Journal of Organometallic Chemistry, 382 (1990) 345–359
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20467

Contributions to the chemistry of halosilane adducts

XIX *. Temperature dependent equilibrium between pentacoordinate and ionic tetracoordinate structures of an organochlorosilane-nitrogen base adduct. Synthesis and structural investigations of (*N–Si*)-silicon-functional (1-(2-pyridone(2′-pyridyl)imine)methyl)silanes. The crystal and molecular structure of (*N–Si*)-chloro(1-(2-pyridone-(2′-pyridyl)imine)methyl)dimethylsilane, (*N–Si*)-(1-(2-pyridone(2′-pyridyl)imine)methyl)trichlorosilane and 1-methyl-2-(2′-pyridyl)aminopyridinium chloride

Dieter Kummer *, **Subhash C. Chaudhry, Joachim Seifert,**
Institut für Anorganische Chemie der Universität (TH), D-7500 Karlsruhe (B.R.D.)

Bernhard Deppisch and Günter Mattern
Institut für Kristallographie der Universität (TH), D-7500 Karlsruhe (Germany)

(Received July 25th, 1989)

Abstract

2,2′-Dipyridyltrimethylsilylamine reacts with chloro- and bromomethyl(methyl) chlorosilanes to give Si-functional 1-(2-pyridone-(2′-pyridyl)imine) methylsilanes. Their solid state and solution structures have been determined. Depending on the halogen and the number of halogen atoms neutral pentacoordinate Si-species, $R\overline{N\text{-}2\text{-}(C_5H_4NCH_2Si}Me_xCl_{3-x})$ ($R = 2\text{-}C_5H_4N$; $x = 1$ (**2**); $x = 0$ (**3**)) or ionic tetracoordinate Si-species $[R\text{-}\overline{N\text{-}2\text{-}(C_5H_4NCH_2Si}Me_2)]^+Br^-$ (**4**) are obtained in solution and as solids. The solid compound with $x = 2$ (**1**) is also pentacoordinate at Si. In solution there is an interesting temperature-dependent equilibrium between the neutral pentacoordinate and the ionic tetracoordinate structure (at lower temperature, NMR) of **1**. For the pentacoordinate species dissociation of the coordinative Si–N bond and formation of the neutral tetravalent silanes is suggested at higher

---

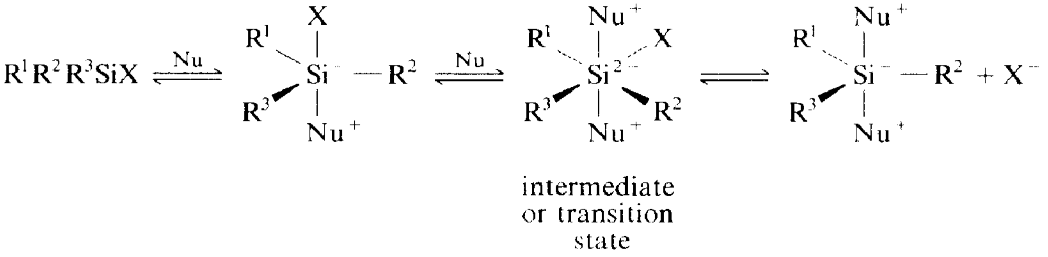
* For part XVIII see ref. 5.

0022-328X/90/$03.50

temperature in solution. The temperature-dependent equilibrium between the isomers of **1** thus follows reversibly the S_N2 pathway of nucleophilic substitution at silicon. The solid state structures of **1** and **3** and of 1-methyl-2-(2′-pyridyl)aminopyridinium chloride (**5**) are discussed. Structural differences between solid **1** and **3** are interpreted in terms of different stages of the S_N2 reaction at silicon.

Introduction

There has been much recent interest in investigation of the mechanism of nucleophilic substitution at silicon. Three mechanisms have been proposed for nucleophilically-activated racemisation and solvolysis of halosilanes. One mechanism involves expansion of coordination at silicon, involving ultimately hexacoordinated intermediate species (Scheme 1) [1], while another involves intermediate tetracoordinate ionic silicon species with ionization of Si–halogen bonds [2]. Recently, an alternative pathway for nucleophile-assisted racemization of halosilanes involving halide exchange has been suggested [3]. This has led to an extension of the second mechanism as shown in Scheme 2. In spite of many studies in this field no clear distinction between the first two mechanisms can yet be made. In the course of our investigations of coordination compounds of silicon we were able to obtain compounds with properties which may throw light on these questions and give a better understanding of the factors determining either coordination expansion or ionization of Si–halogen bonds as a consequence of coordination. This has been discussed recently [4,5]. We now report the preparation and structural investigations of these compounds.



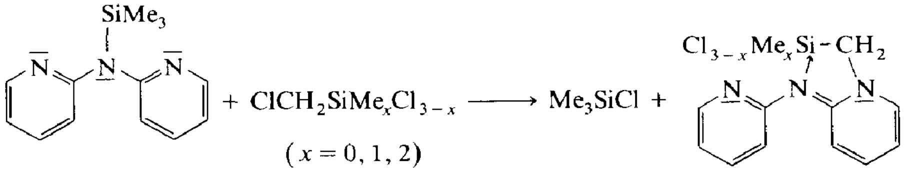
Scheme 1

$$\begin{tikzcd}[column sep=huge, row sep=large]
R_3SiX + Nu \arrow[r, shift left, "inv"] \arrow[d, shift right, "Hal^-\ (inv)"'] & {[\overline{R_3Si}(Nu)]^+\ X^-} \arrow[l, shift left, "inv"] \arrow[d, shift right, "Nu\ (inv)"'] \\
\overline{R_3Si}X + Nu \arrow[r, shift left, "inv"] \arrow[u, shift right, "Hal^-\ (inv)"'] & {[R_3Si(Nu)]^+\ X^-} \arrow[l, shift left, "inv"] \arrow[u, shift right, "Nu\ (inv)"']
\end{tikzcd}$$

Scheme 2

Results and discussion

When *N*-trimethylsilyl-2,2′-dipyridylamine is treated with chloromethylchlorosilanes, *N*-pyridylsubstituted derivatives (**1**, **2**, **3**) are obtained, with liberation of one equivalent of Me_3SiCl (eq. 1).



(1)

(**1**: $x = 2$,
2: $x = 1$,
3: $x = 0$)

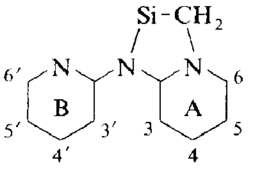
Structural investigations of the new compounds have revealed interesting facts, especially in the case of the chloromethyldimethylchlorosilane derivative (**1**). The ^1H and ^{13}C and ^{29}Si NMR spectra of **1** show major changes between −100 and +140 °C. The ^1H NMR spectra (Table 1) are consistent with the proposed bonding of the silylmethyl group to one of the pyridyl rings. The signals from the protons of this ring (A) are strongly shifted down-field at low temperature and to high-field at high temperature.

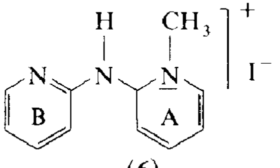
At −70 °C the chemical shifts approach those of pyridinium compounds, whereas at +140 °C they correspond to typical shifts of pyridones or pyridone imines. Thus, the 6H signal is shifted 1.22 ppm upfield from 9.15 ppm at −70 °C to 7.93 ppm at +140 °C. The signals from the protons of the other pyridyl ring (B) show only a small temperature dependence, and remain in the typical pyridine proton region.

This result and the temperature dependence of the CH_2 proton shifts (see below) are interpreted in terms of a temperature-dependent equilibrium between two or possibly three isomers of the compound (Scheme 3), the aminopyridinium chloride formed by ionisation of the Si–Cl bond at low temperature with four-coordinate silicon, and the pyridone-imine derivatives with penta-coordination at silicon by Si–N interaction (corresponding to a pyridone-2-immonium derivative) at intermediate temperatures and possibly four coordinate silicon at high temperatures by dissociation of the Si–N bond. Although no direct evidence of Si–N dissociation has been found the substantial high field shift of the CH_2 protons upon increase of temperature is in accord with this assumption. The NMR-data may also be interpreted in terms of a continuous transition of the ligand system from the aminopyridinium to the pyridone-imine extreme upon increase of temperature, which is consistent with the ^1H and ^{13}C spectra, and a concomitant increase of the Si–N bond length and decrease of the Si–Cl bond length which determine the ^{29}Si shift. For a relatively stronger decrease (for Si–Cl) than increase (for Si–N) a high field shift of the ^{29}Si resonance is expected [6]. No distinction can be made between the two possibilities, both of which may in fact be present. The indications of the ^1H NMR data are supported by those from the ^{13}C spectra (Table 2). The temperature dependence of the ring and methylene carbon resonances (in particular the high field shifts of the CH_2 and 5C (N-substituted ring A) signals and a strong low field shift of the 3C signal with increase of temperature) are in accord with the proposed

Table 1

^{1}H and ^{29}Si NMR chemical shifts (δ (ppm)) for compounds **1**, **2**, **3**, **4**, and **6** ($CDCl_3$ solutions, TMS internal standard)

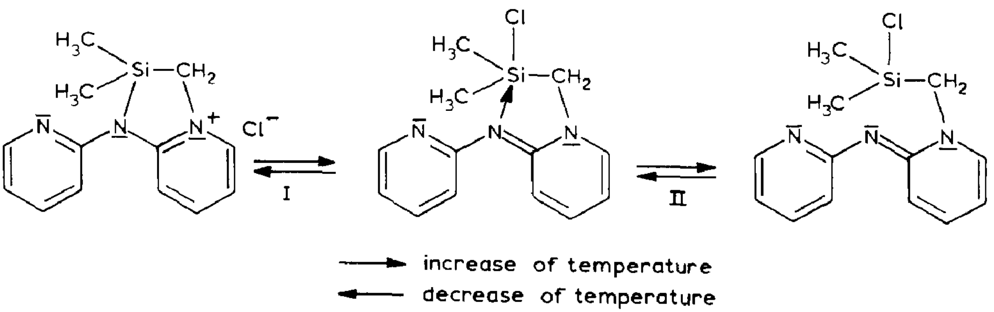




(6)

Compound	Temp. (°C)	^{29}Si	^{1}H Ring A						^{1}H Ring B			
			6H	5H	4H	3H	CH_2	CH_3	6'H	5'H	4'H	3'H
1	+140		7.93	6.58	7.46	6.88	4.06	0.78	8.44	7.10	7.73	7.14
	+80	−6.2 [a]	8.36	6.85	7.72	7.11	4.22	0.79	8.47	7.19	7.82	7.25
	+25	+6.4	8.69	7.02	7.92	7.33	4.33	0.79	8.45	7.23	7.88	7.32
	−70	+18.4 [b]	9.15	7.22	8.16	7.63	4.45	0.82	8.51	7.32	7.97	7.41
2	+80		7.76	6.59	7.45	6.60	4.08	0.92	8.51	7.21	7.81	7.55
	+25		7.84	6.68	7.53	6.64	4.13	0.95	8.52	7.27	7.87	7.58
	−70		8.00	6.83	7.68	6.79	4.26	0.95	8.56	7.35	7.93	7.64
3	+80		7.75	6.65	7.48	6.50	4.10	–	8.51	7.23	7.80	7.63
	+25		7.82	6.70	7.53	6.50	4.15	–	8.54	7.28	7.84	7.65
	−70		7.92	6.80	7.63	6.53	4.25	–	8.59	7.37	8.01	7.68
4	+80	+19.2 [c]	8.88	7.22	8.20	7.66	4.44	0.78	8.43	7.25	7.93	7.55
	+25	+19.9 [d]	8.95	7.25	8.25	7.73	4.42	0.78	8.45	7.27	7.96	7.55
	−70	+20.4 [b]	9.04	7.27	8.30	7.78	4.40	0.80	8.47	7.29	7.97	7.51
6	+25		8.04	6.86	7.81	7.24	–	3.88	8.37	7.17	7.94	7.85

[a] At 100 °C. [b] At −80 °C. [c] At +80 °C. [d] At 0 °C. [e] In $CDCl_3/CH_3CN$ 1/1 v/v $^{1}H^{1}H$ coupling constants (not listed) in agreement with postulated structures:



Scheme 3

equilibria. Corresponding shifts of the 5C and 3C resonances are generally observed for related 2-pyridyl ether vs. 2-pyridone structures [20]. The smaller difference of the ^{13}C shift values compared to the corresponding ^{1}H shift values of the present aminopyridinium vs. the pyridone-imine or immonium species may be due mainly to the different effects of the aromatic ring current on ring ^{1}H and ^{13}C resonances. Furthermore, a high field shift of the ^{29}Si resonance (a single signal in the accessible temperature range) with increase of temperature is observed, as expected for an increase in penta-coordinate relative to tetra-coordinate Si species [7] (in terms of equilibrium I (Scheme 3) alone or of I and II). For the exclusive presence of equilibrium II a low field ^{29}Si shift with increase of temperature would be expected. This is not observed in the accessible temperature range (up to 80 °C). Thus, while clear evidence for equilibrium I is given by the ^{29}Si spectra this is not the case for equilibrium II (Si–N dissociation).

Further support for the suggested equilibria of Scheme 3 comes from the nature of compounds **2**, **3** and **4**. Compound **4** was obtained from (bromomethyl)dimethyl-

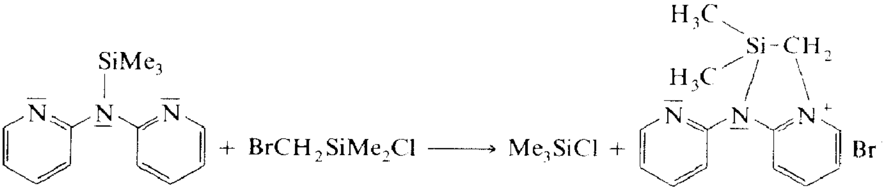
Table 2

^{13}C NMR chemical shifts (δ (ppm)) for compounds **1**, **2**, **3** and **4** ($CDCl_3$ solutions, TMS internal standard)

Compound	Ring	Temp. (°C)	2C	3C	4C	5C	6C	CH_2	CH_3
1	A	+80	153.4	117.3	143.1	114.3	142.0	44.8	3.5
	B		156.1	121.2	139.2	112.9	149.3		
	A	25	152.3	116.2	143.8	115.0	142.3	44.0	2.1
	B		155.4	121.2	139.4	112.6	149.1		
	A	−70	150.5	113.9	144.5	115.9	142.8	42.2	−0.2
	B		154.2	120.9	139.2	111.8	148.6		
2	A	25	157.1	121.4 [a]	139.1 [a]	113.5	141.8	46.4	11.7
	B		155.0	121.6 [a]	139.8 [a]	112.3	149.7		
3	A	25	156.3	122.8 [a]	142.0	113.7	143.9	46.0	–
	B		154.7	122.6 [a]	139.3	111.5	149.8		
4	A	25	151.8	115.3	145.4	116.8	144.0	43.9	0.6
	B		155.0	121.5	140.0	113.0	149.1		

[a] Tentative assignments.

chlorosilane according to eq. 2.


(2)

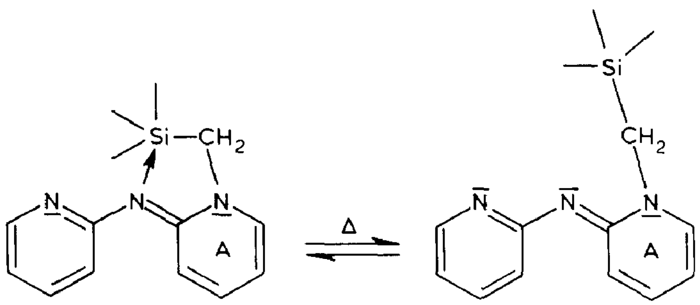
The ^1H and ^{13}C NMR spectra of **4** (Tables 1 and 2) correspond closely to the low temperature spectra of **1**, and vary only little with temperature (the proton shifts for the free pyridyl-ring (B) and the CH_2 group not more than 0.04 ppm, and the shifts of the *N*-substituted pyridyl ring A not more than 0.16 ppm between −70 and +80 °C). The shift values are in accord with the presence of a pyridinium structure which is retained over the whole temperature range up to 140 °C. The pyridinium structure is in accord with the greater ease of ionization of the Si–Br than of the Si–Cl bond.

The fact that the chemical shifts of **1** and **4** (^1H, ^{13}C, ^{29}Si) differ slightly even at low temperature but apparently converge with further decrease of temperature, as well as the greater temperature dependence of the shifts of the pyridinium protons (ring A) of **4** compared with those for pyridyl protons (ring B) may be due to contact ion pair/solvent-separated ion pair equilibria. Partial dissociation may also occur. The ionic structure of **4** is also present in the solid state, as evidenced interalia by the absence of IR bands in the 500–200 cm region assignable to Si–Br vibrations.

On the other hand the ^1H NMR spectra of **2** and **3** (Table 1) are very similar to the high temperature spectrum of **1** and thus are consistent with the presence of pyridone-imine species. Since a formal analogy exists between the SiN coordinated compounds **2** and **3** and 1-methyl-2-(2′-pyridyl)aminopyridinium halides the proton chemical shifts for the iodide **6** (obtained from 2,2′-dipyridylamine and methyliodide) were determined for comparison (Table 1). They are similar to those of **2** and **3**, confirming the analogy, but shifted slightly to lower field. They suggest that the bonding in **6** is between the aminopyridinium and the pyridone-immonium forms, and perhaps closer to the latter. This is confirmed by X-ray structure investigations (see below). The similarity is also in accord with strong N–Si coordination for **2** and **3** at −70 °C, where the best agreement of δ-values with those for **6** is observed. Increase in temperature causes high field (and converging) shifts of corresponding CH_2 and pyridone ring A protons of **2** and **3**. They are greater than expected for the usual temperature effect, the magnitude of which can be estimated from the temperature dependence of the pyridyl ring B proton shifts for **4**, and approach the pyridone shift region (1-methyl-2-pyridone: δ (ppm) 6H 7.31, 5H 6.15, 4H 7.26, 3H 6.57 [8]). Also, the pyridyl-ring B proton shifts of **2** and **3** exhibit a greater temperature dependence than those for **4**.

These observations may be interpreted in terms of the Si–N coordination/dissociation equilibrium already suggested for **1** (eq. 3) and/or of a lengthening of the Si–N bond, as discussed for **1**, involving a gradual shift of the bonding arrangement from the pyridone-immonium to the pyridone-imine extreme.

Proton shifts (ring A) are expected to be at higher field for IV than for III. For **2** pentacoordination of silicon at low temperature is directly revealed by the ap-



(III) (IV)

(3)

pearance of an AB multiplet of the CH_2 protons below −40 °C (in xylene/$CDCl_3$ 1/4) due to their diastereotopy in the pentacoordinate structure.

X-ray structure determinations of **1** and **3** (see experimental) support the results discussed for the solution state. Bond lengths and angles are given in Tables 3 and 4 with the numbering schemes in Fig. 1 and 2. **1** and **3** have similar structures in the solid state with pentacoordination at silicon (Fig. 1, 2). The coordination polyhedron is a (more **1** or less **3**) distorted trigonal bipyramid (tbp), with the electronegative atoms (N, Cl) in axial positions. Since ionization of the Si–Cl bond observed in solution for **1** leads to tetrahedral silicon, the distortion of the tbp towards a tetrahedral structure is of interest. This may be estimated from the

Table 3

Bond lengths (Å) in **1**, **3** and **5**, e.s.d. in parentheses

Compound	**1**	**3**	**5**
Si–Cl(3)	2.598(1)	2.238(2)	–
Si–N(1)	1.898(2)	1.901(3)	–
Si–C(11)	1.890(4)	1.876(4)	–
Si–C(12)	1.862(4)	–	–
Si–Cl(1)	–	2.073(2)	–
Si–C(13)	1.865(4)	–	–
Si–Cl(2)	–	2.073(2)	–
N(1)–C(5)	1.350(4)	1.349(5)	1.355(3)
N(1)–C(6)	1.413(5)	1.439(5)	1.405(3)
N(2)–C(1)	1.359(4)	1.368(5)	1.362(3)
N(2)–C(5)	1.365(4)	1.358(5)	1.361(3)
N(2)–C(11)	1.486(4)	1.468(6)	1.477(3)
N(3)–C(6)	1.334(4)	1.319(5)	1.327(2)
N(3)–C(10)	1.344(6)	1.353(6)	1.338(3)
C(1)–C(2)	1.351(4)	1.338(7)	1.357(4)
C(2)–C(3)	1.400(5)	1.409(6)	1.392(4)
C(3)–C(4)	1.358(5)	1.367(6)	1.355(3)
C(4)–C(5)	1.410(4)	1.419(6)	1.404(3)
C(6)–C(7)	1.384(4)	1.397(6)	1.377(3)
C(7)–C(8)	1.388(6)	1.389(6)	1.379(4)
C(8)–C(9)	1.380(6)	1.350(8)	1.373(4)
C(9)–C(10)	1.368(5)	1.391(6)	1.366(4)

Table 4

Bond angles (deg.) in **1**, **3** and **5**, e.s.d. in parentheses

Compound	1	3	5
Cl–Si–N(1), Cl(3)–Si–N(1)	166.2(1)	171.1(1)	–
Cl–Si–C(11), Cl(3)–Si–C(11)	81.1(1)	86.9(1)	–
N(1)–SI–C(11)	85.4(1)	84.9(2)	–
Cl–Si–C(12)	87.7(1)	–	–
Cl(1)–Si–Cl(3)	–	92.0(1)	–
N(1)–Si–C(12)	100.6(1)	–	–
Cl(1)–Si–N(1)	–	94.8(1)	–
C(11)–Si–C(12)	115.2(2)	–	–
Cl(1)–Si–C(11)	–	117.8(2)	–
Cl–Si–C(13)	85.6(1)	–	–
Cl(2)–Si–Cl(3)	–	90.7(1)	–
N(1)–Si–C(13)	98.5(1)	–	–
Cl(2)–Si–N(1)	–	91.9(1)	–
C(11)–Si–C(13)	118.3(2)	–	–
Cl(2)–Si–C(11)	–	128.3(2)	–
C(12)–Si–C(13)	124.2(2)	–	–
Cl(1)–Si–Cl(2)	–	113.9(1)	–
Si–N(1)–C(5)	113.5(2)	114.8(2)	–
Si–N(1)–C(6)	122.9(2)	126.9(2)	–
Si–C(11)–N(2)	107.5(2)	110.2(3)	–
C(5)–N(1)–C(6)	123.4(2)	117.6(3)	124.2(2)
C(1)–N(2)–C(5)	123.4(2)	122.7(4)	121.3(2)
C(1)–N(2)–C(11)	120.9(3)	121.8(3)	118.0(2)
C(5)–N(2)–C(11)	115.7(3)	115.5(3)	120.7(2)
C(6)–N(3)–C(10)	118.0(3)	117.1(4)	116.9(2)
N(2)–C(1)–C(2)	120.2(3)	121.1(4)	121.6(2)
C(1)–C(2)–C(3)	118.4(3)	118.5(4)	117.9(2)
C(2)–C(3)–C(4)	121.5(3)	120.8(4)	121.0(2)
C(3)–C(4)–C(5)	119.8(3)	119.7(4)	120.3(2)
N(1)–C(5)–N(2)	114.3(2)	114.4(3)	117.8(2)
N(1)–C(5)–C(4)	128.9(3)	128.4(3)	124.4(2)
N(2)–C(5)–C(4)	116.7(3)	117.2(3)	117.8(2)
N(1)–C(6)–N(3)	113.9(3)	116.6(3)	116.5(2)
N(1)–C(6)–C(7)	123.8(3)	119.0(4)	119.9(2)
N(3)–C(6)–C(7)	122.1(3)	124.2(4)	123.5(2)
C(6)–C(7)–C(8)	118.3(3)	116.9(4)	118.4(2)
C(7)–C(8)–C(9)	120.3(3)	120.2(4)	118.9(2)
C(8)–C(9)–C(10)	117.0(4)	118.9(4)	118.6(2)
N(3)–C(10)–C(9)	124.2(4)	122.6(4)	123.8(2)

displacement of silicon from the trigonal plane of the three equatorial ligand atoms (C(11) C(12) C(13) (**1**), C(11) Cl(1) Cl(2) (**3**)), which is 0.167 Å (towards the axial Cl atom) for **1**, or about 40% towards the (distorted) tetrahedron expected for complete ionization of the SiCl bond. For **3** the displacement is only 0.01 Å. The more tetrahedral and thus more ionic character of **1** is also supported by the axial Si–Cl bond lengths (Table 3); whereas the value for **3** (2.238 Å) is in the range observed for other trigonal bipyramidal chlorosilane adducts, that for **1** is extremely large (2.598 Å) and much larger than expected even when the general bond lengthening of Si–Cl (and other) bonds on introduction of less electronegative substituents at

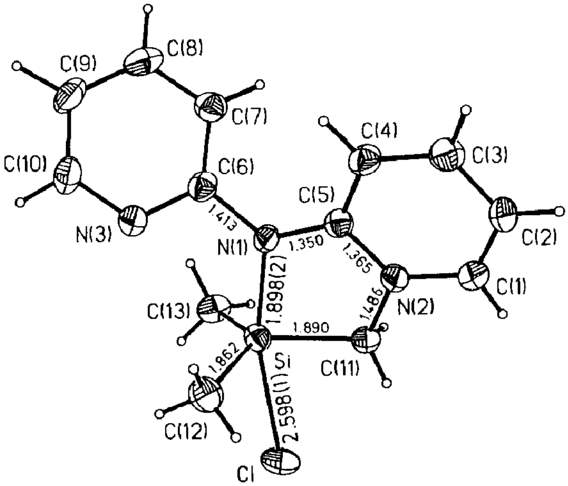


Fig. 1. ORTEP drawing of the molecular structure of **1**; the thermal ellipsoids are the 50% probability surfaces.

silicon is taken into account. The unusual bond length is in accord with the ease of ionization of the Si–Cl bond in solution. The Si–Cl distance, however, is significantly shorter than the sum of the Van der Waals radii (3.75 Å [9], 3.68 Å [10]), indicating that complete ionization has not taken place in the solid. This is supported by the results of a recent X-ray investigation of the ionic compound $[Me_3Si \cdot NMI]^+Cl^-$ (NMI = *N*-methylimidazole), for which the shortest Si–Cl distance of 4.024 Å is found [11]. Although the structure is better described in terms of a slightly distorted tetrahedral coordination around silicon and a separate chloride ion [11], it can also be regarded as involving strongly distorted trigonal bipyramidal coordination around silicon with the closest chlorine atom occupying one axial

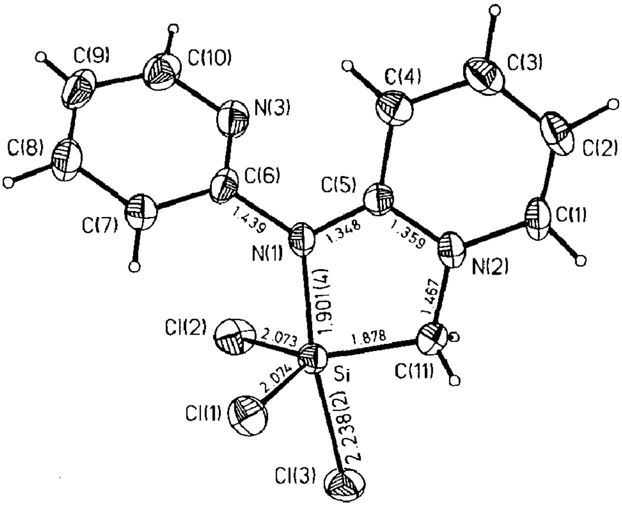


Fig. 2. ORTEP drawing of the molecular structure of **3**; the thermal ellipsoids are the 50% probability surfaces.

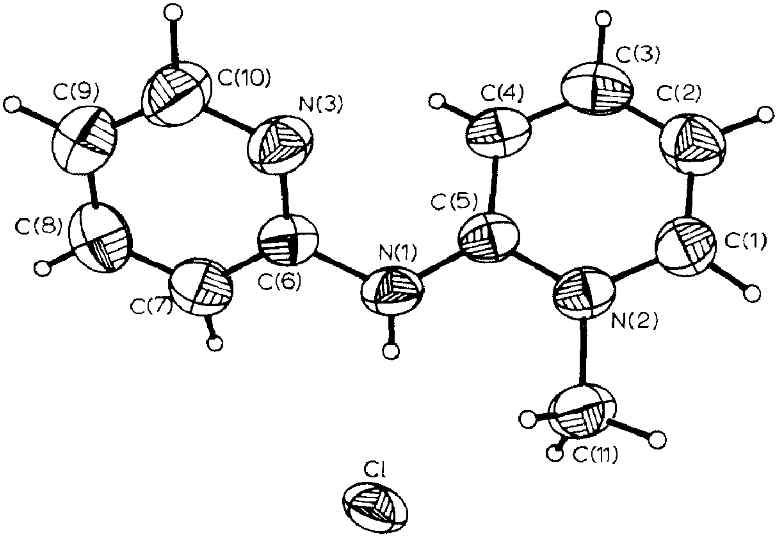


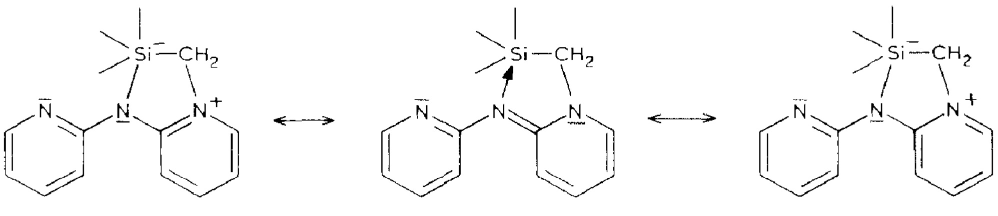
Fig. 3. ORTEP drawing of the molecular structure of **5**; the thermal ellipsoids are the 50% probability surfaces.

position. The structure is thus directly comparable to the (less distorted) tbp coordination of silicon in **1** showing the ionic Si...Cl distance to be significantly longer.

In view of the significant differences between the Si–Cl bond lengths in **1** and **3** a shorter Si–N bond length might have been expected for **1** than for **3**. However, the Si–N bond lengths in **1** and **3** are almost equal, and consistent with those in other penta-coordinate compounds. This may be due to the counteracting effects of Si–N bond shortening upon increase in Si–Cl bond ionization (lengthening) and Si–N lengthening upon introduction of less electronegative substituents at silicon. Other structural investigations have shown a similar dependence of Si–N bond length on Si substitution [12].

The bond lengths of the organic ligand system also agree well with the postulated structure. While the bond lengths in the free pyridyl ring B are close to those in 2,2′-dipyridylamine [13], those in the *N*-methylated ring A are intermediate between those in 1-methyl-2-pyridone [14] and pyridinium salts or pyridine [15], and indicate a bonding situation between the pyridone immonium and the aminopyridinium extremes (Scheme 4).

Interestingly, the corresponding bond lengths in the dipyridylamine systems of **1** and **3** vary only slightly, in spite of significant changes in bond lengths at the silicon



(V) (VI) (VII)

Scheme 4

atom. This is also true for the bond lengths in the related 1-methyl-2-(2′-pyridyl)amino-pyridinium chloride (**5**), which correspond closely to those in **1** and **3**. Bond lengths and angles of the X-ray structure determination of **5** are given in Tables 3 and 4, with the numbering system shown in Fig. 3. Although the observed differences of the bond length in **1**, **3** and **5** appear not to be sufficiently significant to justify a conclusive interpretation it noteworthy that they are in accord with the postulated structural changes, **1** corresponding more closely to **5**, with less pyridone immonium character than **3**. Further structural results not related to the present discussion are considered below.

The structures of **1** and **3** can be associated with successive stages along the S_N2 reaction pathway for substitution at silicon [16], the structural changes being due to the change in the substituents at silicon. Similar structural changes have been reported for other series of pentacoordinate Si compounds [16,17]. The structural results are consistent with interpretation of the solution behaviour of the compounds. In the case of **1** the strong inductive effect of the methyl groups leads to the lengthening of the axial Si–Cl bond (the chlorine atom being more polarizable than the N atom), and this facilitates ionization in solution on lowering of the temperature (entropy effect). Warming of the solution reverses the process. Since related chlorosilanes containing coordinative Si–N bonds do not show this type of interconversion another important factor is the nature of the nitrogen ligand. Charge delocalization may be an important factor. When one or two further chlorines are introduced in place of methyl at silicon, no ionization is observed even at −130 °C in keeping with the change in the inductive effect. In relation to the question of the mechanism of nucleophilically-assisted substitution at silicon, it is important, however, that in favourable cases (**1**) the energy difference between the ionic tetracoordinate and coordination expanded species is small, and one or the other species may be obtained by changing the experimental conditions only slightly. The implications of this result for the mechanistic question have been discussed elsewhere [5]. It is interesting in this context that related systems involving halosilane/oxygen donor interactions have been reported for which similar temperature dependent interconversions were suggested [18].

Finally, it is noted that the temperature dependent equilibrium between the isomers of **1** in solution follows reversibly the S_N2 pathway of nucleophilic substitution at silicon.

Structure determination of 1, 3 and 5

Single crystals were obtained as described in the Experimental section. Data were collected on a Syntex R3 diffractometer with graphitemonochromated Mo-K_α radiation at the temperatures indicated. Three representative reflections monitored at regular intervals showed no significant variation in intensity. The structures were solved and refined by the SHELXTL program system [19]. The non-hydrogen atoms were included in the block cascade refinement with anisotropic temperature factors, the H atoms with isotropic temperature factors and the methyl groups as geometrically rigid groups. The refinement converged at the indicated reliability values.

Crystal data: **1**: $C_{13}H_{16}ClN_3Si$, $M = 277.83$, monoclinic, space group $P2_1/n$, $Z = 4$, a 13.972(7), b 6.537(2), c 16.300(8) Å, $\alpha = \gamma = 90°$, β 108.45(4) at −45 °C,

Table 5

Atom coordinates ($\times 10^{-4}$) for **1**, **3**, and **5**

Atom	x	y	z
1			
Si	3316(1)	6610(2)	6095(1)
Cl	4085(1)	5873(2)	7747(1)
N(1)	2467(2)	6895(4)	4926(2)
N(2)	1566(2)	4465(4)	5364(2)
N(3)	3653(2)	8717(5)	4522(2)
C(1)	854(3)	2982(5)	5259(2)
C(2)	237(3)	2486(6)	4457(2)
C(3)	364(3)	3506(5)	3745(2)
C(4)	1075(3)	4987(6)	3849(2)
C(5)	1705(2)	5521(5)	4689(2)
C(6)	2672(2)	8290(5)	4342(2)
C(7)	1928(3)	9264(6)	3682(2)
C(8)	2227(3)	10667(6)	3174(2)
C(9)	3240(3)	11095(6)	3339(2)
C(10)	3914(3)	10103(7)	4024(2)
C(11)	2250(2)	5031(5)	6242(2)
C(12)	4381(3)	5113(6)	5945(2)
C(13)	3403(3)	9361(6)	6415(2)
3			
Si	4258(2)	5802(1)	6937(1)
Cl(1)	3118(2)	5228(1)	8025(1)
Cl(2)	5365(2)	4461(1)	6227(1)
Cl(3)	7103(2)	6108(1)	7502(1)
N(1)	1910(4)	5765(3)	6370(2)
N(2)	2421(5)	7743(3)	6319(2)
N(3)	638(5)	4730(3)	5265(2)
C(1)	2004(7)	8883(3)	6120(3)
C(2)	374(7)	9158(4)	5750(3)
C(3)	−928(6)	8247(4)	5581(3)
C(4)	−515(6)	7104(4)	5772(3)
C(5)	1243(5)	6830(3)	6147(2)
C(6)	966(5)	4741(3)	6051(3)
C(7)	558(7)	3803(4)	6571(3)
C(8)	−246(7)	2805(4)	6225(3)
C(9)	−648(7)	2780(4)	5426(3)
C(10)	−197(6)	3756(4)	4955(3)
C(11)	4208(6)	7424(4)	6720(3)
5			
Cl	7781(1)	1773(1)	7621(1)
N(1)	5525(1)	1545(2)	6339(1)
N(2)	5514(1)	−490(2)	6219(1)
N(3)	4140(1)	2667(2)	5504(1)
C(1)	5073(2)	−1562(2)	6235(2)
C(2)	4105(2)	−1672(2)	6314(2)
C(3)	3572(2)	−651(2)	6394(2)
C(4)	4007(2)	419(2)	6389(1)
C(5)	5012(1)	517(2)	6309(1)
C(6)	5043(1)	2645(2)	6142(1)
C(7)	5532(2)	3635(2)	6574(2)
C(8)	5053(2)	4706(2)	6342(2)
C(9)	4111(2)	4743(2)	5692(2)
C(10)	3688(2)	3716(2)	5296(2)
C(11)	6565(2)	−451(2)	6115(2)

U 1408 Å^3; 4291 reflections collected in the range $4.5° \leq 2\theta \leq 40°$, 1542 unique reflections with intensity $I > 3\sigma(I)$, $R = 0.036$

3: $C_{11}H_{10}Cl_3N_3Si$, $M = 316.97$, orthorhombic, space group $P2_12_12_1$, $Z = 4$, a 7.046(1), b 11.351(3), c 16.519(4) Å, $\alpha = \beta = \gamma = 90°$ at $-40°$C, U 1321 Å^3, 6683 reflections collected in the range of $5° \leq 2\theta \leq 60°$, 2658 unique reflections with intensity $I > 3\sigma(I)$, $R = 0.0412$.

(5) $C_{11}H_{12}ClN_3$, $M = 221.07$, monoclinic, space group $C2/c$, $Z = 8$, a 13.524(5), b 11.394(3), c 15.416(6)Å, $\alpha = \gamma = 90°$, β 106.93(3)°, U 2273 Å^3 at 22°C, 4875 reflections collected in the range of $4° \leq 2\theta \leq 50°$, 1391 unique reflections with intensity $I > 3\sigma(I)$, $R = 0.0336$

Supplementary material, lists of anisotropic temperature factors and the observed and calculated structure factors are available from the Fachinformationszentrum Energie, Physik, Mathematik, D 7514 Eggenstein-Leopoldshafen, upon citation of the deposit number CSD 54005, and the journal reference.

Structural results: Atom coordinates for **1**, **3** and **5** are given in Table 5. Structural data relevant to the question of molecular penta-coordination vs. ionic tetra-coordination at silicon have already been discussed. In addition we note that the bond distances to the equatorial substituents of silicon are only slightly longer than the tetrahedral distances (for standard bond lengths see ref. 14). For **1** the Si–CH_2 distance is slightly longer than the Si–CH_3 distances. This may be due to steric strain in the five-membered cycle which incorporates the $SiCH_2$ group (and this may also be responsible for the fact that the angle between the axial atoms (Cl–Si–N(1)), is less than 180° (166.2° **1**, 171.1° **3**). The pyridyl-rings including N(1) (for the free pyridyl ring) and N(1) and C(11) (for the bound ring) are essentially planar, whereas in the five-membered ring Si–N(1)–C(5)–N(2)–C(11) the silicon is displaced out of the plane of the four other atoms (angle between normals to planes Si–N(1)–C(11) and N(1)–C(5)–N(2)–C(11) 17.8°(**1**) resp. 4.7° (**3**). This may be due to steric interactions between the free pyridyl ring and the equatorial ligands on silicon (close interatomic contacts between N(3) and hydrogen H(131) of one methylgroup of **1** (2.737 Å) and H(7) and equatorial Cl(1) of **3** (2.686 Å)). The two pyridyl-rings are not in the same plane. Their normals include angles of 41.7° (**1**) and 53.7° (**3**), and this relieves the strong steric interactions between H(4) and H(7) of **1** and H(4) and N(3) of **3** in a planar arrangement of the two rings. The observed distances are 2.234 Å (H(4), H(7), **1**) and 2.501 Å (H(4), N(3), **3**). In accord with steric and electrostatic requirements, N(3) of the pyridyl-ring in **1** is adjacent to the equatorial methyl groups of silicon, while the pyridyl-ring in **3** is twisted by about 180°, with C(7)H neighbouring the equatorial Cl atoms. N(1) of **1** and **3** is almost planar (displacement from the trigonal plane Si–C(5)–C(6) 0.08 Å (**1**) and 0.04 Å (**3**)). In **5** chloride is hydrogen-bonded to the bridging NH group (Cl...H 2.36 Å, N–H 0.76 Å).

Experimental

All manipulations were carried out on a standard vacuum line. Special precautions were taken to exclude moisture. $ClCH_2SiMe_2Cl$, $BrCH_2SiMe_2Cl$, $ClCH_2SiMeCl_2$ and $ClCH_2SiCl_3$ were purified by distillation and stored in a vessel on the vacuum line. Before they were used a considerable amount of the silane was condensed off to ensure complete removal of traces of hydrogen chloride. 2,2′-Dipyridylamine (Fluka AG) was used without further purification, but dried under vacuum by gentle warming.

Elemental analysis was carried out by Mikroanalytisches Labor Pascher, Remagen. The ^{1}H and ^{29}Si NMR spectral measurements were recorded on a Bruker WH-300 (300 MHz, ^{1}H; 59.62 MHz, ^{29}Si) and a Bruker WP 80 (80 MHz, ^{1}H) spectrometer. Infrared spectra were recorded on a Perkin–Elmer IR spectrophotometer 283, using Nujol mulls on CsI optics. Mass spectra were determined with a Varian MAT 711 mass spectrometer.

Preparation of N-trimethylsilyl-bis(2-pyridyl)amine ($(C_5H_4N)_2NSiMe_3$) (TMSDPA)

To a stirred solution of 5.76 g (0.034 *M*) of 2,2′-dipyridylamine (DPA) in 125 ml of benzene, cooled in an ice bath 20 ml of 1.69 *M* n-BuLi in hexane (Ventron) was added dropwise. A cream solid precipitated. The suspension was stirred for about 2 h. The solid ($(C_5H_4N)_2NLi$) was filtered off and dried under vacuum. It was then suspended in 120 ml of n-pentane and a solution of 3.8 g (0.035 *M*) of trimethylchlorosilane in 40 ml of n-pentane was added dropwise with stirring. The mixture was then refluxed for 2 h to complete the reaction:

$$(C_5H_4N)_2NLi + Me_3SiCl \longrightarrow (C_5H_4N)_2NSiMe_3(\text{TMSDPA}) + LiCl$$

Finely divided lithium chloride was filtered off. The residue was extracted four times with 35 ml of pentane, to remove any TMSDPA sticking to the finely divided LiCl. The extracts were filtered and the pentane removed, to leave a colourless crystalline solid, m.p. 46.5 °C; microanalysis (found (calcd.)) N 17.4 (17.27); mass spectrum $m/e = 243.1193$ ($^{12}C_{13}H_{17}N_3{}^{28}Si$ calcd. 243.1192); NMR: (ppm) ^{1}H: 0.27 ($SiMe_3$), 6.51 (3H), 7.46 (4H), 6.85 (5H), 8.33 (6H); ^{29}Si: +6.5; $CDCl_3$ solutions, TMS internal standard.

Reactions of TMSDPA with $BrCH_2SiMe_2Cl$ and $ClCH_2SiMe_xCl_{3-x}$ ($x = 0, 1, 2$)

An equimolar amount of silane was condensed onto a known amount of solid TMSDPA at liquid nitrogen temperature. The mixture was then slowly warmed to room temperature at which a reaction took place. The mixture was stirred continuously for three days during which a white solid was formed. The trimethylchlorosilane was condensed off directly into a NMR tube. An equimolar amount of Me_3SiCl was obtained in each case, leaving behind pure white solids which were dried under vacuum.

Analytical data: Microanalysis (found (calcd)): **1**: N, 15.0 (15.13), Cl, 12.9 (12.76); (**2**: N, 13.9 (14.09), Cl, 24.0 (23.77); **3**: N, 13.1 (13.19); Cl, 32.7 (33,37); **4**: N, 12.9 (13.04); Br, 25.0 (24.79).

Mass spectra (molecular ion peaks) m/e (found (calcd.)): **1**: 277.0790 (277.0778) $C_{13}H_{16}N_3ClSi$; **2**: 297.0241 (297.0227). $C_{12}H_{13}N_3Cl_2Si$; **3**: 316.9709 (316.9702) $C_{11}H_{10}N_3Cl_3Si$; **4**: 321.0288 (321.0280) $C_{13}H_{16}N_3BrSi$; (for all formulae ^{12}C, ^{35}Cl, ^{28}Si, ^{80}Br). IR spectra show the expected bands. For **4** only weak broad bands appear in the region from 600–200 cm^{-1}; for NMR data see Tables 1 and 2.

Preparation of single crystals of 1 and 3

A solution of **1** in acetonitrile was concentrated by slow evaporation under vacuum until colourless needle-like crystals appeared in the solution. The crystals were separated from the mother liquid by filtration and dried under vacuum.

A concentrated solution of **3** was prepared in chloroform and left undisturbed for about four months, after which column-shaped colourless crystals were present. These were filtered off and washed three times with toluene and dried under vacuum.

Monoglyme was slowly added to a concentrated solution of **5** in CH_2Cl_2 until a turbidity appeared. A layer of monoglyme was then cautiously placed above the liquid. Diffusion of the monoglyme produced suitably shaped crystals in the solution within 3 days, and these were separated, washed three times with Et_2O, and dried in a stream of dry nitrogen.

Acknowledgement

This work was financially supported by the Fonds der Chemischen Industrie. One of us (SCC) is grateful to the A. von Humboldt Foundation for the award of a Humboldt Fellowship and to the Himachal Pradesh University, Shimla (India) for granting study leave.

References

1 R.J.P. Corriu and G. Guerin, Adv. in Organomet. Chem., 2 (1982) 265; R.J.P. Corriu, G. Guerin and J.J.E. Moreau, Topics Stereochem., 15 (1984) 43.
2 J. Chojnowski, M. Cypryk and M. Michalski, J. Organomet. Chem., 161 (1978) C31.
3 A.R. Bassindale, J.C.-Y. Lan and P.G. Taylor, J. Organomet. Chem., 341 (1988) 213.
4 D. Kummer, J. Seifert, S.C. Chaudhry, B. Deppisch and G. Mattern, Abstracts B19, 8th Intern. Symp. Organosilicon Chem., St. Louis USA, 1987.
5 S.C. Chaudhry and D. Kummer, J. Organomet. Chem., 359 (1988) 241.
6 V.H. Flygare, Chem. Rev., 74 (1974) 653.
7 (a) H. Marsmann, in P. Diehl, E. Fluck and R. Koesfeld (Eds.), NMR Basic Principles and Progress, Vol. 17, Springer Verlag, Berlin, Heidelberg, New York, 1981, p. 65; (b) V.F. Sidorkin, V.A. Pestunovich and M.G. Voronkov, Magn. Res. Chem., 23 (1985) 491; (c) R.K. Harris, J. Jones and Soon Ng, J. Magn. Resonance, 30 (1978) 521.
8 J.A. Elvidge and L.M. Jackman, J. Chem. Soc., (1961) 859.
9 L. Pauling, Die Natur der chemischen Bindung, Verlag Chemie, Weinheim, 1964.
10 A. Bondi, J. Phys. Chem., 68 (1964) 441.
11 K. Hensen, Th. Zengerly, Th. Müller and P. Pickel, Z. Anorg. Allg. Chem., 558 (1988) 21, and personal communication Prof. Hensen.
12 G. Klebe, J.W. Bats and K. Hensen, J. Chem. Soc. Dalton Trans., (1985) 1.
13 J.E. Johnson and R.A. Jacobson, Acta Cryst. B, 29 (1973) 1669.
14 B.R. Penfold, Acta Cryst., 6 (1953) 591.
15 C.D. Johnson in A.R. Katritzky and C.W. Rees (Eds.), Comprehensive Heterocyclic Chemistry, Vol. 2, Pergamon Press, Oxford 1984, p. 109.
16 G. Klebe, J. Organomet. Chem., 293 (1985) 147.
17 A.A. Macharashvili, V.E. Shklover, Yu.T. Struchkov, G.I. Oleneva, E.P. Kramarova, A.G. Shipov and Yu.I. Bankov, J. Chem. Soc. Chem. Commun., (1988) 683; A.A. Macharashvili, V.E. Shklover, Yu.T. Struchkov, B.A. Gostevskii, I.D. Kalikhman, O.B. Bannikova, M.G. Voronkov and V.A. Pestunovich, J. Organomet. Chem. 356 (1988) 23; A.A. Macharashvili, V.E. Shklover, Yu.T. Struchkov, M.G. Voronkov, B.A. Gostevskii, I.D. Kalikhman, O.B. Bannik and V.A. Pestunovich, J. Organomet. Chem. 340 (1988) 23.
18 (a) V.A. Pestunovich, M.F. Larin, A.I. Albanov, M.G. Voronkov and Yu.I. Bankov, Abstr. Papers, 7th Intern. Symp. Organosilicon Chemistry, Kyoto, Sept. 1984, 2C1150; (b) I.D. Kalikhman, V.A. Pestunovich, R.A. Gostevskii, O.B. Bannikova and M.G. Voronkov, J. Organomet. Chem. 338 (1988) 169.
19 G.M. Sheldrick, SHELXTL-Programmsystem, Universität Göttingen, Germany (1982)
20 M. Shamma and D.M. Hindenlang, Carbon-13 NMR Shift Assignments of Amines and Alkaloids Plenum Press, New York 1979