

Synthesis and Structure of (Hydridosilyl)hydrazines

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A series of (hydridosilyl)hydrazines **1**–**12** has been prepared from the corresponding chloro- or bromosilanes and hydrazines in the presence of triethylamine as an auxiliary base. Methylsilyl (MeH₂Si-), dimethylsilyl (Me₂HSi-), and phenylsilyl (PhH₂Si-) groups have been introduced as substituents. NMR spectra (¹H, ¹³C, ¹⁵N, ²⁹Si) have been measured and used

to determine the rotation barrier about the N–N bond in (PhH₂Si)(Me₂HSi)N–N(SiHMe₂) (**9**), which has been found to be 75 kJmol⁻¹. The crystal structure of (PhH₂Si)₂N–N(SiH₂Ph)₂ (**7**) features each of the two NNSi₂ groups as nearly planar, but with a dihedral angle close to orthogonal. Such a structure is also implied for **9** on the basis of the NMR spectra.

Layers of amorphous silicon nitride, Si₃N₄, may serve as dielectric components in microelectronic devices. Conventionally, these materials are produced by deposition from the gas phase by PECVD (plasma-enhanced chemical vapor deposition)^[1] from mixtures of N₂ or NH₃ with SiH₄. There is currently an interest, however, in "single-source" silicon-nitrogen compounds, which would allow a simplification of the process and safer handling. The Si/N stoichiometry of such compounds should approach that of Si₃N₄ with few or no Si–C bonds present in order to reduce carbon incorporation into the silicon nitride layer. Together with some simple silyl- or disilanylaminines, (hydridosilyl)hydrazines appeared to be promising candidates as single-source precursors of silicon nitride thin films.

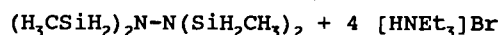
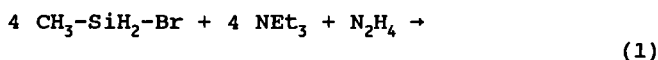
Tetrakis(silyl)hydrazine, (H₃Si)₂N–N(SiH₃)₂, was prepared by Aylett in 1956^[2] as a colorless, volatile liquid which is explosive on contact with air. The compound is difficult to prepare and only accessible via halosilanes H₃SiX (X = Br, I), which are of limited stability and difficult to manipulate. No other (hydridosilyl)hydrazines are known to date, but there were numerous investigations, mainly by Wannagat et al.^[3], on (triorganosilyl)hydrazines. The sterically overcrowded tetrakis(trimethylsilyl)hydrazine, (Me₃Si)₂N–N(SiMe₃)₂, was finally synthesized by Wiberg et al.^[4] in 1968.

(Hydridosilyl)hydrazines containing N–H bonds could also serve in dehydrocoupling reactions as precursors of polysilazanes which can be converted into Si–N ceramics by pyrolysis^[5].

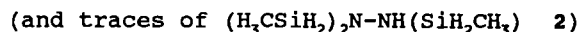
(Methylsilyl)hydrazines

The most volatile, yet alkyl-substituted silylhydrazines can be derived from the partially methylated silyl substituents. Monomethylsilyl compounds are readily prepared from bromo(methyl)silane, H₃C–SiH₂Br, which is available in a two-step synthesis from commercial dichloro(methyl)phenylsilane by chlorine/hydrogen substitution followed by Si–Ph cleavage with liquid HBr according to the method of Fritz and Kummer^[6a]. Bromo(methyl)silane reacts in pen-

tane with hydrazine in the presence of triethylamine to give tetrakis(methylsilyl)hydrazine (**1**) (Eq. (1)) and traces of tris(methylsilyl)hydrazine (**2**).

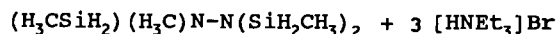
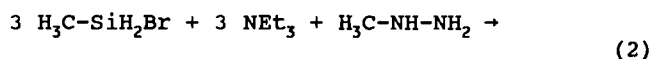


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The reaction proceeds also in the absence of the auxiliary base, since the hydrazine itself serves as the dehydrohalogenating agent, but the yields are not as high as with triethylamine.

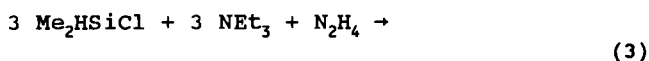
When methylhydrazine is treated in the same way, methyltris(methylsilyl)hydrazine (**3**) is formed exclusively (Eq. (2)).



3

(Dimethylsilyl)hydrazines

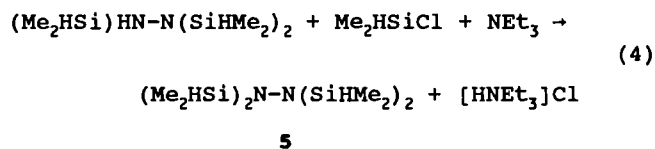
Similar syntheses can also be carried out with chlorodimethylsilane, Me₂HSiCl. However, the reaction of hydrazine with Me₂HSiCl in the presence of Et₃N in boiling THF gives only tris(dimethylsilyl)hydrazine (**4**) (Eq. (3)).



4

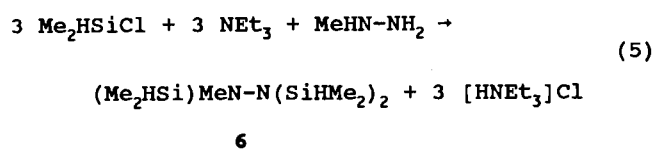
Even with a large excess of the chlorosilane and four days of reaction time only traces of tetrakis(dimethylsilyl)hydra-

zine (**5**) are detectable in the GC of the reaction mixture. If **4** is heated with NEt_3 and Me_2HSiCl in a sealed tube to 150°C for three days, **5** is formed in 83% yield (Eq. (4)).



While hydrazine adds three of the dimethylsilyl groups, only two of the more space-filling trimethylsilyl groups⁽⁷⁾ are taken up under similar conditions.

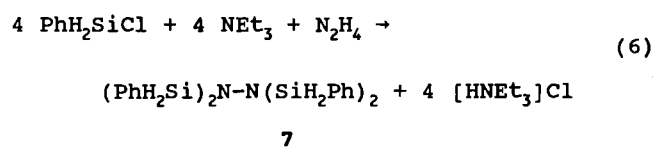
Methylhydrazine is triply silylated without the application of rigorous temperature and pressure conditions to yield tris(dimethylsilyl)methylhydrazine (**6**) (Eq. (5)).



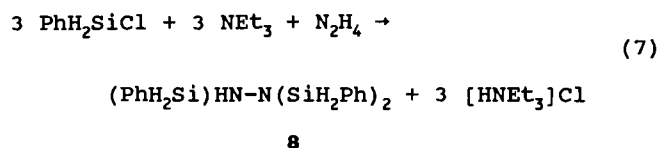
The (dimethylsilyl)hydrazines **4**, **5**, and **6** are colorless liquids, which can be distilled under reduced pressure. They are readily hydrolyzed to the corresponding siloxanes and hydrazines. In dry air they are stable for some time, but the action of oxidants like HNO_3 may even lead to explosive oxidation. Such hypergolic properties have also been reported for (trimethylsilyl)hydrazines⁽⁸⁾.

(Phenylsilyl)hydrazines

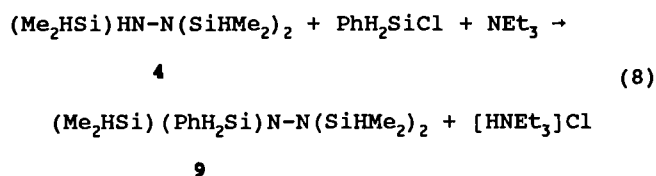
Hydrazine reacts with chloro(phenyl)silane, PhH_2SiCl , in the presence of NEt_3 to give tetrakis(phenylsilyl)hydrazine (**7**) in high yields (Eq. (6)).



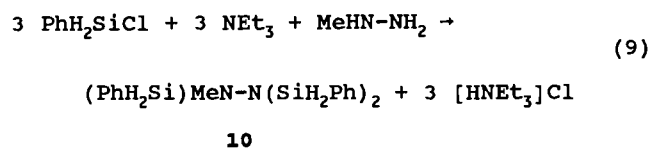
Even if hydrazine is present in excess, complete silylation prevails, and tris(phenylsilyl)hydrazine (**8**) is formed only in small amounts (Eq. (7)).



The fact that the sterical requirement of the dimethylsilyl groups is greater than that of the phenylsilyl group, is also evident from the observation that the reaction of PhH_2SiCl with **4** leading to tris(dimethylsilyl)(phenylsilyl)hydrazine (**9**) (Eq. (8)) is proceeding more readily than the reaction shown in Eq. (4).

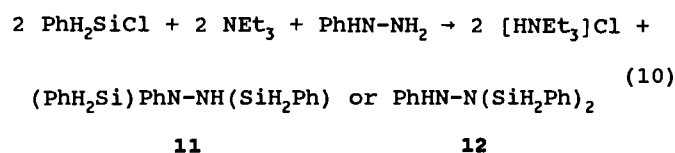


At elevated temperature this process is accompanied by transsilylation as a secondary reaction. Dimethylsilyl groups are replaced by phenylsilyl groups, which results in the formation of traces of the two isomers of (dimethylsilyl)bis(phenylsilyl)hydrazine and also of the two isomers of bis(dimethylsilyl)bis(phenylsilyl)hydrazine, as detected by GC-MS in the product mixture and — in enriched form — in the distillation residue. Silylation of methylhydrazine with PhH_2SiCl leads to methyltris(phenylsilyl)hydrazine (**10**) (Eq. (9)).



No doubly silylated methylhydrazine is detectable in the reaction mixture.

Silylation of phenylhydrazine with PhH_2SiCl gives two isomeric products: 1-phenyl-1,2-bis(phenylsilyl)hydrazine (**11**) and 1-phenyl-2,2-bis(phenylsilyl)hydrazine (**12**) (Eq. (10)) in a ratio of 72:28.



No triply substituted product is detectable. Compounds **11** and **12** cannot be separated by distillation, but pure **11** is obtained by fractional crystallisation.

The (phenylsilyl)-hydrazines **7** and **10–12** can be purified only by means of kugelrohr distillation, since decomposition ensues at elevated temperatures. Compound **7** decomposes at temperatures of about 300°C to phenylsilane and a colorless polymer.

Crystal Structure of **7**

The result of the structure determination is shown in Figure 1 and represents the first crystal structure of a silylhydrazine. Both N atoms show an almost completely trigonal planar coordination geometry. The geometry is comparable to the Si_2NNSi_2 skeleton of tetrasilylhydrazine as determined by means of electron diffraction⁽⁹⁾. The dihedral angle of $87.0(2)^\circ$ enclosed by the two Si_2N planes is close to orthogonal (Figure 2) separating the nitrogen lone pairs perpendicular to the planes. The equivalent angle in tetrasilylhydrazine is only 82.5° , but that difference may result from strong torsional vibrations in the gas phase. The N–N bond

length of 1.483(3) Å is only slightly longer than the corresponding distances found in tetrasilylhydrazine [1.457(16) Å] or hydrazine [1.449(4) Å]^[10]. The average Si–N bond distance is found to be 1.728 Å and is therefore within the range of data found by X-ray diffraction of other silylamines^[11]. This distance does not appear to be affected by the different formal oxidation state of nitrogen in hydrazines and amines, respectively. The bond angles C–C–C at the *ipso*-C atoms of the phenyl rings are compressed to an average of 117.2(3)°, which agrees with the prediction by the VSEPR model^[12].

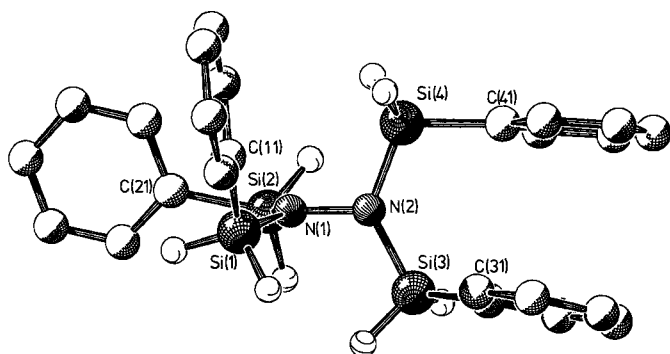


Figure 1. Molecular structure of tetrakis(phenylsilyl)hydrazine (7) projected perpendicularly to the N–N bond with atomic numbering. The molecule has no crystallographic symmetry. Phenyl hydrogen atoms have been omitted for clarity. – Selected bond distances [Å] and angles [°]: Si1–N1 1.726(2), N1–N2 1.482(3), Si1–C11 1.862(3), C11–C12 1.393(4), C12–C13 1.382(4), C13–C14 1.371(5), Si1–H101 1.34(3); Si1–N1–Si2 103.3(1), Si1–N1–N2 114.1(2), N1–Si1–C11 114.9(1), N1–Si1–H101 107(1), C11–Si1–H101 109(1), C12–C11–C16 116.7(3), C11–C12–C13 122.0(3), C12–C13–C14 119.7(4), C13–C14–C15 120.1(4)

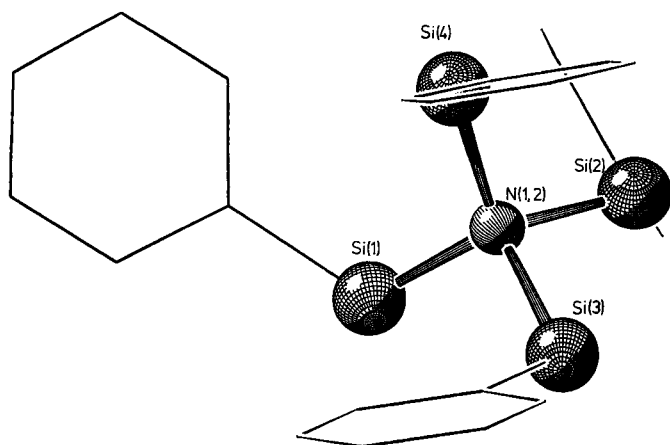


Figure 2. Molecular structure of compound 7 projected parallel to the N–N axis

NMR Studies and Molecular Dynamics of (Hydridosilyl)hydrazines

In the typical fragment of (hydridosilyl)hydrazines, the NNSiH sequence, all atoms have spin $\frac{1}{2}$ isotopes, ^1H , ^{15}N and ^{29}Si , which are used as probes for the electronic and structural properties.

The resonances of the NH protons are not detectable for every compound because of severe line broadening. In general, the signals appear at higher field for compounds with silylated N atoms ($\delta = 2.5$ for **8**, 2.91 for **11**) but are shifted to lower field in cases with an organic substituent at the N atom. However, the δ values are always larger than for comparable silylamines. The resonances of the hydrazine NH protons show couplings to the silyl protons with $^3J(\text{HSiNH})$ values of 1.8 Hz in **2** and 3.1 Hz in **5** (2.0 Hz in **11** and 2.5 Hz in **8**). The NH protons also cause a splitting of the ^{29}Si resonances into doublets with $^2J(\text{SiNH})$ values of ca. 11 Hz.

However, ^{29}Si -NMR spectroscopic studies are greatly facilitated by sensitivity enhancement by using INEPT and DEPT pulse sequences whereby polarization is transferred by means of the $^1J(\text{HSi})$ coupling, which amounts to between 196 and 218 Hz for the title compounds. Independent of the nature of the substituents, the ^{29}Si -chemical shifts of the tetrasilylhydrazines appear at lower field than any of the ^{29}Si resonances of the triply substituted analogs. For the trisilylhydrazines **3**, **6**, and **10** the resonances of the Si atoms at the doubly silylated N atoms are shifted to higher fields relative to the corresponding signals of the atoms bound to the methylated nitrogen atom, while the signals of the Si atoms at the monosilylated N atoms in **2**, **5**, and **8** appear at higher fields than in the hydrazines **3**, **6**, and **10**, respectively, with methylated nitrogen. These effects reflect the higher electronegativity of carbon relative to H and Si. The ^1H -coupled ^{15}N -NMR spectra (INEPT or DEPT technique) are direct evidence for the connectivity of the molecules. These spectra are most straightforward for an analysis of the (phenylsilyl)hydrazines with their relatively simple coupling patterns. If methyl groups are bound to either nitrogen or silicon the ^{15}N resonance is split into a very complex multiplet structure, which is more difficult to assign. The ^{15}N

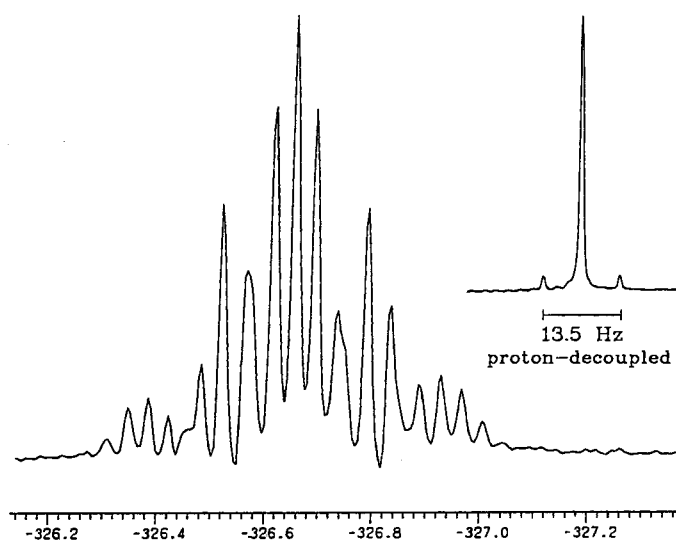


Figure 3. ^{15}N -DEPT spectrum of compound **7** recorded with 0.38-Hz digital resolution and a delay of 96.15 ms in the DEPT pulse sequence. The FID was zero-filled and apodized with a sin^2 function before Fourier transformation. In the inset the proton-decoupled signal with satellite lines of the $^1J(^{15}\text{N}^{29}\text{Si})$ coupling is shown

resonance of **7** consists of a quintet of quintets at $\delta = -326.5$ (see Figure 3). These quintets are the result of the $^2J(\text{NSiH})$ coupling (6.3 Hz) with four silyl protons bound to the two geminal silicon atoms and of the $^3J(\text{NNSiH})$ coupling (1.5 Hz) with the silyl protons at the vicinal $^{14}\text{NSi}_2$ group. As mentioned above, the NH-resonance in the spectrum of **8** appears at $\delta = 2.50$, which is at lower field relative to the NH resonance of $(\text{PhH}_2\text{Si})_2\text{NH}$ ($\delta = 0.12$).

In order to determine whether the rotation around the NN bond in compound **9** is hindered, $^1\text{H-NMR}$ spectra have been recorded at variable temperatures for this model compound with its diagnostic substituent pattern. At 20°C three doublets are observed for the methyl groups, each with the same intensity. One of these doublets is assigned to the unique dimethylsilyl group next to the phenylsilyl group. The two geminal dimethylsilyl groups give rise to two doublets because of the diastereotopic character of the two methyl groups at each of these silicon atoms. With increasing temperature these two doublets collapse to give one broad signal, with a coalescence temperature at 80°C corresponding to an estimated N–N rotation barrier of 75 kJ mol^{-1} . This value is comparable to the data available for other silylhydrazines from the work of Scherer et al.^[13] The result confirms an orthogonal orientation of the NSi_2 planes in the ground state of **9** as already suggested by the crystal structure of **7**.

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Experimental

All reactions were carried out under dry nitrogen. The solvents were dried with CaH_2 or K/Na and distilled prior to use. All glassware was heated to 160°C , evacuated and filled with dry nitrogen. – NMR: Jeol JNM GX-270 and Jeol JNM GX-400. – IR: Perkin Elmer 1650 FT-IR. – MS: Varian MAT 112 S and MAT 311. – GC/MS: Hewlett Packard HP 5890 with mass-selective detector 5971 A. – Anhydrous hydrazine was prepared by drying concentrated hydrazine (95%, Raschig distillation over NaOH) with BaO , followed by trap-to-trap condensation in vacuo. Bromo(methyl)silane and chloro(phenyl)silane were obtained as described^[6b].

Tetrakis(dimethylsilyl)hydrazine (5): 10.0 ml of tris(dimethylsilyl)hydrazine (**4**) (39.8 mmol) is placed together with 5.5 ml of triethylamine (40 mmol) and 4.33 ml of chlorodimethylsilane (39.8 mmol) into a thick-walled tube which is sealed and heated to 140°C in an autoclave filled with hexane for 3 d. After cooling to ambient temp. the tube is opened and the ammonium salt filtered from the slurry. The filtrate is subjected to fractional distillation to yield 8.76 g (83%) of **5**, b.p. $96^\circ\text{C}/1 \text{ mbar}$. – $^1\text{H NMR}$ (399.78 MHz, C_6D_6 , TMS, 25°C): $\delta = 0.25$ [d, $^3J(\text{HCSiH}) = 3.2 \text{ Hz}$, 24H, H_3C], 4.47 [sept, $^3J(\text{HSiCH}) = 3.2 \text{ Hz}$, 4H, HSi], – $^{13}\text{C NMR}$ (100.54 MHz, C_6D_6 , TMS, 25°C): $\delta = 0.32$ [qdd, $^1J(\text{CH}) = 119.5$, $^2J(\text{CSiH}) = 10.6$, $^4J(\text{CSiNSiH}) = 1.8 \text{ Hz}$]. – $^{15}\text{N}\{^1\text{H}\}$ NMR (INEPT, 40.51 MHz, C_6D_6 , CH_3NO_2 external, 25°C): $\delta = -319.15$ [s, $^1J(\text{NSi}) = 13.7 \text{ Hz}$]. – $^{29}\text{Si NMR}$ (INEPT, 79.43 MHz, C_6D_6 , TMS, 25°C): $\delta = -2.09$ [d sept d, $^1J(\text{SiH}) = 199.5$, $^2J(\text{SiCH}) = 6.8$, $^3J(\text{SiNSiH}) = 1.8 \text{ Hz}$]. – IR (Film): $\tilde{\nu} = 2146 \text{ s}$ (νSiH), 974 ss ($\nu_{\text{as}}\text{SiNSi}$). –

MS (GC-coupled), m/z (%): 264 [M^+], 204 (100) [$\text{M}^+ - \text{Me}_2\text{SiH}$], 189, 175, 132 [$(\text{Me}_2\text{HSi})_2\text{N}^+$], 130 [$\text{C}_4\text{H}_{12}\text{NSi}_2^+$], 116, 100, 73, 59 [Me_2HSi].

Tris(dimethylsilyl)(phenylsilyl)hydrazine (9): 20.0 ml of tris(dimethylsilyl)hydrazine (**4**) (79.6 mmol) is heated together with 10.3 ml of chloro(phenyl)silane (79.8 mmol) and 10.9 ml of triethylamine (79.8 mmol) to 130°C for 3 h. After cooling to ambient temp. 50 ml of pentane is added. The suspension is stirred for several min, then filtered and the solvent removed under reduced pressure. The residue is subjected to fractional distillation to yield 16.0 g (71%) of **9**, b.p. $90^\circ\text{C}/0.1 \text{ mbar}$. – $^1\text{H NMR}$ (399.78 MHz, C_6D_6 , TMS, 25°C): $\delta = 0.19$ [d, $^3J(\text{HCSiH}) = 3.4 \text{ Hz}$, 6H, $(\text{H}_3\text{CSi})_2\text{N}$], 0.20 [d, $^3J(\text{HCSiH}) = 3.4 \text{ Hz}$, 6H, $(\text{H}_3\text{CSi})_2\text{N}$], 0.23 [d, $^3J(\text{HCSiH}) = 3.4 \text{ Hz}$, 6H, $\text{H}_3\text{CSiNSiPh}$], 4.76 [sept, $^3J(\text{SiCH}) = 3.4 \text{ Hz}$, 2H, $(\text{HSi})_2\text{N}$], 4.79 [sept, $^3J(\text{SiCH}) = 3.4 \text{ Hz}$, 2H, HSiNSiPh], 5.19 (s, 2H, H_2SiPh), 7.16–7.18 (m, 2H, *o*-H), 7.67–7.70 (m, 3H, *m,p*-H). – $^{13}\text{C}\{^1\text{H}\}$ NMR (100.54 MHz, C_6D_6 , TMS, 25°C): $\delta = 0.21$ (s, $\text{C}_2\text{SiNSiPh}$), 0.44 [s, $(\text{CSi})_2\text{N}$], 0.54 [s, $(\text{CSi})_2\text{N}$], 128.18 (s, *o*-C), 130.49 (s, *p*-C), 134.68 (s, *i*-C), 135.93 (s, *m*-C). – $^{29}\text{Si NMR}$ (INEPT, 79.43 MHz, C_6D_6 , TMS, 25°C): $\delta = -23.81$ [ttm, $^1J(\text{SiH}) = 208.8$, $^3J(\text{SiCH}) = 6.2 \text{ Hz}$, SiH_2PH], -1.81 [d sept t, $^1J(\text{SiH}) = 200.2$, $^2J(\text{SiCH}) = 6.9$, $^3J(\text{SiNSiH}) = 2.1 \text{ Hz}$, Si_2N], 0.41 [d sept t, $^1J(\text{SiH}) = 202.0$, $^2J(\text{SiCH}) = 6.9$, $^3J(\text{SiNSiH}) = 1.5 \text{ Hz}$, SiNSiH_2Ph]. – IR (film): $\tilde{\nu} = 2146 \text{ ss}$ (νSiH), 963 s ($\nu_{\text{as}}\text{SiNSi}$). – MS (GC-coupled), m/z (%): 360 (100) [M^+], 300 [$\text{M}^+ - \text{H} - \text{Me}_2\text{HSi}$], 267, 252, 221, 178, 148, 135, 116.

General Procedure for Preparing the (Hydridosilyl)hydrazines 1–4, 7, 8, 10–12: The solvent, the hydrazine, and a stoichiometric amount of triethylamine are placed into a two-necked flask equipped with a reflux condenser and a dropping funnel. The chlorosilane, diluted with the same volume of solvent, is added dropwise to the flask while stirring the content vigorously. The mixture is heated to reflux for 4 h, and the white precipitate of triethylammonium chloride is filtered after cooling to -30°C . The solvent is removed from the filtrate by distillation, and the remaining liquid is distilled. In the following section details for the individual compounds are presented.

Tetrakis(methylsilyl)hydrazine (1): Pentane (700 ml), N_2H_4 (3.89 ml, 0.125 mol), Me_2SiBr (62.93 g, 0.503 mol), NEt_3 (80.8 ml, 0.503 mol), yield 18.3 g (62%), b.p. $76^\circ\text{C}/33 \text{ mbar}$. – $^1\text{H NMR}$ (399.78 MHz, C_6D_6 , TMS, 25°C): $\delta = 0.22$ [t, $^3J(\text{HCSiH}) = 3.7 \text{ Hz}$, 12H, H_3C], 4.70 [q, $^3J(\text{HSiCH}) = 3.7 \text{ Hz}$, 12H, H_2Si]. – $^{13}\text{C NMR}$ (100.54 MHz, C_6D_6 , TMS, 25°C): $\delta = -2.87$ [qt, $^1J(\text{CH}) = 121.0$, $^2J(\text{CSiH}) = 9.4 \text{ Hz}$]. – $^{29}\text{Si NMR}$ (INEPT, 79.43 MHz, C_6D_6 , TMS, 25°C): $\delta = -21.49$ [tqt, $^1J(\text{SiH}) = 208.7$, $^2J(\text{SiCH}) = 7.4$, $^3J(\text{SiNSiH}) = 1.6 \text{ Hz}$]. – IR (film): $\tilde{\nu} = 2147 \text{ ss}$ (νSiH), 967 s ($\nu_{\text{as}}\text{SiNSi}$). – MS (GC-coupled), m/z (%): 208 [M^+], 162 (100) [$\text{M}^+ - \text{H} - \text{CH}_3\text{SiH}_2$], 147 [$\text{C}_2\text{H}_{11}\text{Si}_3\text{N}_2^+$], 145, 116 [$\text{C}_2\text{H}_8\text{Si}_2\text{N}_2^+$], 102, 88, 86, 59. – In lower-boiling fractions small amounts of *tris(methylsilyl)hydrazine (2)* are detectable besides **1**. The following data have been tentatively assigned to **2**: $^1\text{H NMR}$ (399.78 MHz, C_6D_6 , TMS, 25°C): $\delta = 0.08$ [t, $^3J(\text{HCSiH}) = 3.6 \text{ Hz}$, 3H, H_3CSiN], 0.15 [t, $^3J(\text{HCSiH}) = 3.5 \text{ Hz}$, 6H, $(\text{H}_3\text{CSi})_2\text{N}$], 4.59 [qd, $^3J(\text{HSiCH}) = 3.7$, $^3J(\text{HSiNH}) = 1.8 \text{ Hz}$, 2H, H_2SiNH], 4.61 [q, $^3J(\text{HSiCH}) = 3.6 \text{ Hz}$, 4H, $(\text{H}_2\text{Si})_2\text{NH}$]. – $^{13}\text{C NMR}$ (100.54 MHz, C_6D_6 , TMS, 25°C): $\delta = -4.95$ [qt, $^1J(\text{CH}) = 120.9$, $^2J(\text{CSiH}) = 9.0 \text{ Hz}$, $(\text{CSi})_2\text{N}$], -4.19 [qt, $^1J(\text{CH}) = 120.4$, $^2J(\text{CSiH}) = 9.4 \text{ Hz}$, CSiNH]. – $^{29}\text{Si NMR}$ (INEPT, 79.43 MHz, C_6D_6 , TMS, 25°C): $\delta = -26.11$ [tdq, $^1J(\text{SiH}) = 204.0$, $^2J(\text{SiNH}) = 11.5$, $^2J(\text{SiCH}) = 7.4 \text{ Hz}$, SiNH], -24.02 [tqt, $^1J(\text{SiH}) = 202.9$, $^2J(\text{SiCH}) = 7.4$, $^3J(\text{SiNSiH}) = 1.5 \text{ Hz}$, Si_2N]. – MS (GC-coupled), m/z (%): 164 (100) [M^+], 145, 118 [$\text{M}^+ - \text{H} - \text{CH}_3\text{SiH}_2$], 103 [$\text{CH}_7\text{N}_2\text{Si}_2^+$], 86, 74, 70, 59.

Methyltris(methylsilyl)hydrazine (3): Pentane (500 ml), MeNHNH₂ (2.50 ml, 46.8 mmol), MeH₂SiBr (17.55 g, 140 mmol), NEt₃ (19.5 ml, 140 mmol), yield 4.26 g (51%), b.p. 75 °C (40 mbar). — ¹H NMR (399.78 MHz, C₆D₆, TMS, 25 °C): δ = 0.17 [t, ³J(HCSiH) = 3.5 Hz, 3H, H₃CSiNC], 0.20 [t, ³J(HCSiH) = 3.5 Hz, 6H, (H₃CSi)₂N], 2.62 (s, 3H, H₃CN), 4.65 [q, ³J(HSiCH) = 3.5 Hz, 4H, (H₂Si)₂N], 4.66 [q, ³J(HSiCH) = 3.5 Hz, 2H, H₂SiNC]. — ²⁹Si NMR (INEPT, 79.43 MHz, C₆D₆, TMS, 25 °C): δ = -20.99 [tqt, ¹J(SiH) = 202.7, ²J(SiCH) = 7.4, ³J(SiNSi) = 1.6 Hz, Si₂N], -13.39 [tqq, ¹J(SiH) = 202.5, ²J(SiCH) = 7.3, ³J(SiNCH) = 3.1 Hz, SiNC]. — IR (film): $\tilde{\nu}$ = 2142 ss broad (νSiH), 1012 ss, 970 s (ν_{as}SiNSi). — MS (GC-coupled), *m/z* (%): 178 [M⁺], 148 [M⁺ - 2 CH₃], 132 (100) [M⁺ - H - Me₂Hsi], 117 [M⁺ - H - Me₂Hsi - CH₃], 104 [C₂H₁₀NSi₂], 102, 78, 72.

Tris(dimethylsilyl)hydrazine (4): THF (1.2 l), N₂H₄ (8.70 ml, 0.284 mol), Me₂HSiCl (150 ml, 1.38 mol), NEt₃ (191.3 ml, 1.38 mol), yield 48.68 g (83%), b.p. 60 °C/15 mbar. — ¹H NMR (399.78 MHz, C₆D₆, TMS, 25 °C): δ = 0.10 [d, ³J(HCSiH) = 3.1 Hz, 6H, (H₃C)₂SiNH], 0.17 [d, ³J(HCSiH) = 3.1 Hz, 12H, ((H₃C)₂Si)₂N], 2.16 (s, 3H, HN), 4.67 [sept, ³J(HSiCH) = 3.1 Hz, 2H, (HSi)₂N], 4.76 [sept, ³J(HSiCH) = 3.1 Hz, 1H, HSiNH]. — ¹³C NMR (67.94 MHz, C₆D₆, TMS, 25 °C): δ = -2.16 [qd, ¹J(CH) = 129.7, ²J(CSiH) = 10.1 Hz, (CH₃Si)₂N], -1.48 [qd, ¹J(CH) = 119.7, ²J(CSiH) = 11.8 Hz, CH₃SiNH]. — ²⁹Si NMR (INEPT, 79.43 MHz, C₆D₆, TMS, 25 °C): δ = -7.77 [d sept d, ¹J(SiH) = 203.1, ²J(SiCH) = 6.9, ³J(SiNSiH) = 1.4 Hz, Si₂N], -7.36 [d d sept, ¹J(SiH) = 203.4, ²J(SiNH) = 10.6, ²J(SiCH) = 6.5 Hz, SiNH]. — IR (Film): $\tilde{\nu}$ = 3362 w (νNH), 2133 s (νSiH), 990 s (ν_{as}SiNSi). — MS (EI), *m/z* (%): 206 [M⁺], 193, 133 [C₄H₁₅NSi₂⁺], 119 (100), 103, 75, 61.

Tris(dimethylsilyl)methylhydrazine (6): THF (500 ml), MeNHNH₂ (8.0 ml, 0.15 mol), Me₂HSiCl (50.0 ml, 0.46 mol), NEt₃ (63.8 ml, 0.46 mol), yield 16.47 g (50%), b.p. 106 °C/75 mbar. — ¹H NMR (399.78 MHz, C₆D₆, TMS, 25 °C): δ = 0.16 [d, ³J(HCSiH) = 3.1 Hz, 6H, H₃CSiNC], 0.22 [d, ³J(HCSiH) = 3.1 Hz, 12H, (H₃CSi)₂N], 2.61 (s, 3H, H₃CN), 4.73 [sept, ³J(HSiH) = 3.1 Hz, 2H, (HSi)₂N], 4.75 [sept, ³J(HSiCH) = 3.1 Hz, 1H, HSiNC]. — ¹³C{¹H} NMR (100.54 MHz, C₆D₆, TMS, 25 °C): δ = -1.21 [s, (CH₃Si)₂N], 0.07 (s, H₃CSiNC), 40.85 (s, CH₃N). — ¹⁵N{¹H} NMR (INEPT, 40.51 MHz, C₆D₆, CH₃NO₂ external, 25 °C): δ = -331.08 [s, ¹J(NSi) = 19.4 Hz, NCSi], -307.33 [s, ¹J(NSi) = 14.5 Hz, NSi₂]. — ²⁹Si NMR (INEPT, 79.43 MHz, C₆D₆, TMS, 25 °C): δ = -8.06 [d sept d, ¹J(SiH) = 196.3, ²J(SiCH) = 6.9, ³J(SiCH) = 1.1 Hz, Si₂N], -3.15 [d sept q, ¹J(SiH) = 197.6, ²J(SiCH) = 6.8, ³J(SiNCH) = 3.3 Hz, SiNC]. — IR (film): $\tilde{\nu}$ = 2124 s (νSiH), 995 s (ν_{as}SiNSi). — MS (GC-coupled), *m/z* (%): 220 [M⁺], 160 (100) [M⁺ - H - Me₂Hsi], 145 [C₄H₁₃N₂Si₂], 132, 116, 102, 86, 73, 59.

Tetrakis(phenylsilyl)hydrazine (7) and Tris(phenylsilyl)hydrazine (8): THF (600 ml), N₂H₄ (5.0 ml, 0.16 mol), PhH₂SiCl (64.5 ml, 0.632 mol), NEt₃ (65.5 ml, 0.632 mol), yield of **8** 5.62 g (10%), b.p. 165 °C/0.02 mbar, yield of **7** 48.37 g (67%), purified by kugelrohr distillation (air bath temp. 180 °C, 0.01 mbar), m.p. 14 °C. Single crystalline material is obtained from concentrated solutions in pentane or THF at -20 °C.

7: ¹H NMR (399.78 MHz, C₆D₆, TMS, 20 °C): δ = 5.15 [s, ¹J(HSi) = 217.7 Hz, 8H, SiH₂], 7.10–7.15 (m, 12H, *m,p*-H), 7.50–7.51 (m, 8H, *o*-H). — ¹³C{¹H} NMR (100.54 MHz, C₆D₆, TMS, 25 °C): δ = 127.94 (s, *o*-C), 130.33 (s, *p*-C), 134.94 (s, *i*-C), 136.54 (s, *m*-C). — ¹⁵N{¹H} NMR (INEPT, 40.51 MHz, C₆D₆, CH₃NO₂ external, 25 °C): δ = -326.47 [s, ¹J(NSi) = 13.5, ²J(NSiH) = 6.3, ³J(NNSiH) = 1.5 Hz]. — ²⁹Si NMR (DEPT, 79.43 MHz, C₆D₆, TMS, 25 °C): δ = -21.55 [tt, ¹J(SiH) = 217.5, ³J(SiCCH) = 5.7 Hz]. — IR (film): $\tilde{\nu}$ = 2153 ss (νSiH), 992 m (ν_{as}SiNSi). — MS (CI), *m/z* (%):

456 (100) [M⁺], 423, 378, 377 [M⁺ - 2H - PhH₂Si], 299, 271, 226, 183, 150, 107.

C₂₄H₂₈N₂Si₄ (456.8)

Calcd. C 63.09 H 6.18 N 6.13 Si 24.59

Found C 63.33 H 6.39 N 6.42 Si 23.12

8: ¹H NMR (399.78 MHz, C₆D₆, TMS, 25 °C): δ = 2.50 (s, broad, 1H, NH), 4.79 [d, ³J(HSiNH) = 2.5 Hz, 2H, H₂Si-NH], 5.16 [s, ¹J(HSi) = 210.5 Hz, 4H, (H₂Si)₂N], 7.10–7.18 (m, 9H, *m,p*-H), 7.46–7.49 (m, 2H, *o*-C₆H₅SiNH), 7.57–7.60 [m, 4H, (*o*-C₆H₅Si)₂N]. — ¹³C{¹H} NMR (100.54 MHz, C₆D₆, TMS, 25 °C): δ = 128.08 (s, *o*-C-SiNH), 128.27 [s, (*o*-C-Si)₂N], 130.43 [s, (*p*-C-Si)₂N], 130.49 (s, *p*-C-SiNH), 132.94 (s, *i*-C-SiNH), 133.67 [s, (*i*-C-Si)₂N], 135.42 [s, (*m*-C-Si)₂N], 135.57 (s, *m*-C-SiNH). — ¹⁵N NMR (INEPT, 40.51 MHz, C₆D₆, CH₃NO₂ external, 25 °C): δ = -330.21 [quint d t, ²J(NSiH) = 6.1, ²J(NNH) = 1.2, ³J(NNSiH) = 1.2 Hz, NSi₂], -324.99 [d t quint, ¹J(NH) = 82.9, ²J(NSiH) = 6.0, ³J(NNSi) = 2.0 Hz, NHSi]. — ²⁹Si NMR (INEPT, 79.43 MHz, C₆D₆, TMS, 25 °C): δ = -28.01 [tdt, ¹J(SiH) = 217.4, ²J(SiNH) = 11.5, ³J(SiCCH) = 6.5 Hz, SiNH], -25.13 [ttt, ¹J(SiH) = 210.5, ³J(SiCCH) = 6.0, ²J(SiNH) = 0.9 Hz, Si₂N]. — IR (film): $\tilde{\nu}$ = 3361 m (νNH), 2151 ss (νSiH), 1018 s, 920 s (ν_{as}SiNSi). — MS (CI), *m/z* (%): 350 [M⁺], 244 [M⁺ - C₆H₆Si], 229 (100) [C₁₂H₁₅NSi₂], 167, 153, 107.

Methyltris(phenylsilyl)hydrazine (10): THF (250 ml), MeNHNH₂ (6.46 ml, 0.12 mol), PhH₂SiCl (50.0 ml, 0.37 mol), NEt₃ (50.9 ml, 0.37 mol), yield 33.13 g (82%), purified by kugelrohr distillation (air bath temp. 135–145 °C, 0.01 mbar). — ¹H NMR (399.78 MHz, C₆D₆, TMS, 25 °C): δ = 2.54 (s, 3H, CH₃), 5.08 (s, 2H, H₂SiNC), 5.21 [s, 4H, (H₂Si)₂N], 7.10–7.16 (m, 9H, *m,p*-C₆H₅), 7.49–7.51 (m, 2H, *o*-C₆H₅NC), 7.61–7.64 [m, 4H, (*o*-C₆H₅Si)₂N]. — ¹³C{¹H} NMR (69.94 MHz, C₆D₆, TMS, 25 °C): δ = 39.73 (s, CH₃), 128.07 (s, *o*-C), 130.29 (s, *p*-C), 133.46 (s, *i*-C-SiNC), 134.06 [s, (*i*-C-Si)₂N], 135.40 (s, *m*-C-SiNC), 135.48 [s, (*m*-C-Si)₂N]. — ¹⁵N NMR (INEPT, 27.39 MHz, C₆D₆, CH₃NO₂ external, 25 °C): δ = -332.78 [s, ¹J(NSi) = 19.7 Hz, NSi₂], -315.36 [s, ¹J(NSi) = 15.1 Hz, NSiC]. — ²⁹Si NMR (INEPT, 79.43 MHz, C₆D₆, TMS, 25 °C): δ = -27.91 [tt, ¹J(SiH) = 210.0, ³J(SiCCH) = 6.2 Hz, Si₂N], -21.34 [tm, ¹J(SiH) = 211.9 Hz, SiNC]. — IR (film): $\tilde{\nu}$ = 2147 s (νSiH), 1012 m (ν_{as}SiNSi). — MS (CI), *m/z* (%): 364 [M⁺], 258 [M⁺ - PhH₂Si - H], 229 (100) [C₁₂H₁₅NSi₂], 181, 153, 107 [C₆H₇Si].

C₁₉H₂₄N₂Si₃ (336.6)

Calcd. C 62.58 H 6.63 N 7.68 Si 23.10

Found C 61.87 H 6.61 N 7.75 Si 21.61

1-Phenyl-1,2-bis(phenylsilyl)hydrazine (11) and 2-Phenyl-1,1-bis(phenylsilyl)hydrazine (12): THF (500 ml), PhHNNH₂ (12.0 ml, 0.12 mol), PhH₂SiCl (50.0 ml, 0.37 mol), NEt₃ (50.9 ml, 0.37 mol); purification by kugelrohr distillation (air bath temp. 150 °C, 0.01 mbar) gives 30.1 g of a mixture of both isomers (27.8% of **12** and 72.2% of **11**, according to GC). Compound **11** is obtained in pure form by fractional crystallisation from pentane at -20 °C.

11: ¹H NMR (399.78 MHz, C₆D₆, TMS, 25 °C): δ = 2.91 (broad, 1H, NH), 4.95 [d, ³J(HSiNH) = 2.0 Hz, 2H, H₂SiNH], 5.33 (s, 2H, H₂SiNPh), 7.07–7.14 and 7.45–7.50 (m, 15H, C₆H₅). — ¹⁵N{¹H} NMR (INEPT, 40.51 MHz, C₆D₆, CH₃NO₂ external, 25 °C): δ = -322.71 [s, ¹J(NSi) = 19.1 Hz, NHSi], -300.41 [s, ¹J(NSi) = 12.3 Hz, NPhSi]. — ²⁹Si NMR (INEPT, 79.43 MHz, C₆D₆, TMS, 25 °C): δ = -29.48 [tt, ¹J(SiH) = 216.02, ³J(SiCCH) = 6.2 Hz, SiNPh], -28.39 [tdt, ¹J(SiH) = 212.2, ²J(SiNH) = 12.6, ³J(SiCCH) = 6.1 Hz, SiNH]. — MS (GC-coupled), *m/z* (%): 320 (100) [M⁺], 212 [M⁺ - PhSiH₃], 183, 150, 135, 120, 107 [PhH₂Si⁺], 105.

12 (from a mixture with **11**): ¹H NMR (399.78 MHz, C₆D₆, TMS, 25 °C): δ = 4.70 (broad, 1H, NH), 5.12 (s, 4H, H₂Si), 7.07–7.14

and 7.45–7.50 (m, 15H, C₆H₅). – ¹⁵N{¹H} NMR (INEPT, 40.51 MHz, C₆D₆, CH₃NO₂ external, 25°C): δ = –326.85 [s, ¹J(NSi) = 14.3 Hz, NSi₂], –287.36 (s, NHPh). – ²⁹Si NMR (INEPT, 79.43 MHz, C₆D₆, TMS, 25°C): δ = –25.96 [tt, ¹J(SiH) = 212.1, ³J(SiCCH) = 5.8 Hz]. – MS (GC-coupled), m/z (%): 320 (100) [M⁺], 241 [M⁺ – 2H – Ph], 226, 211 [M⁺ – PhSiH₃ – H], 183, 163, 148, 120, 107 [PhH₂Si], 105.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for 7. $U(\text{eq}) = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2, U_3 are the Eigenvalues of the $U(ij)$ Matrix. E.s.d.'s in parentheses

ATOM	X/A	Y/B	Z/C	U(eq.)
Si(1)	0.33974(7)	–0.20124(8)	0.47386(5)	0.044
Si(2)	0.26376(8)	0.07054(8)	0.41391(4)	0.047
Si(3)	0.38027(6)	0.06306(9)	0.60346(4)	0.042
Si(4)	0.14953(7)	–0.0395(1)	0.55354(6)	0.053
N(1)	0.2833(2)	–0.0537(2)	0.4752(1)	0.035
N(2)	0.2737(2)	–0.0161(2)	0.5470(1)	0.037
C(11)	0.2527(2)	–0.3394(3)	0.4745(2)	0.039
C(12)	0.1461(3)	–0.3392(3)	0.4388(2)	0.045
C(13)	0.0844(3)	–0.4456(3)	0.4369(2)	0.055
C(14)	0.1288(4)	–0.5564(4)	0.4693(2)	0.062
C(15)	0.2323(4)	–0.5605(4)	0.5045(2)	0.063
C(16)	0.2948(3)	–0.4527(3)	0.5074(2)	0.057
C(21)	0.2451(2)	0.0077(3)	0.3213(2)	0.039
C(22)	0.1557(3)	–0.0597(3)	0.2857(2)	0.045
C(23)	0.1411(3)	–0.1045(3)	0.2162(2)	0.051
C(24)	0.2160(3)	–0.0826(3)	0.1811(2)	0.055
C(25)	0.3043(3)	–0.0158(4)	0.2153(2)	0.056
C(26)	0.3188(3)	0.0283(3)	0.2844(2)	0.048
C(31)	0.3975(2)	0.0194(3)	0.6992(1)	0.035
C(32)	0.4063(2)	–0.1073(3)	0.7217(2)	0.042
C(33)	0.4194(3)	–0.1398(4)	0.7925(2)	0.050
C(34)	0.4245(3)	–0.0455(4)	0.8433(2)	0.054
C(35)	0.4158(3)	0.0797(4)	0.8228(2)	0.053
C(36)	0.4025(2)	0.1117(3)	0.7515(2)	0.044
C(41)	0.1346(2)	0.0433(3)	0.6351(2)	0.039
C(42)	0.1218(2)	0.1738(3)	0.6370(2)	0.050
C(43)	0.1163(3)	0.2332(4)	0.6993(2)	0.058
C(44)	0.1240(3)	0.1662(4)	0.7600(2)	0.056
C(45)	0.1358(3)	0.0379(5)	0.7599(2)	0.061
C(46)	0.1406(3)	–0.0244(4)	0.6977(2)	0.052

Crystal Structure Determination for Compound 7: Suitable crystals of 7 were grown from *n*-pentane at –20°C (needle-shaped, m.p. 14°C), sealed under argon in a glass capillary and mounted on a Syntex P2₁ diffractometer. Compound 7 crystallizes in the monoclinic spacegroup $P2_1/c$ (No. 14 in the International Tables for Crystallography). – Crystal data: $a = 13.379(2)$, $b = 10.490(1)$, $c = 19.304(3)$ Å, $\beta = 106.75(1)^\circ$, $V = 2594.1$ Å³, $M_r = 456.848$, $Z = 4$, $\rho_{\text{calc}} = 1.170$ g·cm^{–3}, $\mu(\text{Mo-K}\alpha) = 2.4$ cm^{–1}, $T = -60^\circ\text{C}$, $(\sin \Theta/\lambda)_{\text{max}} = 0.572$ Å^{–1}, $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å. After check for

higher symmetry 4219 reflections were measured of which 3832 were unique. 3191 reflections with $F_o \geq 2\sigma(F_o)$ were used for structure solution and refinement. The structure was solved by direct methods and completed by Fourier synthesis. After anisotropic refinement of all heavier atoms the hydrogen atoms could be found in difference Fourier maps and were refined isotropically. The structure could be refined to a R (R_w) value of 0.050 (0.049) [$w = 1/(\sigma^2(F_o) + k \cdot F_o^2)$, $l = 1.5969$, $k = 0.000301$] for 383 parameters, convergence of $(\text{shift/error})_{\text{max}} = 0.002$ and a residual electron density of $+0.34/-0.39$ e·Å^{–3}. Atomic coordinates are listed in Table 1. Further information on the X-ray structure determination can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56706, the names of the authors, and the journal citation.

[1] E. Unger, *Chem. Unserer Zeit* **1991**, 25, 148–158.

[2] B. J. Aylett, *J. Inorg. Nucl. Chem.* **1956**, 2, 325.

[3] [3a] U. Wannagat, W. Liehr, *Z. Anorg. Allg. Chem.* **1959**, 299, 341–348. – [3b] F. Höfler, U. Wannagat, *Monatsh. Chem.* **1966**, 97, 1598–1610.

[4] N. Wiberg, W.-Ch. Joo, W. Uhlenbrock, *Angew. Chem.* **1968**, 80, 661–662; *Angew. Chem. Int. Ed. Engl.* **1968**, 7, 640.

[5] M. Peuckert, T. Vaahs, M. Brück, *Adv. Mater.* **1990**, 2, 398–404.

[6] [6a] G. Fritz, D. Kummer, *Z. Anorg. Allg. Chem.* **1960**, 306, 191. – [6b] J. Zech, H. Schmidbaur, *Chem. Ber.* **1990**, 123, 2087–2091.

[7] U. Wannagat, W. Liehr, *Z. Anorg. Allg. Chem.* **1958**, 297, 126–136.

[8] U. Wannagat, F. Höfler, *Monatsh. Chem.* **1966**, 97, 1157–1162.

[9] C. Glidewell, D. W. H. Rankin, A. G. Robiette, G. M. Sheldrick, *J. Chem. Soc. (A)* **1970**, 318–320.

[10] Y. Morino, T. Iijima, Y. Murata, *Bull. Chem. Soc. Jpn.* **1960**, 33, 46.

[11] N. W. Mitzel, A. Schier, H. Beruda, H. Schmidbaur, *Chem. Ber.* **1992**, 125, 1053–1059.

[12] A. Domenicano, A. Vaciano, C. A. Coulson, *Acta Crystallogr., Sect. B*, **1975**, 31, 221.

[13] O. J. Scherer, U. Bültjer, *Angew. Chem.* **1971**, 83, 364–365; *Angew. Chem. Int. Ed. Engl.* **1971**, 10, 343.

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