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An NMR Spectroscopic and X-ray Crystallographic Study of the Reaction of Tris(dimethylamino)chlorosilane with Aluminum Chloride. A Quest for the Elusive Silicenium Cation

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Abstract: The reaction of $(Me_2N)_3SiCl$ with Al_2Cl_6 in CH_2Cl_2 has been carried out over a range of stoichiometries in an effort to prepare the $[(Me_2N)_3Si]^+$ ion. In the solid phase the product forms as colorless crystals of $(Me_2N)_3SiCl{\cdot}AlCl_3$ in orthorhombic space group *Pbca*, with unit cell constants at −35 °C $a = 14.718$ (14) Å, $b = 12.379$ (7) Å, and $c = 33.442$ (21) Å. The calculated density of 1.441 g cm^{-3} is reasonable for 16 molecules of $(Me_2N)_3SiCl{\cdot}AlCl_3$ per unit cell. Full-matrix least-squares refinement of the structure, using the 3646 symmetry-independent reflections for $4 < 2\theta < 48°$ which have $I_o > 2.0\sigma(I_o)$, has converged with a conventional R index (on $|F|$) of 0.060. The bonding in each $(Me_2N)_3SiCl{\cdot}AlCl_3$ is such that one of the Me_2N groups is involved in a donor–acceptor bond with an $AlCl_3$ unit. In solution the reaction has been investigated by ^1H, ^{13}C, ^{27}Al, and ^{29}Si NMR spectroscopy. A preliminary study of the interaction of $(Me_2N)_3SiF$ with the fluoride ion acceptors PF_5 and AsF_5 revealed that these reactions are apparently complex and do not result in significant fluoride ion abstraction.

Introduction

The literature records numerous unsuccessful attempts to isolate tricoordinate silicon (silicenium) cations.[1] Despite this body of negative results, it is interesting to note that silicenium cations are readily observable in the vapor phase by mass spectrometry[2] and ion cyclotron resonance (ICR)[3] techniques. Indeed, it has been found both experimentally[3] and theoretically[4] that in the gas phase the parent silicenium ion, SiH_3^+, is more stable than the analogous carbocation. Since amino groups are widely recognized to function as effective π donors,[5] we decided to attempt stabilization of the tricoordinate Si^+ center with Me_2N ligands. Since halide ion abstraction has proved to be an effective means of synthesizing two-coordinate phosphorus cations,[6] one obvious approach to the corresponding silicon chemistry was to treat tris(dialkylamino)silyl halides with halide ion acceptors. The present paper describes the reactions of $(Me_2N)_3SiX$ (X = Cl, F) with Al_2Cl_6, PF_5, and AsF_5. Reactions in solution were investigated by NMR spectroscopy. A single-crystal X-ray diffraction study has been performed on the solid resulting from the reaction of $(Me_2N)_3SiCl$ with Al_2Cl_6.

Experimental Section

General Procedures. Virtually all the materials described herein are moisture sensitive. Accordingly, volatile compounds were manipulated in a high-vacuum system of conventional design and less volatile materials were handled in an inert atmosphere.

Spectroscopic Measurements. The ^1H and ^{19}F NMR spectra were recorded on A-60 and A-56/60 spectrometers, respectively. The ^1H and ^{19}F chemical shifts were measured relative to internal CH_2Cl_2 (δ 5.34 ppm relative to Me_4Si) and external CCl_3F, respectively. The ^{13}C NMR spectra were measured on a Bruker WH-90 spectrometer operating at 22.6 MHz and referenced to internal CH_2Cl_2 (δ 54.2 ppm relative to Me_4Si). The ^{27}Al spectra were recorded on a Varian HA-100 spectrometer operating at 26.05 MHz and featuring a locally built cross-correlation system and external deuterium lock. Hydrated Al^{3+} and $[Me_4N]^+[AlCl_4]^-$ were employed as primary and secondary external references, respectively. The ^{29}Si NMR experiments were performed on a Varian XL-100 spectrometer at the University of Houston.[7] This instrument was operated in the Fourier transform mode and featured a tunable probe. The ^{29}Si chemical shifts are referenced to external Me_4Si. For all the above nuclei a positive chemical shift implies that the resonance occurs at higher frequency than that of the primary reference.

Infrared spectra were obtained using a Perkin-Elmer Model 337 grating spectrophotometer.

Materials. Tris(dimethylamino)chlorosilane, Al_2Cl_6, *n*-BuLi, Me_2NH, SiF_4, PF_5, and AsF_5 were procured commercially. All volatile materials were purified by trap-to-trap distillation in vacuo prior to use. The aluminum chloride was sublimed at least twice in evacuated sealed tubes using a Scientific Instrument Accessories Model 240 thermal gradient sublimer. Reagent grade CH_2Cl_2 was distilled from CaH_2 at reduced pressure and stored over CaH_2 in the dark. Anhydrous diethyl ether was used without further purification.

Preparation of Tris(dimethylamino)fluorosilane. The procedure employed is similar to the one described by Wannagat et al.[8] for the synthesis of $(Et_2N)_3SiF$. Dimethylamine (55.5 mmol) and ca. 60 mL of dry Et_2O were condensed in vacuo at −196 °C into a 250-mL round-bottomed flask equipped with a magnetic stirring bar. The reaction vessel was removed from the vacuum line and charged with 55.5 mmol of *n*-BuLi (*n*-hexane solution) while the contents were maintained at −196 °C. The reaction mixture was then allowed to warm to ambient temperature, stirring being maintained for 1.0 h. Following this, the reactor was connected to the vacuum system, cooled to −22 °C, and exposed to 46.25 mmol of SiF_4. When the pressure in the system reached equilibrium, all volatiles were condensed into the reaction vessel. The flask was then allowed to warm to ambient temperature and was heated subsequently for ca. 5 min at 60 °C before fractionating the volatiles with U-traps held at −22, −50, and −196 °C. Clear, colorless liquid $(Me_2N)_3SiF$ (1.52 g, 8.5 mmol) was isolated, representing a yield of 46.0%. NMR: ^1H, doublet, δ 2.46 ppm, $J_{FSiNCH} = 1.3$ Hz; ^{19}F, broad singlet, δ 152.4 ppm. IR: $\nu(SiF)$ 862 cm^{-1}; $\nu(SiN)$ 739 cm^{-1}.

Reaction of $(Me_2N)_3SiCl$ with Al_2Cl_6. In a typical experiment 0.464 g (2.37 mmol) of $(Me_2N)_3SiCl$ was condensed in vacuo onto 0.316 g (1.185 mmol) of Al_2Cl_6 contained in a 10-mL round-bottomed flask at −196 °C. After condensation of ca. 2 mL of CH_2Cl_2, the reaction mixture was agitated frequently and allowed to assume ambient temperature. This treatment resulted in a colorless solution. NMR: ^1H, singlet, δ 2.74 ppm; ^{13}C, singlet, δ 40.4 ppm; ^{27}Al, broad singlet, δ +107 ppm; ^{29}Si (−60 °C), singlet, δ −25.3 ppm.

Reaction of $(Me_2N)_3SiF$ with MF_5 (M = P, As). In a typical experiment 0.095 mmol of $(Me_2N)_3SiF$, 0.05 mL of $C_6H_5CF_3$, and ca. 0.2 mL of CH_2Cl_2 were condensed at −196 °C into a 5-mm o.d. NMR tube connected to a vacuum system by means of a stopcock and standard taper joint. The mixture was thawed, mixed thoroughly by agitation, and recooled to −196 °C prior to the addition of 0.095 mmol of MF_5 (M = P, As). Following this, the NMR tube was sealed and allowed to warm to ambient temperature while the contents were mixed by vigorous shaking. ^1H and ^{19}F NMR spectroscopic assays revealed (a) the presence of at least ten ^1H or ^{19}F resonances and (b) the virtual absence of PF_6^- or AsF_6^-.

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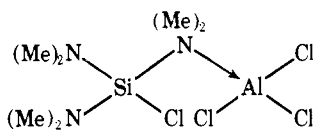
Crystallographic Section. Single crystals of the solid obtained from the reaction of $(Me_2N)_3SiCl$ with Al_2Cl_6 were grown by allowing a supersaturated CH_2Cl_2 solution to stand for several hours at −30 °C. A satisfactory specimen cut from a large, colorless tablet was glued to a glass fiber which was affixed to a brass pin and joined to a goniometer head. The crystal was then quickly transferred to a Syntex $P2_1$ automated diffractometer where it was maintained in a stream of cold (−35 °C), dry nitrogen during the course of all subsequent crystallographic experiments. Preliminary examination of the crystal with the diffractometer indicated orthorhombic symmetry consistent with space group *Pbca* (no. 61). Crystal data and data collection details are summarized in Table I. The measured X-ray diffraction intensities were reduced and assigned standard deviations (with $p = 0.03$) as described previously.[9]

Although the density of these crystals was not determined experimentally because of the aforementioned air/moisture sensitivity, the calculated value of 1.441 g cm^{-3} assuming 16 formula weights per unit cell of $[(Me_2N)_3Si]AlCl_4$ is plausible. Since solution of the crystal structure requires the location of two (crystallographically independent) formula weights of $[(Me_2N)_3Si]AlCl_4$ per asymmetric unit in space group *Pbca*, it was deemed expedient to initiate structure solution by direct methods (MULTAN).[10] Satisfactory solution of the structure was ultimately obtained by the application of direct and heavy-atom methods.[11] However, as confirmed by successful full-matrix least-squares refinement of the structure (discussed below), the crystal structure consists not of the desired $[(Me_2N)_3Si]^+$ and $AlCl_4^-$ ions but rather of the Lewis acid–base adduct **1**. (Consistent with the calculated density, there are two molecules of **1** per asymmetric unit.)



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The function minimized in least-squares refinement is $\sum w(|F_o| - |F_c|)^2$, where the weight w is $\sigma(|F_o|)^{-2}$, the reciprocal square of the standard deviation of each observation, $|F_o|$. Neutral atom scattering factors for Cl, Si, Al, N, and C[12] were used in these calculations, and the real ($\Delta f'$) and imaginary ($\Delta f''$) corrections[12] for anomalous scattering were applied to the Cl, Si, and Al scattering curves. Least-squares convergence was attained using only those 3646 data with $I_o/\sigma(I_o) > 2.0$ for a structure in which all nonhydrogen atoms were ultimately refined anisotropically, with $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.060$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.081$, and a standard deviation of an observation of unit weight $= [\sum w(|F_o| - |F_c|)^2/(m - s)]^{1/2} = 3.38$, for $m = 3646$ observations and $s = 271$ variables. No attempt was made to locate the hydrogen atoms. Despite omission of the contributions of the hydrogen atoms to the calculated structure factors, examination of the data near the conclusion of refinement indicated that several low-angle reflections were possibly affected by secondary extinction. However, since the incorporation of Zachariasen's coefficient[13] for this effect produced no significant changes in the structural parameters or the values of the calculated structure factor amplitudes and since it refined to a value not significantly different from zero, it was not included in the final cycles of refinement. A structure-factor calculation using the atomic parameters obtained at least-squares convergence with all 4775 reflections measured during data collection gave R and R_w values of 0.089 and 0.082, respectively.

In the final cycle of refinement no shift in an atomic parameter exceeded 25% of a corresponding estimated standard deviation (esd). The largest peaks on a final difference Fourier map were 0.3–0.6 e Å^{-3} and were associated with the methyl carbon atoms (and presumably their omitted hydrogen atoms).

Table II presents atomic positional and thermal parameters, with corresponding esd's as estimated from the least-squares inverse matrix. A tabulation of observed and calculated structure factor amplitudes is available.[14]

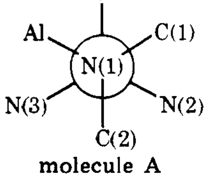
Table I. Crystallographic Summary

Crystal Data at −35 °C[a]	
a, Å	14.718 (14)
b, Å	12.379 (7)
c, Å	33.442 (21)
V, Å^3	6093 (13)
d_{calcd}, g cm^{-3}	1.441[b]
empirical formula	$C_6H_{18}AlCl_4N_3Si$
crystal system	orthorhombic
systematic absences	$0kl$, $k = 2n + 1$ $h0l$, $l = 2n + 1$ $hk0$, $h = 2n + 1$
space group	*Pbca* (no. 61)
Z	16
F(000), electrons	2720
formula wt	329.14
Data Collection at −35 °C[c]	
radiation (Mo Kα), Å	0.710 69
mode	ω scan
scan range	symmetrically over 1.0° about K$\alpha_{1,2}$ maximum
background	offset 1.0 and −1.0° in ω from K$\alpha_{1,2}$ maximum
scan rate, deg min^{-1}	variable, 3.0–6.0
check reflections	4 remeasured after every 96 reflections; analysis[d] of these data indicated a continuous decline in intensity to a maximum of ca. 8% at the conclusion of data collection (64 h of X-ray exposure), for which the appropriate correction was applied
2θ range, deg	4.0–48.0
total reflections measd	4775
data crystal dimensions, mm	0.40 × 0.74 × 0.82
absorption coeff, μ(Mo Kα), cm^{-1}	8.84[e]

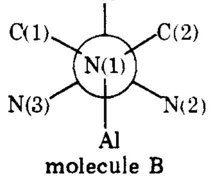
[a] Unit cell parameters were obtained by least-squares refinement of 30 reflections with $22.0 < 2\theta < 23.9°$. [b] Owing to air/moisture sensitivity an experimental density was not obtained. [c] Syntex $P2_1$ autodiffractometer equipped with a graphite monochromator and a Syntex LT-1 inert-gas low-temperature delivery system. [d] Henslee, W. H.; Davis, R. E. *Acta Crystallogr., Sect. B* **1975**, *31*, 1511. [e] Since the data crystal was cut from a larger specimen and since the crystal faces were severely eroded at the conclusion of data collection as a consequence of the decay mentioned above, an absorption correction based upon the diffractometer setting angles of the crystal faces was not applied to the data. The range in transmission factors based upon the extreme dimensions of the crystal is 0.48–0.70.

Results and Discussion

The crystal structure consists of discrete molecules of $(Me_2N)_3SiCl{\cdot}AlCl_3$, each formed by the coordination of an $AlCl_3$ moiety to one of the nitrogen atoms of a $(Me_2N)_3SiCl$ molecule. All nonbonded intermolecular distances (exclusive of those involving the unlocated hydrogen atoms; see Experimental Section) are greater than the accepted van der Waals contact distances. There is no apparent pseudosymmetry which approximately relates the atoms of the two molecules (A and B) of the asymmetric unit. Figure 1 provides a stereoscopic view of molecule A and indicates the atom numbering scheme used for both molecule A and molecule B. As shown by comparison of the bond lengths and bond angles in Table III, the molecular geometries of the two independent molecules are in excellent agreement. Furthermore, these values for $(Me_2N)_3SiCl{\cdot}AlCl_3$ agree with values obtained for numerous other structural determinations of similar molecules. The only significant difference in the structures of molecules A and B



molecule A



molecule B

Table II. Fractional Coordinates and Anisotropic Thermal Parameters ($\times 10^3$) for Atoms of $(Me_2N)_3SiCl{\cdot}AlCl_3$[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(A1)	0.8639 (1)	0.6348 (2)	0.8742 (1)	53 (1)	54 (1)	39 (1)	−3 (1)	7 (1)	12 (1)
Cl(A2)	0.9065 (1)	0.4437 (1)	0.7973 (1)	64 (1)	34 (1)	59 (1)	4 (1)	−2 (1)	7 (1)
Cl(A3)	1.0226 (1)	0.6055 (2)	0.7276 (1)	48 (1)	73 (1)	60 (1)	−3 (1)	18 (1)	−11 (1)
Cl(A4)	0.7961 (1)	0.5460 (2)	0.7146 (1)	60 (1)	57 (1)	61 (1)	−1 (1)	−22 (1)	−12 (1)
Si(A)	0.9229 (1)	0.7347 (1)	0.8328 (0)	28 (1)	32 (1)	31 (1)	1 (1)	−1 (1)	1 (1)
Al(A)	0.8990 (1)	0.5770 (2)	0.7579 (1)	34 (1)	33 (1)	39 (1)	1 (1)	−2 (1)	−2 (1)
N(A1)	0.8582 (3)	0.7086 (4)	0.7870 (1)	23 (3)	29 (3)	37 (3)	1 (2)	−2 (2)	4 (2)
N(A2)	0.9143 (4)	0.8656 (4)	0.8458 (2)	36 (3)	35 (3)	50 (3)	2 (3)	−6 (3)	−7 (3)
N(A3)	1.0314 (4)	0.6979 (4)	0.8265 (2)	28 (3)	45 (3)	41 (3)	5 (3)	−2 (2)	6 (3)
C(A1)	0.7550 (4)	0.6967 (6)	0.7948 (2)	18 (3)	52 (4)	74 (5)	−1 (3)	2 (3)	−6 (4)
C(A2)	0.8727 (5)	0.7997 (5)	0.7568 (2)	61 (5)	33 (4)	49 (4)	0 (4)	−4 (4)	14 (3)
C(A3)	0.8317 (5)	0.9314 (6)	0.8452 (2)	55 (5)	43 (4)	63 (5)	19 (4)	−4 (4)	−9 (4)
C(A4)	0.9832 (6)	0.9125 (6)	0.8728 (2)	61 (5)	54 (5)	70 (5)	3 (4)	−24 (4)	−28 (4)
C(A5)	1.0768 (5)	0.6026 (6)	0.8427 (2)	49 (5)	54 (5)	67 (5)	18 (4)	−16 (4)	13 (4)
C(A6)	1.0975 (5)	0.7744 (7)	0.8069 (2)	36 (4)	70 (5)	79 (6)	−17 (4)	10 (4)	8 (5)
Cl(B1)	0.4911 (1)	0.9606 (1)	0.9429 (1)	50 (1)	30 (1)	60 (1)	−14 (1)	−2 (1)	0 (1)
Cl(B2)	0.3876 (1)	0.5107 (1)	0.9558 (1)	46 (1)	32 (1)	67 (1)	−1 (1)	10 (1)	−9 (1)
Cl(B3)	0.1959 (1)	0.6776 (2)	0.9498 (1)	29 (1)	56 (1)	70 (1)	−7 (1)	−3 (1)	−4 (1)
Cl(B4)	0.2836 (1)	0.6087 (2)	1.0418 (1)	69 (1)	57 (1)	50 (1)	0 (1)	21 (1)	12 (1)
Si(B)	0.4479 (1)	0.8039 (1)	0.9340 (1)	27 (1)	25 (1)	35 (1)	−2 (1)	0 (1)	−1 (1)
Al(B)	0.3164 (1)	0.6415 (2)	0.9814 (1)	32 (1)	29 (1)	40 (1)	−4 (1)	6 (1)	−1 (1)
N(B1)	0.3965 (3)	0.7690 (4)	0.9823 (1)	25 (3)	27 (3)	34 (3)	−1 (2)	0 (2)	−4 (2)
N(B2)	0.5357 (4)	0.7247 (4)	0.9216 (2)	30 (3)	40 (3)	50 (3)	4 (3)	6 (3)	5 (3)
N(B3)	0.3702 (4)	0.8043 (4)	0.8971 (2)	35 (3)	36 (3)	38 (3)	0 (2)	−6 (2)	−2 (3)
C(B1)	0.3314 (5)	0.8612 (5)	0.9950 (2)	40 (4)	29 (4)	59 (5)	13 (3)	4 (3)	−14 (3)
C(B2)	0.4676 (5)	0.7580 (6)	1.0151 (2)	44 (4)	59 (5)	36 (3)	3 (4)	−15 (3)	−3 (4)
C(B3)	0.5939 (5)	0.6543 (6)	0.9464 (2)	34 (4)	51 (5)	73 (5)	13 (4)	−5 (4)	3 (4)
C(B4)	0.5828 (6)	0.7589 (7)	0.8836 (2)	55 (5)	83 (6)	59 (5)	5 (5)	31 (4)	13 (5)
C(B5)	0.3043 (5)	0.8909 (6)	0.8888 (2)	50 (5)	37 (4)	67 (5)	6 (4)	−18 (4)	7 (4)
C(B6)	0.3592 (5)	0.7140 (6)	0.8691 (2)	58 (5)	59 (5)	41 (4)	−11 (4)	−4 (4)	−14 (4)

[a] See Figure 1 for identity of the atoms. Numbers in parentheses throughout the table are the estimated standard deviations in the units of the least significant digits for the corresponding parameter. The U_{ij} are the mean-square amplitudes of vibration in Å^2 from the general temperature factor expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

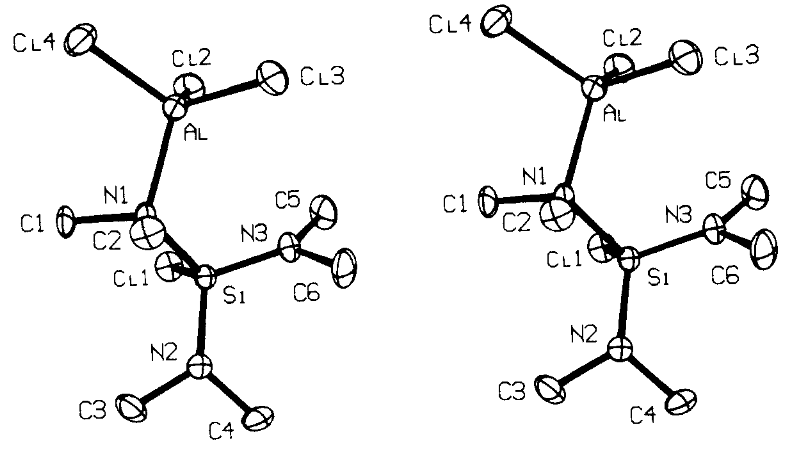


Figure 1. Stereoscopic view of molecule A of $(Me_2N)_3SiCl{\cdot}AlCl_3$, illustrating the atom-numbering scheme used for both independent molecules of the structure. Atoms are shown as ellipsoids of 30% probability. As stated in the text, the hydrogen atoms were not located in this study.

is conformational, as shown below, which is consistent with the presumed low barrier of rotation about the Si-N(sp^3) single bond.

The structure of the donor fragment $(Me_2N)_3SiCl$ has been determined by gas-phase electron diffraction methods.[15] When nitrogen atom N(1) undergoes coordination with an $AlCl_3$ unit, three major structural modifications ensue (see Table IV): (1) the coordination geometry of N(1) changes from trigonal planar to tetrahedral, (2) the Si-N(1) bond lengthens by 0.12-0.16 Å, and (3) the C-N(1) bonds increase by ca. 0.07 Å. The major point of interest in the structure of $(Me_2N)_3SiCl{\cdot}AlCl_3$ concerns the fact that both tetrahedral and trigonal planar nitrogen atoms are bonded to the same silicon atom. Thus, N(1) is virtually tetrahedral (average bond angle 109.4° in both molecules A and B), while the average sums (for molecules A and B) of bond angles are 356.4 and 359.8° for N(2) and N(3), respectively. Furthermore, the average N(1)-Si bond length (1.836 Å) is significantly larger than the average N(2)-Si or N(3)-Si bond length (1.679 Å). The sensitivity of N-X bond lengths to the geometry at the nitrogen center is now well documented for compounds with, e.g., N-P[16] and N-Si[17] bonds. Typically, for a tetrahedrally coordinated nitrogen atom the N-X bond lengths approach the sum of the covalent radii (1.87 Å[18] in the case of the N-Si bond), whereas for a trigonal planar nitrogen atom this bond is shortened appreciably. These observations can be rationalized by postulating a pπ-dπ component to the N-X bond when the nitrogen atom is trigonal planar.[19] However, it is sometimes possible to discuss the

Table III. Bond Lengths (Å) and Bond Angles (deg)[a]

	molecule A	molecule B
Si-Cl(1)	2.050 (2)	2.062 (2)
Si-N(1)	1.832 (5)	1.835 (5)
Si-N(2)	1.684 (6)	1.674 (6)
Si-N(3)	1.674 (5)	1.683 (5)
N(1)-C(1)	1.549 (8)	1.550 (8)
N(1)-C(2)	1.528 (8)	1.522 (8)
N(2)-C(3)	1.465 (9)	1.478 (9)
N(2)-C(4)	1.478 (10)	1.510 (10)
N(3)-C(5)	1.460 (9)	1.472 (9)
N(3)-C(6)	1.510 (9)	1.468 (9)
Al-N(1)	1.990 (5)	1.972 (5)
Al-Cl(2)	2.115 (3)	2.111 (3)
Al-Cl(3)	2.111 (3)	2.112 (3)
Al-Cl(4)	2.130 (3)	2.118 (3)
Cl(1)-Si-N(1)	103.8 (2)	102.8 (2)
Cl(1)-Si-N(2)	112.0 (2)	110.4 (2)
Cl(1)-Si-N(3)	109.0 (2)	108.2 (2)
N(1)-Si-N(2)	110.3 (3)	113.5 (3)
N(1)-Si-N(3)	110.1 (2)	111.4 (2)
N(2)-Si-N(3)	111.5 (3)	110.2 (3)
Si-N(1)-Al	113.3 (3)	115.0 (3)
Si-N(1)-C(1)	112.7 (4)	108.9 (4)
Si-N(1)-C(2)	110.5 (4)	111.8 (4)
Al-N(1)-C(1)	107.5 (4)	102.9 (4)
Al-N(1)-C(2)	103.9 (4)	110.5 (4)
C(1)-N(1)-C(2)	108.5 (5)	107.0 (5)
Si-N(2)-C(3)	126.4 (5)	130.9 (5)
Si-N(2)-C(4)	119.0 (5)	113.5 (5)
C(3)-N(2)-C(4)	111.1 (5)	111.8 (5)
Si-N(3)-C(5)	127.7 (5)	126.1 (4)
Si-N(3)-C(6)	119.9 (5)	122.7 (4)
C(5)-N(3)-C(6)	111.9 (5)	111.2 (5)
N(1)-Al-Cl(2)	110.5 (2)	108.8 (2)
N(1)-Al-Cl(3)	111.0(2)	109.9 (2)
N(1)-Al-Cl(4)	105.4 (2)	106.0 (2)
Cl(2)-Al-Cl(3)	112.6 (1)	112.1 (1)
Cl(2)-Al-Cl(4)	108.6 (1)	110.7 (1)
Cl(3)-Al-Cl(4)	108.5 (1)	109.1 (1)

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figure 1 for identity of the atoms.

structural trends in such molecules in terms of other orbital interactions.[20]

The increase of N-C bond lengths upon coordination of the nitrogen atom has been observed previously. In fact, using Me_3N as a reference base it has been suggested[21] that the increase of the N-C distances is an indication of the stability of the X_3Al complex.

The N → Al and Al-Cl bond lengths in $(Me_2N)_3SiCl{\cdot}AlCl_3$ are very similar to those in other monoamine complexes such as $Me_3N{\cdot}AlCl_3$.[21]

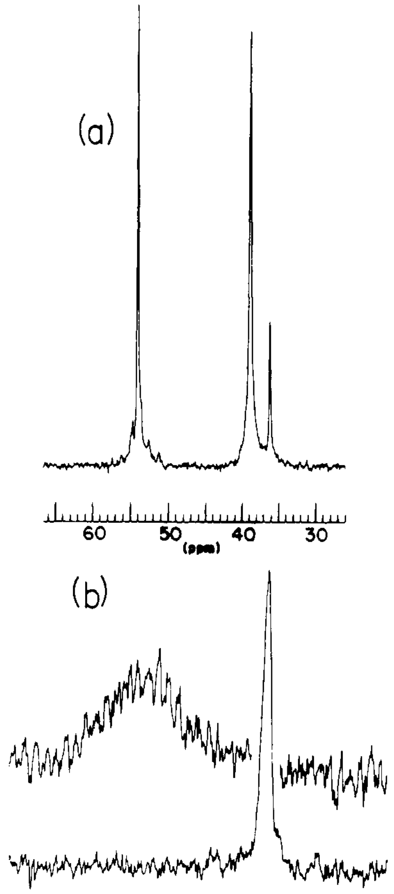


Figure 2. (a) ^{13}C NMR spectrum of $(Me_2N)_3SiCl{\cdot}AlCl_3$ with a 33% excess of $(Me_2N)_3SiCl$ in CH_2Cl_2 solution at −90 °C. (b) ^{27}Al NMR spectra of $AlCl_4^-$ (sharp resonance) and $(Me_2N)_3SiCl{\cdot}AlCl_3$ (broad resonance).

The identity of the solution species resulting from the reaction of $(Me_2N)_3SiCl$ with Al_2Cl_6 has not been established as well as that of the solid-state material. At ambient temperature the ^1H and ^{13}C NMR spectra of 1:1 mixtures of $(Me_2N)_3SiCl$ and $AlCl_3$ units consist of singlets shifted downfield by 0.24 and 3.1 ppm, respectively, from those of unreacted $(Me_2N)_3SiCl$. In the presence of excess $(Me_2N)_3SiCl$ two resonances are clearly apparent in both the ^1H and ^{13}C spectra, thus indicating that, on the NMR time scale, the exchange between free and coordinated $(Me_2N)_3SiCl$ is not significant. Examination of the integrated areas of free and complexed $(Me_2N)_3SiCl$ indicates a composition of 1:1 stoichiometry, viz., $(Me_2N)_3SiCl{\cdot}AlCl_3$. The ^{13}C spectrum of $(Me_2N)_3SiCl$ in solution with a 30% excess of $AlCl_3$ units exhibits a sharp singlet shifted downfield by only 0.5 ppm from that of $(Me_2N)_3SiCl{\cdot}AlCl_3$. This small shift could indicate the presence of a small amount of a bis adduct, $(Me_2N)_3SiCl{\cdot}2AlCl_3$, in dynamic equilibrium with the mono adduct. However, it is probably due to the presence of Al_2Cl_6 in the solution. Figure 2a illustrates the observation that sig-

Table IV. Comparison of Structural Data for $(Me_2N)_3SiCl$ and $(Me_2N)_3SiCl{\cdot}AlCl_3$[a]

		$(Me_2N)_3SiCl{\cdot}AlCl_3$[c]					
		molecule A			molecule B		
	$(Me_2N)_3SiCl$[b]	N(1)	N(2)	N(3)	N(1)	N(2)	N(3)
Si-N, Å	1.715 (2)	1.832 (5)	1.684 (6)	1.674 (5)	1.835 (5)	1.674 (6)	1.683 (5)
C-N, Å[d]	1.462 (5)	1.538 (10)	1.472 (6)	1.485 (25)	1.536 (14)	1.494 (16)	1.470 (2)
S_N, deg	359.5		356 (2)	360 (2)		356 (2)	360 (1)
deviations of N from its Si, C, C plane, Å		0.512 (5)	0.164 (5)	0.063 (5)	0.547 (5)	0.173 (5)	0.008 (5)
ϕ, deg	22.5	38	15	15	8	20	33

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. S_N corresponds to the sum of the angles about the nitrogen atoms. ϕ represents the angle of twist from the conformation in which the Si, Cl, N(i) (i = 1, 2, or 3) plane is perpendicular to the C, N(i), C plane. [b] Reference 15. [c] See Figure 1 for identity of the atoms. [d] Mean C-N bond lengths are listed. Omission of the hydrogen atoms in structure refinement tends to lengthen artificially the determined C-N distances (see text).

nificant exchange broadening does not occur in the ^{13}C resonance of a typical mixture containing excess $(Me_2N)_3SiCl$ even at −90 °C. Thus, if the structure of $(Me_2N)_3SiCl{\cdot}AlCl_3$ in solution is the same as that in the solid state, the $AlCl_3$ moiety must be averaging among all three nitrogen sites fairly rapidly. The foregoing conclusions are consistent with the ^{27}Al NMR data for a 1:1 mixture of $(Me_2N)_3SiCl$ and $AlCl_3$ units (Figure 2b), since the ^{27}Al chemical shift of $(Me_2N)_3SiCl{\cdot}AlCl_3$ (+107 ppm) is close to that of other $R_3E{\cdot}AlCl_3$ complexes, such as $Me_3P{\cdot}AlCl_3$.[22] The ^{29}Si NMR data were difficult to obtain, possibly owing to quadrupolar relaxation effects associated with the ^{14}N nuclei. However, on cooling the samples (equimolar in $(Me_2N)_3SiCl$ and $AlCl_3$ units) to −60 °C it was possible to detect singlet resonances. The chemical-shift difference between $(Me_2N)_3SiCl$ and that which we attribute to $(Me_2N)_3SiCl{\cdot}AlCl_3$ is surprisingly small.

The interaction of $(Me_2N)_3SiF$ with the fluoride ion acceptors PF_5 and AsF_5 was explored as a potential synthetic route to the $[(Me_2N)_3Si]^+$ ion. These reactions are apparently complex, resulting in the appearance of several new resonances. However, none of these resonances was attributable to PF_6^- or AsF_6^-; hence, this line of experimentation was not pursued further.

Current efforts to synthesize silicenium ions involve the use of cyclic precursor halides and silyl halides with both bulky and π-donor substituents.

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Supplementary Material Available: A tabulation of observed and calculated structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal Structure of Bis(triphenylantimony catecholate) Hydrate. A New Square-Pyramidal Antimony(V) Compound

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Abstract: Reaction between triphenylantimony dichloride and catechol in the presence of ammonia yields the partially hydrated product $(Ph_3SbO_2C_6H_4)_2{\cdot}H_2O$, the crystal structure of which has been determined by single-crystal X-ray diffraction methods. The compound, bis(2,2,2-triphenyl-1,3,2-benzodioxastibole) hydrate, crystallized in the monoclinic space group $P2_1/c$ with cell constants a = 9.78 (1) Å, b = 21.10 (1) Å, c = 19.95 (1) Å, β = 105.28 (5)°, Z = 4. Antimony atoms in both five- and sixfold coordination are present with the central atom in the former being attached to three carbon and two oxygen atoms in a distorted square-pyramidal arrangement. Distortion of this polyhedron arises basically from the presence of the dioxo chelating group. The second polyhedron is distorted octahedral and is derived from the square-pyramidal arrangement above with the addition of a water molecule weakly coordinated in the sixth position.

Trigonal bipyramidal or square pyramidal based structures are generally considered possible for compounds in which the central atom has ten electrons in its valence shell. The difference in energy between these two forms is apparently small but, while both arrangements are found when the central atom is a transition element, compounds derived from main-group elements have with very few exceptions the trigonal-bipyramidal configuration. The major exception is the square-pyramidal structure found for pentaphenylantimony[1] where crystal-packing effects are thought to stabilize this geometry at the expense of the "expected" trigonal-bipyramidal form.[2] It is worth stressing the unusual situation with $SbPh_5$, as the p-tolyl antimony derivative[3] and pentaphenyl derivatives of arsenic and phosphorus[5] all have trigonal-bipyramidal

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