Methylsilylhydroxylamines: Preparative, Spectroscopic and *Ab initio* Studies†

Norbert W. Mitzel,[a] Matthias Hofmann,[b] Eckhard Waterstradt,[c] Paul von Ragué Schleyer[b] and Hubert Schmidbaur*,[a]

[a] *Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany*

[b] *Institut für Organische Chemie der Friedrich Alexander Universität Erlangen-Nürnberg, Henkestrasse 42, D-91054 Erlangen, Germany*

[c] *Institut für Theoretische und Physikalische Chemie der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany*

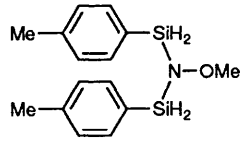
Methylsilylhydroxylamines [$(MeH_2Si)_2NOMe$, $(MeH_2Si)MeNOMe$, Me_2NOSiH_2Me] have been prepared from bromo(methyl)silane and the corresponding methylhydroxylamines in the presence of an auxiliary base (triethylamine or *N,N,N',N'*-tetramethylethylenediamine). The compounds were studied by NMR spectroscopy of all elements present (^1H, ^{13}C, ^{15}N, ^{17}O, ^{29}Si). The magnitude of the one-bond coupling constants $^1J(^{15}N^{29}Si)$ is interpreted in terms of the hybridization associated with the pyramidal co-ordination of nitrogen, a unique structural feature in Si/N chemistry. *Ab initio* studies confirmed these structural predictions. Singly silylated hydroxylamines have been shown to be more strongly pyramidal than doubly silylated ones. Calculations on the model compound $(H_3Si)_2NOMe$ gave a barrier to inversion at nitrogen of 9.7 kcal mol^{-1}. This inversion is accompanied by a partial rotation around the N–O bond. The NMR chemical shifts of the compounds have been calculated and the results are in good agreement with the experimental data. The unusually low chemical shifts $\delta(^{17}O)$ of hydroxylamines have thus been confirmed by theory. A comparison of the calculated normal modes of vibration with experimental data leads to a complete assignment of the IR spectra.

The considerable interest in the nature of the Si–N bond ensuing in 1955, when Hedberg[1] showed that trisilylamine, $N(SiH_3)_3$, has a planar co-ordination at the nitrogen atom, has been maintained ever since, and during the last 40 years the structures of a large number of silylamines have been determined.[2] As a general rule it was derived from these results that *all* compounds with *doubly* and *triply* silylated nitrogen atoms exhibit a planar geometry at nitrogen.[3] Only for a few *mono*silylated amines deviations from a planar arrangement of the nitrogen substituents[4] occur, but with significant variations for the gas phase and the solid state.

$p_\pi d_\pi$ Bonding,[5] formerly the most widespread hypothesis to explain this and other unique properties of silylamines, like low basicity at nitrogen and short Si–N bonds, was shown to be rather insignificant, and p_σ* interactions[6] (negative hyperconjugation, anomeric effect) and an electrostatic repulsion model[7] have since been introduced as more meaningful approaches.

Compounds with a wide variety of substituents at the *silicon* part of the molecules have been structurally studied, but the variations of *nitrogen* substituents have been limited to silylated hydrazines some of which were presented in previous papers from this laboratory.[8] For this class of Si/N compounds with nitrogen in its oxidation state -II, planarity at nitrogen induced by silyl substituents appears to be also well established.[9] As a continuation of these studies we have now investigated silylated hydroxylamines bearing oxygen as a very electronegative substituent at nitrogen in its oxidation state -I. In this context we recently reported the unique structure of *O*-methyl-*N,N*-bis(*p*-tolylsilyl)hydroxylamine **1**,[10] one of only a few doubly N-silylated compounds with a pyramidal co-ordination sphere at nitrogen.[11]

† *Non-SI unit employed:* cal = 4.184 J.



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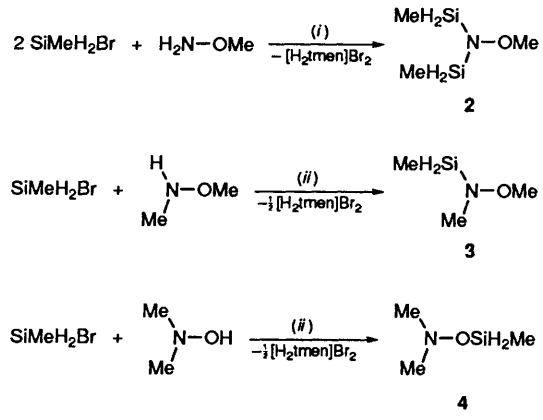
As a follow-up to this work, and as a part of our current search for new single-source feedstock precursors for chemical vapour deposition[12] (CVD) of silicon nitride and oxynitride films,[13] we are now examining low-molecular-weight silylhydroxylamines with low carbon contents and high volatilities. These small molecules should also allow a direct comparison of experimental data with the results of more sophisticated theoretical calculations of structure and bonding.

Results and Discussion

Preparation of Methylsilylhydroxylamines.—Since compounds with silyl groups H_3Si are generally pyrophoric, methylsilyl groups, the organosilyl groups with the lowest carbon content, were chosen for this study. Bromo(methyl)silane is a powerful silylating agent for NH and OH functions and reacts with *O*-methyl, *N,O*-dimethyl- and *N,N*-dimethylhydroxylamine in the presence of triethylamine to give the silylated hydroxylamines **2**, **3** and **4**, respectively (Scheme 1).

The compounds have low boiling points (97, 61 and 58 °C, respectively), and separation from the solvents and from the excess of triethylamine is difficult. These complications can be overcome by a solvent-free reaction mode and by using *N,N,N',N'*-tetramethylethylenediamine (tmen) as the dehydrohalogenating agent. The advantage of tmen is its dibasic nature. Since both di- and mono-protonated tmen salts are non-volatile,



Scheme 1 (*i*) tmen; (*ii*) ½tmen

a small excess of tmen can be used without causing separation problems. The yields of products are generally higher as compared with the NEt_3 procedure.

Compounds **2–4** can be purified by distillation and stored at room temperature for long periods of time without decomposition; **2** and **3** are readily hydrolysed, while **4** (with no substitution labile Si–N bond) is more stable towards moisture. Oxidation in dry air is slow, but stronger oxidants like HNO_3 react violently.

All attempts to generate tris(methylsilyl)hydroxylamine from the reaction of anhydrous H_2NOH and $SiMeH_2Br$ have been unsuccessful. The main component of the volatile products is 1,3-dimethyldisiloxane.

Solution NMR Studies.—Compounds **2–4** have been completely characterized by their NMR spectra employing the complete set of nuclei (^1H, ^{13}C, ^{15}N, ^{17}O, ^{29}Si). Selected data are shown in Table 3. The main interest lies in the $^1J(^{15}N^{29}Si)$ coupling constants. We have recently reported the mode of dependence of this parameter on the degree of silylation at the nitrogen atom of silyl-amines and -hydrazines.[14] In the series of silyl-amines and -hydrazines bearing simple silyl substituents comparable to the methylsilyl group employed here the $^1J(^{15}N^{29}Si)$ values for *doubly* silylated nitrogen units were found to be about 14 Hz, for *mono*silylated ones about 20 Hz. For the hydroxylamines **2** and **3** the values for $^1J(^{15}N^{29}Si)$ (11.5 and 10.4 Hz) are smaller than those of comparable silyl-hydrazines and -amines, and equally surprisingly the $^1J(^{15}N^{29}Si)$ coupling constant of the *singly* silylated **3** is less than that of **2** with *two* silyl substituents attached to nitrogen. Referring to the correlation of $^1J(^{15}N^{29}Si)$ with the s character of the Si–N bond,[15] these results are indicative of a reduced s character in **2** and **3** associated with a change in geometry towards a pyramidal nitrogen configuration as compared with planar Si/N systems. These qualitative considerations are confirmed by the natural bond orbitals (NBO) analyses discussed below.

Even compound **2** is suggested to be pyramidal at nitrogen. In order to verify these conclusions, quantum-chemical calculations on the geometries, NMR chemical shifts and vibrational frequencies have been carried out.

Ab Initio *Calculations.*—All computations were performed with the GAUSSIAN 92[16] and CADPAC 5.0[17] program packages. Structures were first optimized at the SCF/6-31G* level, and the nature of stationary points was characterized by subsequent frequency calculations. Geometries were then refined at the MP2(fc)/6-31 + G* level.[18]

The calculated geometries of compounds **2** and $(H_3Si)_2NOMe$ **5** are in good agreement with the crystal structure data for **1**[10] which is also a doubly N-silylated hydroxylamine (see Table 1 and Figs. 1 and 2). The sums of the bond angles at

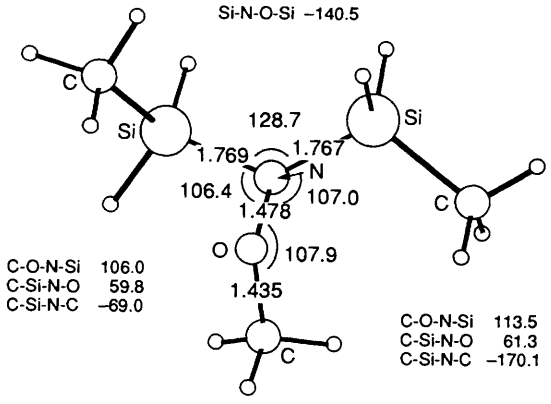


Fig. 1 Calculated molecular geometry (lengths in Å, angles in °) of compound **2** (minimum-energy conformation)

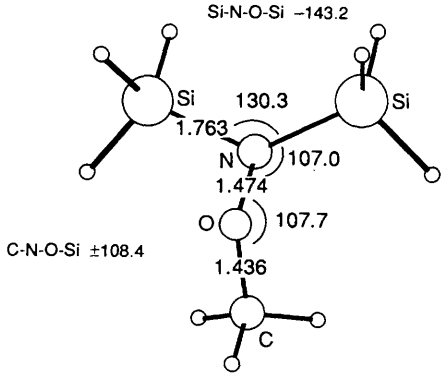


Fig. 2 Calculated molecular geometry of compound **5** (minimum-energy conformation)

nitrogen are similar, indicating a similar hybridization state of nitrogen. The singly *N*-silylated hydroxylamine **3** (Fig. 3) is clearly more strongly pyramidal as compared with **2** and **5**, as also deduced from NMR data (above). According to an NBO analysis[19] of the electronic wavefunctions of the pyramidal compounds **2** and **3**, their N–Si bonds have less s character than have completely flattened systems like $NH(SiH_3)_2$. Fig. 4 shows the different contributions of Si and N s orbitals to the hybrid orbitals forming the N–Si bonds of **2**, **3** and $NH(SiH_3)_2$. The N atom of **2** contributes slightly more s character to the N–Si bond than does that of **3**, resulting in a lower $^1J(^{15}N^{29}Si)$ coupling constant for **3**, as also observed in the NMR experiment (see above). The planar compound $NH(SiH_3)_2$ has a much larger amount of s character in the N–Si bond, mainly originating from a larger amount of s in the silicon atomic orbital. Therefore, planar Si–N systems show larger $J(^{15}N^{29}Si)$ coupling constants than do the non-planar silylhydroxylamines, as discussed later. The different hybridization state of the nitrogen lone pair in $NH(SiH_3)_2$ (pure p) as compared with those of **2** and **3** is indicative of the different co-ordination geometries of nitrogen.

The results show that even the presence of two silyl substituents does not induce a flat geometry at nitrogen in silylhydroxylamines. The structure of these compounds is thus clearly determined by the electronic influence of the oxygen atoms. By contrast, the MP2(fc)/6-31 + G* geometry of **4** (Fig. 5) shows a clearly pyramidal nitrogen configuration (sum of angles at N is 321.2°) as expected for a non-silylated nitrogen atom in hydroxylamines.

Geometric parameters computed for compounds **2**, **3** and **5** compare well with those determined by X-ray diffraction for **1**. The greatest deviations occur for the Si–N distances. This can be attributed to the different substitution patterns, or to insufficiencies in the level of theory employed in the calculations.

Table 1 MP2(fc)/6-31 + G* (**2**, **3**, **5**) and crystallographic (**1**) molecular structure data (lengths in pm, angles in °)

	$(MeH_2Si)_2NOMe$ **2**	$(MeH_2Si)MeNOMe$ **3**	$(H_3Si)_2NOMe$ **5**	$[(p\text{-}MeC_6H_4)H_2Si]_2NOMe$ **1**
N–O	147.8	146.3	147.4	146.3
N–Si	176.8 (average)	177.7	176.3	172.8 (average)
O–C	143.5	143.2	143.6	142.4
Si–N–Si	128.7		130.3	131.1
Si–N–C		119.3		
Si–N–O	106.7 (average)	104.4	107.0	109.3
C–N–O		107.3		
C–O–N	107.9	107.8	107.7	109.3
Sums of angles at N				
	342.1	331.0	344.3	347.9

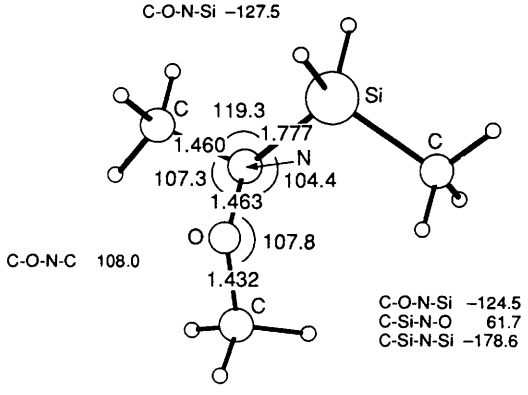


Fig. 3 Calculated molecular geometry of compound **3** (minimum-energy conformation)

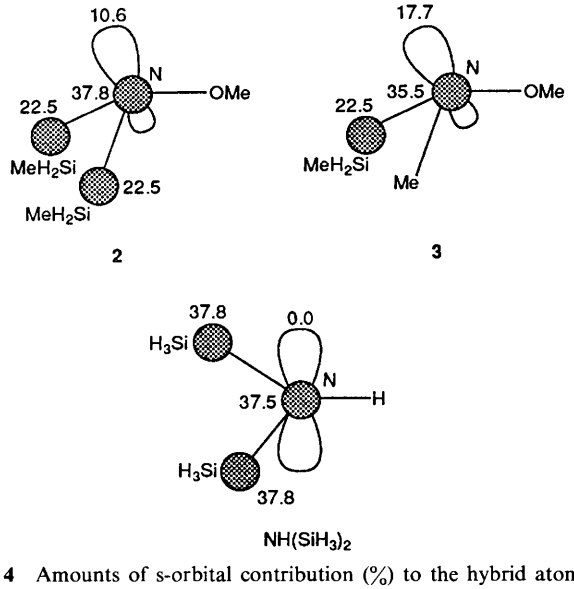


Fig. 4 Amounts of s-orbital contribution (%) to the hybrid atomic orbitals forming the N–Si bond, and s character of the nitrogen lone pairs in compounds **2**, **3** and $NH(SiH_3)_2$

The calculated barrier for nitrogen inversion in compound **5** amounts to as much as 9.7 kcal mol^{-1} at the MP4/6-311 + G*//MP2(fc)/6-31 + G* level and is thus much higher than that of NH_3 (5.8 kcal mol^{-1}) and $NH_2(SiH_3)$ (1 kcal mol^{-1}).[20] The discrepancy can be ascribed to lone-pair repulsion effects at neighbouring nitrogen and oxygen atoms. This effect seems also to be the major origin of the pyramidal co-ordination geometry at nitrogen. The calculated contour plots of the NLMOs (natural localized molecular orbitals) show a strong overlap of the lone pairs at N and O in the ground state and increased overlap for a planar configuration as in the transition state for

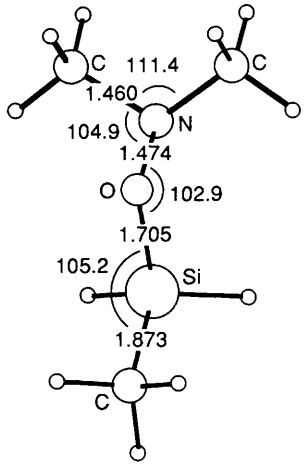


Fig. 5 Calculated molecular geometry of compound **4** (minimum-energy conformation)

nitrogen inversion (see above). The inversion at nitrogen must be accompanied by a rotation of the methoxy group around the N–O bond in order to yield another staggered conformation. A planar arrangement of the Si_2NOC skeleton (see Fig. 6 for optimized geometry) was confirmed to be a first-order saddle point on the potential-energy hypersurface by frequency calculation at the RHF/6-31G* level. The imaginary frequency (-172 cm^{-1}) corresponds to the combination of nitrogen inversion and rotation of the methoxy group around the N–O bond.

In the ground state calculated for compound **5** the H_3C group is placed in an antiparallel position relative to the silicon substituents at the nitrogen atom (*trans* conformation of lone pairs at N and O). For molecules **2** and **3** similar conformations are predicted. This conformation has been confirmed experimentally for compound **1** by a crystal-structure determination and for the methylated derivatives of hydroxylamine by an electron-diffraction study in the gas phase[21] and by *ab initio* studies.[22]

Calculations of NMR Chemical Shifts.—Compound **5**, which is the simplest of the molecules considered in the present paper, seemed to be a suitable candidate for chemical shift calculations at different levels of theory. We have calculated its ^{13}C, ^{15}N, ^{17}O and ^{29}Si NMR chemical shifts with the individual gauge for different localized orbitals (IGLO)[23] and the gauge-including atomic orbitals (GIAO)[24] method at the self consistent field (SCF) level, and in addition with the newly available GIAO-MP2 method[25] with t.z.p./d.z. basis sets (t.z.p. = triple zeta plus polarization for non-hydrogen atoms, d.z. = double zeta for hydrogen atoms)[26] for calculations including the effects of electron correlation. The results are shown in Table 2. The largest differences Δ between calculations at different levels of

theory are observed for $\delta(^{15}N)$ (25 ppm) and $\delta(^{17}O)$ (63 ppm), while Δ for $\delta(^{13}C)$ and $\delta(^{29}Si)$ are within the range of confidence for the comparison of calculated with experimental data. The calculated $\delta(^{15}N)$ value (at the highest level of theory) for the transition state of nitrogen inversion of molecule **5** is significantly different (10 ppm upfield) from $\delta(^{15}N)$ for **5** in the ground state. This indicates clearly the influence of the co-ordination geometry at the N atom on $\delta(^{15}N)$. As the transition state is less symmetrical than the ground state, the silicon atoms show different chemical shifts.

In order to reproduce the experimental chemical shift values of compounds **2–4**, IGLO calculations on these compounds were performed. The values of $\delta(^{15}N)$ and $\delta(^{17}O)$ were corrected for the level of theory by addition of the differences Δ listed in Table 2 and for the use of different standards in calculations and measurements [$\delta(^{15}N)$ of gaseous NH_3 is +400.9 *vs.* liquid $MeNO_2$;[27] $\delta(^{17}O)$ of gaseous H_2O is −36.1 *vs.* liquid H_2O[28]]. The corrected data are listed in Table 3 together with the experimentally obtained chemical shifts of **2–4**. The calculated $\delta(^{13}C)$ and $\delta(^{29}Si)$ chemical shifts fit excellently the experimental data, and after correction as mentioned above the $\delta(^{15}N)$ and $\delta(^{17}O)$ chemical shifts are also in the range of confidence of about 10 and 20 ppm respectively.[25b] The experimentally observed downfield shift of $\delta(^{29}Si)$ in the series of compounds **2–4** is also shown by the calculated $\delta(^{29}Si)$ values. The calculations confirm the unexpectedly low values of $\delta(^{17}O)$ for compounds with an oxygen atom bound to an electronegative nitrogen atom.[29]

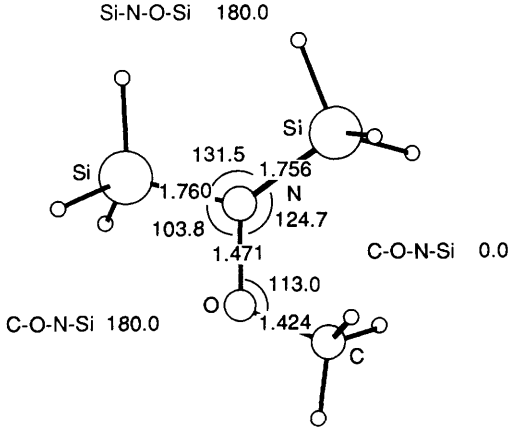


Fig. 6 Geometry of the transition state of the nitrogen inversion of compound **5** accompanied by a partial rotation around the N–O bond

Table 2 Dependence of calculated chemical shift data on the level of theory for compound **5** (transition state in parentheses) [standards: $\delta(^{13}C)$ and $\delta(^{29}Si)$, $SiMe_4$; $\delta(^{15}N)$, NH_3(gas); $\delta(^{17}O)$, H_2O(gas)]; Δ is the difference between the chemical shifts calculated with IGLO (II') and the GIAO-MP2 method

	IGLO (II')	GIAO-SCF/ t.z.p./d.z.	GIAO-MP2/ t.z.p./d.z.	Δ
$\delta(^{13}C)$	61.2 (57.9)	59.0 (54.9)	66.4 (62.3)	5
$\delta(^{15}N)$	109.1 (97.0)	122.1 (112.5)	134.3 (123.9)	25
$\delta(^{17}O)$	28.0 (27.7)	49.7 (47.8)	90.9 (89.0)	63
$\delta(^{29}Si)$	−48.9	−48.8	−56.5	−8
	(−46.5, −55.9)	(−45.6, −55.0)	(−51.0, −63.4)	

Vibrational Spectroscopy.—Normal modes of vibration of compounds **2** and **3** were deduced from the *ab initio* calculations and visualized by using a modified version of the program VIBRATE.[30] The results with assignments are listed in Table 4, and calculated and measured IR data for **3** are also presented in Fig. 7. Theoretical IR frequencies are scaled by 0.9 to correct for the harmonic oscillator model assumed in the computations.[19] Differences in states of aggregation (calculations, 'gas phase'; experiments, 'liquid phase') are additional sources for deviations.

The results are in good agreement with those of experimental IR studies and normal co-ordinate analyses of trimethylsilylhydroxylamines.[31,32] The ν(NO) band is at 1089w cm^{-1} for **2** and at 1061w cm^{-1} for **3**, while tris(trimethylsilyl)hydroxylamine shows this vibration at 1057 cm^{-1}.[32] In an earlier

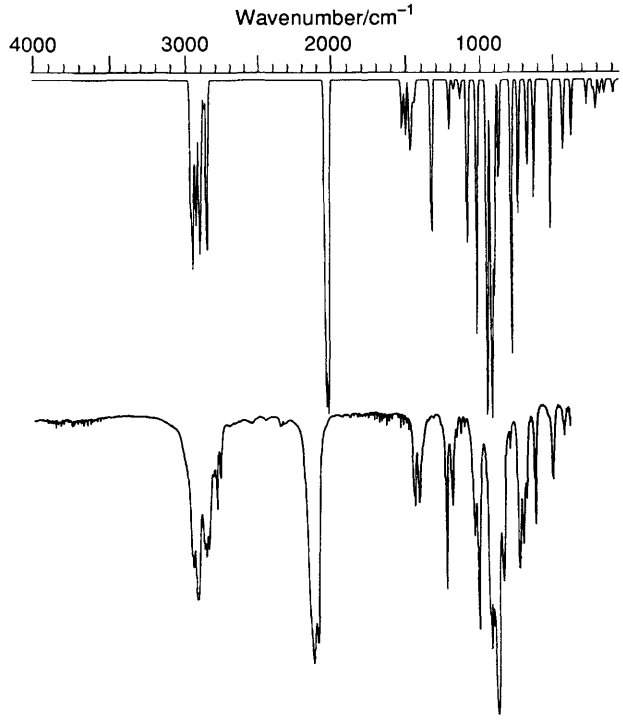


Fig. 7 Calculated (upper) and measured (lower) vibrational spectra of compound **3**

Table 3 Estimated theoretical* NMR chemical shifts of compounds **2–4** and experimental data for comparison [standards: $\delta(^{13}C)$ and $\delta(^{29}Si)$, $SiMe_4$; $\delta(^{15}N)$, $MeNO_2$(l); $\delta(^{17}O)$, H_2O(l)]. The $^1J(^{15}N^{29}Si)$ coupling constants of **2** and **3** are also listed

	2		**3**		**4**	
	calc.	exptl.	calc.	exptl.	calc.	exptl.
$\delta(^{13}C)$	62.3 (MeO)	63.0	60.1 (MeO)	60.7		
	−2.8 (MeSi)	−5.0	38.8 (MeN)	37.7	48.5 (MeN)	49.6
	−3.0 (MeSi)	−5.0	−4.5 (MeSi)	−7.1	−2.4 (MeSi)	−4.2
$\delta(^{15}N)$	−247	−248.1	−249	−249.1	−254	−247.9
$\delta(^{17}O)$	44	58.8	73	83.9	119	128.2
$\delta(^{29}Si)$	−26.7 (2×)	−29.4	−18.3	−21.8	−14.9	16.4
$^1J(^{15}N^{29}Si)$/Hz		11.5		10.4		

* Chemical shifts were estimated by correcting IGLO(II') results for the differences Δ (see Table 2) between IGLO(II') and GIAO-MP2/t.z.p./d.z. for compound **5** and taking into account the different references used in the calculations and experiments.

Table 4 Calculated and experimental IR spectroscopic data (cm^{-1}) for compounds **2** and **3** with assignments (calculated wavenumbers scaled by an empirical factor of 0.9)

2			3		
calc.	exptl.	Assignment	calc.	exptl.	Assignment
			2973, 2957	2966m	ν_{asym}[CH(O)]
2978, 2961	2951m	ν_{asym}[CH(O)]	2949, 2948	2943m	ν_{asym}[CH(Si)]
2946, 2943					
2934	2894w	ν_{asym}[CH(Si)]	2938, 2929	2879m	ν_{asym}[CH(N)]
2932	2807w	ν_{sym}[CH(O)]			
2899			2890, 2877,	2806m	ν_{sym}(CH)
2874, 2872	2767w	ν[CH(Si)]	2870	2779w	ν_{sym}(CH)
2147, 2136,					
2133, 2120	2150s	ν(SiH)	2133	2150s	ν_{asym}(SiH)
1496			2111	2121s	ν_{sym}(SiH)
1471	1465w	δ_{sym}[H_3C(O)]	1501, 1494,		
			1472, 1466,		
			1458		
			1448, 1442	1464w	δ_{sym}[H_3C(N,O)]
1456, 1447					
1440	1436w	δ_{sym}[H_3C(O)]	1439	1437w	δ_{sym}[H_3C(N,O)]
1445, 1442					
1308, 1307	1252s	δ_{sym}[H_3C(Si)]	1307	1253m	δ_{sym}[H_3C(Si)]
1206, 1169	1181w		1228, 1209	1212m	
			1169, 1150		
1123	1089w	ν(NO)	1128	1061w	ν(NO)
975	1031m	ν_{asym}(SiNSi)	1065	1035s	ν_{asym}(SiNC)
955, 950	974s	δ_{sym}(SiH_2)	965	952s	δ_{sym}(SiH_2)
942	935s	δ_{sym}(SiH_2)			
928	894s	ω(SiH_2), τ(CH_3Si)	921	908s	ω(SiH_2),τ(CH_3Si)
903					
879, 874	866s	ν_{sym}(NOC),τ(CH_3Si)	905	862m	ρ(CH_3Si)
			873		
760,748	751s	ρ(CH_3Si)	753	751m	ρ(CH_3Si)
			724	723m	τ(SiH_2)
726	697w	τ(SiH_2)	672		
675, 660, 646			622	641m	δ_{sym}(NSiCO)
550	561w	ω(SiNSi)			
497	515w	ρ(SiH_2)	502	522w	ρ(SiH_2)
488, 401, 300			441	444w	ω(SiNO)
241, 207, 180			378, 269, 222,		
176, 153, 134			207, 176, 153,		
128, 103, 52, 51			144, 99, 72		

investigation[31] ν(NO) of a series of (trimethylsilyl)hydroxylamines was assigned to strong absorptions at *ca.* 950 cm^{-1}. Unsubstituted H_2NOH exhibits the ν(NO) vibration at 895 cm^{-1} in the gas phase (926 cm^{-1} in the solid state).[33]

Experimental

All the reactions were carried out under an atmosphere of dry nitrogen. The solvents and triethylamine were dried over CaH_2 and distilled prior to use. All glassware was heated to 160 °C, evacuated and filled with dry nitrogen several times. NMR: JEOL JNM GX-400 spectrometer; spectra were taken from solutions in C_6D_6 at 25 °C with internal $SiMe_4$ (^1H, ^{13}C, ^{29}Si) and external $MeNO_2$ (^{15}N) or water (^{17}O) as standards. IR: Perkin-Elmer 1650 FT-IR spectrometer. GC–mass spectrometry: Hewlett-Packard HP 5890 chromatograph with 5971A mass-selective detector. Bromo(methyl)silane was prepared according to a published procedure[34] by protodesilylation of methylphenylsilane with liquid HBr. The free methylated hydroxylamines were prepared by modified literature methods.[35]

O-Methyl-N,N-bis(methylsilyl)hydroxylamine **2**.—A solution of *O*-methylhydroxylamine (4.50 cm^3, 86.8 mmol) and *N,N,N',N'*-tetramethylethylenediamine (12.9 cm^3, 86.8 mmol) was added dropwise to bromo(methyl)silane (21.7 g, 174 mmol) cooled to −78 °C. The mixture was allowed to warm slowly to ambient temperature and then heated to 60 °C for 2 h. All volatile products were condensed into a trap cooled with liquid nitrogen in a vacuum. After a second trap-to-trap condensation, distillation over a Vigreux column (20 cm) yielded 5.23 g (45%) of compound **2**, b.p. 97 °C. NMR: ^1H (399.78 MHz), δ 0.20 [t, 6 H, ^3J(HCSiH) = 3.6, H_3CSi], 3.39 (s, 3 H, H_3CO) and 4.58 (q, 4 H, H_2Si); ^{13}C (100.54 MHz), δ −5.0 [qt, ^1J(CH) = 121.0, ^2J(CSiH) = 9.2, CSi] and 63.0 [q, ^1J(CH) = 142.3, CO]; ^{15}N [distortionless enhancement of polarization transfer (DEPT), 40.51 MHz], δ −248.1 [s, ^1J(NSi) = 11.5]; ^{17}O-{^1H} (54.21 MHz), δ 58.8 (s); ^{29}Si, (DEPT, 79.43 MHz), δ −29.4 [tqt, ^1J(SiH) = 205.6, ^2J(SiCH) = 7.5, ^3J(SiNSiH) = 3.8 Hz]. Mass spectrum (GC coupled): *m/z* = 135 [M^+], 120 [$M^+ - CH_3$], 104 [100%, $(MeH_2Si)_2N^+$] and 90 [$M^+ - MeH_2Si$].

N,O-*Dimethyl-N-(methylsilyl)hydroxylamine* **3**.—The procedure was the same as described for compound **2**. Substances used: bromo(methyl)silane (10.0 g, 80 mmol), *N,O*-dimethylhydroxylamine (4.88 g, 80 mmol), tmen (6.5 cm^3, 44 mmol, 10% excess). Yield: 4.63 g (55%), b.p. 60–62 °C. NMR: ^1H (399.78 MHz), δ 0.12 [t, 3 H, ^3J(HCSiH) = 3.5, H_3CSi], 2.68 (s, 3 H, H_3CN), 3.33 (s, 3 H, H_3CO) and 4.33 (q, 2 H, H_2Si); ^{13}C (100.54 MHz), δ −7.1 [qt, ^1J(CH) = 115.2, ^2J(CSiH) = 8.7, CSi], 37.7 [qt, ^1J(CH) = 134.6, ^3J(CNSiH) = 1.6, CN] and 60.7 [q, ^1J(CH) = 141.7, CO]; ^{15}N-{^1H} (DEPT, 40.51 MHz), δ −249.1 [s, ^1J(NSi) = 10.4]; ^{17}O-{^1H} (54.21 MHz), δ 83.9 (s); ^{29}Si (DEPT, 79.43 MHz), δ −21.8 [tqq, ^1J(SiH) = 203.6, ^2J(SiCH) = 7.4, ^3J(SiNCH) = 5.4 Hz].

N,N-*Dimethyl*-O-(*methylsilyl*)*hydroxylamine* **4**.—The procedure was the same as described for compound **2**, bromo(methyl)silane (21.9 g, 175 mmol), *N*,*N*-dimethylhydroxylamine (10.7 g, 175 mmol) and tmen (13.0 cm^3, 86 mmol). Yield: 2.07 g (11%), b.p. 57–58 °C. NMR: ^1H (399.78 MHz), δ 0.18 [t, 3 H, ^3J(HCSiH) = 3.2, H_3CSi], 2.38 (s, 6 H, H_3CN) and 4.67 (q, 2 H, H_2Si); ^{13}C (100.54 MHz), δ −4.2 [qt, ^1J(CH) = 120.9, ^2J(CSiH) = 10.1, CSi] and 49.6 [qq, ^1J(CH) = 129.6, ^3J(CNCH) = 5.5, CN]; ^{15}N-{^1H} (DEPT, 40.51 MHz), δ −247.9 (s); ^{17}O-{^1H} (54.21 MHz), δ 128.2 (s); ^{29}Si (DEPT, 79.43 MHz), δ 16.4 [tq, ^1J(SiH) = 212.0, ^2J(SiCH) = 7.3 Hz].

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