# Synthesis, Properties, and Structure of Poly(silyl)pyridines. The Phantom of Intramolecular Si−N Bonding

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2- and 3-silylpyridine (**2**, **3**) have been prepared from the corresponding bromopyridines either directly by metathesis reaction with $KSiH_3$ or via the lithiated pyridines and their reaction with halosilanes (in poorer yield). 3-Silylquinoline **4** was obtained from 3-lithioquinoline and tetra(ethoxy)silane followed by reduction with $LiAlH_4$. 4-Silylpyridine (**5**), 2,6-disilylpyridine (**9**), 5/6-methyl-2-silylpyridine (**6**, **7**), and 2-bromo-6-silylpyridine (**8**) were also obtained via the $KSiH_3$ route, and traces of pentasilylpyridine (**15**) have been detected among the products of the analogous reaction with pentabromopyridine. These compounds and the di- and tripyridylsilanes **10**−**13** have been characterized by their analytical and spectroscopic data. The crystal structures of **6**, **9**, and 5-methyl-2-*trimethylsilyl*pyridine (**16**) have been determined by low-temperature ("in situ") X-ray diffraction techniques. In all cases the silyl substituents in the 2-position show bending toward the nitrogen atom of the ring (with angles N−C−Si much smaller than 120°), suggesting a coordinative bonding of nitrogen to silicon. The structures are in excellent agreement with results of ab initio calculations (MP2/6-31G*) carried out for 2-silyl-, 3-silyl-, and 2,6-disilylpyridine. These calculations indicate, however, that the distortions are *not* due to direct (exocyclic) Si−N donor−acceptor bonding (as also suggested in the literature for *trimethylsilyl*pyridines), but originate from the changes in the electronic configuration of the heterocycle (as compared to benzene). This conclusion is supported by a review of structural data for methylpyridines and finally for pyridine itself: all these compounds show small N−C−X angles (X = H, C, Si in *ortho*-position to N) and similar distortions of the heterocycle. Ab initio quantum chemical calculations for pyridine (in the literature) and for 2,6-dimethylpyridine (this work) further corroborate the findings for these analogues. In summary therefore, there is no special "silicon effect" in the molecular and electronic structure of *ortho*-silylated pyridines. The physical properties of the compounds are best interpreted through the effect of the heteroatom N on the structure of the arene ring. In the crystal structures there is also no evidence for *inter*molecular donor−acceptor interactions, e.g., as described for the pentameric $[Me_3Si-NH_2]_5$.



## Introduction

There are many very pronounced differences in the chemistry of carbon and silicon compounds, and these differences are perhaps best reflected in a comparison of simple methyl and silyl analogues with the C/Si atoms solely substituted by hydrogen ($CH_3$/$SiH_3$). Classical examples are dimethyl ether versus methoxysilane and disiloxane,[1,2] trimethyl- versus dimethyl(silyl)-[3] and trisilylamine,[4] methyl- versus silylhydrazines[5,6] and -hydroxylamines,[7,8] neopentane versus tetrasilylmethane,[9] methylated versus silylated ylides,[10] dimethyl- versus disilylnaphthalines,[11] or finally hexamethyl- versus hexasilylbenzene.[12]

The reactivity pattern of the compounds not only is determined by the consequences of an *umpolung* of the E−H bond but also shows ready access to transition

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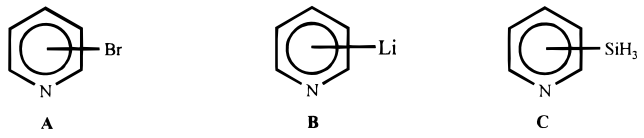
**Scheme 1**



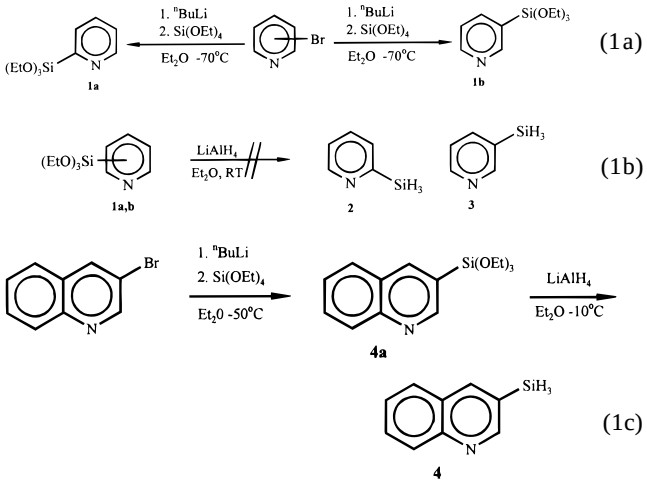

states with larger coordination numbers at silicon in nucleophilic substitution reactions or even to regular pentacoordinate silicon compounds as ground-state species. These phenomena are clearly associated with the smaller electronegativity, the larger atomic radius, and a different electronic configuration of silicon as compared to carbon. For several decades pertinent theoretical treatments have focused on d-orbital participation, and this picture is still the most descriptive model, even though advanced calculations have shown that this aspect may have been overestimated and should be complemented by a consideration of $\pi/\sigma^*$ interactions.[13]

There appears to be evidence from previous spectroscopic studies of *alkyl*silyl-substituted nitrogen heterocycles, like trimethylsilylpyridines, that *intra*molecular interactions between the nitrogen donor centers and the substituents in *ortho*-positions may modify the electronic and structural properties of such molecules.[14] The present report gives an account of our recent studies of *fully hydrogenated silylpyridines and related compounds*, which were undertaken not only for the above reasons but also because compounds of this type may be interesting substrates for dehydrogenative[15] and desilanative[16] coupling and similar reactions of synthetic interest.[17]

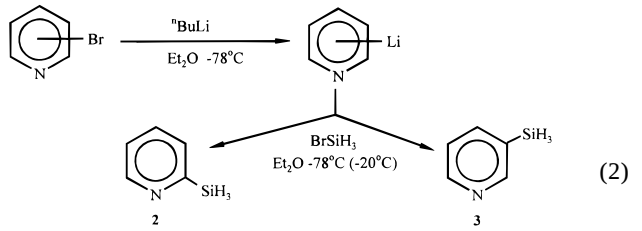
In the course of these studies the molecular structures of the C/Si-analogous picolines and of pyridine itself were reconsidered in order to treat the results on the silicon compounds in the proper context.

## Preparative Concepts

The literature has no report on the preparation of perhydrosilylated nitrogen heteroarenes such as silylpyridines, $C_5H_4N-SiH_3$ (**C**, Scheme 1). In the present work three approaches to silylpyridines **C** have been tested, as represented by eq 1−3. All three syntheses have bromopyridines **A** as the starting materials. These were metalated using organolithium reagents to give lithiopyridines **B**, which were treated with a tetraalkoxysilane to give the trialkoxysilyl systems **1a,b** (eq 1a) following procedures reported in the literature for silylarenes.[18] However, attempts to carry out a reduction of these intermediates using lithium aluminum hydride were not successful (eq 1b) except for the quinoline systems **4a, 4** (eq 1c).

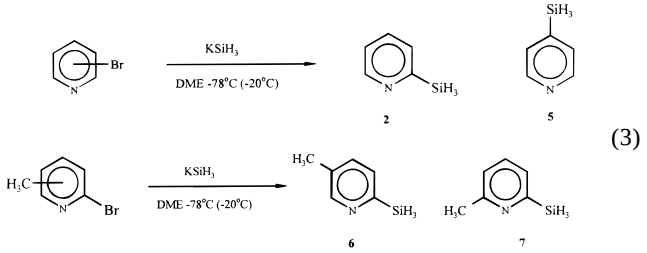



Because of this failure, the lithiopyridines **B** were reacted with bromosilane at very low temperature, and in the product mixture the expected target molecules 2- and 3-silylpyridine (**2, 3,** respectively) could indeed be identified, but the yields were low and purification of the products turned out to be extremely tedious (eq 2). The procedure is generally not a very attractive synthesis because of the adverse properties of bromosilane, $H_3SiBr$.




Compounds **A** were therefore treated with silylpotassium, obtained by reductive cleavage of disilane by potassium metal. This approach requires access to preparative quantities of disilane, and great care must be taken while handling solutions of the extremely sensitive reagent $KSiH_3$ (eq 3). With these precautions, the procedure gives the best results, and the two isomeric silylpyridines **2** and **5** and two isomeric silylmethylpyridines **6** and **7** could be prepared and isolated as colorless, distillable, air-sensitive liquids.

Depending on the molar ratio of the reagents, di- and triarylated silanes **10**−**13** were also obtained in small yields.




In exploratory experiments with dibromo- and pentachloropyridine as the staring materials, small quantities of the di- and pentasilylated pyridines **9** and **15** have also been detected, but only 2,6-disilylpyridine (**9**) could be isolated as a colorless liquid by fractional condensation. Partial silylation of 2,6-dibromopyridine gave the

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**Table 1. Crystal Data, Data Collection, and Structure Refinement for 6, 9, and 16**

| | 6 | 9 | 16 |
|---|---|---|---|
| **Crystal Data** | | | |
| empirical formula | $C_6H_9NSi$ | $C_5H_9NSi_2$ | $C_9H_{15}NSi$ |
| fw | 123.13 | 139.31 | 165.31 |
| cryst syst | monoclinic | orthorhombic | monoclinic |
| space group | $P2_1$ (No. 4) | $P2_12_12$ (No. 18) | $P2_1/c$ (No. 14) |
| $a$, Å | 6.1938(8) | 14.131(1) | 13.440(1) |
| $b$, Å | 6.6782(6) | 4.463(1) | 10.999(1) |
| $c$, Å | 8.8677(7) | 6.372(1) | 7.249(1) |
| $\beta$, deg | 99.962(9) | 90 | 95.64(1) |
| $V$, Å$^3$ | 361.27(6) | 401.82(5) | 1066.4(2) |
| $D_{calcd}$, g cm$^{-3}$ | 1.133 | 1.151 | 1.030 |
| Z | 2 | 2 | 4 |
| $\mu$ (Mo K$\alpha$), cm$^{-1}$ | 2.24 | 3.50 | 1.66 |
| cryst dimens, mm | 0.4 × 0.4 × 0.5 | 0.4 × 0.4 × 0.6 | 0.35 × 0.35 × 0.6 |
| **Data Collection** | | | |
| temp, K | 179 | 164 | 185 |
| scan mode | $\omega$-$\theta$ | $\omega/\theta$ | $\omega/\theta$ |
| $hkl$ ranges | 0→6; −8→8; −10→10 | −18→18, −5→5, −8→8 | 0→17, 0→14, −9→9 |
| measured reflns | 1360 | 3838 | 2408 |
| unique reflns | 1352 ($R_{int}$ = 0.0000) | 970 ($R_{int}$ = 0.0450) | 2315 ($R_{int}$ = 0.1041) |
| reflns used for refinement | 1352 | 970 | 2314 |
| **Refinement** | | | |
| least-squares parameters | 105 | 56 | 160 |
| final $R$ values [$I > 2\sigma(I)$]: | | | |
| R1[a] | 0.0467 | 0.0308 | 0.0539 |
| wR2[b] | 0.1167 | 0.0770 | 0.1381 |
| goodness-of-fit on $F^2$ | 1.069 | 1.153 | 1.056 |
| $\rho_{fin}$(max/min), e Å$^{-3}$ | 0.580/−0.160 | 0.385/−0.332 | 0.519/−0.391 |

[a] $R1 = \sum(||F_o|| - ||F_c||)/\sum|F_o|$. [b] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[s^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a$ = 0.0930 (**6**), 0.0535 (**9**), 0.1009 (**16**); b = 0.0543 (**6**), 0.0097 (**9**), 0.0905 (**16**).



2-bromo-6-silylpyridine (**8**). Likewise, 5-bromopyrimidine gave 5-silylpyrimidine (**14**) after treatment with $KSiH_3$.

All isolated silylpyridines were identified employing standard mass spectrometry and NMR and IR spectroscopy techniques. In representative cases, elemental analysis data have also been obtained (Experimental Section).

## Structural and Theoretical Studies

The simple (mono)silylpyridines **2**−**7** are colorless liquids with low melting points. It was only in the cases of 5-methyl-2-silylpyridine (**6**) and 2,6-disilylpyridine (**9**) that crystal growth experiments were successful, and the structures of these prototypes could therefore be determined (Table 1 and the Supporting Information). The single crystals were grown "in-situ" in a capillary on the diffractometer at low temperature using techniques that were successfully applied already for other silylated compounds.[19]

Crystals of 5-methyl-2-silylpyridine (**6**) are monoclinic, space group $P2_1$, with two formula units in the unit cell (at 179 K). In the lattice there is only one independent molecule with no crystallographically imposed symmetry.

A projection parallel to the pyridine ring (Figure 1) shows that both the methyl carbon and the silyl silicon atom are in the molecular plane. However, a projection perpendicular to the plane of the pyridine ring (Figure 2) reveals a striking distortion of the standard geometry by a leaning over of the *silyl* group toward the nitrogen atom. This leads to an increase of the Si−C1−C2 angle from ideally 120° to 124.0(2)° and a narrowing of the angle Si−C1−N to 114.79(14)°. Consequently, this bending produces a shortening of the peripheral exocyclic Si−N distance to 2.723(2) Å, which gives the impression of a sub-van der Waals contact.

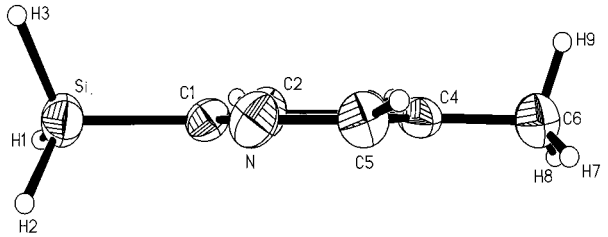


**Figure 1.** Molecular structure of **6** (ORTEP drawing with 50% probability ellipsoids). Projection parallel to the plane of the pyridine ring.

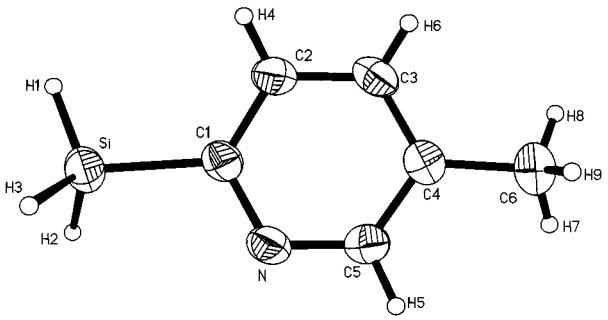


**Figure 2.** Molecular structure of **6** (ORTEP drawing with 50% probability ellipsoids). Projection perpendicular to the plane of the pyridine ring. Selected bond lengths [Å] and angles [deg]: Si−C1 1.869(2), N−C1 1.346(2), N−C5 1.334(3), C1−C2 1.388(3), C2−C3 1.380(3), C3−C4 1.377(3), C4−C5 1.386(3), C4−C6 1.507(3); Si−C1−N 114.79(14), Si−C1−C2 124.0(2), N−C1−C2 121.1(2), C3−C4−C5 116.9(2), C3−C4−C6 122.5(2), C5−C4−C6 120.6(2).

(19) Rudman, R. *Low-Temperature X-ray Diffraction Apparatus and Techniques*; Plenum Press: New York and London, 1976.

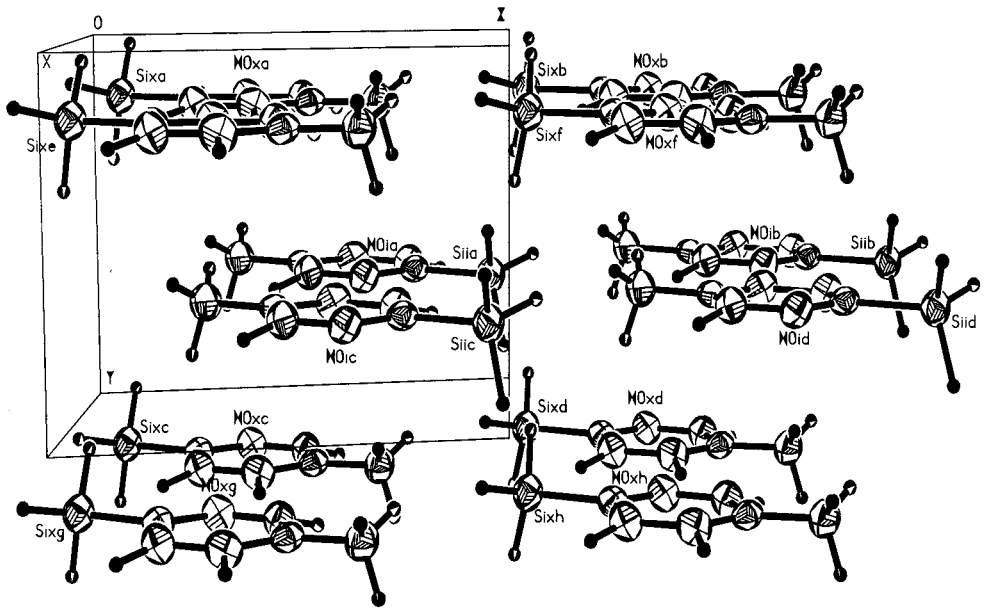


**Figure 3.** Packing diagram of **6**.

It should be noted that the 5-methyl group in the present compound **6** has angles C6−C4−C3/C5 very close to 120°.

The positions of the hydrogen atoms of the molecule have been found in the difference Fourier syntheses and refined isotropically to a precision that justifies a discussion of their location. It appears that the silyl group has a conformation that is roughly staggered relative to the nitrogen lone pair of electrons and thus has the right orientation for a donor−acceptor interaction (dihedral angle H1−Si−C1−N 168.5°; Figure 2). This orientation is preferred, although it puts the hydrogen atom H1 at silicon in an eclipsed position relative to the hydrogen atom H4 at the aryl ring.

By contrast, the conformation of the methyl group attains the standard methyl−arene orientation in which all short contacts of methyl and aryl hydrogen atoms are avoided. In the molecule **6** these contacts are minimized further and very significantly, by a bending of all three pyridine hydrogen atoms (H4, H5, H6) out of the molecular plane (Figure 1).

Intermolecular distances within the lattice are all rather large, and there is no indication that the distortions discussed above are caused by packing forces (Figure 3).

Crystals of 2,6-$(H_3Si)_2C_6H_3N$ (**9**) are orthorhombic, space group $P2_12_12$, with $Z = 2$ molecules in the unit cell. The geometry of the molecule follows the symmetry of a crystallographic 2-fold axis passing through the nitrogen atom and through the *para*-carbon atom C3 and its hydrogen atom H5 (Figure 4). As shown in a projection down this 2-fold axis (Figure 5), the two silicon atoms deviate slightly from the pyridine plane, and the $SiH_3$ groups are rotated away from the fully eclipsed conformation, thereby reducing the contacts between hydrogen atoms H1/H1′ and H4/H4′. There is no evidence for significant intermolecular contacts that could be held responsible for the configuration of the individual molecules (Figure 6).

The angles N−C1/C1′−Si/Si′ = 114.63(9)° and C2/C2′−C1/C1′−Si/Si′ = 123.85(11)° are again smaller and larger, respectively, than the 120° standard and lead

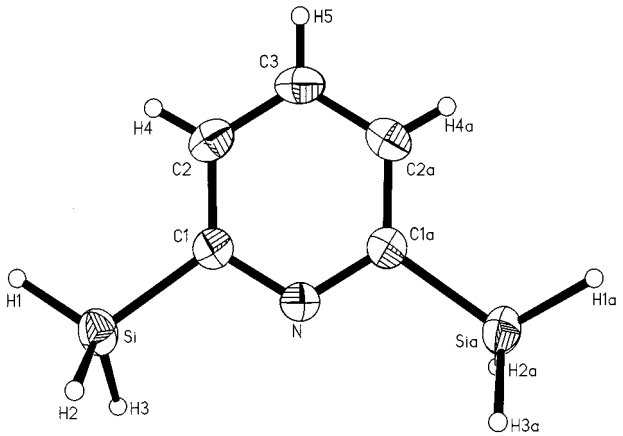


**Figure 4.** Molecular structure of **9** (ORTEP drawing with 50% probability ellipsoids). Projection perpendicular to the plane of the pyridine ring. Selected bond lengths [Å] and angles [deg]: Si−C1 1.8728(13), N−C1 1.3550(14), C1−C2 1.395(2), C2−C3 1.383(2); Si−C1−N 114.63(9), Si−C1−C2 123.85(11), N−C1−C2 121.51(12), C1−N−C1A 118.78(14), C1−C2−C3 119.85(14), C2−C3−C2A 118.5(2).

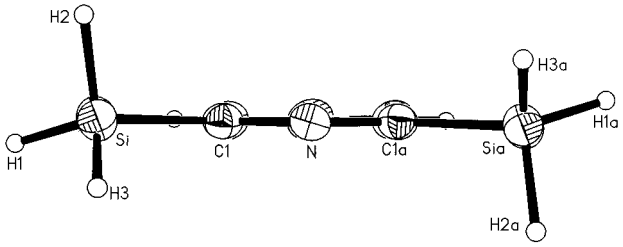


**Figure 5.** Molecular structure of **9** (ORTEP drawing with 50% probability ellipsoids). Projection down the 2-fold axis.

to peripheral distances Si/Si′−N = 2.731 Å, very similar to the dimensions found for 5-methyl-2-silylpyridine (**6**). This shows that the geometrical features are probably quite general for *ortho*-silylated pyridines.

To confirm this generalization a *trimethylsilylated* homologue (with a $SiMe_3$ instead of a $SiH_3$ group) was also included into the structural studies.

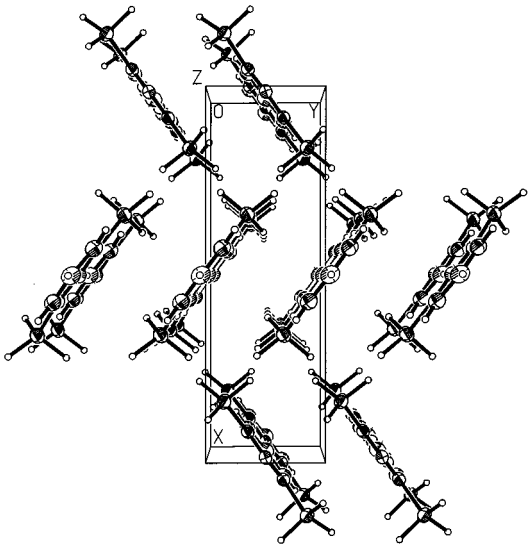


**Figure 6.** Packing diagram of **9**.

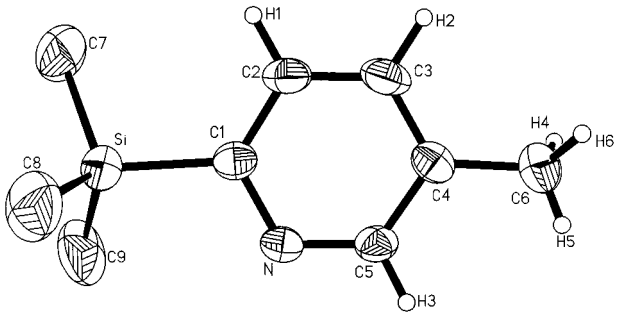


**Figure 7.** Molecular structure of **16** (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å] and angles [deg]: Si−C1 1.873(2), Si−C7 1.858(3), Si−C8 1.849(4), Si−C9 1.863(4), N−C1 1.357(3), N−C5 1.327(3), C1−C2 1.394(3), C2−C3 1.376(3), C3−C4 1.372(3), C4−C5 1.395(3), C4−C6 1.500(3); Si−C1−N 115.8(2), Si−C1−C2 124.6(2), N−C1−C2 119.6(2), C1−C2−C3 120.6(2), C2−C3−C4 120.0(2), C3−C4−C5 116.5(2), C4−C5−N 124.7(2), C5−N−C1 118.6(2), C3−C4−C6 122.3(2), C5−C4−C6 121.2(2), C1−Si−C7 108.5(2), C1−Si−C8 109.1(2), C1−Si−C9 108.3(2), C7−Si−C8 110.6(2), C7−Si−C9 109.8(3), C8−Si−C9 110.3(3).

5-Methyl-2-trimethylsilylpyridine (**16**) was synthesized following the literature procedure[14] for other trimethylsilylpyridines, and single crystals were grown using low-temperature techniques described above. The crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell. The molecular structure is shown in Figure 7 with selected geometrical details in the figure caption. It is obvious that it closely resembles that of the $H_3Si$-substituted analogue with an angle Si−C−N = 115.8(2)° and the corresponding angle Si−C1−C2 at 124.6(2)°. This tilting of the trimethylsilyl group toward the nitrogen atom leads to a Si−N distance of 2.749 Å, as compared to 2.723(2) Å for the 5-methyl-2-silylpyridine (**6**). By comparison, the exocyclic angles at C4 show only small deviations from the ideal 120° standard. The pyridine ring atoms and their hydrogen atoms are largely coplanar, and the conformation of the trimethylsilyl group relative to the ring nitrogen atom is close to staggered [C7−Si−C1−N 161.6°]. The rotational position is opposite that of the 5-methyl group.

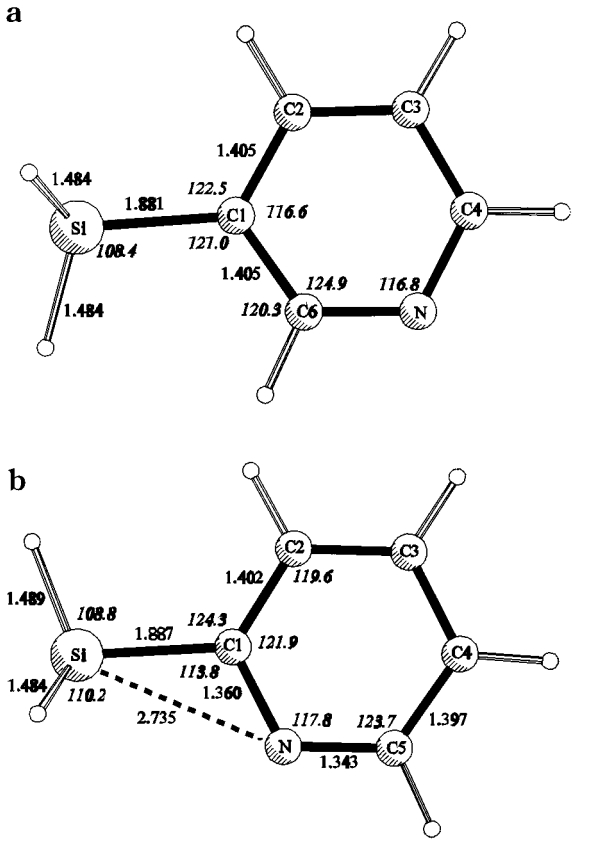


**Figure 8.** Molecular geometries of (a) **3** and (b) **2** as calculated ab initio (MP2/6-31G*).

In summary, the structures of 2-$H_3Si$− (**6**) and 2-$Me_3$-Si-5-methylpyridine (**16**) are surprisingly similar and show little sign of a marked influence of the methyl substitution at silicon.

Thus, tentatively, the results of the present structural study could be taken as evidence that there is indeed a significant intramolecular interaction of the silyl groups with the pyridine function as proposed in the literature.[14]

The experimental findings were therefore followed up by ab initio calculations[20] (up to the MP2/6-31G* level of theory) of the electronic configuration and the molecular ground-state geometry for both 3- and 2-silylpyridine (**3, 2**) and for 5-methyl-2-silylpyridine **(6)**. The results are shown in Figures 8a,b and 9. Clearly, the calculations have reproduced the experimental data for 5-methyl-2-silylpyridine (**6**) in a very satisfactory way. Calculated and experimentally determined Si−C−C/N angles agree within the experimental standard deviations, and the Si−N contacts are arrived at 2.735/2.737 Å for **2**/**6**, which compare very favorably with the X-ray value of 2.723(2) Å for **6**.

It is particularly noteworthy that no distortions of Si−C−C angles are calculated for 3-silylpyridine (**3**), where

(20) Calculations were performed using standard methods implemented in Gaussian 94: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople J. A. *Gaussian 94, Revision C.3*; Gaussian, Inc.: Pittsburgh, PA, 1995.

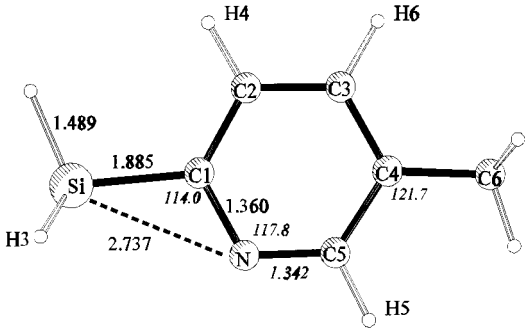


**Figure 9.** Molecular geometry of **6** calculated ab initio (MP2/6-31G*).

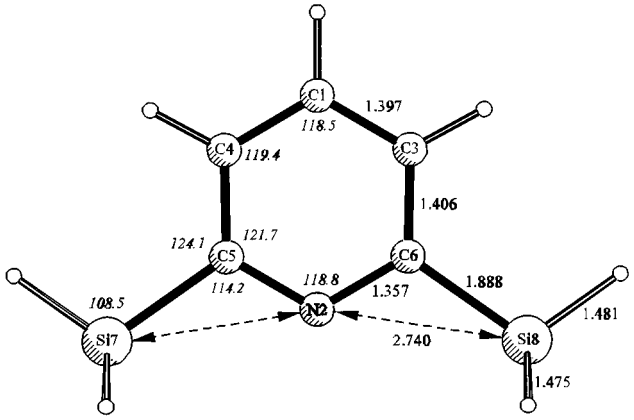


**Figure 10.** Molecular geometry of **9** calculated ab initio (MP2/6-31G*).

the nitrogen atom is "out of reach" of the silyl group (Figure 8a).

Ab initio calculations have also been carried out for 2,6-disilylpyridine (**9**). The results are shown in Figure 10. A bending of both silyl groups toward the nitrogen atom is predicted with angles Si−C−C and Si−C−N of 124.1° and 114.2°, respectively. The Si−N contacts (2.740 Å) are calculated to be not much longer than in 2-silylpyridine (**2**).

A natural bond orbital analysis (NBO) of **9** indicates that there is no significant interaction (through-space) between the nitrogen lone pair and the $\sigma^*$-orbitals of the Si−C/Si−H bonds of the exocyclic silyl groups of the type $lp_N \rightarrow \sigma^*$, whereas contributions of the type $lp_N \rightarrow \sigma^*_{C-C}$ (ring) seem to be important.

### NMR and IR Parameters of Silylpyridines

All silyl-pyridines and related compounds prepared in this study have been investigated by multinuclear NMR spectroscopy ($^1$H, $^{13}$C, $^{14}$N, $^{15}$N, $^{29}$Si) primarily in order to confirm their composition and structure. However, the chemical shift data and coupling constants are also instrumental to support the conclusions drawn from the structural data. Lukevics and his group have pointed out previously that the NMR data of some *trimethylsilyl*pyridines indicate abnormal values for the isomers with the substituent in 2-position possibly owing to intramolecular complexation.[14] The results of the present study not only show the same trend but even feature a much stronger effect.

The chemical shift $\delta(^{29}\text{Si})$ for 2-silylpyridine (**2**) is 4.9 ppm upfield from that of 3-silylpyridine (**3**), indicating a much stronger shielding of the silicon nucleus in the *ortho*-substituted compound. Conversely, the chemical

**Table 2. NMR Data [ppm] of Silyl-, Trimethylsilyl-, and Methylpyridines[14]**

| | R = $SiH_3$ | | R = $SiMe_3$ | | R = $CH_3$ |
|---|---|---|---|---|---|
| | $\delta(^{29}\text{Si})$ | $\delta(^{14}\text{N})$ | $\delta(^{29}\text{Si})$ | $\delta(^{14}\text{N})$ | $\delta(^{14}\text{N})$ |
|  | -62.4 | -68.5 | -3.75 | -71.1 | -61.7 |
|  | -67.3 | -38.7 | -5.46 | -50.5 | -62.6 |
|  | -62.9 | --- | -3.39 | -69.9 | --- |
|  | -64.2 | -15.4 | --- | --- | -62.4 |
|  | -63.0 | -42.7 | --- | --- | --- |
|  | -64.1 | -39.3 | --- | --- | -62.4 |
|  | -64.4 | -41.3 | -6.21 | --- | -62.2 |

shift $\delta(^{14}\text{N})$ for 2-silylpyridine (**2**) is −29.8 ppm downfield from the value for 3-silylpyridine (**3**), meaning a strong deshielding of the nitrogen nucleus in the former. For the $Me_3Si$-substituted reference compounds the effects are smaller, but in the same direction, with $\Delta\delta(^{29}\text{Si}) = 1.6$ ppm and $\Delta\delta(^{14}\text{N}) = -20.6$ ppm. Effects of the same direction and order of magnitude are observed for 2,6-disilylpyridine (**9**) and pentasilylpyridine (**15**) (Experimental Section). Finally, the data for *methyl*pyridines show only very minor variations in their $\delta(^{14}\text{N})$ data, barely exceeding the standard deviations of the measurements (Table 2). All data were measured consistently in benzene solvent with similar concentrations at ambient temperature.

Based on the geometries obtained in the ab initio calculations, the IR spectrum of 2-silylpyridine (**2**) has been simulated using standard programs. The agreement with the experimental spectrum is very satisfactory, proving the validity of the model chosen for the treatment of the data.

### Molecular and Electronic Structure of Pyridine and Methylpyridines

It is very tempting to deduce from the above structural and spectroscopic data (but ignoring the results of the theoretical calculations) that there is a significant intramolecular bonding interaction between the pyridine nitrogen atoms and the silicon atoms of substituents in the *ortho*-positions. A crucial test for the validity of this concept is of course the unbiased comparison with data for the carbon analogues, in particular of the *ortho*-methylpyridines and of pyridine itself.

The molecular structure of 2-methylpyridine is not known, neither for the gas phase nor for the crystal. 2,6-Dimethylpyridine has only been cocrystallized with hydrates of lithium salts, but 2-methylquinoline[21] and its 7-bromo derivative[22] have been structurally investigated as pure phases.

(21) Ribar, B.; Dijakovic, V.; Janic, J.; Argay, G.; Kalman, A.; Djuvic, S. *Cryst. Struct. Commun.* **1974**, *3*, 323.
(22) Sinha, D. P.; Gupta, S. B. *Z. Kristallogr.* **1981**, *155*, 47−52.

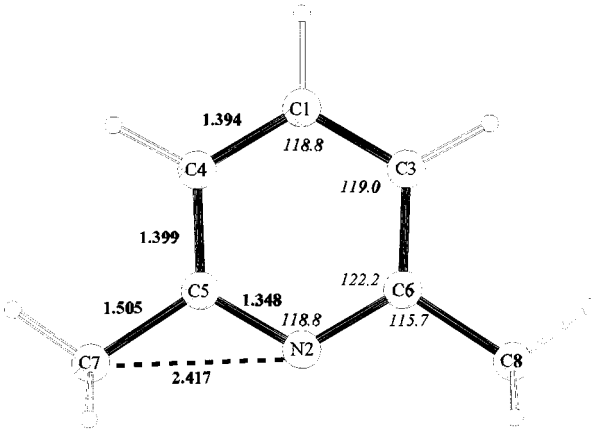


**Figure 11.** Molecular geometry of 2,6-dimethylpyridine calculated ab initio (MP2/6-31G*).

The literature data for 2,6-dimethylpyridine cocrystallized with $[Li(H_2O)_4)]^+ Cl^-$ show an N−C−$CH_3$ angle of 116.4°, while for 2-methylquinoline N−C−$CH_3$ = 115.3°.[23]

From these experimental data we therefore have every reason to believe that N−C−$CH_3$ angles in *ortho-methyl*pyridines are virtually the same as N−C−$SiH_3$ angles in *ortho-silyl*pyridines.

This suggestion is finally also supported by ab initio calculations using the same methods as employed for the silyl compounds (MP2/6-31G* level of theory). The result for 2,6-dimethylpyridine is shown in Figure 11. The N−C−$CH_3$ angle is predicted to be 115.7°, in good agreement with the experimental data. Like for the silyl analogues, the calculations show that the *trans*−*trans* conformation is the ground state (i.e., with the lone pair of electrons at the nitrogen atom and the methyl hydrogen atoms in the plane of the molecule in *trans*-positions), but *cis*−*trans* and *cis*−*cis* conformations are not much higher in energy (0.73 and 1.80 kJ $mol^{-1}$, respectively).

As for 2,6-disilylpyridine (**9**), the NBO analysis of 2,6-dimethylpyridine indicates that there is no significant direct interaction (through-space) between the nitrogen lone pair and the $\sigma^*$-orbitals of the C−C/C−H bonds of the exocyclic methyl group ($lp_N \rightarrow \sigma^*$). The distortion of the molecule away from the symmetrical benzene geometry is largely due to changes in the electronic configuration of the heterocycle.

This idea is finally also borne out by the structure of pyridine itself:[24] Electron diffraction, microwave, and infrared data, as well as ab initio calculations, have consistently shown that the *ortho*-hydrogen atoms of pyridine are bent toward the nitrogen atom, giving two angles N−C−H of 115.2°. There are also alternating endocyclic C−N−C, N−C−C, and C−C−C angles of 120 ± 5° as compared to benzene with its full $D_{6h}$ symmetry.

## Conclusions

The results of the present experimental and theoretical studies on silylpyridines, taken together with literature data for pyridine and methylpyridines, indicate that there is no experimental or theoretical basis for the assumption of direct (through-space, peripheral) silicon−nitrogen donor−acceptor bonding in these systems. The geometrical distortions of the pyridine rings and of their substituents away from benzene-type symmetry are common to hydrogen, methyl, and silyl substituents and not unique for the silicon compounds. The structural and spectroscopic characteristics are best explained through changes in the electronic configuration of the six-membered ring core upon introduction of the nitrogen heteroatom. It thus appears that silylpyridines are another class of organosilicon compounds where there is no need to invoke a special "silicon effect" (e.g., related to d-orbital participation) to rationalize experimental data.

## Experimental Section

**General Methods.** All experiments were carried out under a dry nitrogen atmosphere. Solvents were appropriately dried, distilled, and saturated with dry nitrogen; glassware was dried in an oven and filled with nitrogen. Starting materials were commercially available or prepared and purified according to published procedures: bromosilane,[25] potassium silanide.[26] $^1H$ NMR, $^{13}C$ NMR, $^{29}Si$ NMR, and $^{14}N$ NMR spectra were recorded with a JEOL JNM-GX 270 spectrometer ($^1H$ at 270.17 MHz, $^{13}C$ at 67.94 MHz, $^{29}Si$ at 53.67 MHz) or a JEOL JNM-GX 400 spectrometer ($^1H$ at 399.78 MHz, $^{13}C$ at 100.54 MHz, $^{29}Si$ at 79.43 MHz, $^{14}N$ at 28.90 MHz). Mass spectra were recorded with an analytical GLC-MS Hewlett-Packard 5890 Series II chromatograph (column HP1, cross-linked methylsilicon gum 12 m/0.2 mm, thickness of film 0.33 $\mu$m) with a mass-selective detector HP MS 5971 A (EI-MS 70 eV). IR spectra were recorded on a Midac FT-IR Prospect spectrometer. Microanalyses were performed in-house by combustion.

**3-Triethoxysilylpyridine (1b).** To a solution of 3-bromopyridine (8.5 g, 0.054 mol) in 30 mL of diethyl ether is added a solution of *n*-butyllithium in hexane (34.3 mL, 1.567 M, 0.054 mol) dropwise with cooling (−78 °C). A pale yellow solid is formed. After stirring at −78 °C for 45 min the mixture is added slowly to precooled (−78 °C) tetraethoxysilane (24.0 mL, 0.108 mol). After 1 h of stirring at this temperature the mixture is allowed to warm to room temperature. The solvent is evaporated and the residue extracted with 40 mL of pentane. The suspension is filtered, the solvent removed in vacuo, and the product separated by fractional distillation. The pale yellow liquid product (**1b**, yield 16%, 2.1 g) is collected at bp 75−78 °C/0.1 mbar. $^1H$ NMR ($C_6D_6$, 20 °C): $\delta$ 1.07 (t, $^3J_{HH}$ = 7 Hz, 9H, $CH_3$), 3.74 (q, $^3J_{HH}$ = 7 Hz, 6H, $CH_2$), 6.91 (dd, $^3J_{HH}$ = 7/5 Hz, 1H, pyridine−$H_5$), 7.80 (dm, $^3J_{HH}$ = 7 Hz, 1H, pyridine−$H_4$), 8.55 (dm, $^3J_{HH}$ = 5 Hz, 1H, pyridine−$H_6$), 9.04 (s, 1H, pyridine−$H_2$). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 20 °C): $\delta$ 18.3 ($CH_3$), 59.0 ($CH_2$), 123.3 ($C_5$), 128.2 ($C_3$ ipso), 142.3 ($C_4$), 151.6 ($C_6$), 155.6 ($C_2$). $^{29}Si\{^1H\}$ NMR ($C_6D_6$, 20 °C): $\delta$ −59.3 [s, Si(OEt)$_3$]. MS (EI, 70 eV): *m*/*z* 241 [$M^+$], 240 [$M^+$ − H, 100%], 226 [$M^+ - CH_3$], 212 [$M^+ - CH_2CH_3$], 196 [$M^+ - OCH_2CH_3$], 182 [$M^+ - OCH_2CH_3 - CH_3$], 168 [$M^+ - OCH_2CH_3 - CH_2CH_3$], 152 [$M^+ - 2OCH_2CH_3$], 106 [$M^+ - 3OCH_2CH_3$], 79 [$C_5H_5N^+$], 140, 63, 51. IR (KBr, film): $\nu$ 3035 [w, $\nu(CH)_{Aryl}$], 2980 and 2950 [w, $\nu(CH)_{Et}$], 1600/1580/1400 [s, $\nu$(C=C)], 967 [s, $\nu$(Si−O−C)]. $C_{11}H_{19}NO_3Si$ (241.4): found C 54.0, H 7.9, N 5.2; calcd C 54.8, H 7.9, N 5.8.

**2-Triethoxysilylpyridine (1a).** As described for **1b**, **1a** is prepared from 10 g (0.063 mol) of 2-bromopyridine and *n*-butyllithium (40.4 mL of a 1.567 M solution in hexane, 0.063 mol), followed by tetraethoxysilane (33 g, 0.158 mol). After

(23) Raston, C. L.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1988**, *41*, 413.
(24) Pyckhout, W.; Horemans, N.; Van Alsenoy, C.; Geise, H. J.; Rankin, D. W. H. *J. Mol. Struct.* **1987**, *156*, 315−329.
(25) Ward, L. G. L. *Inorg. Synth.* **1968**, *11*, 159.
(26) Feher, F.; Plichta, P.; Guillery, R. *Tetrahedron Lett.* **1970**, *51*, 4443.

purification by fractional distillation (96 °C/0.1 mbar), a pale yellow liquid is obtained. Yield: 1.52 g (10%). $^1$H NMR ($C_6D_6$, 22 °C): $\delta$ 1.22 (t, $^3J_{HH}$ = 7 Hz, 9H, $CH_3$), 4.04 (q, $^3J_{HH}$ = 7 Hz, 6H, $CH_2$), 6.68 (dd, $^3J_{HH}$ = 7/5 Hz, 1H, pyridine−$H_5$), 7.07 (dm, $^3J_{HH}$ = 7 Hz, 1H, pyridine−$H_4$), 7.72 (dm, $^3J_{HH}$ = 7 Hz, 1H, pyridine−$H_3$), 8.66 (s, 1H, pyridine−$H_6$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 22 °C): $\delta$ 18.5 ($CH_3$), 59.3 ($CH_2$), 123.7 ($C_5$), 130.9 ($C_3$), 133.8 ($C_4$), 150.4 ($C_6$), 163.1 ($C_2$ ipso). $^{29}$Si{$^1$H} NMR ($C_6D_6$, 22 °C): $\delta$ −66.6 [s, $Si(OEt)_3$]. MS (EI, 70 eV): *m/z* = 241 [$M^+$], 240 [$M^+$ − H, 100%], 226 [$M^+$ − $CH_3$], 212 [$M^+$ − $CH_2CH_3$], 196 [$M^+$ − $OCH_2CH_3$], 182 [$M^+$ − $OCH_2CH_3$−$CH_3$], 168 [$M^+$ − $OCH_2CH_3$−$CH_2CH_3$], 153 [$M^+$ − $2OCH_2CH_3$], 107 [$M^+$ − $3OCH_2CH_3$], 79 [$C_5H_5N^+$], 140, 125, 87, 63, 52. $C_{11}H_{19}NO_3Si$ (241.4): found C 54.5, H 7.7, N 5.4; calcd C 54.8, H 7.9, N 5.8.

**3-Triethoxysilylquinoline (4a).** To a cooled solution (−50 °C) of *n*-butyllithium in hexane (30.6 mL, 1.567 M, 0.048 mol) is added dropwise a solution of 3-bromoquinoline (10 g, 0.048 mol) in diethyl ether (30 mL). A yellow solid is formed. The mixture is stirred at −50 °C for about 15 min and then added dropwise to a cooled (−78 °C) solution of tetraethoxysilane (21.4 mL, 0.096 mol) with vigorous stirring. Stirring and cooling is continued for 1 h, and then the reaction mixture is allowed to warm to room temperature. The solvent is removed under reduced pressure, and the residue is extracted three times with a total of 50 mL of pentane. The salts are removed by filtration, and the solvent is distilled off using a slight vacuum. The residue is fractionized at 111 °C/0.1 mbar to give 2.98 g (yield 21%) of 3-triethoxysilylquinoline as a slightly orange liquid. $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 1.26 (t, $^3J_{HH}$ = 7 Hz, 9H, $CH_3$), 3.92 (q, $^3J_{HH}$ = 7 Hz, 6H, $CH_2$), 7.47 (dd, $^3J_{HH}$ = 7 Hz, 1H, quinoline−$H_6$), 7.66 (dd, $^3J_{HH}$ = 7 Hz, 1H, quinoline−$H_7$), 7.77 (d, $^3J_{HH}$ = 8 Hz, 1H, quinoline−$H_5$), 8.12 (d, $^3J_{HH}$ = 8 Hz, 1H, quinoline−$H_8$), 8.50 (s, 1H, quinoline−$H_4$), 9.16 (s, 1H, quinoline−$H_2$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 20 °C): $\delta$ 17.9 ($CH_3$), 58.5 ($CH_2$), 124.0 ($C_3$ ipso), 126.2 ($C_6$), 127.2 ($C_{4a}$), 127.6 ($C_5$), 129.1 ($C_7$), 130.0 ($C_8$), 144.1 ($C_4$), 148.6 ($C_{8a}$), 154.0 ($C_2$). $^{29}$Si-{$^1$H} NMR ($C_6D_6$, 20 °C): $\delta$ −59.2 [s, $Si(OEt)_3$]. MS (EI, 70 eV): *m/z* = 291 [$M^+$], 290 [$M^+$ − H, 100%], 276 [$M^+$ − $CH_3$], 262 [$M^+$ − $CH_2CH_3$], 246 [$M^+$ − $OCH_2CH_3$], 218 [$M^+$ − $OCH_2$-$CH_3$−$CH_2CH_3$], 202 [$M^+$ − $2OCH_2CH_3$], 156 [$M^+$ − $3OCH_2$-$CH_3$], 129 [$C_9H_6N^+$], 147, 102, 95, 63. $C_{15}H_{21}NO_3Si$ (291.9): found C 61.0, H 7.3, N 4.4; calcd C 61.7, H 7.2, N 4.8.

**3-Silylquinoline (4).** To a solution of 2.5 g (9 mmol) of **4a** in 30 mL of diethyl ether is added a suspension of lithium aluminum hydride (268 mg, 7 mmol) in 10 mL of diethyl ether at −10 °C with stirring. After 15 min, the temperature is allowed to reach 20 °C, and stirring is continued for 3 h. A 30 mL portion of pentane is added, the mixture is filtered, and the solvent is removed in vacuo. The remaining oil is fractionally distilled to give a nearly colorless liquid. Yield: 342 mg (25%; mp ca. −20 °C). $^1$H NMR ($C_6D_6$, 19 °C): $\delta$ 4.06 (s, $^1J_{SiH}$ = 206 Hz, 3H, $SiH_3$), 7.15 (dd, $^3J_{HH}$ = 7 Hz, 1H, quinoline−$H_6$), 7.30 (dd, $^3J_{HH}$ = 7 Hz, 1H, quinoline−$H_7$), 7.35 (dm, $^3J_{HH}$ = 7 Hz, 1H, quinoline−$H_5$), 7.79 (s, 1H, quinoline−$H_8$), 8.21 (d, $^3J_{HH}$ = 7 Hz, 1H, quinoline−$H_4$), 8.93 (s, 1H, quinoline−$H_2$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 19 °C): $\delta$ 121.1 ($C_3$ ipso), 126.6 ($C_6$), 127.7 ($C_{4a}$), 127.8 ($C_5$), 129.4 ($C_7$), 130.3 ($C_8$), 144.8 ($C_4$), 149.2 ($C_{8a}$), 154.8 ($C_2$). $^{29}$Si NMR (DEPT, $C_6D_6$, 19 °C): $\delta$ −61.5 [q, $^1J_{SiH}$ = 204 Hz, $^3J_{SiH}$ = 6.8/3 Hz, $SiH_3$]. $^{15}$N NMR (DEPT, $C_6D_6$, 19 °C): $\delta$ = −67.6 [dd, $^2J_{NH}$ = 11 Hz, $^3J_{NH}$ = 2 Hz, quinoline−N]. MS (EI, 70 eV): *m/z* = 159 [$M^+$], 158 [100%, $M^+$ − H], 130 [$M^+$ − SiH], 128 [$M^+$ − $SiH_3$], 115, 105, 89, 79, 63, 55. IR (KBr, film): $\nu$ 3061 [m, $\nu$(CH)$_{Aryl}$], 2160 [s, $\nu$(SiH)], 1618/1580/1566/1487 [s, $\nu$(C=C) and $\nu$(C=N)$_{Aryl}$]. $C_9H_9NSi$ (159.8): found C 67.2, H 5.5, N 11.0; calcd C 67.6, H 5.6, N 11.4.

**3-Silylpyridine (3).** A solution of 3-bromopyridine (12.8 g, 0.081 mol) in 80 mL of diethyl ether is added dropwise with stirring to a solution of *n*-butyllithium (48.7 mL, 1.567 M, 0.081 mol) in hexane at − 40 °C. Stirring is continued for 15 min, and then 9.0 g (0.081 mol) of bromosilane is condensed into the mixture at −196 °C. The reaction mixture is allowed to warm to −78 °C with vigorous stirring. After stirring for 90 min at −40 °C the formation of a white solid can be observed. Subsequently, the mixture is allowed to warm to room temperature. After condensing off all volatile products from the salts, the product can be isolated by fractional condensation (−20 °C, −78 °C, −96 °C, −196 °C). The product **3** is a colorless liquid (bp ca. 142 °C, yield 1.23 g, 14%). $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 4.15 (s, $^1J_{SiH}$ = 205 Hz, 3H, $SiH_3$), 7.21 (dd, $^3J_{HH}$ = 7/5 Hz, 1H, pyridine−$H_5$), 7.81 (dt, $^3J_{HH}$ = 7 Hz, 1H, pyridine−$H_4$), 8.56 (dd, $^3J_{HH}$ = 5 Hz, 1H, pyridine−$H_6$), 8.69 (s, 1H, pyridine−$H_2$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 20 °C): $\delta$ 123.4 ($C_5$), 128.2 ($C_3$ ipso), 143.4 ($C_4$), 150.9 ($C_6$), 155.7 ($C_2$). $^{29}$Si NMR (DEPT, $C_6D_6$, 20 °C): $\delta$ −62.4 [q, $^1J_{SiH}$ = 205 Hz, $SiH_3$]. $^{14}$N NMR ($C_6D_6$, 20 °C): $\delta$ −68.5 [s, pyridine−N]. MS (EI, 70 eV): *m/z* 110 [$M^+$ + 1], 109 [100%, $M^+$], 108 [$M^+$ − H], 80 [$M^+$ − SiH], 78 [$C_5H_4N^+$], 74, 68, 59, 63, 55. IR (gas): $\nu$ 3070 [m, $\nu$(CH)$_{Aryl}$], 2169 [s, $\nu$(SiH)], 1580/1566/1463 [s, $\nu$(C=C) and $\nu$-(C=N)$_{Aryl}$].

**2-Silylpyridine (2).** As described for **3, 2** is prepared from 8.54 g (0.054 mol) of 2-bromopyridine, *n*-butyllithium (31.8 mL of a 1.7 M solution in hexane, 0.054 mol), and 6.0 g of bromosilane (0.054 mol). After purification by fractional condensation (−20 °C, −78 °C, −96 °C, −196 °C), a colorless liquid is isolated in the − 20 °C trap. Yield: 0.30 g (5%). $^1$H NMR ($C_6D_6$, 18 °C): $\delta$ 4.17 (s, $^1J_{SiH}$ = 203 Hz, 3H, $SiH_3$), 6.88 (dd, $^3J_{HH}$ = 7/5 Hz, 1H, pyridine−$H_5$), 7.22 ($\psi$t, $^3J_{HH}$ = 7 Hz, 1H, pyridine−$H_4$), 7.32 (d, $^3J_{HH}$ = 5 Hz, 1H, pyridine−$H_3$), 8.55 (d, $^3J_{HH}$ = 5 Hz, 1H, pyridine−$H_6$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 18 °C): $\delta$ 122.4 ($C_5$), 128.3 ($C_3$), 134.1 ($C_4$), 150.4 ($C_6$), 158.6 ($C_2$ ipso). $^{29}$Si NMR (DEPT, $C_6D_6$, 18 °C): $\delta$ −67.3 [q, $^1J_{SiH}$ = 202 Hz, $SiH_3$]. $^{14}$N NMR ($C_6D_6$, 18 °C): $\delta$ −38.7 [s, pyridine−N]. MS (EI, 70 eV): *m/z* 110 [$M^+$ + 1], 109 [100%, $M^+$], 107 [$M^+$ − 2H], 80 [$M^+$ − SiH], 78 [$C_5H_4N^+$], 67, 57, 54. IR (gas): $\nu$ 3030 [m, $\nu$(CH)$_{Aryl}$], 2163 [s, $\nu$(SiH)], 1580/1566/1463 [s, $\nu$(C=C) and $\nu$(C=N)$_{Aryl}$].

**Alternative Synthesis.** To a solution of 2-bromopyridine (2.0 g, 0.013 mol) in 20 mL of dimethoxyethane (DME) is added rapidly a precooled solution of potassium silanide in DME (16.2 mL, 0.82 M, 0.013 mol) with cooling (−78 °C). A white solid is formed. The resulting suspension is stirred for 3 h and then allowed to warm to room temperature. The precipitate is separated and the solvent removed by distillation. The residue is fractionally condensed (−20 °C, −78 °C, −96 °C, −196 °C) to give **2** as a colorless liquid in the −20 °C-trap. Yield: 400 mg (28%). $^{13}$C NMR (DEPT, $C_6D_6$, 19 °C): $\delta$ 122.4 (d$\psi$t, $^1J_{CH}$ = 163 Hz, $^2J_{CH}$ = 7 Hz, $C_5$), 128.5 (d, $^1J_{CH}$ = 161 Hz, $C_3$), 133.9 (dd, $^1J_{CH}$ = 161 Hz, $^2J_{CH}$ = 7 Hz, $C_4$), 150.8 (d, $^1J_{CH}$ = 174 Hz, $C_6$). $C_5H_7NSi$ (109.3): found C 54.5, H 6.5, N 12.4; calcd C 54.9, H 6.4, N 12.8.

**4-Silylpyridine (5).** To a suspension of 4-bromopyridine hydrochloride (3.13 g, 16.1 mmol) in 50 mL of pentane, triethylamine (2.5 mL, 17.7 mmol) is added slowly and then the mixture is refluxed overnight. The white precipitate is separated, and the product is distilled. 4-Bromopyridine is dissolved in 20 mL of dimethoxyethane (DME) and cooled to −78 °C. The reaction with $KSiH_3$ is carried out as described for **2** (alternative synthesis) with potassium silanide (21.6 mL of a 0.82 M solution in DME, 17.7 mmol). Product **5** can be isolated by fractional condensation (−10 °C, −22 °C, −196 °C) and collected at −10 °C as a colorless liquid. Yield: 142 mg (8%). $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 4.23 (s, $^1J_{SiH}$ = 205 Hz, 3H, $SiH_3$), 6.68 (dd, $^3J_{HH}$ = 6 Hz, 2H, pyridine−$H_{3,5}$), 8.51 (d, $^3J_{HH}$ = 6 Hz, 2H, pyridine−$H_{2,6}$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 20 °C): $\delta$ 123.5 ($C_{3,5}$), 135.2 ($C_4$ ipso), 150.3 ($C_{2,6}$). $^{29}$Si NMR (DEPT, $C_6D_6$, 20 °C): $\delta$ −62.9 [q, $^1J_{SiH}$ = 204 Hz, $SiH_3$]. MS (EI, 70 eV): *m/z* = 110 [$M^+$ + 1], 109 [100%, $M^+$], 107 [$M^+$ − 2H], 80 [$M^+$ − SiH], 79 [$C_5H_4N^+$], 68, 58.

**5-Methyl-2-silylpyridine (6).** As described for **2 (5)**, **6** is prepared from 2-bromo-5-methylpyridine (3.0 g, 17.4 mmol) in 75 mL of dimethoxyethane (DME) and a solution of potassium silanide in DME (23.3 mL, 0.82 M, 19.2 mmol).

After purification by fractional condensation (0 °C, −15 °C, −196 °C) **6** can be separated as a colorless liquid (mp −15 °C, 365 mg, 17%). $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 1.73 (s, 3H, $CH_3$), 4.38 (s, $^1J_{SiH}$ = 203 Hz, 3H, $SiH_3$), 6.75 (d, $^3J_{HH}$ = 7 Hz, 1H, pyridine−$H_4$), 7.13 (d, $^3J_{HH}$ = 7 Hz, 1H, pyridine−$H_3$), 8.51 (s, 1H, pyridine−$H_6$). $^{13}$C NMR ($C_6D_6$, 20 °C): $\delta$ 18.0 (q, $^1J_{CH}$ = 127 Hz, $CH_3$), 131.2 (d, $^1J_{CH}$ = 160 Hz, $C_3$), 133.0 ($C_5$ ipso), 134.4 (d, $^1J_{CH}$ = 159 Hz, $C_4$) 151.7 (d, $^1J_{CH}$ = 175 Hz, $C_6$), 154.4 ($C_2$ ipso). $^{29}$Si NMR (DEPT, $C_6D_6$, 20 °C): $\delta$ −64.4 [q, $^1J_{SiH}$ = 203 Hz, $SiH_3$]. $^{14}$N NMR ($C_6D_6$, 18 °C): $\delta$ −41.3 [s, pyridine−N]. MS (EI, 70 eV): *m/z* 123 [$M^+$], 122 [$M^+$ − H], 120 [100%, $M^+$ − 3H], 108 [$M^+$ − $CH_3$], 106 [$M^+$ − $CH_3$−2H], 94 [$M^+$ − SiH], 92 [$M^+$ − $SiH_3$], 79 [$C_5H_4N^+$]. IR (gas): $\nu$ 3007 [m, $\nu$-$(CH)_{Aryl}$], 2980 [m, $\nu(CH)_{Alkyl}$], 2181 [s, $\nu$(SiH)], 1562/1460/1372 [s, $\nu$(C═C) and $\nu(C{=}N)_{Aryl}$]. $C_6H_9NSi$ (123.2): found C 58.3, H 7.3, N 11.2; calcd C 58.5, H 7.3, N 11.4.

**6-Methyl-2-silylpyridine (7).** As described for **6**, **7** is prepared from 2-chloro-6-methylpyridine (3.0 g, 23.5 mmol) in 75 mL of DME and a solution of potassium silanide in DME (31.5 mL, 0.82 M, 25.9 mmol). The product **7** can be isolated by fractional condensation (0 °C, −15 °C, −196 °C) as a colorless liquid collected at −15 °C (mp ca. −18 °C; yield 0.35 g, 12%). $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 2.15 (s, 3H, $CH_3$), 4.34 (s, $^1J_{SiH}$ = 203 Hz, 3H, $SiH_3$), 6.30 (d, $^3J_{HH}$ 7 Hz, 1H, pyridine−$H_4$), 6.65 (d, $^3J_{HH}$ = 7 Hz, 2H, pyridine−$H_{3,5}$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 20 °C): $\delta$ 24.5 ($CH_3$), 123.0 ($C_5$), 128.8 ($C_3$), 134.3 ($C_4$) 157.5 ($C_6$ ipso), 159.2 ($C_2$ ipso). $^{29}$Si NMR (DEPT, $C_6D_6$, 20 °C): $\delta$ −64.1 [q, $^1J_{SiH}$ = 202 Hz, $SiH_3$]. $^{14}$N NMR ($C_6D_6$, 18 °C): $\delta$ −39.3 [s, pyridine−N]. MS (EI, 70 eV): *m/z* 123 [$M^+$], 122 [100%, $M^+$ − H], 120 [$M^+$ − 3H], 109 [$M^+$ − $CH_3$], 106 [$M^+$ − $CH_3$−2H], 94 [$M^+$ − SiH], 79 [$C_5H_4N^+$].

**2-Bromo-6-silylpyridine (8).** To a solution of 2,6-dibromopyridine (3.0 g, 0.013 mol) in 80 mL of dimethoxyethane (DME) is added a precooled solution of potassium silanide in DME (16.2 mL, 0.82 M, 0.013 mol) over 30 min with cooling (−60 °C). A white precipitate is formed. The resulting white suspension is stirred for 2 h and then warmed to room temperature. After stirring overnight, the salt is separated by filtration, and the filtrate is distilled in a vacuum. The residue contains dibromopyridine and product **8,** which is isolated by sublimation. Compound **8** solidifies to a white solid (mp 28 °C; yield 90 mg, 4%). $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 4.22 (s, $^1J_{SiH}$ = 202 Hz, 3H, $SiH_3$), 6.84 ($\psi$t, $^3J_{HH}$ = 7 Hz, 1H, pyridine−$H_5$), 7.06 (d, $^3J_{HH}$ = 7 Hz, 1H, pyridine−$H_4$), 7.22 (d, $^3J_{HH}$ = 7 Hz, 1H, pyridine−$H_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 19 °C): $\delta$ 128.1 ($C_5$), 130.5 ($C_3$), 136.6 ($C_4$), 143.6 ($C_2$ ipso), 160.3 ($C_6$ ipso). $^{29}$Si NMR (DEPT, $C_6D_6$, 20 °C): $\delta$ −63.0 [q, $^1J_{SiH}$ = 202 Hz, $SiH_3$]. $^{14}$N NMR ($C_6D_6$, 18 °C): $\delta$ −42.7 [s, pyridine−N]. MS (EI, 70 eV): *m/z* = 189 [$M^+$ + 1], 188 [100%, $M^+$], 158 [$M^+$ − $SiH_3$], 107 [$M^+$ − Br], 79 [$C_5H_4N^+$], 53, 51. $C_5H_6BrNSi$ (188.2): found C 31.6, H 3.3, N 7.2; calcd C 31.9, H 3.2, N 7.4.

**2,6-Disilylpyridine (9).** As described for **8**, **9** is prepared from 2,6-dibromopyridine (3.0 g, 0.013 mol) in 60 mL of DME with 2 equiv of potassium silanide in DME (34 mL, 0.82 M, 0.028 mmol). After filtration the product **9** can be isolated by fractional condensation (0 °C, −10 °C, −196 °C). The colorless liquid product is collected at −10 °C (yield 126 mg, 7%). $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 4.28 (s, $^1J_{SiH}$ = 204 Hz, 6H, $SiH_3$), 6.77 (dd, $^3J_{HH}$ 7.5 Hz, 1H, pyridine−$H_4$), 7.02 (d, $^3J_{HH}$ = 7.5 Hz, 2H, pyridine−$H_{3,5}$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 19 °C): $\delta$ 131.0 ($C_{3,5}$), 132.4 ($C_4$), 159.6 ($C_{2,6}$ ipso). $^{29}$Si NMR (DEPT, $C_6D_6$, 20 °C): $\delta$ −64.2 [q, $^1J_{SiH}$ = 203 Hz, $SiH_3$]. $^{14}$N NMR ($C_6D_6$, 18 °C): $\delta$ −15.4 [s, pyridine−N]. MS (EI, 70 eV): *m/z* 140 [$M^+$ + 1], 139 [$M^+$], 138 [100, $M^+$ − H], 108 [$M^+$ − SiH], 106 [$M^+$ − $SiH_3$], 80 [$M^+$ − $SiH_2$−$SiH_3$] 79 [$C_5H_4N^+$], 70, 55, 53. IR (gas): $\nu$ 3042 [m, $\nu(CH)_{Aryl}$], 2160 [s, $\nu$(SiH)], 1659/1562/1453/1382 [s, $\nu$(C═C) and $\nu(C{=}N)_{Aryl}$]. $C_5H_9NSi_2$ (139.2): found C 43.0, H 6.3, N 9.8; calcd C 43.1, H 6.5, N 10.1.

**Bis(5-methylpyridyl-2)silane (10) and Tris(5-methylpyridyl-2)silane (11).** 2-Bromo-5-methylpyridine (6.0 g, 34.8 mmol) is dissolved in 75 mL of dimethoxyethane (DME) and cooled to −78 °C. A precooled solution of potassium silanide (23.3 mL, 0.82 M, 19.2 mmol) in DME is added slowly. A white precipitate is formed. With vigorous stirring the mixture is warmed to room temperature after 30 min and filtered. The filtrate is fractionally condensed (0 °C, −196 °C) to give the product **10** as a colorless liquid (yield 1.04 g; 14%). The major byproduct is tris(3-methylpyridyl-6)silane **11**. $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 1.79 (s, 3H, $CH_3$), 5.32 (s, $^1J_{SiH}$ = 204 Hz, 2H, $SiH_2$), 6.89 (d, $^3J_{HH}$ = 7 Hz, 2H, pyridine−$H_4$), 7.51 (d, $^3J_{HH}$ = 7 Hz, 2H, pyridine−$H_3$), 8.56 (s, 2H, pyridine−$H_6$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 20 °C): $\delta$ 18.3 ($CH_3$), 131.6 ($C_3$), 133.1 ($C_5$ ipso), 134.6 ($C_4$), 151.6 ($C_6$), 157.0 ($C_2$ ipso). $^{29}$Si NMR (DEPT, $C_6D_6$, 20 °C): $\delta$ −44.3 [**10**, t, $^1J_{SiH}$ = 204 Hz, $SiH_2$], $\delta$ = −36.3 [ **11**, d, $^1J_{SiH}$ = 205 Hz, SiH ]. $^{14}$N NMR ($C_6D_6$, 20 °C): $\delta$ −41.3 [s, pyridine−N]. MS (EI, 70 eV): *m/z* 123 [$M^+$], 122 [$M^+$ − H], 108 [$M^+$ − $CH_3$], 94 [$M^+$ − SiH], 92 [$M^+$ − $SiH_3$], 79 [$C_5H_4N^+$].

**Bis(6-methylpyridyl-2)silane (12) and Tris(6-methylpyridyl-2)silane (13).** As described for **10 (11)**, **12 (13)** are prepared from 2-chloro-6-methylpyridine (6.0 g, 47.0 mmol) in 75 mL of DME and potassium silanide in DME (31.5 mL, 0.82 M, 25.9 mmol). After filtration the products are isolated by fractional condensation (0 °C, −15 °C). $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 1.81 (s, 3H, $CH_3$), 5.30 (s, $^1J_{SiH}$ = 204 Hz, 2H, $SiH_2$), 6.59 (d, $^3J_{HH}$ = 7 Hz, 2H, pyridine−$H_4$), 6.95 (d, $^3J_{HH}$ = 7 Hz, 2H, pyridine−$H_5$), 7.27 (s, 2H, pyridine−$H_3$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 20 °C): $\delta$ 24.6 ($CH_3$), 123.1 ($C_5$), 129.2 ($C_3$), 134.0 ($C_4$), 159.0 ($C_6$ ipso), 160.0 ($C_2$ ipso). $^{29}$Si NMR (DEPT, $C_6D_6$, 20 °C): $\delta$ −43.9 [**12**, t, $^1J_{SiH}$ = 204 Hz, $SiH_2$], $\delta$ −35.0 [**11**, d, $^1J_{SiH}$ = 206 Hz, SiH]. $^{14}$N NMR ($C_6D_6$, 20 °C): $\delta$ −39.3 [s, pyridine−N]. MS (EI, 70 eV): *m/z* 123 [$M^+$], 122 [$M^+$ − H], 108 [$M^+$ − $CH_3$], 106 [$M^+$ − $CH_3$−2H], 94 [$M^+$ − SiH], 92 [$M^+$ − $SiH_3$], 79 [$C_5H_4N^+$].

**Reaction of 5-Bromopyrimidine with Potassium Silanide.** As described for **8**, **14** can be obtained by the reaction of 5-bromopyrimidine (2.5 g, 15.72 mmol) in DME (75 mL) with 1 equiv of potassium silanide (21.1 mL, 0.82 M in DME, 17.3 mmol). After evaporation of the solvent a pale yellow liquid remains. MS (EI, 70 eV): *m/z* 110 [100%, $M^+$], 78 [$M^+$ − $SiH_3$ −H], 60, 55, 51.

**Reaction of Pentachloropyridine with Potassium Silanide.** A solution of pentachloropyridine (1.5 g, 5.97 mmol) in 80 mL of DME is added to a solution of potassium silanide (40 mL, 0.82 M, 32.8 mmol) in DME with cooling (−78 °C) and stirring. A brown precipitate is formed. After vigorous stirring for 2 h the mixture is allowed to warm to room temperature. The precipitate is filtered and the solvent removed in vacuo to leave a yellow oil that contains compound **15** as identified by the following data. $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 4.72 (s, 6H, $SiH_3$ meta), 4.81 (s, 3H, $SiH_3$ para), 4.85 (s, 6H, $SiH_3$ ortho). $^{29}$Si NMR (DEPT, $C_6D_6$, 20 °C): $\delta$ −43.5 [q, $^1J_{SiH}$ = 207 Hz, $SiH_3$ para], −76.8 [q, $^1J_{SiH}$ = 188 Hz, $SiH_3$ meta], −79.1 [q, $^1J_{SiH}$ = 190 Hz, $SiH_3$ ortho]. MS (EI, 70 eV): *m/z* 201 [$C_5N(SiH_3)_4^+$], 170 [$C_5N(SiH_3)_3^+$], 138 [100%, $C_5N(SiH_3)_2^+$], 108 [$C_5NSiH_2^+$], 70.

**5-Methyl-2-trimethysilylpyridine (16).** The synthesis follows the literature procedure for other trimethylsilylpyridines.[14] A colorless liquid is obtained (mp −23 °C). $^1$H NMR ($C_6D_6$, 20 °C): $\delta$ 0.35 (s, 9H, $SiMe_3$), 1.85 (s, 3H, $CH_3$), 6.96 (d, $^3J_{HH}$ = 7 Hz, 1H, pyridine−$H_4$), 7.20 (d, $^3J_{HH}$ = 7 Hz, 1H, pyridine−$H_3$), 8.63 (s, 1H, pyridine−$H_6$). $^{13}$C{$^1$H} NMR ($C_6D_6$, 19 °C): $\delta$ −1.63 ($SiMe_3$), 17.6 ($CH_3$), 128.8 ($C_4$), 133.5 ($C_3$), 128.8 ($C_4$), 151.2 ($C_6$), 164.7 ($C_2$ ipso). $^{29}$Si NMR ($C_6D_6$, 20 °C): $\delta$ −6.21 [s, $SiMe_3$]. MS (EI, 70 eV): *m/z* 165 [$M^+$], 164 [$M^+$ − H], 150 [$M^+$ − $CH_3$, 100%], 134 [$M^+$ − 2$CH_3$], 120 [$M^+$ − 3$CH_3$], 107 [$M^+$ − 4$CH_3$], 94 [$M^+$ − $SiMe_3$], 79 [$C_5H_4N^+$], 72, 67, 59, 51. IR (gas): $\nu$ 3030 [m, $\nu(CH)_{Aryl}$], 2967 [s, m, $\nu$-$(CH)_{Alkyl}$], 1652/1467/1259 [s, $\nu$(C═C) and $\nu(C{=}N)_{Aryl}$]. $C_9H_{15}$-NSi (165.2): found C 65.4, H 9.1, N 8.5; calcd C 63.8, H 9.2, N 8.5.

**Crystal Structure Determinations.** A solid−liquid equilibrium was established (at 258 K for **6**, at 253 K for **9**, and at 250 K for **16**) in a sample of the compound held in a capillary. Single crystals grew on cooling at 1 K $h^{-1}$. The specimens were used for measurement of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (graphite-monochromated Mo-$K_\alpha$ radiation, $\lambda$(Mo-$K\alpha$) = 0.710 73 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. The structures were solved by direct methods (SHELXS-86 [27]) and completed by full-matrix least-squares techniques against $F^2$ (SHELXL-93[28]). The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms of **6**, **9**, and **16** were found and refined with isotropic contributions. Further information on crystal data, data collection, and structure refinement are summarized in Table 1. Important interatomic distances and angles are given in the corresponding figure captions. For further details, see the Supporting Information. Moreover, anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited at Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD No. 408957 (**6**), 408958 (**9**), and 408959 (**16**).

**Ab Initio Calculations.** Ab initio molecular orbital calculations were carried out using the Gaussian 94 program.[20] Geometry optimizations (SCF and MP2 level of theory) and vibrational frequency calculations (up to SCF/6-31G*) were performed from analytical first and second derivatives. Calculations were undertaken at the SCF level using the standard 3-21G* [29,30] and 6-31G* [31−33] basis sets, the larger basis sets being used for calculations at the MP2 level of theory. NBO calculations were undertaken with the NBO 3.0 facilities built into Gaussian 94.[34,35]

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**Supporting Information Available:** Tables of atomic coordinates and isotropic thermal parameters, all bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, and thermal parameters for **6**, **9**, and **16** (11 pages). Ordering information is given on any current masthead page.

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