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Articles

Hypervalent Silicon via Intramolecular Coordination in a Four-Membered Ring in Complexes of Substituted Pyridyl Ligands

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Reaction of SiX_nCl_{4-n} (X = H, Me) with “Li(C(SiMe$_3$)$_2$(2-C$_5$H$_4$N))” or “Li(C(SiMe$_3$)$_2$(6-Me-2-C$_5$H$_3$N))” yields hypervalent five-coordinate compounds, established in the solid state for Si*R*HCl$_2$ (**5** and **7**), which show strong intramolecular Si−N interactions in the four-membered chelate ring (NSiC$_2$) that persist in solution (Si−N = 2.066(9) and 2.072(4) Å, X = H). Complexes based on HCPh$_2$(2-C$_5$H$_4$N) form four-coordinate species, whereas complexes based on HCPh(SiMe$_3$)(2-C$_5$H$_4$N) afford either four- or five-coordinate complexes; the *rac* isomers of Si(CH(SiMe$_3$)(2-C$_5$H$_4$N))$_2$Me$_n$Cl$_{2-n}$ (**26** and **27**), formed stereospecifically, are four-coordinate.

Introduction

The main-group-metal chemistry of the bulky alkyl ligand $^-$C(SiMe$_3$)$_2$(2-C$_5$H$_4$N) (R$^-$) has been extensively investigated. Such bulky ligands, devoid of a β-hydrogen, are important in the search for new classes of main-group complexes. The effect of the steric hindrance at the ligating C-center combined with the potential for stabilizing N-donation to any metal(loid) center has resulted in the formation of monomeric, subvalent, hypervalent, electron-deficient, low-coordinate, and ionic species.[1,2]

The synthesis and chemistry of hypervalent silicon complexes have received much attention in recent years.[3−6] Five-coordinate silicon is found in silicates (siliconates) and in neutral compounds via intramolecular complexation of oxygen[4] or nitrogen[5] centers as part of five- or six-membered chelate ring systems.[4−6] Such compounds are usually considered as model compounds for intermediates in nucleophilic substitution at four-coordinate silicon.[6]

Herein we report the synthesis and structural studies of an array of functionalized pyridine complexes of silicon based on a range of ligands with varying substitution and show that five-coordinate silicon is accessible for some four-membered chelate rings (despite ring strain) not only in the solid state but also in solution even at room temperature, while a number of related ligand systems exhibit no Si−N interaction and have four-coordinate silicon centers.

Results and Discussion

Compounds **1** and **2** were prepared from 2,6-dimethylpyridine by metalation using LiBu^n, in Et$_2$O (Scheme 1), a modification of the procedure described by Izod.[7] Higher yields were obtained when **2** was prepared from **1**, rather than from preparation in one step, as in the analogous preparation of 2-(bis(trimethylsilyl)methyl)-

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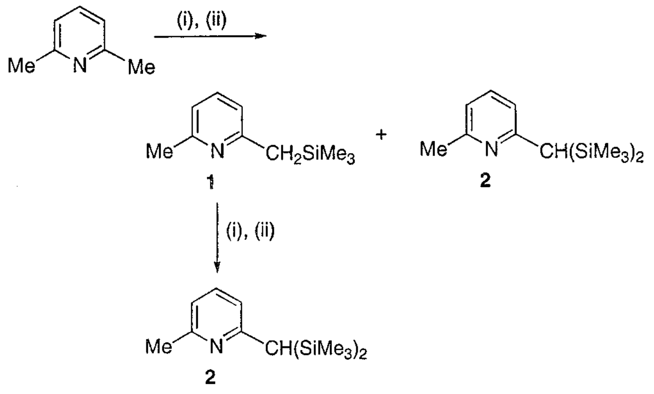
10.1021/om0005497 CCC: $19.00

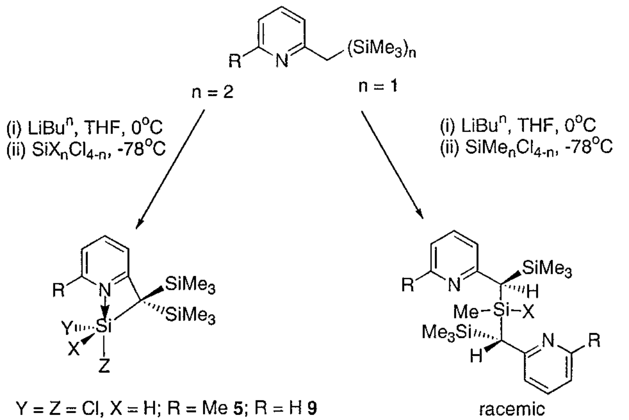
Scheme 1



(i) LiBu^n, Et$_2$O, 0°C

(ii) ClSiMe$_3$

Scheme 2



Y = Z = Cl, X = H; R = Me **5**; R = H **9**
Y = Z = Cl, X = Me; R = Me **6**; R = H **10**
Z = Cl, X = Y = Me; R = Me **7**; R = H **11**
X = Z = Y = Me; R = Me **8**; **R** = H **12**

X = Cl; R = Me **24**; R = H **26**
X = Me; R = Me **25**; R = H **27**

pyridine (**3**).[8] In the preparation of **3**, optimum conditions required the slow addition of chlorotrimethylsilane in hexane to Li(TMEDA)(2-$CH_2C_5H_4N$) (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine), during which the supply of chlorotrimethylsilane is continually consumed and the generated (2-(trimethylsilyl)methyl)-pyridine (**4**) is metalated to form Li(TMEDA)(2-$SiMe_3$-CHC_5H_4N).[7] In contrast, the preparation of **4** requires the slow addition of Li(TMEDA)(2-$CH_2C_5H_4N$) in Et_2O to a solution of excess chlorotrimethylsilane in Et_2O.[8] Yields were not enhanced by slow addition of the silane in the preparation of **2**.

Izod et al.[7] prepared **2** by the method described for **3**,[8] but as yields were not quoted, it is not possible to determine whether similar results were obtained from their studies. In the present study, reactions under these conditions gave a mixture of the mono- and disubstituted ligands and starting material in a ratio of 40:40:20, respectively. Variation in the rates or order of addition resulted in only slight variations in product ratios. The reaction of 2,6-dimethylpyridine with 1.1 mol equiv of LiBu^n, followed by quenching with chlorotrimethylsilane, gave a mixture of unreacted starting material and mono- and disilylated ligand in a ratio of 5:85: 10. Metalation of **1** with LiBu^n followed by quenching gave the disubstituted ligand **2** in >90% yield with little or no starting monosilylated pyridine.

Metalation of **2** with LiBu^n in thf afforded a deep orange solution of “Li(C($SiMe_3$)$_2$(6-Me-2-C_5H_3N))” of unknown structure (the complex not being isolated), although coordination of thf to the metal center is likely. Reaction of “Li(C($SiMe_3$)$_2$(6-Me-2-C_5H_3N))” with SiX_nCl_{4-n} (X = H, n = 1; X = Me, n = 1−3) in thf at −78 °C afforded colorless crystals of **5**, **6**, or **7** and **8**, the last compound being a colorless liquid (Scheme 2). Unlike the reaction of Izod et al.,[7] the above-mentioned reactions occur at the trimethylsilyl-substituted carbon. Izod found that the reaction of chlorotrimethylsilane with a TMEDA adduct of the lithium reagent of “Li(C($SiMe_3$)$_2$-(6-Me-2-C_5H_3N))” resulted in substitution occurring at the methyl carbon, rather than at the trimethylsilyl-substituted carbon.[7] Similarly, reaction of SiX_nCl_{4-n} (X = H, n = 1; X = Me, n = 1−3) with “Li(C($SiMe_3$)$_2$(2-C_5H_4N))” gave the five-coordinate species **9**, **10**, or **11** or the four-coordinate species **12**.[8] Complexes of the ligand **3** based on silicon show strong intramolecular Si−N interactions in the solid and in solution with a rapid equilibrium between four- and five-coordinate species, ΔG = 51(4) kJ mol^{-1}.[9]

The analogous compounds **14**−**17**, based on the related ligand 2-(diphenylmethyl)pyridine (**13**), were prepared similarly from the reaction of “Li(C(Ph)$_2$-(C_5H_4N))” with the corresponding silane SiX_nCl_{4-n} (X = H, n = 1; X = Me, n = 1−3) in thf at −78 °C. These complexes have seemingly similar steric hindrance and ligand bite but are devoid of Si−N interactions as found in the X-ray structure of complex **15**.[9] It appears that the Si−N interaction in **9**−**11** arises from minimization of steric buttressing between the proton attached to C(2) (C α to substituted C) of the pyridyl ring and the trimethylsilyl groups of the ligand. In general, less strained ring systems are required for stabilizing hypervalent species possessing N-donation.[5,10]

An electronic effect must also be in operation since compounds **8** and **12**, which have three methyl groups attached to the central silicon, are four-coordinate, whereas with one or two chlorines, and in some cases hydrogen, the complexes are five-coordinate. Thus, the hypervalent state requires at least one electronegative center, the associated polarization resulting in an increase in the Lewis acidity of the central silicon.

In an attempt to understand whether the bulk of the ligand and/or the stabilization of the silicon on the ligand results in the formation of five-coordinate species, preliminary investigation of the new ligand 2-(phenyl-(trimethylsilyl)methyl)pyridine (**18**), incorporating both trimethylsilyl and phenyl substituents on pyridine, was carried out. Compound **18** was prepared in high yield by metalation of 2-benzylpyridine (**19**) with LiBu^n in Et_2O, affording a deep red solution, followed by quenching with chlorotrimethylsilane (Scheme 3). The same compound, **18**, was prepared similarly in thf or TMEDA in high yield.

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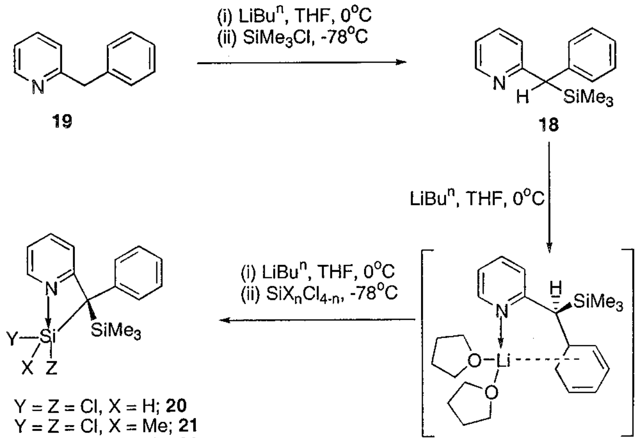
Scheme 3



19

18

Y = Z = Cl, X = H; **20**
Y = Z = Cl, X = Me; **21**
Z = Cl, X = Y = Me; **22**
X = Z = Y = Me; **23**

(stereochemistry undefined)

Metalation of **18** with LiBu^n in thf afforded a deep red solution of "Li(CPh(SiMe$_3$)(2-C$_5$H$_4$N))". The thf adduct has been isolated and its X-ray structure determined, albeit for weakly diffracting crystals. It is comprised of discrete monomeric species with one molecule of (thf)$_2$Li(CPh(SiMe$_3$)(2-C$_5$H$_4$N) devoid of crystallographic symmetry in the asymmetric unit, with two thf molecules coordinated to lithium.[11] Reaction of "Li(CPh(SiMe$_3$)(2-C$_5$H$_4$N))" with SiX$_n$Cl$_{4-n}$ (X = H, n = 1; X = Me, n = 1−3) in thf at −78 °C afforded dark red solutions of **20**−**23** (Scheme 3). Various attempts to crystallize these silanes were unsuccessful.

Silicon compounds of the less substituted ligands **1**, **4**, and **19** have also been prepared. Two different approaches were carried out in an attempt to isolate these silicon derivatives. Addition of a solution of the lithium reagent to a solution of the silane SiX$_n$Cl$_{4-n}$ (X = H, Me) at −78 °C, as in similar reactions mentioned above, on workup gave oils at 25 °C of composition SiRX$_n$Cl$_{3-n}$. These compounds often decomposed around 0 °C. Characterization of these compounds was thwarted by this decomposition and the difficulty of isolation of the reaction products from starting material. Attempts to distill the complexes from excess starting material resulted in decomposition of the products to dark brown oils.

A second strategy for the preparation of the less substituted complexes involved the addition of 1 mol equiv of the silane to a solution of "Li(CH(SiMe$_3$)(2-C$_5$H$_4$N))" or "Li(CH(SiMe$_3$)(6-Me-2-C$_5$H$_3$N))" at 0 °C. Workup gave crystalline complexes **24**−**27** (Scheme 2). Complexes based on **18** decomposed rapidly at room temperature, resulting in difficulty in obtaining satisfactory data for full characterization. Similar reactions based on the disubstituted ligands **2**, **3**, **13**, and **19** resulted in only low yields of SiRX$_n$Cl$_{3-n}$ and starting material, with no detected formation of the dialkyl compounds.

The preferential formation of racemic isomers in high yields is attributed to the stereochemistry of the trimethylsilyl group and the pyridine ring (Figure 1). The pyridine ring of the first attached alkyl group may direct the delivery of the second alkyl group to give the racemic isomer.

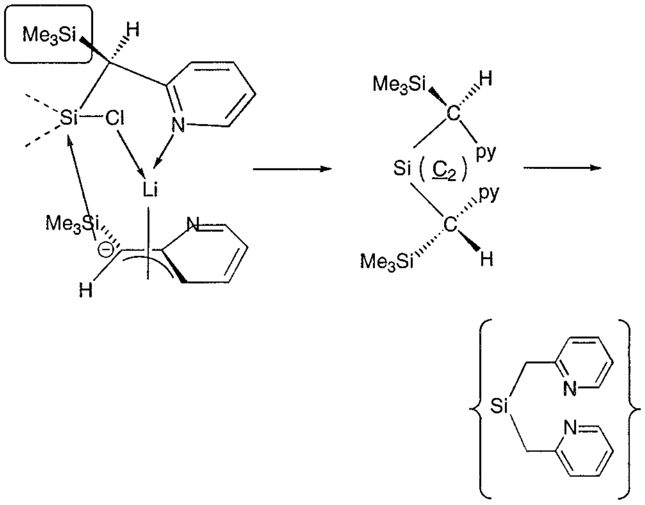


Figure 1. Formation of the racemic isomer.

Table 1. ^{29}Si NMR Chemical Shifts of Silicon Complexes

compd		chem shift (ppm)	
		central Si	SiMe$_3$
1	$H_2CSiMe_3(6\text{-}Me\text{-}2\text{-}C_5H_3N)$		1.36
2	$HC(SiMe_3)_2(6\text{-}Me\text{-}2\text{-}C_5H_3N)$		1.63
5	$Si(C(SiMe_3)_2(6\text{-}Me\text{-}2\text{-}C_5H_3N))HCl_2$	−64.82	1.94
6	$Si(C(SiMe_3)_2(6\text{-}Me\text{-}2\text{-}C_5H_3N))MeCl_2$	−33.06	1.73
7	$Si(C(SiMe_3)_2(6\text{-}Me\text{-}2\text{-}C_5H_3N))Me_2Cl$	−14.72	1.00
8	$Si(C(SiMe_3)_2(6\text{-}Me\text{-}2\text{-}C_5H_3N))Me_3$		−2.06
9	$Si(C(SiMe_3)_2(2\text{-}C_5H_4N))HCl_2$	−18.0	−5.68, −5.52
10	$Si(C(SiMe_3)_2(2\text{-}C_5H_4N))MeCl_2$	−30.9	2.4
11	$Si(C(SiMe_3)_2(2\text{-}C_5H_4N))Me_2Cl$	−11.18	2.48
14	$Si(C(Ph)_2(2\text{-}C_5H_4N))HCl_2$	−2.5	
15	$Si(C(Ph)_2(2\text{-}C_5H_4N))MeCl_2$	5.9	
16	$Si(C(Ph)_2(2\text{-}C_5H_4N))Me_2Cl$	20.07	
17	$Si(C(Ph)_2(2\text{-}C_5H_4N))Me_3$	8.56	
18	$HCPhSiMe_3(2\text{-}C_5H_4N)$		2.1
20	$Si(CPhSiMe_3(2\text{-}C_5H_4N))HCl_2$	−27.03	6.15
21	$Si(CPhSiMe_3(2\text{-}C_5H_4N))MeCl_2$	5.32	2.29
22	$Si(CPhSiMe_3(2\text{-}C_5H_4N))Me_2Cl$	15.59	3.74
23	$Si(CPhSiMe_3(2\text{-}C_5H_4N))Me_3$		1.21
24	$Si(HCSiMe_3(6\text{-}Me\text{-}2\text{-}C_5H_3N))_2MeCl$	28.8	2.5
25	$Si(HCSiMe_3(6\text{-}Me\text{-}2\text{-}C_5H_3N))_2Me_2$	3.81	1.3
26	$Si(HCSiMe_3(2\text{-}C_5H_4N))_2MeCl$	22.89	1.49
27	$Si(HCSiMe_3(2\text{-}C_5H_4N))_2Me_2$	3.18	0.82

NMR Analysis of Silicon Complexes. Series of NMR data of six-membered aromatic heteocycles, including substituted pyridines, have been compiled by Batterham[12] and Katritzky.[13] Changes in the electronegativity of the substituent result in only slight changes in the resonances of pyridine ring protons and carbons. The ^{13}C and ^{1}H NMR spectra of the above silanes are similar to those of the conjugate acids of the ligand; slight perturbations of 1 ppm are evident in the ^{13}C NMR spectra, except for the α-carbon (C$_7$), whereby the C$_7$ resonances of complexes based on **1**−**4** are found at δ 29−40 ppm, those based on **13** occur at δ 57−65 ppm, and those based on **18** are at δ 39−49 ppm.

Table 1 contains ^{29}Si NMR data for the silicon complexes in the present study. An apparent trend is evident with the value of the silicon shift, suggestive of the likely coordination environment about the silicon center. The trimethylsilyl groups of the ligand tend to

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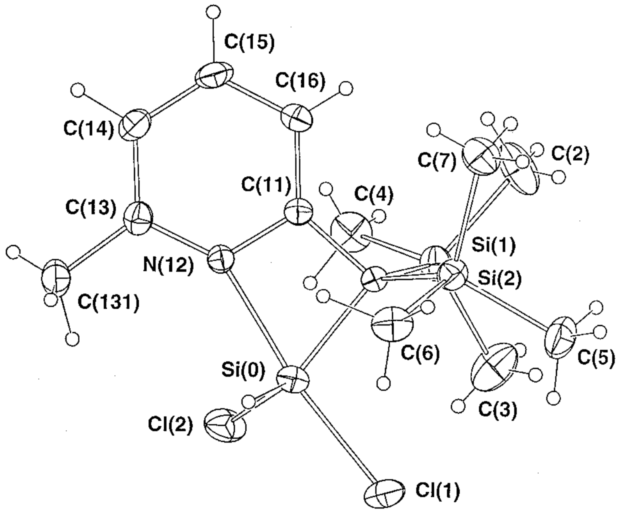

Figure 2. Molecule 1 of **5** (molecule 2 is closely similar) projected normal to the pyridine plane. In this figure and in Figure 3, non-hydrogen atoms are shown with 20% thermal ellipsoids, hydrogen atoms having arbitrary radii of 0.1 Å.

have ^{29}Si NMR chemical shifts close to δ 0 ppm, ranging between δ −5.7 and 6.2 ppm, as expected for slight changes in the electronic environment of the trimethylsilyl groups between complexes without change in the coordination number. On the other hand, large changes in the shift of the central silicon atom range between δ −64.8 and 28.8 ppm.

Complexes bearing two trimethylsilyl groups have negative values for the ^{29}Si chemical shift of the central silicon atom, whereas the diphenyl counterparts have positive values. The ligand containing one phenyl and one trimethylsilyl group has both negative and positive values. On the basis of crystallographic results and the positive/negative values for the ^{29}Si NMR chemical shift, a trend is apparent. Negative values of ^{29}Si NMR chemical shift correlate with five-coordination, and positive ^{29}Si NMR chemical shift values correlate with four-coordination, similar results having been found for other systems.[5] These findings suggest that the silicon atom of complex **20** is likely to be five-coordinate, whereas those in other complexes in the series **21**−**23** are most likely four-coordinate.

Changes in the bulk of the ligand and the substituent silane both play an important role in the determination of the coordination environment about the central silicon. In the present study silyl-substituted pyridines are required for the formation of five-coordinate species, and increases in the bulk of the central silane can result in the formation of four-coordinate species.

Molecular Structures of 5, 26, and 27. The results of the room-temperature single-crystal X-ray studies are consistent with the above formulations of the three complexes in terms of stoichiometry, connectivity, and stereochemistry. Complex **5** crystallizes with two independent molecules in the asymmetric unit, both devoid of crystallographic symmetry, and with similar substituent dispositions/conformations (that of molecule 1 being depicted in Figure 2) and geometries (Table 2). Complexes **26** and **27** are isomorphous, modeled in the monoclinic space group *C*2/*c* with the central silicon atom disposed on a crystallographic 2-axis so that half of the molecule comprises the asymmetric unit of the structure. For the dimethyl adduct **27**, this model is unproblematic, all hydrogen atoms being refined in $(x,y,z,U_{\mathrm{iso}})_{\mathrm{H}}$; for the Me, Cl adduct **26**, such a disposition is incompatible with 2-fold symmetry and the two substituents, of similar sizes and not infrequently found disordered in the present manner elsewhere, are treated thus. The true structure of **26** may, in fact, be of lower symmetry, but it has not been found possible to initiate meaningful refinement in such a model, and the disordered version is retained. Even with the disordered model, data quality is such as to permit meaningful

Table 2. Selected Molecular Geometry Data for $MeC_6H_4Cl_2NSi(SiMe_3)_2$ (5) and $C_6H_5Cl_2NSi(SiMe_3)_2$ (9)

atoms	param[a]	atoms	param[a]
Distances (Å)			
C(1)−Si(1)	1.912(4), 1.919(4); 1.932(8)	N(12)−C(13)	1.345(6), 1.343(5); 1.34(1)
C(1)−Si(2)	1.921(4), 1.915(4); 1.936(8)	C(13)−C(14)	1.377(8), 1.375(8); 1.36(1)
C(1)−C(11)	1.506(6), 1.501(5); 1.49(1)	C(14)−C(15)	1.358(7), 1.378(9); 1.39(1)
C(1)−Si(0)	1.906(4), 1.904(5); 1.905(8)	C(15)−C(16)	1.354(8), 1.368(7); 1.37(1)
C(11)−N(12)	1.342(5), 1.350(6); 1.36(1)	N(12)−Si(0)	2.072(4), 2.069(4); 2.066(9)
C(11)−C(16)	1.383(8), 1.380(7); 1.38(1)	Si(0)−Cl(1)	2.163(2), 2.165(2); 2.167(7)
C(13)−C(131)	1.495(8), 1.493(9); −	Si(0)−Cl(2)	2.071(2), 2.075(2); 2.077(3)
Angles (deg)			
Si(1)−C(1)−Si(2)	114.7(2), 114.8(2); 114.7(4)	C(1)−C(11)−N(12)	107.3(4), 107.1(4); 106.4(7)
Si(1)−C(1)−Si(0)	116.2(2), 115.6(3); 115.0(4)	C(1)−C(11)−C(16)	132.7(4), 133.2(4); 133.8(7)
Si(2)−C(1)−Si(0)	110.9(2), 111.2(2); 111.2(4)	N(12)−C(11)−C(16)	119.9(4), 119.7(4); 119.7(7)
C(11)−C(1)−Si(0)	92.0(2), 92.3(3); 93.1(5)	C(11)−N(12)−C(13)	122.0(4), 122.9(4); 120.6(8)
C(11)−C(1)−Si(1)	108.5(3), 107.8(3); 111.2(5)	C(11)−N(12)−Si(0)	90.1(3), 90.0(2); 90.5(5)
C(11)−C(1)−Si(2)	112.3(2), 113.0(7); 109.5(5)	C(13)−N(12)−Si(0)	147.9(3), 147.1(3); 148.9(6)
C(1)−Si(0)−Cl(1)	101.6(1), 101.5(1); 102.4(3)	N(12)−C(13)−C(14)	118.9(4), 118.1(5); 122.2(8)
C(1)−Si(0)−Cl(2)	120.4(1), 120.5(1); 118.6(3)	N(12)−C(13)−C(131)	116.9(5), 118.1(5); −
Cl(1)−Si(0)−Cl(2)	95.91(8), 95.73(9); 96.9(2)	C(14)−C(13)−C(131)	124.2(5), 123.8(5); −
N(12)−Si(0)−Cl(1)	171.4(1), 171.4(1); 170.4(3)	C(13)−C(14)−C(15)	119.7(5), 120.3(5); 117.7(9)
N(12)−Si(0)−Cl(2)	90.9(1), 91.1(1); 92.0(3)	C(14)−C(15)−C(16)	121.0(6), 120.4(3); 120.8(8)
N(12)−Si(0)−C(1)	70.3(2), 70.4(2); 70.0(3)	C(15)−C(16)−C(11)	118.4(5), 118.6(5); 118.9(3)
Deviations from the C_5N Aromatic Planes (Å)			
δ[C(131)]	−0.030(10), −0.017(10); −	δ[Si(0)]	−0.029(6), −0.029(6); −0.12(1)
δ[C(1)]	0.081(7), 0.072(7); −0.05(1)	δ[Cl(1)]	−0.155(10), −0.158(10); −0.46(2)
δ[Si(1)]	1.753(7), 1.755(7); 1.55(1)	δ[Cl(2)]	1.659(7), 1.669(7); 1.65(1)
δ[Si(2)]	−1.462(8), −1.459(8); −1.71(1)		

[a] The values are given as follows: **5** (molecule 1), **5** (molecule 2); **9**. Values for compound **9** are included for comparative purposes.[9]

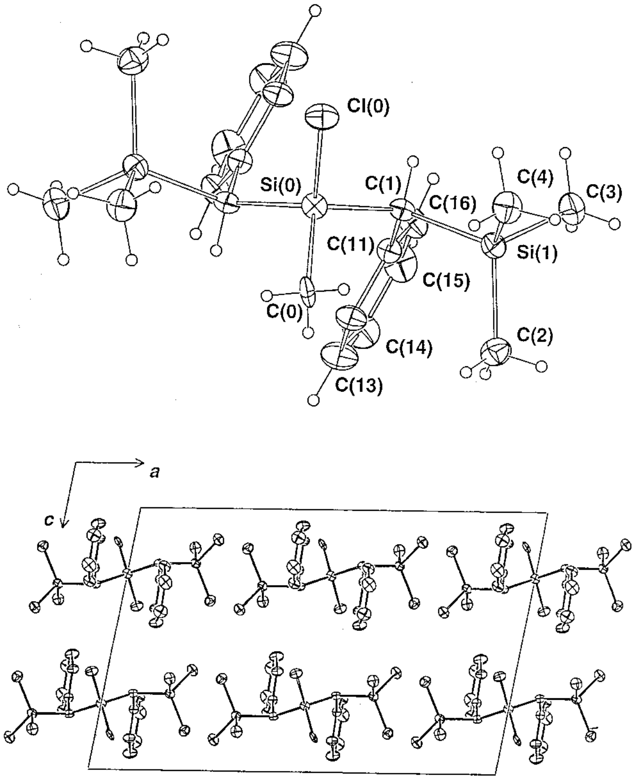

Figure 3. (a) A single ordered component of **27**, projected down the crystallographic 2-axis. (b) The unit cell of the same projected down *b*.

refinement of $(x,y,z,U_{iso})_H$ *inclusive* of those components associated with the disordered methyl group. A molecule of the ordered component is shown projected down its “2-fold” axis (crystallographic *b*) in Figure 3a, the cell contents being depicted in Figure 3b. Relevant geometries are tabulated with those of its dimethyl counterpart, **27**, in Table 3. Differences beyond the central silicon environments, themselves of doubtful value because of the associated disorder, are trivial, the only common feature worthy of comment, perhaps, being the enlargement of the pyridine ring angles to either side of that at the nitrogen (which is diminished below the trigonal value). The structures of **9** and **13** have been briefly reported previously.[9] That of **13** is awkward, the $Ph_2(2\text{-}C_5H_4N)CSiCl_2Me$ molecules crystallizing in a structure modeled as rhombohedral $R\bar{3}$, $Z = 2$, with the C−Si bond disposed on the crystallographic 3-axis. In that model, the phenyl and pyridyl rings are rotationally disordered/scrambled, as are the chlorine and methyl groups, permitting little definitive comment about intramolecular geometries. Among the torsion angles, τ (C/Cl)−Si−C−C is 36.3(4)/36.6(2)° (Cl···C(H$_3$) being 0.21(2) Å) and (N/C)−C−C−Si is 48.0(5)/46.3(4)° (N··· C being 0.057(3) Å).

Rather more features of interest are found within the molecules of **5**, together with **9**. The unsymmetrical disposition of the component moieties, coupled with other aspects, such as the strain associated with the four-membered heterocycle, introduces a number of notable features, observed consistently throughout both molecules of **5** and also **9**. The presence of the pyridyl ring substituent seemingly has little influence on the geometry. We comment on the following particularly, using the more precise study of **5** as a basis for discussion.

(a) The ring silicon, Si(0), is five-coordinate, with a highly distorted environment more nearly the putative trigonal-pipyramidal paradigm (N(12)−Si(0)−C(1) = 171.4(1)° (both molecules, Table 2)). H−Si(0) distances are 1.38(3) and 1.39(3) Å with H−Si(0)−(N(12),Cl(1),Cl(2),C(1)) being as follows for the two molecules: 88(2), 88(1); 94(2), 94(1); 113(1), 113(2); 122(1), 121(2). Cl(2)−Si(0)−C(1) = 120.4(1), 120.5(1)°. Axial and equatorial Si(0)−Cl distances differ appreciably by ca. 0.1 Å, possibly involving some N(12) “trans” effect.

(b) Within the four-membered heterocyclic ring, N(12)−Si(0)−C(1) is the angle about Si(0) differing most dramatically from the trigonal-bipyramidal norm, being 70.3(2), 70.4(2)°. Despite this, Si(0)−C(1) is very similar to the other C(1)−Si(1,2) distances; the angles Si(1,2)−C(1)−Si(0) at the heterocycle periphery differ appreciably. Si(1)−C(1)−Si(0) is the greater, presumably because of the unequally nonsymmetric disposition of the chlorine substituents, notably Cl(1), relative to the “median plane” of the molecule, defined by the C_5N pyridine data. Cl(2), projecting well out of the plane, is straddled by C(3,4) (note that τ Si(0)−C(1)−Si(1)−C(3,4) angles are -53.1(4), −51.3(4)° and 66.8(4), 68.8(3)°; cf. τ Si(0)−C(1)−Si(2)−C(6) = −29.0(3), −29.7(4)°; see Figure 2). C(6) is accommodated by the relatively diminished bulk of the hydrogen on Si(0). The attachment of C(1) to C(11) appears much less strained than that of Si(0) to N(12) of the pyridine ring, as estimated from the asymmetry in the exocyclic angles of the latter. C(1)−C(11) (1.506(6), 1.501(5) Å) is fairly typical of hydrocarbon substituent attachments, whereas N(12)−Si(0) (2.072(4), 2.069(4) Å) is long, approaching Si(0)−Cl(1) (2.163(2), 2.165(2) Å). The latter, despite this, and in keeping with the notion that axial sites in a trigonal-bipyramidal array are more crowded, are longer than Si(0)−Cl(2) (2.071(2), 2.075(2) Å).

(c) Within the pyridine ring, distances are normal, as are the angles, which show no abnormal distortion. An appreciable asymmetry is found at the methyl attachment, however, in keeping with the deviation of the substituent at the nitrogen atom away from proximity. In contrast to the other two complexes, the ring angle at the nitrogen is enlarged above the trigonal value, with those to either side diminished.

There appear to be no direct counterparts of the present systems in the literature. However, five-membered $NSiC_3$ rings have previously been the focus of a crystallographic study by Zybill et al.[5d] The complexes differ from the present in that the array therein is of the form $2\text{-}(Me_2\overline{NCH_2)C_6H_4Si}$, the silicon-bonded carbon, rather than the nitrogen (as in the present compound) being encompassed by the aromatic ring. In those compounds Si−C = 1.895(2), 1.898(2) Å and Si−N = 1.991(2), 2.046(2) Å, N−Si−C being 85.7(1), 83.6(1)°, a geometry appreciably different from the present, as is to be expected.

Experimental Details

General Procedure. All manipulations were carried out using standard Schlenk and glovebox techniques under an atmosphere of high-purity argon or nitrogen. Solvents were dried and then freeze−thaw−degassed prior to use. 2-Benzylpyridine, 2-methylpyridine, 2,6-dimethylpyridine, and TMEDA were purchased from Aldrich and purified by distillation

Table 3. Selected Molecular Geometry Data for $(C_6H_5N(SiMe_3))_2SiMeX$ (27, 26)[a]

atoms	param (X = Me, Cl)	atoms	param (X = Me, Cl)
		Distances (Å)	
Si(0)−C(0)	1.872(4), 1.944(7)	C(1)−C(11)	1.502(4), 1.502(4)
Si(0)−Cl(0)	−, 2.013(2)	C(1)−Si(1)	1.901(3), 1.905(3)
Si(0)−C(1)	1.887(3), 1.868(3)	C(0)···Cl(0)	−, 0.069(7)
		Angles (deg)	
C(0)−Si(0)−C(0′)	108.2(2), 101.5(3)	Si(0)−C(1)−Si(1)	119.0(1), 119.3(3)
C(0)−Si(0)−C(1)	108.3(2), 112.1(2)	Si(0)−C(1)−C(11)	113.5(2), 112.1(2)
C(0′)−Si(0)−C(1)	111.6(2), 109.3(2)	Si(1)−C(1)−C(11)	108.3(2), 108.9(2)
C(1)−Si(0)−C(1′)	109.0(1), 112.2(1)	C(1)−C(11)−N(12)	116.7(2), 116.0(3)
C(11)−N(12)−C(13)	117.7(3), 117.1(3)	C(1)−C(11)−C(16)	122.3(3), 122.8(3)
N(12)−C(13)−C(14)	124.1(4), 124.8(4)	N(12)−C(11)−C(16)	121.1(3), 121.6(3)
C(13)−C(14)−C(15)	118.2(4), 117.8(4)	C(11)−C(16)−C(15)	119.5(3), 120.1(3)
C(14)−C(15)−C(16)	119.4(4), 119.1(3)		

[a] The two values for each entry are for X = Me, Cl. Primed atoms are related by the 2-axis.

prior to use. 2-(Diphenylmethyl)pyridine, $SiHCl_3$, $SiMeCl_3$, $SiMe_2Cl_2$, and $SiMe_3Cl$ were all purchased from Aldrich and used without purification. $LiBu^n$ was obtained from Metallgesellschaft, as a 1.60 M solution in hexane, and was standardized prior to use. **3** and **4** were prepared by literature procedures.[8]

Physical Measurements. ^1H NMR spectra were recorded on a Bruker WM 250 or on a Varian Gemini 200 spectrometer in deuterated chloroform, benzene, or toluene and referenced to the residual ^1H resonances of the solvent (δ 7.24, 7.15, and 6.98 ppm, respectively). ^{13}C NMR spectra were recorded on the same spectrometers using broad-band proton decoupling and referenced to the ^{13}C resonances of the deuterated solvent (δ 77.0, 128.0, and 20.4 ppm, respectively). ^{29}Si NMR spectra were recorded on a Varian Unity 400 or Bruker CXP 300 spectrometer and were referenced externally to tetramethylsilane (δ 0.00 ppm). IR were recorded in the range 4000−400 cm^{-1} using a Perkin-Elmer 1725 Fourier transformed infrared spectrometer, as thin films or Nujol mulls on NaCl or CsI plates. Elemental analyses were determined by the Canadian Microanalytical Services Ltd., Vancouver, Canada, or Micro Analytical Services Pty. Ltd., Melbourne, Australia. Melting points were determined in sealed glass capillaries under argon and are uncorrected. Boiling points are uncorrected.

Structure Determinations. Unique room-temperature single counter/"four-circle" diffractometer data sets were recorded ($2\theta/\theta$ scan mode, $2\theta_{max} = 50°$; monochromatic Mo Kα radiation, $\lambda = 0.710\,7_3$ Å; T ca. 295 K) yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinements after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms, $(x,y,z,U_{iso})_H$ values also being refined. Conventional residuals on $|F|$, R and R_w (statistical weights, derivative of $\sigma^2(I) = (\sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff}))$ are quoted at convergence. Neutral atom complex scattering factors were employed, computation using the Xtal 3.2 program system.[14] Pertinent results are given below and in the figures and tables, full tables of atomic coordinates, and thermal parameters, and molecular non-hydrogen geometries being deposited in the Supporting Information. Individual variations in procedure/abnormalities/idiosyncrasies are noted below ("variata").

Details for the determinations of **9** and **15** have been previously recorded.[9]

Crystal and Refinement Data. Compound 5: $C_7H_7Cl_2NSi(SiMe_3)_2 \equiv C_{13}H_{25}Cl_2NSi_3$, $M_r = 350.5$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 8.866(3)$ Å, $b = 8.874(3)$ Å, $c = 28.597(5)$ Å, $\alpha = 89.08(2)°$, $\beta = 89.35(2)°$, $\gamma = 60.67(2)°$, $V = 1961$ Å^3, $D_c(Z = 4) = 1.19$ g cm^{-3}, $F(000) = 744$, $N = 6924$, $N_o = 4070$, $R = 0.042$, $R_w = 0.040$, $n_v = 543$, $|\Delta\rho_{max}| = 0.28$ e Å^{-3}.

Compound 26. $(C_6H_5N(SiMe_3))_2SiMeCl \equiv C_{19}H_{31}ClN_2Si_3$, $M_r = 407.2$, monoclinic, space group $C2/c$, $a = 19.155(7)$ Å, $b = 9.868(1)$ Å, $c = 12.412(12)$ Å, $\beta = 100.49(6)°$, $V = 2307$ Å^3., $D_c(Z = 4) = 1.17$ g cm^{-3}, $F(000) = 872$, $N = 2024$, $N_o = 1462$, $R = 0.046$, $R_w = 0.049$, $n_v = 192$, $|\Delta\rho_{max}| = 0.44$ e Å^{-3}.

Compound 27. $(C_6H_5N(SiMe_3))_2SiMe_2 \equiv C_{20}H_{34}N_2Si_3$, $M_r = 386.8$, monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), $a = 19.131(7)$ Å, $b = 9.883(3)$ Å, $c = 12.444(8)$ Å, $\beta = 99.97(4)°$, $V = 2317$ Å^3. D_c ($Z = 4$) = 1.11 g cm^{-3}, $F(000) = 840$, $N = 2644$, $N_o = 1745$, $R = 0.047$, $R_w = 0.050$, $n_v = 182$, $|\Delta\rho_{max}| = 0.35$ e Å^{-3}.

Variata. Modeled as isomorphous with the previous compound in space group $C2/c$, the molecule is disposed with the central silicon atom lying on a crystallographic *2*-axis, about which the methyl and chlorine moieties are disordered; attempted modeling in space group Cc was (inherently) fruitless, seemingly retentive of the disorder, so that the $C2/c$ model was retained.

Syntheses. Compound 1. $LiBu^n$ (130 mL, 204 mmol) was added slowly to an ice-cooled solution of 2,6-dimethylpyridine (20.0 g, 187 mmol) in Et_2O (200 mL), and the resulting orange slurry was stirred for 1 h. $SiMe_3Cl$ (30 mL, 237 mmol) was then slowly added over 30 min at 0 °C, yielding a pale yellow solution, and the mixture was stirred overnight at room temperature. The mixture was filtered, solvents were removed in vacuo, and the product was distilled (23 g, 70%); bp 60 °C, 5 mmHg. ^1H NMR (200 MHz, $CDCl_3$): δ 0.03 (18H, s, $Si(CH_3)_3$), 2.28 (2H, s, CH_2SiMe_3), 2.44 (3H, s, CH_3), 6.70 (1H, m, Ar H), 7.33 (1H, m, Ar H), 6.78 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ −1.7 ($Si(CH_3)_3$), 30.1 (CH_2SiMe_3), 24.5 (CH_3), 118.5, 119.0, 136.0, 157.4, 160.5 (C_5H_3N).

Compound 2. $LiBu^n$ (83 mL, 130 mmol) was added slowly to an ice-cooled solution of **1** (19 g, 110 mmol) in Et_2O (250 mL), and the resulting orange slurry was stirred for 1 h. $SiMe_3Cl$ (19 mL, 150 mmol) was then added over 30 min, yielding a pale yellow solution which on stirring for 12 h became colorless. The mixture was filtered, the solvent was removed in vacuo, and the product was distilled (24 g, 94% yield); bp 80 °C, 5 mmHg. ^1H NMR (200 MHz, $CDCl_3$): δ 0.03 (9H, s, $Si(CH_3)_3$), 1.86 (1H, s, $CHSiMe_3$), 2.43 (3H, s, CH_3), 6.66 (1H, m, Ar H), 6.75 (1H, m Ar H), 7.32 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 0.2 ($Si(CH_3)_3$), 24.6 (CH_3), 33.1 ($CHSiMe_3$), 117, 119.3, 135.6, 157.2, 163.2 (C_5H_3N).

Compound 5. $LiBu^n$ (7.4 mL, 11.3 mmol) was added slowly to an ice-cooled solution of **2** (2.68 g, 10.7 mmol) in thf (25 mL). The resulting solution was stirred for 1 h and then added to a solution of $SiHCl_3$ (2.0 mL, 20 mmol) in thf (25 mL) at −78 °C over 1 h. The yellow solution was warmed to room temperature overnight. Volatiles were removed in vacuo, yielding a yellow oil which was extracted into hexane (60 mL); the extracts were filtered, concentrated, and cooled to −30 °C, giving colorless crystals (2.95 g, 79%); mp 121 °C. Anal. Calcd for $C_{13}H_{25}NSi_3Cl_2$: C, 44.55; H, 7.19; N, 4.00, Found: C, 46.06;

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[14] *The Xtal 3.2 Reference Manual*; Hall, S. R., Flack, H. D., Stewart, J. M., Eds.; Universities of Western Australia, Geneva, and Maryland, 1992.

H, 6.67; N, 4.61. ^{1}H NMR (200 MHz, C_6D_6): δ 0.31 (18H, s, $Si(CH_3)_3$), 2.06 (3H, s, CH_3), 6.21 (1H, m, Ar H), 6.66 (1H, m, Ar H), 6.92 (1H, m Ar H), 6.36 (1H, s, SiH). ^{13}C NMR (50.3 MHz, C_6D_6): δ 1.5 ($Si(CH_3)_3$), 19.2 (CH_3), 40.6 ($C(SiMe_3)_2$), 119.3, 120.8, 139.8, 154.1, 163.0 (C_5H_3N), ^{29}Si NMR (79.45 MHz, C_6H_6): δ 1.94 ($SiMe_3$), −64.82 (SiH) (doublet), IR (Nujol): 2189 cm^{-1} (SiH).

Compound 6. This preparation follows that of **5**, using **2** (1.15 g, 4.6 mmol), LiBu^n (3.1 mL, 4.9 mmol), and $SiMeCl_3$ (0.8 mL, 7 mmol) as colorless crystals (1.2 g, 72%), mp 123 °C dec. Anal. Calcd for $C_{14}H_{27}NSi_3Cl_2$: C, 46.13; H, 7.47; N, 4.84. Found: C, 46.43; H, 7.56; N, 5.06. ^{1}H NMR (200 MHz, C_6D_6): δ 0.31 (18H, s, $Si(CH_3)_3$), 1.20 (3H, s, $SiCH_3$), 2.07 (3H, s, CH_3), 6.20 (1H, m, Ar H), 6.65 (1H, m, Ar H), 6.83 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, C_6D_6): δ 2.3 ($Si(CH_3)_3$), 16.3 ($SiCH_3$), 20.5 ($C_{6'}$), 32.5 ($C(SiMe_3)_2$), 119.1, 120.4, 138.7, 154.3, 163.2 (C_5H_3N).

Compound 7. This preparation follows that of **5**, using **2** (0.8 g, 3.2 mmol), LiBu^n (2.3 mL, 3.5 mmol), and $SiMe_2Cl_2$ (0.9 mL, 7 mmol) as colorless crystals (1.03 g, 94%), mp 76 °C. Anal. Calcd for $C_{15}H_{30}NSi_3Cl$: C, 52.36; H, 8.79; N, 4.07, Found: C, 52.06; H, 9.16; N, 4.65. ^{1}H NMR (200 MHz, C_6D_6): δ 0.31 (18H, s, $Si(CH_3)_3$), 0.94 (6H, s, $Si(CH_3)_2$), 2.00 (3H, s, CH_3), 6.32 (1H, m, Ar H), 6.84 (1H, m, Ar H), 6.92 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, C_6D_6): δ 2.8 ($Si(CH_3)_3$), 11.3 ($Si(CH_3)_2$), 21.6 (CH_3), 29.2 ($C(SiMe_3)_2$), 119.2, 120.2, 137.6, 154.5, 164.5 (C_5H_3N).

Compound 8. This preparation follows that of **5**, using **2** (0.8 g, 3.2 mmol), LiBu^n (2.2 mL, 3.4 mmol), and $ClSiMe_3$ (0.6 mL, 5.0 mmol), giving a yellow oil which was distilled to result in a pale yellow liquid (0.8 g, 78%), bp 100 °C, 0.5 mmHg. ^{1}H NMR (200 MHz, C_6D_6): δ 0.31 (27 H, s, $Si(CH_3)_3$), 2.28 (3H, s, CH_3), 6.45 (1H, m, Ar H), 6.99 (1H, m, Ar H), 7.02 (1H, m Ar H). ^{13}C NMR (50.3 MHz, C_6D_6): δ 4.3 ($Si(CH_3)_3$), 23.7 (CH_3), 30.5 ($C(SiMe_3)_3$), 118.0, 121.5, 135.6, 156.3, 163.8 (C_5H_3N).

Compound 11. This preparation follows that of **5**, using **3** (2.0 g, 8.4 mmol), LiBu^n (5.7 mL, 8.8 mmol) and $SiMe_2Cl_2$ (1.5 mL, 12 mmol), to give colorless crystals (2.1 g, 76%), mp 75 °C. Anal. Calcd for $C_{14}H_{28}NSi_3Cl$: C, 50.94; H, 8.55; N, 4.24. Found: C, 50.68; H, 8.37; N, 4.22. ^{1}H NMR (200 MHz, C_6D_6): δ 0.25 (18H, s, $Si(CH_3)_3$), 0.83 (3H, s, $Si(CH_3)_2$), 6.7 (1H, m, Ar H), 7.0 (1H, m, Ar H), 7,15 (1H, m, Ar H), 7.75 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, C_6D_6): δ 2.7 ($Si(CH_3)_3$), 11.4 ($Si(CH_3)_2$), 34.3 ($C(SiMe_3)_2$), 119.9, 123.2, 137.4, 144.6, 165.1 (C_5H_4N).

Compound 16. This preparation follows that of **5**, using **13** (2.6 g, 10.9 mmol), LiBu^n (7.3 mL, 11.7 mmol) and $SiMe_2Cl_2$ (3.0 g, 20 mmol), to give colorless crystals (2.1 g, 57%), mp 132 °C. Anal. Calcd for $C_{20}H_{20}NSiCl$: C, 71.09; H, 5.97; N, 4.14. Found: C, 70.83; H, 6.05; N, 4.27. ^{1}H NMR (200 MHz, C_6D_6): δ 0.74 (12H, s, $Si(CH_3)_2$), 6.45 (1H, m, Ar H), 6.65 (1H, m, Ar H), 6.85 (1H, m, Ar H), 6.9−7.3 (8H, m, Ph H), 6.3−7.4 (2H, m, Ph H), 8.1 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, C_6D_6, $CDCl_3$): δ 6.6 ($Si(CH_3)_2$), 58.0 (CPh_2), 121.4, 125.4, 136.0, 137.2 (C_5H_4N), 126.4, 128.5, 130.3, 147.1 (Ph).

Compound 17. This preparation follows that of **5**, using **13** (2.0 g, 8.4 mmol), LiBu^n (5.7 mL, 8.8 mmol), and $SiMe_3Cl$ (1.5 mL, 12 mmol) to give colorless crystals (2.1 g, 76%), mp 75 °C. Anal. Calcd for $C_{21}H_{23}NSi_3$: C, 79.44; H, 7.30; N, 4.41. Found: C, 79.25; H, 7.15; N, 4.61. ^{1}H NMR (200 MHz, C_6D_6): δ 0.15 (18H, s, $Si(CH_3)_3$), 6.67 (1H, m, Ar H), 7.02−7.06 (5H, m, Ar and Ph H), 7.22−7.28 (6H, m, Ph H), 7.52 (1H, m, Ar H), 8.62 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, C_6D_6): δ 1.6 ($Si(CH_3)_3$), 57.0 (CPh_2), 120.4, 124.8, 136.2, 148.0, 167.8 (C_5H_4N), 125.4, 128.0, 129.7, 146.2 (Ph).

Compound 18. LiBu^n (20 mL, 32 mmol) was added slowly to an ice-cooled solution of 2-benzylpyridine (5.0 g, 29.5 mmol) in Et_2O (200 mL) and the resulting orange slurry stirred for 1 h. To this solution was added $SiMe_3Cl$ (6.3 mL, 50 mmol) slowly over 30 min at 0 °C, yielding a pale yellow solution. Stirring was continued overnight at room temperature. The mixture was filtered and solvent was removed in vacuo, affording a pale brown oil (6.8 g, 95%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.06 (18H, s, $Si(CH_3)_3$), 3.74 (1H, s, $CHSiMe_3$), 7.04 (1H, m, Ar H), 7.16 (1H, m, Ar H), 7.29 (1H, m, Ar H), 7.40 (1H, m, Ar H), 7.51 (1H, m, H), 8.57 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 1.85 ($Si(CH_3)_3$), 48.7 ($CHSiMe_3$), 123.3, 125.1, 136.1, 148.8, 163.1 (C_5H_4N), 120.1, 128.2, 128.6, 141.7 (Ph).

Compound 20. This preparation follows that of **5**, using **18** (1.2 g, 5.2 mmol), LiBu^n (3.5 mL, 5.5 mmol), and $SiHCl_3$ (1.0 mL, 10 mmol), to give an orange solution which upon concentration gave a dark orange oil (1.2 g, 68%). ^{1}H NMR (250 MHz, C_6D_6/C_7D_8): δ 0.14 (1H, s, $Si(CH_3)_3$), 6.62 (1H, s, SiH), 6.5−7.4 (8H, m, Ar and Ph H), 7.98 (1H, m, Ar H). ^{13}C NMR (62.8 MHz, C_6D_6): δ −0.1 ($Si(CH_3)_3$), 41.0 ($CSiMe_3$), 123.6, 126.4, 137.8, 149.1, 164.5 (C_5H_4N), 121.4, 128.7, 130.0, 146.2 (Ph) (SiH). IR (Nujol): 2235 cm^{-1} (Si−H).

Compound 21. This preparation follows that of **5**, using **18** (1.2 g, 5.2 mmol), LiBu^n (3.5 mL, 5.5 mmol), and $SiMeCl_3$ (1.0 mL, 10 mmol), to give an orange oil (1.1 g, 59%). ^{1}H NMR (200 MHz, C_6D_6/C_7D_8): δ 0.14 (9H, s, $Si(CH_3)_3$), 0.87 (3H, s, $SiCH_3$), 7.1−7.5 (8H, m, Ar and Ph H), 8.55 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, C_6D_6/C_7D_8): δ 3.74 ($Si(CH_3)_3$), 15.6 ($SiCH_3$), 39.0 ($CSiMe_3$), 120.1, 125.1, 135.9, 148.9, 162.6 (C_5H_4N), 125.3, 128.1, 129.9, 141.1 (Ph).

Compound 22. This preparation follows that of **5**, using **18** (1.2 g, 5.2 mmol), LiBu^n (3.5 mL, 5.5 mmol), and $SiMe_2Cl_2$ (1.0 mL, 10 mmol), to give a brown oil (1.2 g, 61%). ^{1}H NMR (200 MHz, C_6D_6/C_7D_8): δ 0.21 (9H, s, $Si(CH_3)_3$), 0.83 (6H, s, $Si(CH_3)_2$), 6.7−7.5 (8H, m, Ar and Ph H), 8.33 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, C_6D_6/C_7D_8): δ 2.7 ($Si(CH_3)_3$), 11.4 ($Si(CH_3)_2$), 34.3 ($CSiMe_3$), 119.9, 123.2, 137.4, 144.6, 165.1 (C_5H_4N), 124.1, 128.4, 130.0, 144.1 (Ph).

Compound 23. This preparation follows that of **5**, using **18** (1.2 g, 5.2 mmol), LiBu^n (3.5 mL, 5.5 mmol), and $SiMe_3Cl$ (1.0 mL, 10 mmol), to give an orange oil (1.8 g, 88%). ^{1}H NMR (200 MHz, C_6D_6): δ 0.25 (18H, s, $Si(CH_3)_3$), 6.88−7.44 (8H, m, Ar and Ph H), 8.45 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, C_6D_6): δ 0.6 ($Si(CH_3)_3$), 33.3 ($CSiMe_3$), 119.1, 124.6, 134.9, 147.7, 167.1 (C_5H_4N), 124.2, 127.5, 130.3, 144.9 (Ph).

Compound 24. This preparation follows that of **5**, using **1** (1.0 g, 5.6 mmol), LiBu^n (3.7 mL, 5.8 mmol), and $SiMeCl_3$ (0.6 mL, 5.1 mmol), to give pale pink crystals (1.05 g, 86%), mp 101 °C. Anal. Calcd for $C_{21}H_{35}N_2Si_3Cl$: C, 57.95; H, 8.11; N, 6.44. Found: C, 57.46; H, 8.27; N, 6.94. ^{1}H NMR (200 MHz, C_6D_6/C_7D_8): δ 0.19 (9H, s, $Si(CH_3)_3$), 0.23 (9H, s, $Si(CH_3)_3$), 1.17 (3H, s, $SiCH_3$), 2.11 (1H, s, $CHSiMe_3$), 2.29 (1H, s, $CHSiMe_3$), 2.37 (3H, s, CH_3), 2.46 (3H, s, CH_3), 6.00 (2H, m, Ar H), 6.41 (2H, m, Ar H), 7.05 (2H, m, Ar H). ^{13}C NMR (50.3 MHz, C_6D_6/C_7D_8): δ 0.12, 0.13 ($Si(CH_3)_3$), 6.2 ($SiCH_3$), 21.8, 22.6 (CH_3), 33.9, 34.4 ($CHSiMe_3$), 118.6, 118.7, 120.8, 121.4, 135.8, 136.0, 151.8, 152.7, 164.0, 164.4 ($2 \times C_5H_4N$).

Compound 25. This preparation follows that of **5**, using **1** (0.8 g, 4.46 mmol), LiBu^n (3.0 mL, 4.7 mmol), and $SiMe_2Cl_2$ (0.55 mL, 4.5 mmol) as colorless crystals (0.88 g, 95%); mp 90 °C. Anal. Calcd for $C_{22}H_{38}N_2Si_3$: C, 63.7; H, 9.23; N, 6.75. Found: C, 63.68; H, 9.65; N, 7.23. ^{1}H NMR (200 MHz, C_6D_6/C_7D_8): δ 0.18 (9H, s, $Si(CH_3)_3$), 0.69 (3H, s, $SiCH_3$), 2.01 (1H, s, $CHSiMe_3$), 6.36 (1H, m, Ar H), 6.50 (1H, m, Ar H), 8.04 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, C_6D_6/C_7D_8): δ 0.5 ($Si(CH_3)_3$), 2.7 ($SiCH_3$), 31.3 ($CHSiMe_3$), 118.0, 121.7, 134.8, 150.3, 164.4 (C_5H_4N).

Compound 26. This preparation follows that of **5**, using **4** (0.7 g, 4.24 mmol), LiBu^n (2.9 mL, 4.6 mmol), and $SiMe_2Cl_2$ (0.5 mL, 4.25 mmol) as pink crystals (0.69 g, 80%); mp 99 °C. Anal. Calcd for $C_{19}H_{31}N_2Si_3Cl$: C, 56.05; H, 7.67; N, 6.88. Found: C, 55.85; H, 7.40; N, 7.01. ^{1}H NMR (200 MHz, C_6D_6): δ 0.16 (9H, s, $Si(CH_3)_3$), 0.19 (9H, s, $Si(CH_3)_3$), 1.07 (3H, s, $SiCH_3$), 2.26 (1H, s, $CHSiMe_3$), 2.43 (1H, s, $CHSiMe_3$), 6.00 (1H, m, Ar H), 6.11 (3H, m, Ar H), 6.75 (2H, m, Ar H), 8.32 (1H, m, Ar H), 8.38 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, C_6D_6): δ 0.07, 0.12 ($Si(CH_3)_3$), 6.2 ($SiCH_3$), 33.8, 34.3 ($CHSiMe_3$), 118.6, 118.7, 123.3, 123.7, 134.9, 135.2, 148.7, 149.0, 162.0, 162.4 ($2 \times C_5H_4N$).

Compound 27. This preparation follows that of **5**, using **4** (0.8 g, 4.85 mmol), LiBu^n (3.2 mL, 5.0 mmol), and SiMe$_3$Cl (0.6 mL, 4.9 mmol), to give white crystals (0.83 g, 89%), mp 86 °C. Anal. Calcd for $C_{20}H_{34}N_2Si_3$: C, 62.11; H, 8.86; N, 7.24. Found: C, 62.85; H, 8.99; N, 7.13. ^{1}H NMR (200 MHz, C_6D_6): δ 0.16 (9H, s, Si(CH$_3$)$_3$), 0.64 (3H, s, SiCH$_3$), 1.99 (1H, s, CHSiMe$_3$), 6.30 (1H, m, H), 6.52 (1H, m, Ar H), 6.83 (1H, m, Ar H), 8.40 (1H, m, Ar H). ^{13}C NMR (50.3 MHz, C_6D_6): δ 0.5 (Si(CH$_3$)$_3$), 1.8 (SiCH$_3$), 31.7 (CHSiMe$_3$), 118.3, 123.9, 135.0, 149.0, 164.6 (C_5H_4N).

Compound 28. LiBu^n (3.1 mL, 4.8 mmol) was added over 10 min to a solution of 2-benzylpyridine (0.74 g, 4.4 mmol) in thf (25 mL) at 0 °C. SiMe$_3$Cl (0.5 mL, 4.1 mmol) was added to the resulting solution and the mixture stirred at room temperature overnight. Volatiles were removed in vacuo, yielding a white solid which was extracted into hexane (35 mL); the extracts were filtered, concentrated, and cooled to −30 °C, giving yellow-pink crystals (0.70 g, 89%), mp 10 °C. ^{1}H NMR (200 MHz, C_6D_6/C_7D_8): δ 0.12 (6H, s, Si(CH$_3$)$_2$), 4.2 (2H, s, CHPh), 7.09−7.63 (16H, m, Ar and Ph H), 8.56 (2H, m, Ar H). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ 1.1 (Si(CH$_3$)$_2$), 44.6 (CHPh), 121.3, 126.5, 136.7, 149.2, 162.9 (C_5H_4N), 123.2, 128.1, 129.2, 148.5 (Ph).

Supporting Information Available: Tables of positional and isotropic displacement parameters, bond lengths, and bond angles for **5**, **26**, and **27**. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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