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Silylhydroxylamines: Compounds with Unusual Nitrogen Coordination

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Five (arylsilyl)hydroxylamines (**1-5**) were prepared from the corresponding arylhalosilanes and alkylated hydroxylamines in the presence of triethylamine as an auxiliary base. The crystal structure of (*p*-tolH$_2$Si)$_2$NOMe (**3**) shows the Si$_2$NO group to be clearly pyramidal, a unique feature in Si/N chemistry. The conformation of the Si$_2$NOC skeleton is found to be the same as in alkylated hydroxylamines. The NMR spectra of all five elements present in the compounds (^{1}H, ^{13}C, ^{15}N, ^{17}O, ^{29}Si) have been measured and are discussed. In this context $^1J(^{15}N^{29}Si)$ coupling constants were found to reflect the unusual nitrogen hybridization in the pyramidal configuration.

Introduction

The coordination geometry of Si/N compounds has been the subject of considerable interest, particularly since almost all of these species exhibit the unusual planar arrangement of substituents at the nitrogen atoms.[1] This and other unique structural and chemical properties, such as short Si-N bonds and poor nitrogen basicity, led to extensive experimental and theoretical studies of this class of compounds.

For a long period of time, it was argued that the special bonding characteristics are the result of $p_\pi d_\pi$ interactions,[2] but a more sophisticated theoretical treatment showed that negative hyperconjugation[3] or an electrostatic repulsion model[4] can also be employed for a rationalization of most of the unexpected features of silylamines. The results of a large number of structural studies led to a widely accepted theorem that all *doubly* and *triply* silylated nitrogen atoms possess planar coordination.[5] It is only for selected *mono*silylated amines that pyramidal nitrogen has been observed,[6] while most of these are also planar.[7] In order to probe the limitations of nitrogen planarization, a large variety of silicon substituents with different steric and electronic effects have been investigated to date. However, only few other substitution patterns at silylated nitrogen atoms have been studied, with a few silyl*hydrazines* being the most important examples. As demonstrated in our laboratory, both tetrakis(phenylsilyl)hydrazine and the bicyclic 1,6-diaza-2,5,7,10-tetrasilabicyclodecane adopt a planar coordination at nitrogen,[8] thus confirming earlier studies.[9]

As a continuation of our systematic investigations on structures of Si/N compounds and of our search for new volatile single-source precursors for the chemical vapor deposition (CVD)[10] of Si$_3$N$_4$ and Si$_2$N$_2$O, we now present the synthesis and structural characterization of some silylated hydroxylamines (**1-5**).

Synthesis of the Silylhydroxylamines

The substitution patterns of the compounds described in the following were chosen such that steric effects at nitrogen (and oxygen) are small and do not obscure the basic electronic effects. Arylsilyl substituents bearing two hydrogen atoms bound to silicon have previously been shown to be sterically nondemanding and easy to accommodate in the packing of a given set of substituents. Moreover, their efficient packing generally leads to good crystallization properties of the compounds.

N,O-Dimethyl-*N*-(phenylsilyl)hydroxylamine (**1**), *O*-methyl-*N,N*-bis(phenylsilyl)hydroxylamine (**2**), and *O*-methyl-*N,N*-bis(*p*-tolylsilyl)hydroxylamine (**3**) have been prepared by silylation of the methylated hydroxylamines with chlorophenylsilane and chloro-*p*-tolylsilane, respectively. Triethylamine has proved to be a suitable dehydrohalogenation reagent. The relatively small phenylsilyl group can also be introduced in the sterically[1] quite crowded *N,O*-bis(dimethylsilyl)hydroxylamine, while in-

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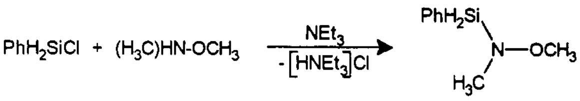

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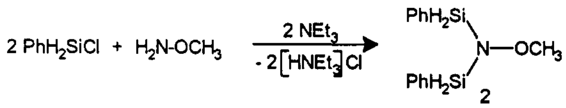

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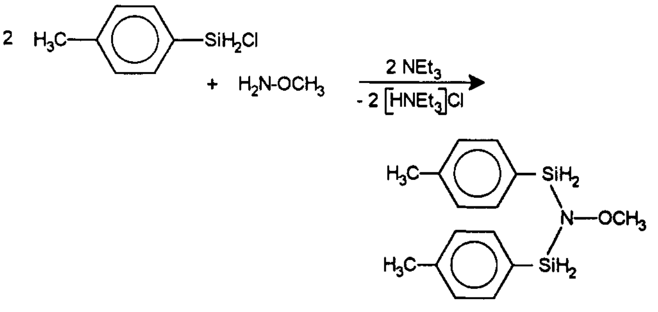

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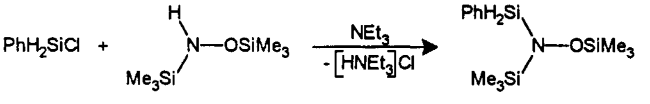
troduction of a third, more bulky trimethylsilyl group requires a metalation step.[11]



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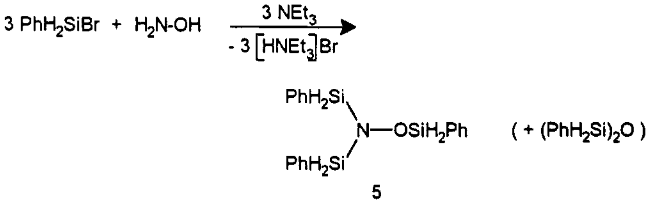
Hydroxylamines such as 4, with different silyl groups, undergo dyotropic rearrangement reactions as reported in more detail by West et al.[12] Silyl and methyl substituents do not exchange in this way. Therefore, distillation of the compounds 1–3 yields these products in high purity, while samples of 4 contain traces of rearrangement products even after careful distillation. All compounds are sensitive to moisture, owing to the hydrolysis of Si–N and Si–H functionalities, but can be stored under an inert atmosphere at ambient temperature for long periods of time.

Experiments aiming at the silylation of anhydrous H_2N–OH with chlorophenylsilane proceeded with vigorous evolution of hydrogen. The main product of the reaction was found to be 1,3-diphenyldisiloxane, and only small amounts of tris(phenylsilyl)hydroxylamine (5) could be detected by GC–MS analysis. 5 could not be separated by distillation.



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NMR Spectroscopic Studies

The compounds have been completely characterized by NMR spectroscopy for isotopes of all elements present in the molecules (^1H, ^{13}C, ^{15}N, ^{17}O, ^{29}Si). The chemical shifts and coupling constants of the nuclei ^1H, ^{13}C, and ^{29}Si are not outside the normal range established for standard silazanes and siloxanes. The chemical shifts of ^{17}O have been found to appear between 56 and 83 ppm and are thus unexpectedly low. Oxygen atoms with electronegative substituents in other classes of compounds such as peroxides or nitroxides (–O—N=O, =N—OH) appear to be less shielded.[13] The ^{15}N NMR shifts of the compounds 1–4 are similar, with the signals shifted downfield as compared with those of silylhydrazines and silylamines.

Table 1. ^{15}N Chemical Shift Values and $^1J(^{15}N^{29}Si)$ Coupling Constants of Arylsilyl-N Compounds

compd (no.)	$\delta(^{15}N)$ (ppm)		$^1J(^{15}N^{29}Si)$ (Hz)	
$(PhH_2Si)N(CH_2Ph)_2$	−355.1		21.2	
(p-tol$H_2Si)N(CH_2Ph)_2$	−364.7		20.9	
$(PhH_2Si)_2NCH_2Ph$	−365.2		14.3	
(p-tol$H_2Si)_2NH$	−389.3		13.8	
(p-tol$H_2Si)_2NCH_2Ph$	−374.7		14.3	
$(PhH_2Si)_2N$–$N(SiH_2Ph)_2$	−326.5		13.5	
$(PhH_2Si)_2N^a$–$N^bMe(SiH_2Ph)$	−332.8	−315.7	15.1 (N^a)	19.7 (N^b)
$(Ph)HN^a$–$N^b(SiH_2Ph)_2$	−287.4	−326.9		14.3 (N^b)
PhH_2SiPhN^a–$N^bH(SiH_2Ph)$	−300.4	−322.7	12.3 (N^a)	19.1 (N^b)
$(PhH_2Si)MeNOMe$ (**1**)	−249.9		11.2	
$(PhH_2Si)_2NOMe$ (**2**)	−249.7		11.9	
(p-tol$H_2Si)_2NOMe$ (**3**)	−248.9		11.6	
$(Me_3Si)(PhH_2Si)NO(SiMe_3)$ (**4**)	−256.0		8.7	

The most informative spectral parameter is the $^1J(^{15}N^{29}Si)$ coupling constant, taken from low-noise ^{15}N NMR spectra recorded using the DEPT technique. In a recent paper we have shown this coupling constant to be clearly dependent on the degree of silylation of a nitrogen atom and on the Si–N bond distance.[14] These correlations are in agreement with the widely quoted proportionality of $^1J(^{15}N^{29}Si)$ and the s character of the Si–N bond.[15]

As compared with other data for arylsilyl nitrogen compounds[8a,14] (Table 1), the $^1J(^{15}N^{29}Si)$ values of 1–4 are far too low, as electronegative substitution (oxygen) of the Si–N bond should generally increase this one-bond coupling constant. The phenomenon can be explained by a change of coordination geometry at nitrogen toward a pyramidal arrangement of the N substituents, which leads to reduced s character in the Si–N bonds (sp^2(planar) → sp^3(pyramidal)). This interpretation is confirmed by the crystal structure of 3, which is discussed in the following section.

It should be noted that a fixed pyramidal configuration at nitrogen requires the SiH_2 protons in all compounds (1–5) to be diastereotopic. From the observation that the NMR spectra (at 20 °C) show these protons to be equivalent on the NMR time scale, it follows that pyramidal inversion is rapid in solution at ambient temperature. This is not surprising, since it is known that N inversions of hydroxylamines have only low energy barriers of ≤ 10 kcal/mol.[16,19]

Crystal Structure of 3

Suitable solvent-free crystals of 3 could be grown by slowly cooling the melt to −20 °C. The resulting crystals

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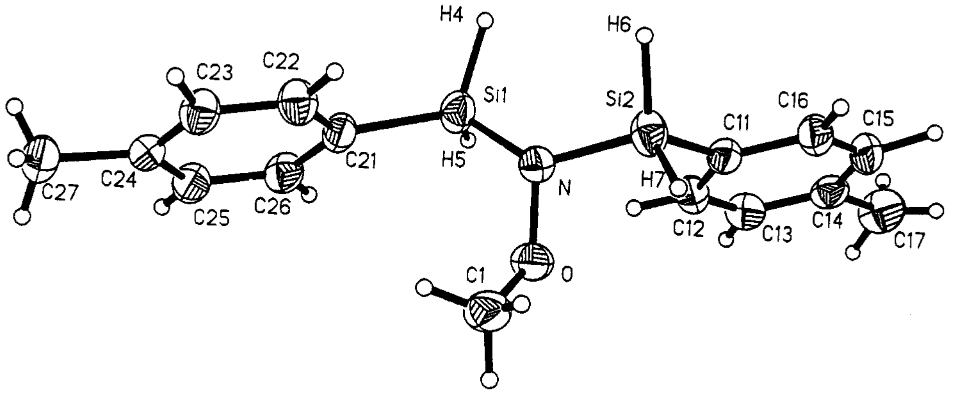

Figure 1. Molecular structure of 3.

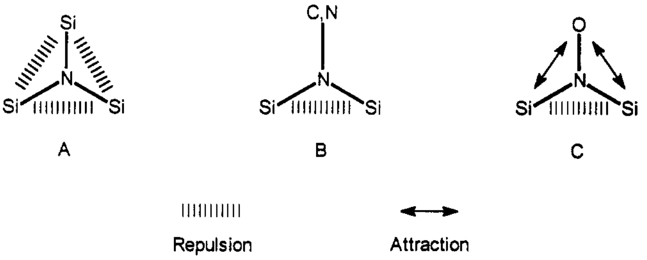

Figure 2. Schematic electrostatic bonding model for Si/N compounds.

Table 2. Selected Structural Data for 3

Bond Lengths (pm)			
N–O	146.3(2)	C11–C12	139.3(2)
N–Si1	172.4(1)	C12–C13	139.1(2)
N–Si2	173.1(1)	C13–C14	138.5(2)
O–C1	142.4(2)	C14–C17	151.6(2)
Si1–C21	184.8(1)	Si1–H4	143.3
Si2–C11	185.5(1)		
Bond Angles (deg)			
N–O–C1	109.3(1)	Si2–C11–C12	120.6(1)
O–N–Si1	108.4(1)	C11–C12–C13	121.6(1)
O–N–Si2	109.3(1)	C12–C13–C14	120.4(1)
Si1–N–Si2	131.1(1)	C13–C14–C15	118.7(1)
N–Si1–C21	114.6(1)	C13–C14–C17	120.0(2)
N–Si2–C11	113.4(1)		

sum of angles at N: 348.8°
dihedral angle (C1,O,N/Si1,N,Si2): 89.4°

belong to the orthorhombic system, space group $P2_12_12_1$ (No. 19). Selected structural parameters are listed in Table 2; the molecular geometry is presented in Figure 1. The molecules of **3** are monomeric in the crystal lattice and show no crystallographic symmetry.

The most striking structural result is the pyramidal coordination of the nitrogen atom. The sum of the angles is as low as 348.8°. This is a unique case in Si/N chemistry, in particular since compound **3** is the first example of a *doubly* silylated nitrogen atom, which is not completely flattened. The general concept that deviations from nitrogen planarity in Si/N systems occur only in singly silylated compounds[5a] should therefore be revised.

The structure of **3** is readily explained by a simple electrostatic model deduced from quantum-chemical calculations[4] (Figure 2). According to this treatment the planarity of trisilylamines (A) is the result of repulsive electrostatic interactions between Si atoms, which are positively polarized owing to the large difference in effective nuclear charges at N and Si.[17] This effect leads to the wide Si–N–Si angle in **3** (131.1(1)°). Conversely, the attraction of the positively polarized silicon and negatively polarized oxygen atoms leads to unusually small Si–N–O angles of 108.4(1) and 109.3(1)°. Similar structural features are to be expected for other Si/N compounds with strongly electron withdrawing substituents bound to nitrogen.

Unaffected by the formal oxidation state of nitrogen and its coordination geometry, both Si–N distances are in the range established for silylamines ($(PhH_2Si)_3N$, 173.5(1) pm;[1b] (p-tol$H_2Si)_3N$ average, 173.3 pm[18]) and silylhydrazines ($(PhH_2Si)_2NN(SiH_2Ph)_2$, average 172.8 pm[8a]). We attribute this finding to a compensation of electronegativity and hybridization effects. The introduction of oxygen causes not only a significant change in the polarization of nitrogen ($N^{\delta+}$–$O^{\delta-}$) but also a change in the configuration of nitrogen (planar → pyramidal) as compared with silylamines and silylhydrazines.

The N–O bond length is 146.3(2) pm and is therefore similar to those of hydroxylamine (147.6(3) pm[19]) and *O*-methylhydroxylamine (146.3(3)[20]). The conformation of the Si_2NOC skeleton shown in Figure 3 can be explained in terms of N- and O-atom lone pair repulsion and is in agreement with the conformations of non-silylated hydroxylamines, which have been the subject of both theoretical[21] and experimental[22] investigations. Our own studies have recently been complemented by ab initio calculations on small model systems, the results of which will be presented in a forthcoming paper.[23] In essence the calculations have shown that N/O lone pair repulsions are minimized in a trans conformation with two pyramidal atoms (O, N), as confirmed by the structural data presented.

Experimental Section

General Considerations. All 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 and evacuated and filled with dry nitrogen several times. NMR spectra were recorded on a JEOL JNM GX-400; the spectra were taken from solutions in C_6D_6 at 25 °C

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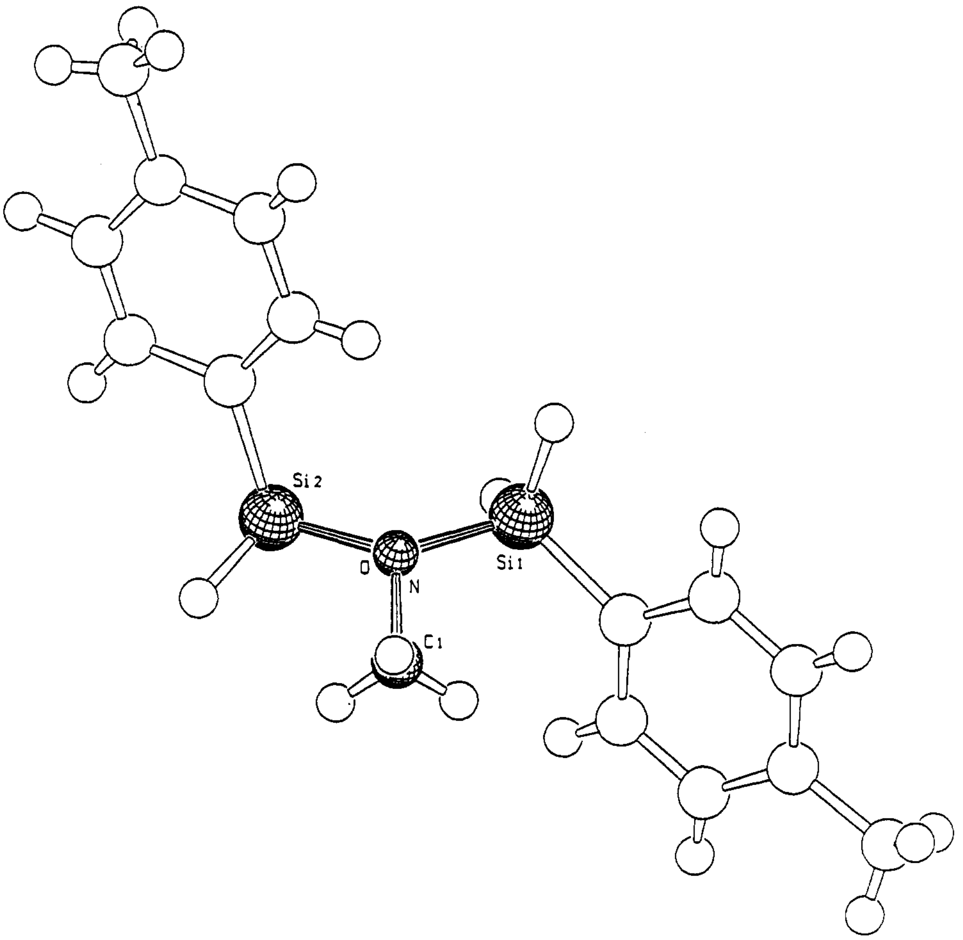

Figure 3. Projection of compound 3 along the O–N bond.

with internal TMS (^1H, ^{13}C, ^{29}Si) and external CH_3NO_2 (^{15}N) and H_2O (^{17}O) as standards, respectively. IR spectra were recorded on a Perkin-Elmer 1650 FT-IR and GC–MS on a Hewlett-Packard HP 5890 with 5971A mass selective detector. The starting materials chloroarylsilanes,[24] bromo(phenyl)silanes,[25] and alkylhydroxylamines[26] were prepared as described in the literature.

***N,O*-Dimethyl-*N*-(phenylsilyl)hydroxylamine (1).** Chlorophenylsilane (10 mL, 81 mmol) is added dropwise to a pentane solution of 4.95 g of *N,O*-dimethylhydroxylamine (81 mmol) and 11.2 mL of triethylamine (81 mmol). The mixture is heated to reflux for 1 h and then cooled to ambient temperature. The ammonium salts are filtered off, and the solvent is removed by distillation. The residue is distilled to yield 3.4 g of 1 (27%), bp 54 °C (1.5 mbar). ^1H NMR (399.78 MHz, C_6D_6, TMS, 25 °C): δ 2.47 [s, 3H, H_3CN], 3.04 [s, 3H, H_3CO], 4.71 [s, 2H, H_2Si], 6.85–6.91 [m, 3H, *m,p*-H], 7.35–7.38 [m, 2H, *o*-H]. $^{13}C\{^1H\}$ NMR (100.54 MHz, C_6D_6, TMS, 25 °C): δ 37.5 [s, CN], 60.6 [s, CO], 128.3 [s, *o*-C], 130.6 [s, *p*-C], 134.6 [s, *i*-C], 135.7 [s, *m*-C]. $^{15}N\{^1H\}$ NMR (DEPT, 40.51 MHz, C_6D_6, CH_3NO_2 external, 25 °C): δ −249.9 [s, $^1J(NSi)$ = 11.2 Hz]. $^{17}O\{^1H\}$ NMR (54.21 MHz, C_6D_6, H_2O external, 25 °C): δ 83.1 [s]. ^{29}Si NMR (DEPT, 79.43 MHz, C_6D_6, TMS, 25 °C): δ −25.3 [t t q m, $^1J(SiH)$ = 210.8 Hz, $^3J(SiCCH)$ = 5.0 Hz, $^3J(SiNCH)$ = 6.1 Hz]. IR (film): 2135 cm^{-1} (ν_{SiH}). Anal. Calcd for $C_8H_{13}NOSi$: C, 57.44; H, 7.83; N, 8.37. Found: C, 56.97; H, 7.61; N, 8.22.

***O*-Methyl-*N,N*-bis(phenylsilyl)hydroxylamine (2).** Bromophenylsilane (26.3 mL, 0.20 mol) is added dropwise to a solution of 5.0 mL of *O*-methylhydroxylamine (0.10 mol) and 27 mL of triethylamine (0.20 mol) in 250 mL of hexane. The mixture is stirred for 2 h and filtered, and the solvent is removed by distillation. The remaining liquid is distilled to yield 14.6 g of 2 (56%), bp 96–98 °C (0.01 mbar). ^1H NMR (399.78 MHz, C_6D_6, TMS, 25 °C): δ 3.29 [s, 3H, H_3C], 5.15 [s, 4H, H_2Si], 7.14–7.18 [m, 6H, *m,p*-H], 7.59–7.62 [m, 4H, *o*-H]. $^{13}C\{^1H\}$ NMR (100.54 MHz, C_6D_6, TMS, 25 °C): δ 62.9 [s, CH_3], 128.2 [s, *o*-C], 130.4 [s, *p*-C], 132.7 [s, *i*-C], 135.2 [s, *m*-C]. $^{15}N\{^1H\}$ NMR (DEPT, 40.51 MHz, C_6D_6, CH_3NO_2 external, 25 °C): δ −249.7 [s, $^1J(NSi)$ = 11.9 Hz]. $^{17}O\{^1H\}$ NMR (54.21 MHz, C_6D_6, H_2O external, 25 °C): δ 56.9 [s]. ^{29}Si NMR (DEPT, 79.43 MHz, C_6D_6, TMS, 25 °C): δ −31.19 [t t t, $^1J(SiH)$ = 212.9 Hz, $^3J(SiCCH)$ = 6.3 Hz, $^3J(SiNSiH)$ = 0.9 Hz]. Anal. Calcd for $C_{13}H_{17}NOSi_2$: C, 60.18; H, 6.60; N, 5.40. Found: C, 59.95; H, 6.73; N, 5.26.

***O*-Methyl-*N,N*-bis(*p*-tolylsilyl)hydroxylamine (3).** Chloro-*p*-tolylsilane (15.0 mL, 99 mmol) is dissolved in 100 mL of pentane and added slowly to a solution of 5.1 mL of *O*-methylhydroxylamine (99 mmol, 100% excess) and 7.4 mL of tetramethylethylenediamine (50 mmol, 100% excess) in 400 mL of pentane. After it is stirred for 1 h, the mixture is filtered, and the solvent is removed under reduced pressure. The remaining oily liquid crystallizes on slow cooling to −20 °C. Liquid impurities are decanted at −20 °C. This procedure is repeated to yield a total of 13.0 g of 3 (91%): mp 1–2 °C; bp 115–119 °C (0.01 mbar). ^1H NMR (399.78 MHz, C_6D_6, TMS, 18 °C): δ 2.06 [s, 6H, H_3C–C], 3.33 [s, 3H, H_3C–O], 5.23 [s, 4H, H_2Si], 6.99 [d, $^3J(HCCH)$ = 7.6 Hz, 4H, *m*-H], 6.59 [d, $^3J(HCCH)$ = 7.6 Hz, 4H, *o*-H]. $^{13}C\{^1H\}$ NMR (100.54 MHz, C_6D_6, TMS, 25 °C): δ 21.5 [s, CH_3–C], 63.0 [s, CH_3–O], 129.1 [s, *o*-C], 129.8 [s, *p*-C], 135.5 [s, *m*-C], 140.4 [s, *i*-C]. $^{15}N\{^1H\}$ NMR (DEPT, 40.51 MHz, C_6D_6, CH_3NO_2 external, 25 °C): δ −248.9 [s, $^1J(NSi)$ = 11.6 Hz]. $^{17}O\{^1H\}$ NMR (54.2 MHz, C_6D_6, H_2O external, 25 °C): δ 70.5 [s]. ^{29}Si NMR (DEPT, 79.43 MHz, C_6D_6, TMS, 25 °C): δ −31.4 [t t, $^1J(SiH)$ = 211.5 Hz, $^3J(SiCCH)$ = 6.1 Hz]. IR (film): 2150 s cm^{-1} (ν_{SiH}). MS (GC-coupled): *m/z* 287 [M$^+$], 271 [M$^+$ − H − CH_3], 254 [M$^+$ − 2H − H_3CO], 194 [100%, M$^+$ − 2H − $C_6H_4CH_3$], 164 [M$^+$ − 2H

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– $H_2SiC_6H_4CH_3$], 135, 119, 102, 91, 70. Anal. Calcd for $C_{15}H_{21}NOSi_2$: C, 62.66; H, 7.36; N, 4.87. Found: C, 62.84; H, 7.50; N, 4.92.

***N*-(Phenylsilyl)-*N,O*-bis(trimethylsilyl)hydroxylamine (4).** *N,O*-Bis(trimethylsilyl)hydroxylamine (8.7 g, 50 mmol) and 6.8 mL of triethylamine (50 mmol) are dissolved in 200 mL of pentane. Bromophenylsilane (6.8 mL, 50 mmol) is added dropwise to this solution, and the mixture is stirred for 3 h, heated to reflux for 20 min, and cooled overnight. The solvents are removed under reduced pressure, and the residue is distilled to yield 5.3 g of **4** (38%), bp 84–85 °C (0.01 mbar). ^1H NMR (100 MHz, C_6D_6, 25 °C): δ 0.14 [s, 9H, HCSiN], 0.18 [s, 9H, HCSiO], 5.13 [s, 2H, H_2Si], 7.05–7.16 [m, 3H, *m,p*-H], 7.51–7.72 [m, 2H, *o*-H]. ^{13}C NMR (100.54 MHz, C_6D_6, 25 °C): δ –0.4 [q, sept, ^1J(CH) = 119.0 Hz, ^3J(CSiCH) = 1.6 Hz, CSiO], 0.5 [q, sept, ^1J[CH) = 119.0 Hz, ^3J(CSiCH) = 1.6 Hz, CSiN], 127.7 [d, m, ^1J(CH) = 158.6 Hz, *o*-C], 129.8 [d t, ^1J(CH) = 159.0 Hz, ^2J(CCH) = 7.4 Hz, *p*-C], 133.5 [m, *i*-C], 134.9 [d m, ^1J(CH) = 158.1 Hz, *m*-C]. $^{15}N\{^1H\}$ NMR (DEPT, 40.51 MHz, C_6D_6, CH_3NO_2 external, 25 °C): δ –256.0 [s, ^1J(NSi) = 8.7 Hz (both Si)]. $^{17}O\{^1H\}$ NMR (54.21 MHz, C_6D_6, H_2O external, 25 °C): δ 63.8 [s]. ^{29}Si NMR (DEPT, 79.43 MHz, C_6D_6, TMS, 25 °C): δ –29.6 [t t pseudo q, ^1J(SiH) = 210.0 Hz, ^3J(SiCCH) = 6.2 Hz, $^{4,5}J$(Si-m,p-H) = 1.0 Hz, SiH_2], 10.3 [dec t, ^2J(SiCH) = 6.7 Hz, ^3J(SiNSiH) = 2.1 Hz, SiC_3–N], 27.7 [dec, ^2J(SiCH) = 6.6 Hz, SiC_3–O]. IR (film): 2156 s (νSiH). Anal. Calcd for $C_{12}H_{25}NOSi_3$: C 50.82, H 8.89, N 4.94. Found: C 50.51, H 9.13, N 5.18.

Reaction of Hydroxylamine with Bromophenylsilane. Hydroxylamine is prepared according to a procedure published by Hurd.[27] Anhydrous hydroxylamine (2.6 g, 79 mmol) is suspended in 500 mL of diethyl ether at 0 °C, and 32.8 g of triethylamine (237 mmol) is added, followed by 32.7 mL of bromophenylsilane. Large amounts of hydrogen are evolved. After the mixture is stirred for 5 h and the precipitate is filtered off, the solution is concentrated under vacuum, filtered again, and traces of solvents removed in vacuo. Distillation yields a fraction at 154 °C (0.01 mbar), which consists of a solution of 5% of tris(phenylsilyl)hydroxylamine (**5**) in 1,3-diphenyldisiloxane (GC/MS). MS (GC-coupled): *m/z* 351 [M^+], 272 [M^+ – Ph – 2H], 244 [M^+ – $PhSiH_2$], 227 [M^+ – PhH_2SiO – H], 195 [100%], 183, 166, 150.

Crystal and structure solution data for $C_{15}H_{21}NOSi_2$, 3: M_r = 287.5, orthorhombic, a = 7.637(1) Å, b = 11.521(1) Å, c = 18.687(1) Å, space group $P2_12_12_1$ (No. 19, *International Tables for X-ray Crystallography*), V = 1644.19 Å^3, Z = 4, D_c = 1.161 g cm^{-3}, T = –80 °C, μ(Mo Kα) = 2.1 cm^{-1}, λ(Mo Kα) = 0.710 69 Å, CAD4 diffractometer, 7744 reflections measured, 7433 unique, and 6987 observed [$F_o \geq 3.0\sigma(F_o)$]; no absorption correction applied. Structure solution by direct methods, with all missing atoms located by successive difference Fourier syntheses; refinement of 255 parameters converged at R = 0.0369 (R_w = 0.0392) ($R = [\sum||F_o| - |F_c||]/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/[wF_o^2]]^{1/2}$ with $w = [\sigma^2(F_o) + 0.000267F_o^2]^{-1}$); maximum and minimum residual electron densities in the difference Fourier map were +1.63 and –1.47 e Å^{-3}, respectively.

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Supplementary Material Available: Tables of crystal data and data collection and refinement details, the atom positions and thermal parameters for the hydrogen and non-hydrogen atoms, and bond distances and angles for **3** (10 pages). Ordering information is given on any current masthead page.

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