Synthesis and Crystal Structure of *tert*-Butylamino(di-*tert*-butyl)silicenio-trichloroaluminate, $(Me_3C)_2Si{=}NCMe_3 \cdot AlCl_3$, and Dimethylazomethine–Aluminium Trichloride, $Me_2C{=}NH \cdot AlCl_3$☆

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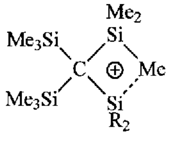
Lithiated *tert*-butylaminofluorosilanes react with aluminium trichloride in ether, eliminating LiF to give $AlCl_3$ adducts of iminosilanes – aminosiliceniotrichloroaluminates ($R_2Si{-}NCMe_3 \cdot AlCl_3$), which thermally form the dimethylazomethine–aluminium trichloride, $Me_2C{=}NH \cdot AlCl_3$.

Although it has been found both theoretically[1] and experimentally[2] that in the gas phase the parent silicenium ion, SiH_3^+, is more stable than the analogous carbenium ion, the literature records numerous unsuccessful attempts to isolate trivalent silyl cations[3]. Early attempts to prepare silicenium ions followed the route of carbenium ions. However, attempts at protonation and dehydration of silanoles proved to be unsuccessful[3]. While the reaction of haloboranes[4] and halophosphanes[5] with Lewis acids, e.g. $AlCl_3$, led to the formation of borinium cations, R_2B^+, and phosphenium cations, R_2P^+, treatment of halosilanes with Lewis acids led to species described as having polarized bonds, for example[6]:

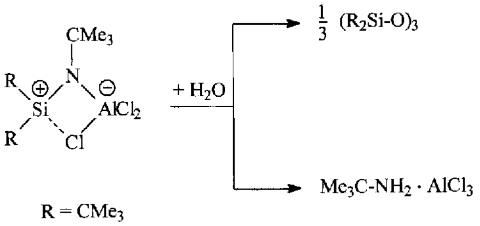
$$Me_3SiBr + AlBr_3 \rightarrow Me_3Si\cdots Br\cdots AlBr_3$$

Eaborn showed in 1981 that the methanolysis of $(Me_3Si)_3CSiR_2I$ might well proceed via a methyl-bridged intermediate silicenium ion[7]. Silicenium ions in solution have been reported by Corey and co-worker[3].



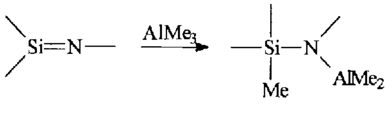
In 1994 Corriu published the first X-ray structure of an intramoleculary coordinated silyl cation using the conformationally rigid 8-(dimethylamino)naphthalene substituent[8], and very recently Belzner reported the synthesis and the solid-state structure of two silyl cations bearing the 2-[(dimethylamino)methyl]phenyl substituent[9].

In 1983, encouraged by the reported adduct of an iminophosphene with $AlCl_3$[10], ($R_2NPNR{-}AlCl_3$, R = $SiMe_3$), we investigated the reaction of LiF adducts of iminosilanes with $AlCl_3$. We isolated compounds that we described as $AlCl_3$ adducts of silicenium ylides: four-membered rings with bridging chlorine atoms[11]. Although these were the first unsaturated Si–N compounds to be reported in the literature, they were not noticed, perhaps because the crystal-structure data were missing. Hydrolysis produced the aminoalane $Me_3CNH_2{-}AlCl_3$ and the cyclic siloxane $(R_2Si{-}O)_3$ due to attack of the oxygen atom (from H_2O) at the electropositive silicon atom.



(1)

In the reaction of an iminosilane with trimethylalane, $AlMe_3$, we previously succeeded in the isolation of a monomeric iminoalane, formed by migration of the nucleophilic methanid ion from the aluminum to the trivalent silicon atom[12]. This reaction and the possibility of obtaining low-temperature X-ray structure data prompted us to renew our study of the above-mentioned $AlCl_3$ adduct.



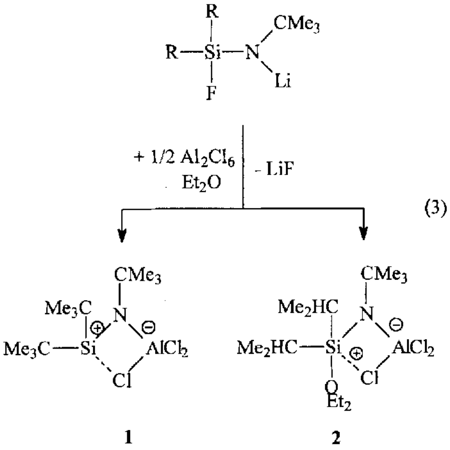
(2)

Reaction of $R_2SiFLiNCMe_3$[13] with $AlCl_3$ in ether leads to elimination of LiF and formation of a 1:1 adduct of the intermediate iminosilane with $AlCl_3$. Compounds **1**[11] and **2** are colourless, extremely moisture-sensitive solids, and can be distilled without decomposition in vacuo. The silicenium character is supported by the low-field ^{29}Si-NMR

[+] Crystal structure.

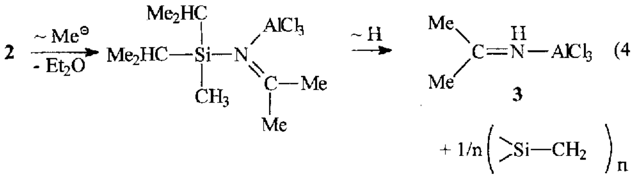
0009–2940/97/0606–0753 $ 17.50+.50/0

chemical shifts (δ = 50.4 for **1** and δ = 49.3 for **2**). In contrast to **1**, compound **2** could be distilled in vacuo without loss of $O(CH_2CH_3)_2$; that means the intermediate iminosilane forms and adduct between a Lewis base and a Lewis acid. In the ^{13}C-NMR spectrum of **2** the C_2O-signal of the ether molecule appears at δ = 71.7, i.e. it is shifted 5 ppm downfield compared with free diethyl ether. This reflects the strong Lewis acid character of the three-coordinate silicon, as was found also in THF adducts of iminosilanes[12,13].



(3)

Experiments to cleave the ether adduct **2** thermally led to the formation of the dimethylazomethine–aluminiumtrichloride, $Me_2C{=}N(H)AlCl_3$ (**3**), and polymers. **3** was also obtained thermally from **1**. Compared with the above-mentioned $Me^{\ominus}$ migration from aluminum to the trivalent silicon atom[12], the formation of **3** can be most satisfactorily interpreted with migration of a $Me^{\ominus}$ ion from the *tert*-butyl group to the silicon atom.



(4)

To our knowledge, the free dimethylazomethine species is still unknown. X-ray structural analyses were carried out with single crystals of **1** and **3**, crystallized from *n*-hexane. The structure determination of **1** confirms the structure suggested on the basis of the NMR data[11]. **1** forms a planar four-membered ring with two significantly long chlorine bridging bonds (Al–Cl 223.2 pm, Si–Cl 231.8 pm). The length of the Si–N bond is found in the normal range for a single bond (170.6 pm); however, the Al–N bond (180.9 pm) is short in comparison to the sum of the aluminium and nitrogen covalent radii (i.g. 200 pm), which suggests the presence of Al–N pπ–pπ bonding. However, the dihedral angle Cl(1)–Al(1)–N(1)–Si(1) of 105.6° makes this limited. Therefore most of the shortening of the Al–N bond should be attributed to the difference between the electronegativities of the atoms. The coordination of the nitrogen atom is planar (sum of the bond angles around N

Figure 1. Molecular structure of **1**, 50% probability level

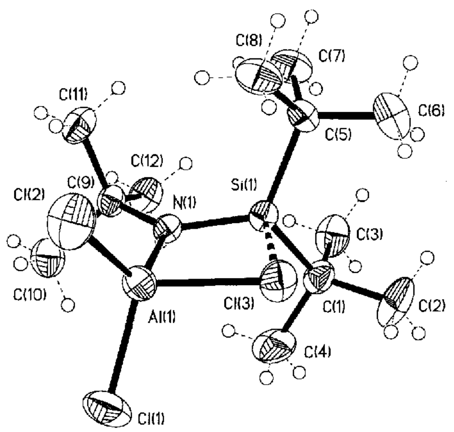


Table 1. Selected bond lengths (pm) and angles (°) for **1**

Al(1)-N(1)	180.9(3)	Al(1)-Cl(2)	210.6(2)
Al(1)-Cl(1)	211.2(2)	Al(1)-Cl(3)	231.8(2)
Cl(3)-Si(1)	223.15(14)	Si(1)-N(1)	170.6(3)
Si(1)-C(5)	189.1(4)	Si(1)-C(1)	190.4(4)
N(1)-C(9)	149.1(5)		
N(1)-Al(1)-Cl(2)	119.47(12)	N(1)-Al(1)-Cl(1)	121.89(12)
Cl(2)-Al(1)-Cl(1)	110.77(7′)	N(1)-Al(1)-Cl(3)	85.66(11)
Cl(2)-Al(1)-Cl(3)	107.87(7)	Cl(1)-Al(1)-Cl(3)	105.57(7)
Si(1)-Cl(3)-Al(1)	76.66(5)	N(1)-Si(1)-C(5)	117.7(2)
N(1)-Si(1)-C(1)	118.4(2)	C(5)-Si(1)-C(1)	117.9(2)
N(1)-Si(1)-Cl(3)	90.91(11)	C(5)-Si(1)-Cl(3)	101.97(13)
C(1)-Si(1)-Cl(3)	101.77(13)	C(9)-N(1)-Si(1)	130.5(2)
C(9)-N(1)-Al(1)	122.6(2)	Si(1)-N(1)-Al(1)	106.8(2)

Figure 2. Molecular structure of **3**, 50% probability level

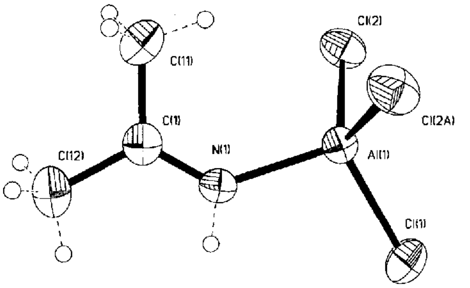


Table 2. Bond lengths (pm) and angles (°) for **3**

Al(1)-N(1)	189.8(3)
Al(1)-Cl(2)	211.79(8)
Al(1)-Cl(1)	211.97(12)
N(1)-C(1)	128.2(4)
C(1)-C(11)	147.3(4)
C(1)- C(12)	148.4(5)
N(1)-Al(1)-Cl(2)	108.81(5)
Cl(2)-Al(1)-Cl(2A)	110.88(5)
N(1)-Al(1)- Cl(1)	102.52(8)
Cl(2)-Al(1)-Cl(1)	112.69(3)
C(1)-N(1)-Al(1)	131.7(2)
N(1)-C(1)-C(11)	120.5(3)
N(1)-C(1)-C(12)	121.8(3)
C(11)C(1)-C(12)	117.7(3)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y + 1/2, z$.

359.9°). The coordination of the aluminium and silicon atoms without the Cl···Al and Cl···Si adduct bond is almost planar (sum of the bond angles around Cl_2AlN 352.1° and around C_2SiN 354.0°). This proves the silicenium character of **1**.

3 exists in the solid state as a simple monomer, the adduct of $Me_2C{=}NH$ wit $AlCl_3$.

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Experimental Section

Compounds were handled in a dry nitrogen atmosphere.

$(C_3H_7)_2SiNCMe_3 \cdot AlCl_3 \cdot O(CH_2CH_3)_2$ (**2**): A solution of 0.01 mol $AlCl_3$ in 100 ml Et_2O was added dropwise at room temperature to a stirred solution of 0.01 mol of the lithiated aminofluorosilane $(C_3H_7)_2SiFNLiCMe_3$ in 100 ml *n*-hexane. When the exothermic reaction was complete, the raw product was separated from LiF and **2** purified by distillation.

2: $C_{14}H_{33}AlCl_3NOSi$ (391.63): 2.1 g (54%) yield, b.p. 106°C/0.01 mbar. MS (field-ion mass spectroscopy): 391 M^+. – ^1H NMR (30% in C_6H_{12}; C_6D_6, TMS int.): $\delta = 1.03$ OCH_2CH_3, 1.2–0.95, C_3H_7, 1.25 CMe_3, 3.90 OCH_2. – ^{13}C NMR: $\delta = 16.4$ OC_2C_2, 16.8 SiC*C*, 17.0 SiC*C*, 17.6 SiC, 35.1 NCC_3, 52.7 NC, 71.7 OC_2C_2. – ^{29}Si NMR: $\delta = 49.2$.

3: $C_3H_7NAlCl_3$ (190.44): Pure **2** (0.5 g) was tempered at 130°C for 5 h and the residue recrystallized from *n*-hexane. 0.2 g (82%) yield. – ^{13}C NMR (C_6D_6, TMS int.): $\delta = 27.5$ CH_3, 27.9 CH_3, 200.6 N=C.

Crystal Data of **1**[14]: Space group $P2_1/n$, monoclinic, $a = 784.6(1)$, $b = 1696.9(2)$, $c = 1413.8(1)$ pm, $\beta = 96.270(10)$, $V = 1.8711(4)$ nm^3, Z = 4, $\rho_{calc.} = 1.231$ Mg/m^3, crystal size 0.3 × 0.3 × 0.1mm, μ (Mo-K_α) = 0.587 mm^{-1}, wavelength = 71.073 pm, 6990 reflections measured in the range $2\Theta = 7.1-40.1°$, of which 1749 independent reflections were used for refinement on $R2 = 172$ parameter, $wR2 = 0.0822$ (all data) and $R1 = 0.0530$ [for $F > 4\sigma(F)$]. Maximal and minimal residual electron density: 198 and −179 e nm^3. Selected bond lengths and angles are compiled in Table 1.

Crystal Data of **3**[14]: Space group *Pnma*, orthorhombic, $a = 1426.8(3)$, $b = 740.5(1)$, $c = 811.5(2)$ pm, $V = 0.8574(3)$ nm^3, $Z = 4$, $\rho_{calc.} = 1.475$ Mg/m^3, crystal size= 0.4 × 0.3 × 0.3 mm, μ (Mo-K_α) = 1.083 mm ^{1}, wavelength = 71.073 pm, 2251 reflections between $\theta = 3.72$ to 22.50° measured, of which 610 independent were used for refinement: 46 parameter, $wR2 = 0.0785$ (all data) and $R1 = 0.0280$ [for $F > 4\sigma(F)$]. Maximal and minimal residual electron density: 275 and −297 e nm^{-3}. Selected bond lengths and angles are compiled in Table 2.

☆ Dedicated to Prof. *A. Meller* on the occasion of his 65th birthday.

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