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Experimental Investigations and *ab Initio* Studies on Hexacoordinated Complexes of Dichlorosilane

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Abstract: Dichlorosilane, SiH_2Cl_2, forms two different kinds of coordination compounds with pyridine and 3-picoline: the simple adduct *trans*-$SiH_2Cl_2(L)_2$ and the ionic complex $[SiH_2(L)_4]Cl_2{\cdot}4CHCl_3$ (L = pyridine, 3-picoline). The adducts *trans*-$SiH_2Cl_2(py)_2$, **1**, and *trans*-$SiH_2Cl_2(3pic)_2$, **2**, form directly from the reaction of bis(dichlorosilyl)methylamine, $NMe(SiHCl_2)_2$ with pyridine (py), and 3-picoline (3pic). Reaction of **1** with an excess of pyridine in chloroform yielded $[SiH_2(py)_4]Cl_2{\cdot}4CHCl_3$, **3**. The molecular and crystal structures of **1**−**3** were investigated by single-crystal X-ray diffraction. The Si atoms of all three compounds are hexacoordinated and lie on centers of inversion. The basic structural parameters are the following: **1** (monoclinic, *C*2/*c*): Si−N 196.9(1) pm, Si−Cl 228.8(1) pm; N−Si−Cl 90.0(1)°, C−N−C 119.0(2)°; Cl−Si−N−C 102.4(1)°. **2** (triclinic, $P\bar{1}$): Si−N 197.5(1) pm, Si−Cl 229.2(1) pm; N−Si−Cl 90.3(1)°, C−N−C 118.8(1)°; Cl−Si−N−C 101.2(1)°. **3** (monoclinic, *C*2/*m*): Si−N 196.2(4) and 197.0(4) pm, Si···Cl 419.9 pm; N−Si−N 90.0°. All three complexes, neutral and cationic, exhibit very similar lengths of the dative Si−N bond. Hartree−Fock calculations with 3-21G(d) and 6-31G(d) basis sets and density functional calculations with the B3LYP functional and a 6-31G(d) basis set were employed for geometry optimizations of *trans*-$SiH_2Cl_2(py)_2$ and $[SiH_2(py)_4]^{2+}$. The optimized structures revealed similar Si−N bond lengths and geometric parameters of the pyridine moieties for both types of complexes as well. Single point energy calculations [B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d)], including corrections for the basis set superposition error, showed that the formation of **1** from SiH_2Cl_2 and pyridine in the gas phase is slightly endothermic ($\Delta H^{298} = 17.2$ kJ mol^{-1}) and endergonic ($\Delta G^{298} = 113.6$ kJ mol^{-1}). The significance of the Lewis acidity of SiH_2Cl_2 is thus questioned and intermolecular interactions (e.g. hydrogen bonds) are held responsible for the existence of **1** in the solid state.

Introduction

Coordination compounds of silicon have in recent years been the subject of many structural,[1−8] spectroscopic,[9,10] reactivity,[11] and *ab initio* studies.[12−20] A subset of that class of compounds, the complexes between chlorosilanes SiH_nCl_{4-n} and simple tertiary amines, are of fundamental interest concerning Lewis acid−base interactions. They were among the first coordination compounds of silicon investigated,[21−24] but little information

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about their molecular structure could be obtained.[25,26] Chlorosilanes form the adducts $\mathrm{SiH}_n\mathrm{Cl}_{4-n}(\mathrm{L})$[22] and $\mathrm{SiH}_n\mathrm{Cl}_{4-n}(\mathrm{L})_2$[23,24] (L = tertiary amine) and ionic complexes such as $[\mathrm{SiH_2(3pic)_4}]\mathrm{Cl_2}\cdot4\mathrm{CHCl_3}$.[27] Most of them are stable only in the solid state and dissociate quantitatively on melting, dissolving, or evaporating. $\mathrm{SiH_2Cl_2(3pic)_2}$ and $[\mathrm{SiH_2(3pic)_4}]\mathrm{Cl_2}\cdot4\mathrm{CHCl_3}$ are the only complexes of this type that have been shown to exist in solution.[27] Thus, it was of interest to perform ab initio calculations on these molecules, to get thermodynamic and structural information on the isolated species. Recently, we reported the reactivity of bis(dichlorosilyl)amine, $\mathrm{NH(SiHCl_2)_2}$, toward 2- and 3-picoline in chloroform solution.[27] We found that both tertiary amines caused a rapid decomposition of $\mathrm{NH(SiHCl_2)_2}$. 2-Picoline led to the formation of $\mathrm{SiHCl_3}$, $\mathrm{SiH_2Cl_2}$, and $\mathrm{SiHCl_3}$, while 3-picoline yielded an equilibrium mixture of **2** and $[\mathrm{SiH_2(3pic)_4}]\mathrm{Cl_2}\cdot4\mathrm{CHCl_3}$ (**4**, 3pic = 3-picoline). We obtained crystals of the latter, the first coordination compound containing a $\mathrm{SiH_2}^{2+}$ dication, and investigated its crystal structure by means of X-ray diffraction (XRD).[27] As crystals of **2** could not be obtained from this solution, we were challenged to find a suitable way to grow them, thus allowing for structural comparison between two fundamental types of hexacoordinated Si complexes, i.e. $\mathrm{SiH_2X_2(L)_2}$ and $[\mathrm{SiH_2(L)_4}]^{2+}$ (L = 3-picoline, X = Cl).

Results

Reaction of $\mathrm{NMe(HSiCl_2)_2}$ with 2-Picoline. No heat of reaction was observed when 2-picoline was added to a solution of $\mathrm{NMe(SiHCl_2)_2}$ in *n*-pentane or chloroform. The reaction was repeated with $\mathrm{CDCl_3}$ as a solvent. The ^{1}H NMR spectrum of this solution was shown to be the addition of the spectra of $\mathrm{NMe(SiHCl_2)_2}$ and 2-picoline.

Reaction of $\mathrm{NMe(HSiCl_2)_2}$ with Pyridine and 3-Picoline. As with 2-picoline, no heat of reaction was observed when either pyridine or 3-picoline was added to a solution of $\mathrm{NMe(HSiCl_2)_2}$ in *n*-pentane or $\mathrm{CHCl_3}$. Nevertheless, a white, powdery solid precipitated from the *n*-pentane solution, soon after the addition of pyridine and 3-picoline, respectively. From the chloroform solution, colorless, well-shaped crystals formed. The time required for the crystals to grow depended on the concentration of the tertiary amine. At higher concentrations, crystals grew within a few hours, while at lower concentrations (i.e. if about equimolar amounts of the tertiary amine and $\mathrm{NMe(SiHCl_2)_2}$ were present), several days passed, before the first crystals appeared. Elemental analysis of the white solid and the crystals showed that they were identical, but were not adducts of $\mathrm{NMe(SiHCl_2)_2}$ with pyridine or 3-picoline, respectively, but in fact dichlorosilanebispyridine, $\mathrm{SiH_2Cl_2(py)_2}$ (**1**), and dichlorosilanebis(3-picoline) $\mathrm{SiH_2Cl_2(3pic)_2}$ (**2**), which thus form according to reaction 1:

$$\mathrm{NMe(SiHCl_2)_2} + 2\mathrm{L} \rightarrow \mathrm{SiH_2Cl_2(L)_2} + 1/n(-\mathrm{SiCl_2}-\mathrm{NMe}-)_n \quad (1)$$

$$(\mathrm{L} = \text{pyridine, 3-picoline})$$

1 also forms either directly from $\mathrm{SiH_2Cl_2}$ and pyridine or from $\mathrm{SiH_3Cl}$ and an excess of pyridine,[23] **2** has recently been prepared by us.[27] The crystals obtained from reaction 1 were suitable for single-crystal XRD (see below). The cyclo- or polysilazanes that form as a side product of reaction 1 were not isolated.

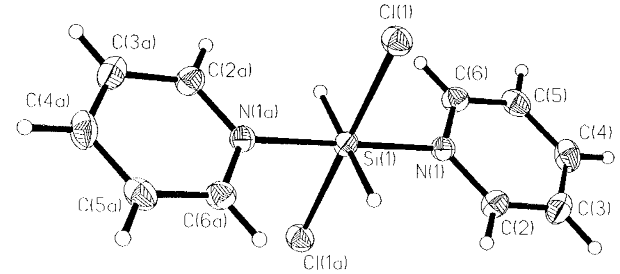

Figure 1. ORTEP diagram of **1**. Displacement ellipsoids are at the 50% probability level. Important structural parameters (distances, pm; angles, deg) of the molecule: Si(1)−N(1) 196.86(14), Si(1)−Cl(1) 228.81(4), N(1)−C(2) 134.6(2), N(1)−C(6) 134.5(2), C(2)−C(3) 137.9(3), C(6)−C(5) 138.2(3), C(3)−C(4) 139.1(3), C(5)−C(4) 138.0(3); N(1)−Si(1)−N(1a) 180.0, N(1)−Si(1)−Cl(1) 90.0(1), Si(1)−N(1)−C(2) 120.6(1), Si(1)−N(1)−C(6) 120.4(1), C(2)−N(1)−C(6) 119.0(2), N(1)−C(2)−C(3) 122.2(2), N(1)−C(6)−C(5) 121.8(2), C(2)−C(3)−C(4) 118.6(2), C(6)−C(5)−C(4) 119.2(2), C(3)−C(4)−C(5) 119.1(2); Cl(1)−Si(1)−N(1)−C(2) 102.3, N(1)−C(2)−C(3)−C(4) 0.0.

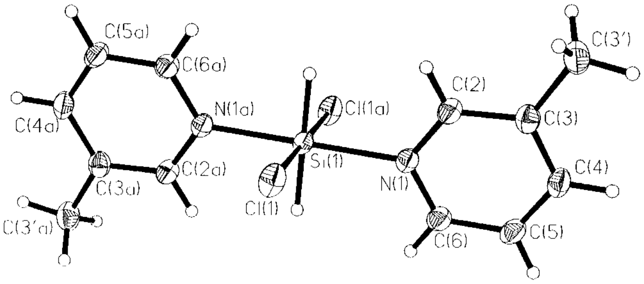

Figure 2. ORTEP diagram of **2**. Displacement ellipsoids are at the 50% probability level. Important structural parameters (distances, pm; angles, deg) of the molecule: Si(1)−N(1) 197.45(12), Si(1)−Cl(1) 229.22(4), N(1)−C(2) 134.7(2), N(1)−C(6) 134.5(2), C(2)−C(3) 138.7(2), C(3)−C(4) 139.5(2), C(3)−C(3′) 150.5(2), C(4)−C(5) 138.7(2), C(5)−C(6) 137.8(2); N(1)−Si(1)−N(1a) 180.0, N(1)−Si(1)−Cl(1) 90.27(4), Si(1)−N(1)−C(2) 119.8(1), Si(1)−N(1)−C(6) 121.4(1), C(2)−N(1)−C(6) 118.79(13), N(1)−C(2)−C(3) 123.52(14), N(1)−C(6)−C(5) 121.42(14), C(2)−C(3)−C(4) 116.85(14), C(6)−C(5)−C(4) 119.5(2), C(2)−C(3)−C(3′) 120.21(14), C(3)−C(4)−C(5) 119.87(14); Cl(1)−Si(1)−N(1)−C(6) 101.2, N(1)−C(2)−C(3)−C(4) 0.1.

Reaction of 1 with an Excess of Pyridine. **1** is not soluble in nonpolar and most aprotic polar solvents such as THF or MeCN. It does dissolve in $\mathrm{CHCl_3}$ if an excess of pyridine is added to the mixture. **1** thus behaved as **2**, which dissolves in $\mathrm{CHCl_3}$ as well, if an excess of 3-picoline is added,[27] but a much higher excess of pyridine is necessary to accomplish the dissolution of **1**. From this solution, a few crystals precipitated, which were characterized as dihydrotetra(pyridine)siliconchloride−tetrakischloroform, $[\mathrm{SiH_2(py)_4}]\mathrm{Cl_2}\cdot4\mathrm{CHCl_3}$ (**3**), by means of single-crystal XRD.

Single-Crystal XRD Investigations. The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. The Si atom in both compounds is hexacoordinated, by two Cl atoms, two H atoms, and two molecules of pyridine or 3-picoline, respectively. The molecules of **1** and **2** exhibit C_i symmetry, due to which only one independent Si−N, Si−H, and Si−Cl bond in the molecules of either compound is present. The pyridine rings are planar within experimental errors and the 3-picoline rings almost so. The two pyridine and 3-picoline moieties in **1** and **2**, respectively, are essentially coplanar. The N−Si−Cl angles are very close to 90.0°.

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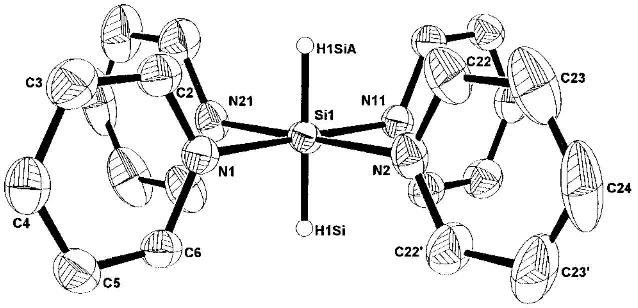

Figure 3. Diagram of $[SiH_2(py)_4]^{2+}$. Hydrogen atoms of the pyridine units are omitted for reasons of clarity. Important structural parameters (distances, pm; angles, deg) of the molecule: Si(1)−N(1) 196.2(4), Si(1)−N(2) 197.0(4), N(1)−C(2) 136.1(7), N(1)−C(6) 134.1(7), N(2)−C(22) 134.3(5), C(2)−C(3) 136.6(8), C(6)−C(5) 137.7(8), C(22)−C(23) 137.5(6), C(3)−C(4) 138.8(8), C(5)−C(4) 138.1(9), C(23)−C(24) 137.1(7); N(1)−Si(1)−N(11) 180.0, N(1)−Si(1)−N(2) 90.0, C(2)−N(1)−C(6) 118.4(5), C(22)−N(2)−C(22′) 119.7(5), N(1)−C(2)−C(3) 122.5(5), N(1)−C(6)−C(5) 121.8(5), N(2)−C(22)−C(23) 120.8(5), C(2)−C(3)−C(4) 118.8(6), C(6)−C(5)−C(4) 119.6(6), C(22)−C(23)−C(24) 118.8(6), C(3)−C(4)−C(5) 118.9(6), C(23)−C(24)−C(23′) 118.1(6); N(2)−Si(1)−N(1)−C(2) 90.0, N(1)−Si(1)−N(2)−C(22′) −87.6(3), N(1)−C(2)−C(3)−C(4) 0.0, N(2)−C(22)−C(23)−C(24) 1.1(7).

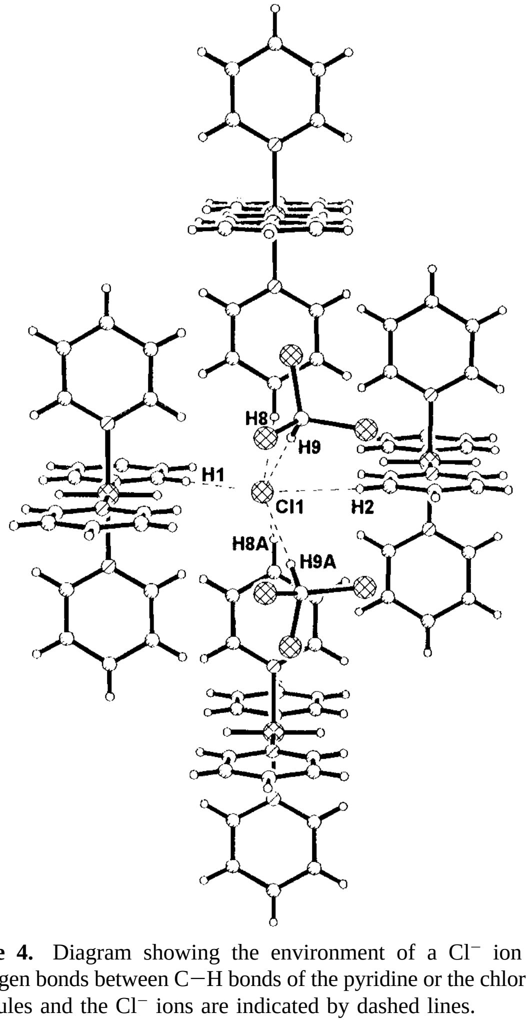

Figure 4. Diagram showing the environment of a Cl^- ion in **3**. Hydrogen bonds between C−H bonds of the pyridine or the chloroform molecules and the Cl^- ions are indicated by dashed lines.

The molecular structure of **3** in the solid state is shown in Figure 4. It exhibits C_i symmetry and consists of a hexacoordinated Si dication, $[SiH_2(py)_4]^{2+}$ (see Figure 3), with slightly distorted D_{4h} symmetry, two Cl^- ions, and four molecules of chloroform.

Each Cl^- ion is coordinated by six H atoms. The difference in lengths between the two independent N→Si bonds is not significant, nor are the differences in bond lengths and angles between the two crystallographically independent pyridine molecules, except for d(N−C2) and d(N2−C22).

Ab initio **Calculations.** *Ab initio* studies allow a closer look at molecular structures and energetics of the complex formation between SiH_2Cl_2 and pyridine, shown in reactions 2 and 3:

$$SiH_2Cl_2 + 2py \rightarrow SiH_2Cl_2(py)_2 \qquad (2)$$

$$SiH_2Cl_2 + 4py \rightarrow [SiH_2(py)_2]^{2+} + 2Cl^- \qquad (3)$$

Neither **2** (which is similar to **1**) nor the interaction of Cl^- with $CHCl_3$ or pyridine was investigated by means of *ab initio* calculations. Initial studies were carried out with the Hartree−Fock (HF) method with 3-21G(d) and 6-31G(d) basis sets, followed by density-functional theory (DFT)[28] calculations as to consider effects of electron correlation. It has been shown[29] that the DFT approach yields very good estimates of several properties of dative bond systems, including geometry and dative bond energy, as well as acceptable vibrational frequencies, if nonlocal corrections to the DFT exchange-correlation potential are used.[30,31] As the N and Cl atoms proved to exhibit highly negative atomic Mulliken and NBO charges at HF and DFT levels with a 6-31G(d) basis, single point energy calculations were performed with a basis set that includes additional polarization and diffuse functions. (For details see the Experimental Section below). Only geometries and vibrational frequencies obtained with B3LYP/6-31G(d) are given (see Table 1), while standard enthalpies of reaction, ΔH^{298}, and standard Gibbs free energies of reaction, ΔG^{298}, for (2) and (3) are given for all levels of calculation employed in the present work (see Table 2). The natural atomic charges,[32] within the pyridine moiety in pyridine itself, **1**, and $[SiH_2(py)_4]^{2+}$, are shown in Figure 5, and the natural charges of the Si, H, and Cl atoms are given in Table 1. Natural atomic charges are directly related to the eigenvalues of the density matrix expressed in terms of natural atomic orbitals and are thus more reliable than Mulliken atomic charges.

Figure 6 shows a plot of the potential energy of **1** (C_{2h}) versus the torsional angle τ(Cl−Si−N−C2). The difference in E_{elec} between the minimum at τ(Cl−Si−N−C2) = 60.4° and the transition state at τ(Cl−Si−N−C2) = 90.0° (Si−H bond eclipsing the N−C2 bond) is 2.6 kJ mol^{-1}, while the energy difference between that minimum and the transition state at τ(Cl−Si−N−C2) = 0° (Si−Cl bond eclipsing the N−C2 bond) is 31.4 kJ mol^{-1}.

Discussion

In contrast to $NH(SiHCl_2)_2$,[27] $NMe(SiHCl_2)_2$ does not react with 2-picoline. It reacts with pyridine and 3-picoline, but much more slowly than $NH(SiHCl_2)_2$ does. These differences must be entirely due to the presence of a Brønsted acidic site, i.e. a N−H group, in $NH(SiHCl_2)_2$. It allows $NH(SiHCl_2)_2$ to form a hydrogen bond with the tertiary amines, in which $NH(SiHCl_2)_2$ acts as a hydrogen bond donor and the tertiary amine as an

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Table 1. Selected B3LYP/6-31G(d) Optimized Geometric Parameters, Natural Atomic Charges q, Si−H Vibrational Frequencies, and B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) Single Point Energies at 0 K

(a) SiH_2^{2+}, H_2SiCl_2, and Pyridine

	C_5H_5N, C_{2v}	H_2SiCl_2, C_{2v}	H_2SiCl_2, D_{2h}	$SiH_2$2+, $D_{\infty h}$
d(Si−H)/pm		147.61	147.75	151.92
d(Si−Cl)/pm		206.54	214.28	
d(N−C^2)/pm	133.93			
d(C^2−C^3)/pm	139.46			
d(C^3−C^4)/pm	139.60			
a(ClSiCl)/deg		110.82	180.00	
a(HSiH)/deg		112.87	180.00	180.00
a(C^{2}NC^6)/deg	117.11			
q_{Si}/1.609 × 10^{-19} C		1.11	1.17	1.94
q_H/1.609 × 10^{-19} C		−0.17	−0.16	0.03
q_{Cl}/1.609 × 10^{-19} C		−0.38	−0.43	
ν^{is}(Si−H)/cm^{-1} [a]		2222.68	2168.39	1988.79
E_{elec}/hartree	−248.3577892	−1211.2763397	−1211.1977867	−289.6905052

(b) $H_2SiCl_2(py)_2$ and $[H_2Si(py)_4]^{2+}$

	1, C_{2h}	**1**, D_2	$[H_2Si(py)_4]^{2+}$, D_{4h}
d(Si−H)/pm	148.26	148.28	148.30
d(Si−Cl)/pm	229.06	229.19	
d(Si−N)/pm	203.87	203.86	201.65
d(N−C^2)/pm	134.24	134.24	135.18
d(C^2−C^3)/pm	138.97	138.97	138.80
d(C^3−C^4)/pm	139.47	139.47	139.62
a(ClSiH)/deg	90.84	90.00	
a(NSiCl)/deg	90.00	90.00	
a(C^{2}NC^6)/deg	119.71	119.77	118.75
t(XSiNC^2)/deg[c]	60.36	58.83	0.0
q_{Si}/1.609 × 10^{-19} C	1.21	1.21	1.54
q_{Cl}/1.609 × 10^{-19} C	−0.57	−0.57	
q_H/1.609 × 10^{-19} C	−0.23	−0.22	−0.26
ν^{is}(Si−H)/cm^{-1} [a]	2110.30	2111.90	2135.00
E_{elec}/hartree	−1708.0045308	−1708.0045578	−1283.7359026

[a] Isolated Si−H bond stretching frequencies, calculated at the B3LYP/6-31G(d) level and scaled according to Wong.[33]

Table 2. Thermochemical Data of Complex Formation for Reactions 2 [**1**(C_{2h}) and **1**(D_2)] and 3 $[SiH_2(py)_4]^{2+}$ [a]

		1(C_{2h})	**1**(D_2)	$[SiH_2(py)_4]^{2+}$
ΔH^{298}	HF/3-21G(d)	−92.2	−93.0	819.7
	HF/6-31G(d)	10.7	9.6	970.8
	B3LYP/6-31G(d)	−31.3	−32.3	1028.9
	B3LYP/6-311+G(2d,p)	−15.9	−16.0	1012.8
	B3LYP/6-311+G(2d,p)[b]	17.2	17.1	1066.5
ΔG^{298}	HF/3-21G(d)	4.7	6.7	965.2
	HF/6-31G(d)	108.0	109.3	1110.5
	B3LYP/6-31G(d)	65.0	65.5	1163.2
	B3LYP/6-311+G(2d,p)	80.5	81.9	1143.1
	B3LYP/6-311+G(2d,p)[b]	113.6	115.0	1196.8
V [c]	B3LYP/6-31G(d)	−294.8		−1698.8
V^{cc} [d]	B3LYP/6-31G(d)	−261.7		−1645.1

[a] ΔH,^{298} ΔG,^{298} V, and V^{cc} are given in kJ mol^{-1}. For details see Experimental Section. [b] ΔH^{298} and ΔG^{298} given here are corrected for the basis set superposition error (bsse). The bsse calculated for **1**(C_{2h}) was taken to correct ΔH^{298} and ΔG^{298} for **1**(C_{2h}) and **1**(D_2). For details see footnotes c and d and Theoretical Methods. [c] $V[\mathbf{1}(C_{2h})] = E_{elec}[\mathbf{1}(C_{2h})] - E_{elec}[SiH_2Cl_2(G1)] - 2E_{elec}[py(G1)]$; $V\{[SiH_2(py)_4]^{2+}\} = E_{elec}\{[SiH_2(py)_4]\} - E_{elec}[SiH_2^{2+}(G3)] - 4E_{elec}[py(G3)]$. G1 refers to the geometry of the SiH_2Cl_2 and pyridine moieties in **1**(C_{2h}), G3 refers to the geometry of the SiH_2^{2+} and pyridine moieties in $[SiH_2(py)_4]^{2+}$. [d] $V^{cc}[\mathbf{1}(C_{2h})] = E_{elec}[\mathbf{1}(C_{2h})] - E^{cc}_{elec}[SiH_2Cl_2(G1)] - 2E^{cc}_{elec}[py(G1)]$; $V^{cc}\{[SiH_2(py)_4]^{2+}\} = E_{elec}\{[SiH_2(py)_4]^{2+}\} - E^{cc}_{elec}[SiH_2^{2+}(G3)] - 4E^{cc}_{elec}[py(G3)]$. For the meaning of G1 and G3, see footnote c. E^{cc}_{elec} is the counterpoise corrected electronic energy. The difference between V and V^{cc} gives a measure for the basis set superposition error.

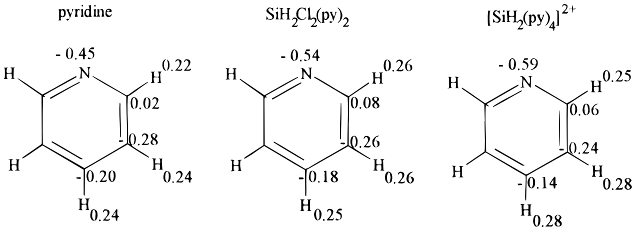

Figure 5. Natural atomic charges in units of the elemental charge of the H, C, and N atoms of the pyridine moiety in pyridine, **1**, and $[SiH_2(py)_4]^{2+}$.

acceptor. This 1:1 reaction, fast and exothermic, immediately leads to a decomposition of $NH(SiHCl_2)_2$ and a subsequent reaction of the released SiH_2Cl_2 with pyridine and 3-picoline.[34] It is likely that $NMe(SiHCl_2)_2$, which does not exhibit a Brønsted acidic site, interacts via one of its Lewis acidic sites, i.e. one of the Si atoms, with the lone pair of the tertiary amine, forming a weak Lewis acid−base complex as an intermediate. As the formation of precipitates of **1** and **2** from $NMe(SiHCl_2)_2$ and pyridine or 3-picoline, respectively, is much quicker in *n*-pentane than in chloroform, we suspect that this or a subsequently formed intermediate prior to the release of SiH_2Cl_2 from $NMe(SiHCl_2)_2$ is better stabilized in a polar solvent with a rather high acceptor number than in a nonpolar solvent.[35] The slow release of SiH_2Cl_2 is seen to be essential for the formation of good quality crystals directly from a chemical reaction.

Comparison of the Molecular Structures of 1, 2, and $[SiH_2(py)_4]^{2+}$. Table 3 gives some characteristic geometric parameters of tetra- and hexacoordinated compounds of silicon with pyridine and 3-picoline. The differences in the Si−Cl bond lengths and in the geometry of the pyridine ring between **1** and

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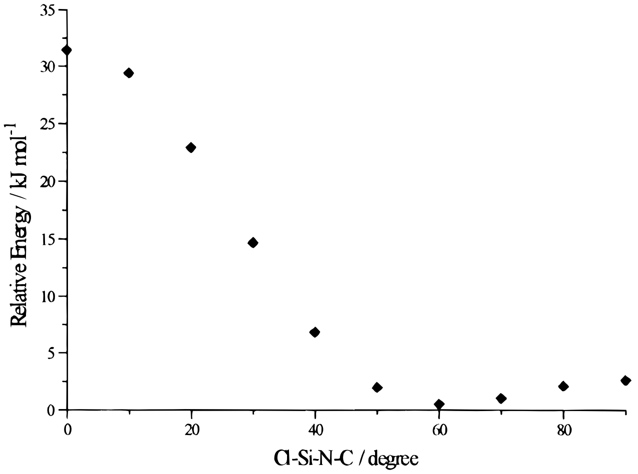

Figure 6. Potenial energy (in kJ mol^{-1} relative to the global minimum) of **1** (C_{2h}) as a function of the Cl−Si−N−C2 torsion.

Table 3. Comparison of Some Geometrical Parameters Taken from the Solid State Structures of Some Coordination Compounds of Si

	d_{av}(Si−N)	d_{av}(Si−Cl)	d_{av}(N−C)	a_{av}(C^2NC^6)	ref
1	196.9(2)	228.8(1)	134.6(3)	119.0(2)	this work
2	197.5(1)	229.2(1)	134.6(4)	118.8(1)	this work
3	196.6(8)		134.7(15)	118.6(14)	this work
4	197.2(6)		134.5(15)	119.0(4)	27
$SiCl_4(py)_2$	197.6(9)	218.3(4)	135(2)	117(1)	26
$[Me_3Si(py)]Br$	185.6(7)		133.5(15)	119.1(8)	1
$[Me_3Si(py)]I$	185.8(9)		133(3)	121(1)	1

2 are not significant; the torsion angles around the Si−N bond of **1** and **2** are similar. Furthermore, the Si−N bond lengths of the hexacoordinated compounds are within a range of 1.6 pm, those of **3** and **4** being slightly shorter than their counterparts in **1** and **2**, and bonds of 3-picoline to Si being on average slightly longer than those of pyridine. These results suggest that the nature of the dative bond between N and Si in hexacoordinated Si compounds hardly depends on the charge of the complex moiety. (See further down for a comparison of the Si atomic charges.) Comparing the hexacoordinated complexes of Si to the tetracoordinated ones, *d*(Si−N) seems to depend greatly on the coordination number, being 10−15 pm smaller in the latter. To introduce covalent radii for Si as a function of the coordination number does not seem reasonable to us as the difference $d(\mathrm{Si}_{\mathrm{CN}=6}-\mathrm{X}) - d(\mathrm{Si}_{\mathrm{CN}=4}-\mathrm{X})$ is not constant but varies with X. The differences in N−C bond lengths and in the C−N−C angles between tetra- and hexacoordinated complexes are, because of the high esds, not significant, but the C−N−C angles are wider and the N−C bonds shorter for the tetracoordinated species (see Table 3).

Despite the basic structural parameters of **1** and **2** being very similar, they exhibit different intermolecular interactions. The crystal structure of **1** exhibits close intermolecular contacts between H atoms of the pyridine ring and Cl atoms, whereas intermolecular contacts in **2** are due to interactions between H atoms of the methyl group and Cl atoms of adjacent molecules. In contrast, the interaction between the $[SiH_2(L)_4]^{2+}$ dication (L = pyridine, 3-picoline), the $CHCl_3$ molecules, and the Cl^- ions, as well as the way the $[SiH_2(L)_4]Cl_2{\cdot}4CHCl_3$ units pack within the crystal, are similar for **3** and **4** (see ref 27 for the crystal structure of **4**).

***Ab initio* Optimized Geometries and Calculated Frequencies.** Before comparing *ab initio* optimized to experimental XRD geometries, their general differences should be stressed. *Ab initio* geometries are so-called r_e structures, i.e. they refer to equilibrium distances between the positions of atomic nuclei corresponding to the minimum of the potential energy. XRD geometries represent distances r_α between average nuclear positions in the thermal equilibrium. Considering the same pair of nuclei, r_e is always smaller than r_α, due to the anharmonicity of interatomic vibrations. Furthermore, *ab initio* methods in general do not give exact but at best accurate solutions of the Schrödinger equation, hence the geometries cannot be taken to represent “the true structure of the isolated molecule”. It can thus be stated that the *ab initio* optimized geometries of **1**(C_{2h}) and $[SiH_2(py)_4]^{2+}$ (see Table 1) and the experimental geometries obtained by XRD (see Figures 1 and 3) do agree quite well. The only significant differences are the lengths of the dative Si−N bond and the Cl−Si−N−C torsion. A potential energy surface scan of the parameter describing the torsion around the Si−N bonds (see Figure 6) revealed that the potential energy curve is rather shallow between the minimum [τ(Cl−Si−N−C) = 60.4°] and the eclipse of the Si−H and N−C bond [τ(Cl−Si−N−C) = 90.0°], i.e. a change of torsion in that region does not require much energy. The shift of this parameter to its value in the solid state [τ(Cl−Si−N−C) = 77.7° = 180.0° − 102.3°] increases the energy by 1.8 kJ mol^{-1} (estimated by a linear interpolation of the potential energy curve between 70.0 and 80.0°) and might well be due to intermolecular forces. The optimized Si−N bond lengths in **1** and $[SiH_2(py)_4]^{2+}$ are similar, which corroborates the results obtained for the solid state by XRD. The increase of *d*(Si−N) from the solid state to the isolated molecule is in accordance with results obtained for other types of dative bonds.[36,37] The lengthening of the Si−Cl bond relative to $SiH_2Cl_2(C_{2v})$ is 3.7% for SiH_2Cl_2 (D_{2h}) and 10.9% for **1**(C_{2h}) (see Table 1). Referring to its value in $SiH_2Cl_2(C_{2v})$, the Si−H bond is stretched by 0.1% in SiH_2Cl_2 (D_{2h}) and by 0.4% in **1**(C_{2h}). The frequency of vibration of the isolated Si−H bonds, ν^{is}(Si−H), of SiH_2Cl_2 (D_{2h}) and **1** is, relative to $SiH_2Cl_2(C_{2v})$, shifted to lower wavenumbers, by approximately 55 and 110 cm^{-1}, respectively (see Table 1). (In an SiH_2 moiety, ν^{is}(Si−H) refers to ν(Si−H) in the corresponding monodeuterated SiHD moiety.) For **1**, the calculated shift is corroborated by experimental infrared bands [(**1**): ν_{as}(Si−H) = 2144 cm^{-1}, (SiH_2Cl_2): ν_{as}(Si−H) = 2231 cm^{-1} [38]]. It is thus *d*(Si−Cl) and ν(Si−H) rather than *d*(Si−H) which give a good indication for the weakening of the Si−Cl and Si−H bonds. Hence, the length of the Si−H bond is much better estimated by IR and/or Raman spectra than by XRD. This refers only to the statistical error of *d*(Si−H) and not to the systematic shrinkage of bonds between heavy elements and hydrogen in XRD experiments. The empirical relationship between the B3LYP/6-31G(d) optimized Si−H bond lengths and the B3LYP/6-31G(d) calculated ν^{is}(Si−H) for all species dealt with in this work (see Table 1) is not linear, as was found if only tetracoordinated Si compounds are considered.[38] The deviation from linearity may be due to qualitatively different potentials between the Si and H nuclei caused by major changes in the local geometry on going from tetra- to hexacoordinated silicon.

Taking the B3LYP/6-31G(d) optimized Si−H, Si−Cl, and Si−N bond lengths, we calculated the valences of the Si atom according to O’Keeffe,[39] which are shown in Table 4. We

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Table 4. Si−H, Si−Cl, and Si−N Bond Valences[a] and Valences of the Si Atom Based on the B3LYP/6-31G(d) Optimized Geometries of SiH_2^{2+}, SiH_2Cl_2 (C_{2v} and D_{2h}), **1**, and $[SiH_2(py)_4]^{2+}$

	υ_{SiH}	υ_{SiCl}	υ_{SiN}	υ_{Si}
SiH_2^{2+}	0.91			1.82
$SiH_2Cl_2(C_{2v})$	1.01	1.01		4.04
$SiH_2Cl_2(D_{2h})$	1.01	0.82		3.66
1(C_{2h})	0.99	0.55	0.54	4.16
1(D_2)	0.99	0.55	0.54	4.16
$[SiH_2(py)_4]^{2+}$	0.99		0.57	4.26

[a] The valence υ_i of an atom *i* is defined according to O'Keeffe et al.[39] as $\upsilon_i = \sum \upsilon_{ij}$, where υ_{ij} is the bond valence of the bond between the atom *i* and its ligand *j*. An empirical relationship between the bond length d_{ij} between atoms *i* and *j* and the bond valence υ_{ij} is given by $\upsilon_{ij} = \exp[(R_{ij} - d_{ij})/b]$. Here, *b* is taken to be a "universal" constant equal to 37 pm. R_{ij} is the so-called bond valence parameter, which gives the length of a bond whose valence is equal to unity.

accepted the *ab initio* data over the XRD data as more precise values of *d*(Si−H).

The valences of the Si atom, υ_{Si}, of **1** and $[SiH_2(py)_4]^{2+}$ are only slightly bigger than υ_{Si} of $SiH_2Cl_2(C_{2v})$. Thus, the term "hypervalent" for **1** and $[SiH_2(py)_4]^{2+}$ does only apply to a small degree. On the other side, changing the symmetry of SiH_2Cl_2 from C_{2v} to D_{2h} decreases υ_{Si}. In terms of relating the Lewis acidity of silicon to a valence υ_i smaller than four, it is much more $SiH_2Cl_2(D_{2h})$ than $SiH_2Cl_2(C_{2v})$ which exhibits that property. How the different lengthening of the Si−H and the Si−X bond (X = F, Cl, Br, I) in different halosilanes corresponds to the energy difference between the ground-state geometry and the planar (transition state) structure and how this relates to the Lewis acidity of the halosilanes is the subject of a current study.

***Ab initio* Energies and Natural Charges.** The effective charges of the Si atoms in **1** and $[SiH_2(py)_4]^{2+}$ (see Table 1) do not differ by 2 units—as the formal charges do—but only by about 0.33. Whereas the positive charge on the Si atom is reduced on going from SiH_2^{2+} to $[SiH_2(py)_4]^{2+}$, it is slightly increased from $SiH_2Cl_2(C_{2v})$ to **1**. The natural atomic charges on the H_{Si}, Cl, and N atoms become more negative as the complexes are formed, that of the H_{Si} and N atoms are even more negative in $[SiH_2(py)_4]^{2+}$ than in **1**. This result of an increased positive atomic charge on the acceptor atom and an increased negative charge on the donor atom corroborates previous investigations.[40] It indicates an increased ionic contribution to the bonds between the central atom and its ligands in compounds with an extended coordination shell. The increased electron density on the H_{Si}, Cl, and N atoms is balanced by an enhanced positive charge not only on the Si atom but also on the C and H atoms of the pyridine ring, which is a good precondition for the formation of intermolecular C−H···Cl hydrogen bridges and Coulombic or local dipole−dipole interactions (see single-crystal XRD investigations above and discussion of the energies below).

The enthalpies $H^{298}$of **1**(C_{2h}) and **1**(D_2) differ by only 0.1 kJ mol^{-1}, and the Gibbs free energy, G^{298}, of **1**(C_{2h}) is 1.4 kJ mol^{-1} lower than that of **1**(D_2). It is thus not surprising that the geometric parameters of **1**(C_{2h}) and **1**(D_2) are very similar. It follows directly that hardly any orbital interaction between the two pyridine rings across the Si atom takes place, as otherwise the D_2 structure would be destabilized by that amount of energy against the C_{2h} structure. It can thus be inferred that pyridine is only a σ- and not a π-donating ligand toward SiH_2Cl_2, a statement that is corroborated by second-order perturbation analyses on a NBO basis (see below). The results obtained from the potential energy surface scan (see Figure 6) imply that the balance between the repulsion of the pyridine moiety by the Si−H and Si−Cl bonds rather than any orbital interactions determines the Cl−Si−N−C2 torsion.

The formation of **1** from SiH_2Cl_2 and pyridine requires a change in symmetry of the SiH_2Cl_2 moiety from the ground-state symmetry C_{2v} to D_{2h}. The latter was shown to be a transition state (the frequency analysis revealed one imaginary frequency) connecting two equivalent C_{2v} geometries, with an energy difference $\Delta E_{elec} = 206.3$ kJ mol^{-1} [B3LYP/6-311+G(2d,p)] between ground and transition state. Forming **1** according to reaction 2, the endothermic process $SiH_2Cl_2(C_{2v}) \rightarrow SiH_2Cl_2(D_{2h})$ is—depending on the model chemistry—more or less compensated by the exothermic interaction of $SiH_2Cl_2(D_{2h})$ with the two pyridine molecules. The formation of $[SiH_2(py)_4]Cl_2$ from SiH_2Cl_2 and pyridine requires two heterolytic cleavages of the Si−Cl bonds, i.e. the reaction $SiH_2Cl_2(C_{2v}) \rightarrow SiH_2^{2+} + 2Cl^-$. The enthalpy to accomplish it is only in part "paid back" by the addition of four molecules of pyridine to SiH_2^{2+}. At the B3LYP/6-31G(d) level, the interaction energies *V* between pyridine and SiH_2Cl_2 and SiH_2^{2+}, respectively, were calculated (see Table 2). $V\{[SiH_2(py)_4]^{2+}\}$ is nearly six times bigger than $V[\mathbf{1}(C_{2h})]$, i.e. the interaction energy for each molecule of pyridine with the Si atom is nearly three times bigger for $[SiH_2(py)_4]^{2+}$ than for **1**. This is remarkable as the dative bond distances have been shown to be very similar (see Table 1). The NBO analyses revealed that the interaction between the pyridine and the silane moiety is—not surprisingly—dominated by the interaction between the lone pair of the N atom and 3p orbitals of the Si atom for **1** and for $[SiH_2(py)_4]^{2+}$. The d-type polarization functions of the Si atom do not contribute to the dative bond. Considering the basis set superposition error that is still included in *V*, an improved interaction energy V^{cc} was obtained performing counterpoise correction calculations.[41,42] The difference between *V* and V^{cc} (i.e. 33.1 kJ mol^{-1} for **1** and 53.6 kJ mol^{-1} for $[SiH_2(py)_4]^{2+}$) is a measure of the basis set superposition error.

The positive value of ΔG^{298} for reaction 2 means that **1** is not stable in the gas phase. This result is in accordance with measurements of the vapor pressure of $SiCl_4(py)_2$[43] and its gas-phase photoelectron spectrum,[44] where no $SiCl_4(py)_2$ could be detected.

Thus **1** and $[SiH_2(py)_4]Cl_2$ require stabilization by additional intermolecular interaction. There are several close contacts between Cl atoms and H atoms of the pyridine and 3-picoline moieties in the crystal structure of **1** and **2**, respectively. As far as the B3LYP/6-31G(d) calculations of the natural atomic charges show, the H atoms of the pyridine ring are more positively and the Cl atoms more negatively charged in **1** than in pyridine and $SiH_2Cl_2(C_{2v})$. This "charge flow" favors the formation of intermolecular C−H···Cl interactions which can be regarded as hydrogen bonds. In **3**, the close contact between the $[SiH_2(py)_4]^{2+}$ dication and the two Cl^- ions (Si···Cl = 419.9 pm)—one could call this a "contact-ion-trio"—must result in substantial Coulombic interaction, in addition to the hydrogen bonds between the Cl^- ions and the $CHCl_3$ and pyridine molecules, respectively. All of these intermolecular interactions must provide enough stabilization effects to make **1** and $[SiH_2(py)_4]Cl_2$ exist.

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Conclusion

SiH_2Cl_2 is not as strong a Lewis acid as its reactivity toward pyridine and its derivatives suggests. It is much more the intermolecular interactions, i.e. hydrogen bonds and Coulombic and dipole forces, between the complex molecules than the formation of dative Si−N bonds that drives SiH_2Cl_2 to act as an electron pair acceptor toward tertiary amines. These stabilizing forces can be provided by the molecular environment in the solid state or in solution.

Experimental Section

General Procedures. All procedures were carried out under argon or nitrogen (dried with activated 4-Å molecular sieves and Sicapent) either on a vacuum line or in a glovebox. Solvents were distilled from CaH_2 and stored over activated molecular sieves; pyridine and 2- and 3-picoline were distilled from CaH_2 and sealed in ampules. H_2SiCl_2 (Aldrich, 99.99%) was used without further purification; bis(dichlorosilyl)methylamine was prepared and purified according to the literature.[34] CHN analyses were performed with a CHN−Rapid (Heraeus) combustion analyzer, Cl was determined potentiometrically with $AgNO_3$. ^1H NMR: Bruker AMX 400, B_1 = 400 MHz. Standard: TMS.

Preparation of Dichlorosilanebispyridine, $SiH_2Cl_2(py)_2$ (1). Bis(dichlorosilyl)methylamine ($NMe(SiHCl_2)_2$, 0.60 mL (3.45 mmol)) was dissolved in 5.0 mL of $CHCl_3$ and 1.0 mL (12.36 mmol) of pyridine was added in portions of 0.2 mL with stirring. From this solution, colorless crystals formed within several days. They were isolated and washed with *n*-pentane, and a single crystal was selected for X-ray diffraction. Anal. Calcd for $C_{10}H_{12}Cl_2N_2Si$: C, 46.5; H, 4.7; N, 10.8; Cl, 27.4. Found: C, 45.5; H, 4.9; N, 10.4; Cl, 27.9. IR (Nujol, NaCl, cm^{-1}): 2920 (vs), 2848 (vs), 2144 (br, s), 1613 (vs), 1458 (s), 1374 (vs), 1195 (s), 1040 (s), 992 (s), 987 (m, sh), 962 (m) 951 (s), 772 (s), 688 (s), 658 (s), 462 (m).

Preparation of Dichlorosilanebis(3-picoline), $SiH_2Cl_2(3pic)_2$, 2. Bis(dichlorosilyl)methylamine ($NMe(SiHCl_2)_2$, 0.60 mL (3.46 mmol)) was dissolved in 5.0 mL of $CHCl_3$ and 1.0 mL (10.24 mmol) of 3-picoline was added in portions of 0.2 mL with stirring. From this solution, colorless crystals formed within several days. They were isolated and washed with *n*-pentane, and a single crystal was selected for X-ray diffraction. Anal. Calcd for $C_{12}H_{16}Cl_2N_2Si$: C, 50.5; H, 5.6; N, 9.8; Cl, 24.7. Found: C, 47.8; H, 5.7; N, 9.2; Cl, 25.1. IR (Nujol, NaCl, cm^{-1}): 2144 (br, s).

Preparation of Dihydrotetra(pyridine)siliconchloride−Tetrakischloroform, $[SiH_2(py)_4]Cl_2\cdot 4CHCl_3$, 3. **1** (30 mg (0.12 mmol)) was suspended in 5.0 mL of $CHCl_3$ and pyridine was added dropwise until the white solid was dissolved. (**1** for this experiment was prepared by adding an excess of pyridine to SiH_2Cl_2 dissolved in *n*-pentane and isolation of the white precipitate.) From this solution at 5 °C a few crystals precipitated and a single crystal was selected for X-ray diffraction.

Attempts To Grow Single Crystals of 1 and 2 by Sublimation. Samples of **1** and **2**, exposed to various temperature gradients, could be sublimed in vacuo, but tended to form thin, white films on the cooler parts of the glassware. In no case could a suitable single crystal for XRD be obtained.

Crystal Structure Determination. The crystal structures were solved by direct methods and difference Fourier technique (SHELXS-86);[45] structural refinement was against F^2 (SHELXL-93).[46] Details of the crystal structure determination of and the crystal data for **1**−**3** are given in Table 5.

Table 5. Crystal Data for Compounds **1**−**3**

	1	**2**	**3**
emprical formula	$C_{10}H_{12}Cl_2N_2Si$	$C_{12}H_{16}Cl_2N_2Si$	$C_{24}H_{26}Cl_{14}N_4Si$
FW/g mol^{-1}	259.21	287.26	894.88
crystal system	monoclinic	triclinic	monoclinic
space group	*C*2/*c*	$P\bar{1}$	*C*2/*m*
temp/K	153	173	130
ρ_{calcd}/g cm^{-3}	1.435	1.391	1.547
a/nm	1.54608(1)	0.60174(2)	1.0508(1)
b/nm	0.61660(1)	0.75422(3)	1.4833(1)
c/nm	1.43313(2)	0.85744(3)	1.2508(1)
α/deg	90	65.954(1)	90
β/deg	118.576(1)	76.746(1)	98.05(1)
γ/deg	90	77.881(1)	90
Z	4	1	2
$R\ [I > 2\sigma(I)]$	0.029	0.0276	0.0641
goodness-of-fit on F^2	1.116	1.056	1.061

Theoretical Methods. The *ab initio* calculations were performed on various servers of the Zentrum für Datenverarbeitung, Universität Mainz, using the GAUSSIAN94 software package.[47] All geometries were fully optimized at a variety of levels of theory including Hartree−Fock [with 3-21G(d) and 6-31G(d) basis sets] and density functional theory (DFT) [with 6-31G(d) basis set].[48] DFT geometry optimizations employed a combination of local, gradient-corrected, and exact exchange functionals according to the prescription of Becke[31] and the gradient-corrected correlation functional of Lee, Yang, and Parr (B3LYP).[30] All stationary points were characterized by calculation of analytic force constants, from which vibrational frequencies were obtained. Only geometries and frequencies obtained with the B3LYP/6-31G(d) model chemistry are given in this paper. With the same model, natural bond orbital analyses were performed.[32] Taking the B3LYP/6-31G(d) optimized geometries, single-point energies were calculated at the B3LYP level of theory with a 6-311+G(2d,p) basis set and tight convergence in the SCF procedure. H^{298} and G^{298} were obtained from unscaled thermal corrections. By the B3LYP/6-31G(d) optimized geometries of **1** and $[SiH_2(py)_4]^{2+}$, counterpoise calculations[41,42] were performed at the same level to correct the energy of interaction between Si and pyridine for the so-called basis set superposition error (bsse).[42] The following symmetry restrictions were used for the single species considered within the present work: SiH_2^{2+}, $D_{\infty h}$; SiH_2Cl_2, C_{2v} and D_{2h}; pyridine, C_{2v}; $[SiH_2(py)_4]^{2+}$, D_{4h}. Two different symmetries of **1** were investigated. In both, the N−Si−Cl angles are rectangular and the pyridine moieties exhibit local C_{2v} symmetry. **1**(C_{2h}) exhibits two coplanar pyridine moieties, while in **1**(D_2) the two pyridine planes form an angle, which is bisected by the N_2SiCl_2 plane. A relaxed potential energy surface scan was performed for **1**(C_{2h}) by using the B3LYP/6-31G(d) model chemistry. Here the parameter describing the torsion of the planes of the pyridine rings against the N_2SiCl_2 plane, τ[C(2)−N−Si−Cl], was changed in steps of 10.0 deg from 0.0 to 90.0 deg. While it was held constant, the other geometrical parameters were optimized.

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Supporting Information Available: Tables of crystal data and positional and isotropic and anisotropic thermal parameters as well as the structure for **3** (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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