*Journal of Organometallic Chemistry*, 249 (1983) 47–54
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# STABILISATION OF SILICENIUM YLIDS BY ADDUCT FORMATION WITH ALUMINIUM TRIHALIDES: THE CRYSTAL STRUCTURE OF $[(Me_3C)_2SiNCMe_3]_2AlClF_2$ *

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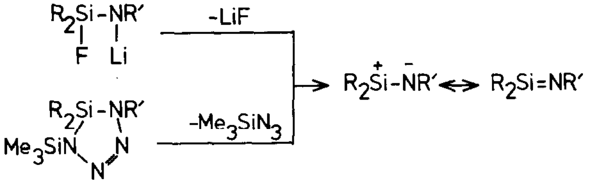
(Received January 18th, 1983)

## Summary

Lithium salts of t-butylamino-diorganylfluorosilanes $[RR'SiFN(CMe_3)Li]$ react with aluminium trichloride in petroleum ether, eliminating LiF, to give $AlCl_3$ adducts of silicenium ylids, $(RR'SiNCMe_3)AlCl_3$. Hydrolysis of these adducts leads to $Me_3CNH_2 \cdot AlCl_3$ and $(RR'SiO)_3$. The compound $[(Me_3C)_2SiNCMe_3]_2AlClF_2$ has been obtained as the major product of the reaction of $(Me_3C)_2SiFN(CMe_3)Li$ with $Al_2Cl_6$ in tetrahydrofuran. It forms orthorhombic crystals, space group *Pnna*, with *a* 16.063(2), *b* 21.896(2), *c* 17.987(2) Å, $Z = 8$. The crystal structure has been determined from 3389 unique diffractometer-measured intensities, and refined to $R = 0.070$. The molecular structure and NMR spectra support the formulation of this compound as a 2 : 1 adduct of a silicenium ylid with $AlClF_2$. The hydrolysis product $Me_3CNH_2 \cdot AlCl_3$ forms monoclinic crystals, space group $P2_1/n$, with *a* 8.348(5), *b* 10.908(4), *c* 11.322(9) Å, *β* 103.63(10)°, $Z = 4$, $R = 0.052$ for 1067 reflections. Molecules are monomeric in the solid state.

## Introduction

Several attempts to stabilise compounds with three-coordinate silicon, or to demonstrate their existence, have been reported [1]. The stabilisation of silaethenes by means of bulky substituents [2] and of disilenes with aryl substituents [3] has



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* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983).

0022-328X/83/$03.00

recently been achieved. In the field of silicon-nitrogen compounds, the quest for three-coordinate silicon has followed three different paths:

(a) elimination of electronegative substituents on Si and electropositive substituents on N [4], or of azides from cyclic silapentazenes [5], according to eq. 1;

(b) photolytic or thermal elimination of $N_2$ from silyl azides, with substituent rearrangement [6], as in eq. 2 (trapping experiments have demonstrated the production of silicenium ylids in such reactions [4–6]);

$$RMe_2SiN_3 \longrightarrow RMeSi{=}NMe + N_2 \qquad (2)$$

(c) the reaction of organo- or aminohalogenosilanes with Lewis acids such as $Al_2Cl_6$, $PF_5$ or $AsF_5$ [7]. Encouraged by the reported stabilisation of a bis(trimethylsilyl)amino-(trimethylsilylamino)phosphane with $Al_2Cl_6$ to produce an adduct $R_2NPNR \cdot AlCl_3$ ($R = Me_3Si$) [8], we have investigated the reaction of lithiated aminofluorosilanes [4] with $Al_2Cl_6$, and report here the results.

## Experimental

Compounds were handled in a dry nitrogen atmosphere. Mass spectroscopy: Varian CH5; NMR spectroscopy: Bruker 60E and FT80 instruments.

### *Silicenium ylid adducts $RR'SiNCMe_3 \cdot AlCl_3$*

A solution of 0.05 mol $Al_2Cl_6$ in 100 ml $Et_2O$ was added dropwise at room temperature to a stirred solution of a lithiated aminofluorosilane $RR'SiFN(CMe_3)Li$ (0.1 mol) in 100 ml petroleum ether (b.p. 40–60°C). When the exothermic reaction was complete, the solvent and LiF were removed and the pure product obtained by distillation.

I: $R = R' = Me_3C$. $C_{12}H_{27}AlCl_3NSi$, yield 20.8 g (60%), b.p. 112°C/0.01 Torr. Mol.wt. 346.8 calcd., 359 obs. (cryoscopy in $C_6H_{12}$), 345 obs. (field-ion mass spectroscopy). Analysis: calcd.: C, 41.56; H, 7.85%; obs.: C, 41.82; H, 7.93%. $^1H$ NMR (30% soln. in $C_6H_6$, TMS internal standard): $\delta$ 1.07 [$Si(CMe_3)_2$], 1.31 [$NCMe_3$] ppm; $^{29}Si$ NMR (30% soln. in $C_6H_6/C_6F_6$, TMS): $\delta$ 50.4 ppm; $^{27}Al$ NMR (30% soln. in $C_6H_6/C_6D_6$, $AlCl_3/H_2O$ external standard): $\delta$ 106.6 ppm.

II: $R = Me_3C$, $R' = Ph$. $C_{14}H_{23}AlCl_3NSi$, yield 27.4 g (75%), b.p. 137°C/0.01 Torr. Mol.wt. = 366.8 calcd., 365 obs. (mass spectroscopy). Analysis: calcd.: C, 45.85; H, 6.32%; obs.: C, 46.51; H, 6.37%. $^1H$ NMR (30% soln. in $CH_2Cl_2$, TMS): $\delta$ 1.29 [$SiCMe_3$], 1.38 [$NCMe_3$], 7.7 [Ph] ppm; $^{29}Si$ NMR (30% soln. in $C_6H_6/C_6F_6$, TMS): $\delta$ 28.2 ppm; $^{27}Al$ NMR (30% soln. in $C_6H_6/C_6D_6$, $AlCl_3/H_2O$): $\delta$ 111.1 ppm.

A solution of 0.025 mol $Al_2Cl_6$ in 50 ml $Et_2O$ was added at room temperature to a stirred solution of 0.1 mol $(Me_3C)_2SiFN(CMe_3)Li$ in 100 ml tetrahydrofuran (THF). After removal of the solvents and LiCl, the crude product was recrystallised from n-hexane, to obtain pure bis(di-t-butylsilyl-t-butylimino)chlorodifluoroalane (III), $[(Me_3C)_2SiNCMe_3]AlClF_2$, yield 21 g (82%), m.p. 138°C. Mass spectrum (70 eV): $m/e = 526$ (relative intensity 5) $[M]^+$, 511 (32) $[M - CH_3]^+$, 469 (100) $[M - C_4H_9]^+$. $^1H$ NMR (30% soln. in $C_6H_6$, TMS): $\delta$ 1.22 [$Si(CMe_3)_2$], 1.43 [$NCMe_3$] ppm; $^{19}F$ NMR (30% soln. in $C_6H_6$, $C_6F_6$ internal standard): $\delta$ 29.5 ppm; $^{29}Si$ NMR

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($Å^2 \times 10^4$) FOR III

| Atom | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| Si(1) | 1228(1) | −745(1) | 3272(1) | 477(4) |
| Al(1) | 2500 | 0 | 3779(1) | 445(6) |
| Cl(1) | 2500 | 0 | 4975(1) | 645(6) |
| F(1) | 1240(1) | 11(1) | 3501(1) | 539(8) |
| N(1) | 2267(2) | −780(2) | 3439(2) | 472(13) |
| C(11) | 877(3) | −754(2) | 2264(2) | 625(18) |
| C(111) | 7(3) | −481(3) | 2175(4) | 929(26) |
| C(112) | 1468(4) | −363(3) | 1813(3) | 861(26) |
| C(113) | 872(4) | −1395(3) | 1919(3) | 979(28) |
| C(12) | 439(3) | −1048(2) | 3959(3) | 589(18) |
| C(121) | 40(3) | −1667(3) | 3728(3) | 846(24) |
| C(122) | 844(3) | −1132(3) | 4728(3) | 772(22) |
| C(123) | −263(3) | −572(3) | 4058(3) | 849(24) |
| C(13) | 2814(3) | −1335(2) | 3430(3) | 634(19) |
| C(131) | 2291(3) | −1913(2) | 3412(4) | 834(25) |
| C(132) | 3354(3) | −1352(3) | 4132(3) | 846(25) |
| C(133) | 3372(3) | −1327(3) | 2740(4) | 916(27) |
| Si(2) | 6682(1) | 8224(1) | 1338(1) | 508(4) |
| Al(2) | 7226(1) | 7500 | 2500 | 526(7) |
| Cl(2) | 8565(1) | 7500 | 2500 | 820(8) |
| F(2) | 6953(2) | 7469(1) | 1357(1) | 651(10) |
| N(2) | 6818(2) | 8263(1) | 2271(2) | 469(12) |
| C(21) | 5568(3) | 8205(2) | 975(3) | 680(20) |
| C(211) | 5509(5) | 7916(3) | 215(3) | 1028(29) |
| C(212) | 5047(3) | 7828(3) | 1524(4) | 888(26) |
| C(213) | 5153(4) | 8826(3) | 945(5) | 1129(32) |
| C(22) | 7485(4) | 8538(3) | 667(3) | 856(24) |
| C(221) | 8303(3) | 8689(3) | 1047(4) | 1099(32) |
| C(222) | 7181(5) | 9140(3) | 260(4) | 1351(39) |
| C(223) | 7675(5) | 8051(3) | 63(4) | 1241(35) |
| C(23) | 6775(3) | 8827(2) | 2748(3) | 527(16) |
| C(231) | 7563(4) | 8871(2) | 3224(3) | 834(24) |
| C(232) | 6014(3) | 8807(2) | 3241(3) | 767(22) |
| C(233) | 6722(3) | 9398(2) | 2261(3) | 705(21) |

(30% soln. in $C_6H_6/C_6F_6$, TMS): $\delta$ 27.6 ppm. $J$(Si–F) 229.7 Hz, $^3J$(Si–F) 4.21 Hz.

Attempts to obtain single crystals of I suitable for X-ray diffraction led to hydrolysis and formation of $Me_3CNH_2 \cdot AlCl_3$ (IV), for which the crystal structure was determined. Crystals of III suitable for X-ray investigation were obtained from n-hexane.

### *Crystal data*

III: $C_{24}H_{54}AlClF_2N_2Si_2$, $M_r = 527.3$, orthorhombic, space group *Pnna*, $a$ 16.063(2), $b$ 21.896(2), $c$ 17.987 (2) Å, $U$ 6326.3 Å$^3$, $Z = 8$, $D_c$ 1.107 g cm$^{-3}$, $F(000) = 2304$, $\lambda$(Mo-$K_\alpha$) 0.71069 Å, $\mu$ 2.46 cm$^{-1}$.

IV: $C_4H_{11}AlCl_3N$, $M_r = 206.5$, monoclinic, space group $P2_1/n$, $a$ 8.348(5), $b$

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($Å^2 \times 10^4$) FOR IV

| Atom | $x$ | $y$ | $z$ | $U$ |
|---|---|---|---|---|
| Al | 2050(1) | 1289(1) | 7133(1) | 540(5) |
| Cl(1) | 2351(2) | −198(1) | 6012(1) | 725(5) |
| Cl(2) | 327(2) | 2584(1) | 6180(1) | 826(6) |
| Cl(3) | 1439(2) | 651(2) | 8726(1) | 972(7) |
| N | 4023(4) | 2262(3) | 7690(4) | 693(16) |
| C(1) | 5690(5) | 2057(4) | 7513(4) | 551(16) |
| C(2) | 6836(6) | 3063(5) | 8137(5) | 794(22) |
| C(3) | 5561(10) | 2076(10) | 6182(6) | 1470(43) |
| C(4) | 6254(8) | 835(5) | 8067(8) | 1302(37) |

10.908(4), $c$ 11.322(9) Å, $\beta$ 103.63(10)°, $U$ 1002.0 $Å^3$, $Z = 4$, $D_c$ 1.369 g $cm^{-3}$, $F(000) = 424$, $\lambda(\text{Mo-}K_\alpha)$ 0.71069 Å, $\mu$ 9.38 $cm^{-1}$.

### *Data collection*

Crystals were sealed in capillaries and examined on a Stoe-Siemens AED diffractometer. Unit cell parameters were obtained from $2\theta$ values of reflections (28 and 12, for III and IV respectively) centred at $\pm\omega$. Intensities were measured by a real-time profile-fitting procedure [9]. No absorption corrections were applied.

III: crystal size 0.9 × 0.5 × 0.5 mm, $2\theta_{max}$ 50°C, 3389 reflections with $F > 4\sigma(F)$.

IV: crystal size 1.0 × 0.6 × 0.6 mm, $2\theta_{max}$45°, 1067 reflections with $F > 4\sigma(F)$.

### *Structure solution and refinement*

Both structures were solved by automatic direct methods, and refined to a minimum value of $\Sigma w\Delta^2$ [$\Delta = |F_0| - |F_c|$; $w^{-1} = \sigma^2(F) + gF^2$, with $g = 0.00069$ for III, 0.00120 for IV]. Hydrogen atoms were constrained to give C–H 0.96, N–H 0.87 Å, H–C–H = H–N–H = 109.5°, $U(H) = 1.2U_{eq}(C)$ or $1.2U_{eq}(N)$, where $U_{eq}$ is the

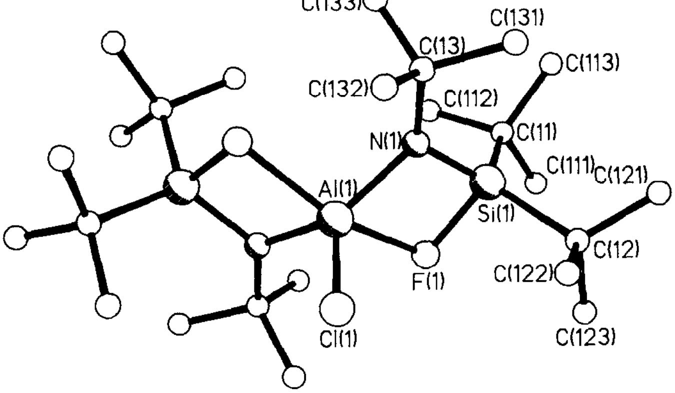


Fig. 1. Molecular structure of III showing the atom numbering scheme for one of the two independent molecules. Hydrogen atoms are omitted for clarity.

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) FOR III (A prime denotes a symmetry-related atom)

| | | | |
|---|---|---|---|
| Si(1)–F(1) | 1.706(3) | Si(2)–F(2) | 1.711(3) |
| Si(1)–N(1) | 1.698(4) | Si(2)–N(2) | 1.695(4) |
| Si(1)–C(11) | 1.898(5) | Si(2)–C(21) | 1.905(5) |
| Si(1)–C(12) | 1.892(5) | Si(2)–C(22) | 1.896(6) |
| Al(1)–Cl(1) | 2.151(3) | Al(2)–Cl(2) | 2.151(3) |
| Al(1)–F(1) | 2.085(2) | Al(2)–F(2) | 2.103(3) |
| Al(1)–N(1) | 1.853(4) | Al(2)–N(2) | 1.842(3) |
| N(1)–C(13) | 1.499(6) | N(2)–C(23) | 1.504(6) |
| C(11)–C(111) | 1.529(7) | C(21)–C(211) | 1.509(8) |
| C(11)–C(112) | 1.513(8) | C(21)–C(212) | 1.537(8) |
| C(11)–C(113) | 1.533(8) | C(21)–C(213) | 1.515(8) |
| C(12)–C(121) | 1.555(8) | C(22)–C(221) | 1.517(9) |
| C(12)–C(122) | 1.540(7) | C(22)–C(222) | 1.584(9) |
| C(12)–C(123) | 1.545(8) | C(22)–C(223) | 1.552(9) |
| C(13)–C(131) | 1.520(7) | C(23)–C(231) | 1.532(7) |
| C(13)–C(132) | 1.534(8) | C(23)–C(232) | 1.511(7) |
| C(13)–C(133) | 1.529(8) | C(23)–C(233) | 1.529(7) |
| F(1)–Si(1)–N(1) | 89.5(2) | F(2)–Si(2)–N(2) | 89.8(2) |
| F(1)–Si(1)–C(11) | 104.2(2) | F(2)–Si(2)–C(21) | 103.0(2) |
| N(1)–Si(1)–C(11) | 117.4(2) | N(2)–Si(2)–C(21) | 117.5(2) |
| F(1)–Si(1)–C(12) | 100.9(2) | F(2)–Si(2)–C(22) | 101.0(2) |
| N(1)–Si(1)–C(12) | 121.8(2) | N(2)–Si(2)–C(22) | 121.7(2) |
| C(11)–Si(1)–C(12) | 114.9(2) | C(21)–Si(2)–C(22) | 115.3(2) |
| Cl(1)–Al(1)–F(1) | 103.9(1) | Cl(2)–Al(2)–F(2) | 102.0(1) |
| Cl(1)–Al(1)–N(1) | 109.3(1) | Cl(2)–Al(2)–N(2) | 110.8(1) |
| F(1)–Al(1)–N(1) | 74.7(1) | F(2)–Al(2)–N(2) | 74.8(1) |
| F(1)–Al(1)–F(1′) | 152.3(2) | F(2)–Al(2)–F(2′) | 156.0(2) |
| N(1)–Al(1)–F(1′) | 96.1(1) | N(2)–Al(2)–F(2′) | 96.6(1) |
| N(1)–Al(1)–N(1′) | 141.4(2) | N(2)–Al(2)–N(2′) | 138.4(2) |
| Si(1)–F(1)–Al(1) | 93.3(1) | Si(2)–F(2)–Al(2) | 92.3(1) |
| Si(1)–N(1)–Al(1) | 102.4(2) | Si(2)–N(2)–Al(2) | 102.7(2) |
| Si(1)–N(1)–C(13) | 127.7(3) | Si(2)–N(2)–C(23) | 126.9(3) |
| Al(1)–N(1)–C(13) | 129.3(3) | Al(2)–N(2)–C(23) | 129.4(3) |
| Si(1)–C(11)–C(111) | 111.5(4) | Si(2)–C(21)–C(211) | 112.2(4) |
| Si(1)–C(11)–C(112) | 108.6(3) | Si(2)–C(21)–C(212) | 107.7(4) |
| C(111)–C(11)–C(112) | 107.2(4) | C(211)–C(21)–C(212) | 108.7(5) |
| Si(1)–C(11)–C(113) | 113.5(4) | Si(2)–C(21)–C(213) | 114.0(4) |
| C(111)–C(11)–C(113) | 108.1(5) | C(211)–C(21)–C(213) | 108.5(5) |
| C(112)–C(11)–C(113) | 107.7(4) | C(212)–C(21)–C(213) | 105.4(5) |
| Si(1)–C(12)–C(121) | 114.0(4) | Si(2)–C(22)–C(221) | 112.3(4) |
| Si(1)–C(12)–C(122) | 110.2(3) | Si(2)–C(22)–C(222) | 112.7(5) |
| C(121)–C(12)–C(122) | 108.0(4) | C(221)–C(22)–C(222) | 107.1(5) |
| Si(1)–C(12)–C(123) | 109.1(4) | Si(2)–C(22)–C(223) | 109.3(4) |
| C(121)–C(12)–C(123) | 108.5(4) | C(221)–C(22)–C(223) | 107.1(5) |
| C(122)–C(12)–C(123) | 106.6(4) | C(222)–C(22)–C(223) | 108.0(5) |
| N(1)–C(13)–C(131) | 110.6(4) | N(2)–C(23)–C(231) | 109.4(4) |
| N(1)–C(13)–C(132) | 110.0(4) | N(2)–C(23)–C(232) | 110.4(4) |
| C(131)–C(13)–C(132) | 108.0(5) | C(231)–C(23)–C(232) | 110.0(4) |
| N(1)–C(13)–C(133) | 110.1(4) | N(2)–C(23)–C(233) | 110.4(4) |
| C(131)–C(13)–C(133) | 108.4(5) | C(231)–C(23)–C(233) | 108.3(4) |
| C(132)–C(13)–C(133) | 109.7(4) | C(232)–C(23)–C(233) | 108.3(4) |

TABLE 4

BOND LENGTHS (Å) AND ANGLES (°) FOR IV

| | | | |
|---|---|---|---|
| Al-Cl(1) | 2.111(2) | Al-Cl(2) | 2.120(2) |
| Al-Cl(3) | 2.104(2) | Al-N | 1.936(4) |
| N-C(1) | 1.469(6) | C(1)-C(2) | 1.516(7) |
| C(1)-C(3) | 1.485(9) | C(1)-C(4) | 1.501(8) |
| Cl(1)-Al-Cl(2) | 111.6(1) | Cl(1)-Al-Cl(3) | 110.4(1) |
| Cl(2)-Cl-Cl(3) | 112.6(1) | Cl(1)-Al-N | 113.8(2) |
| Cl(2)-Al-N | 102.9(1) | Cl(3)-Al-N | 105.2(2) |
| Al-N-C(1) | 129.3(3) | N-C(1)-C(2) | 109.9(4) |
| N-C(1)-C(3) | 106.9(4) | C(2)-C(1)-C(3) | 110.4(5) |
| N-C(1)-C(4) | 107.0(4) | C(2)-C(1)-C(4) | 110.3(4) |
| C(3)-C(1)-C(4) | 112.1(6) | | |

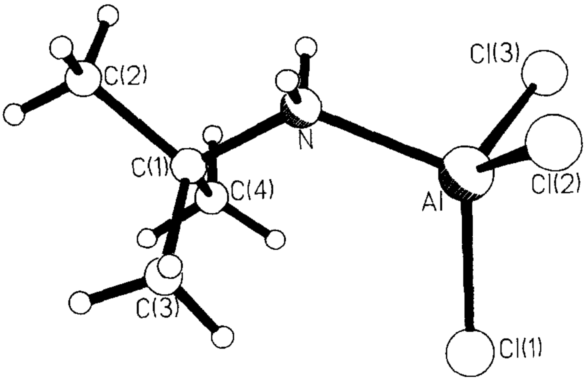


Fig. 2. Molecular structure of IV showing the atom numbering scheme.

equivalent isotropic thermal parameter for a C or N atom, defined as one-third of the trace of the orthogonalised $U_{ij}$ matrix. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Complex scattering factors were used [10]. Final difference syntheses contained no significant features.

III: 345 parameters, $R = 0.070$, $R'$ $[= (\Sigma w\Delta^2/\Sigma w F_0^2)^{1/2}] = 0.077$, mean shift/e.s.d. = 0.01, max. = 0.04; slope of normal probability plot [11] = 1.51.

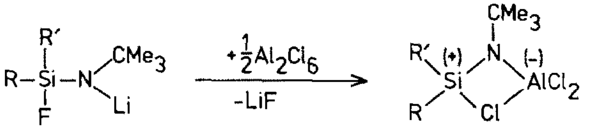
IV: 91 parameters, $R = 0.052$, $R' = 0.066$, mean shift/e.s.d. = 0.08, max. = 0.35, slope = 1.40.

Final atomic coordinates, bond lengths and angles are given in Tables 1-4. Structure factor tables may be obtained from the authors. Figures 1 and 2 show the molecular structures.

## Results and discussion

Reaction of RR'SiFN(CMe$_3$)Li with Al$_2$Cl$_6$ in petroleum ether leads to elimination of LiF and formation of a 1:1 adduct of the silicenium ylid RR' SiNCMe$_3$ with AlCl$_3$ (eq. 3).

I (R = R′ = $Me_3C$) and II (R = $Me_3C$, R′ = Ph) are colourless solids, extremely moisture-sensitive, and can be distilled without decomposition in vacuo. The partial zwitterion character is supported by the very low-field $^{29}Si$ NMR chemical shifts ($\delta$ 50.4 for I, 28.3 ppm for II), which are similar to values found for silaethenes [2]. The $^{27}Al$ NMR chemical shifts ($\delta$ 107 for I, 111 ppm for II) are typical of four-coordinate aluminium [12]. According to cryoscopic measurements, I and II are monomeric in solution in $C_6H_{12}$. We assign the structure shown to I and II, with four-membered ring and bridging chlorine, by analogy with the structure of III, determined by X-ray diffraction and discussed below.

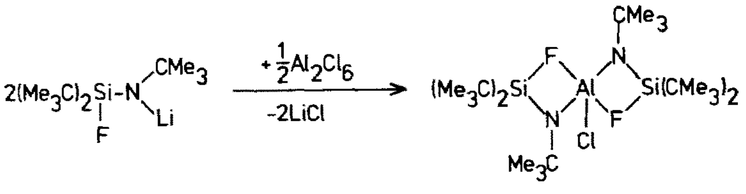


(3)

(I,II)

Attempts to obtain good quality single crystals of I have so far resulted in hydrolysis. This produces $Me_3CNH_2 \cdot AlCl_3$ (IV) and the cyclic siloxane $[(Me_3C)_2SiO]_3$ [13], the water oxygen atom attacking the electropositive silicon atom. IV exists in the solid state as a simple monomer, the adduct of $Me_3CNH_2$ with $AlCl_3$. Bond lengths and angles are very similar to those obtained for $Me_3N \cdot AlCl_3$ [14].

In the synthesis of I, the 2:1 adduct of the silicenium ylid $(Me_3C)_2SiNCMe_3$ with $AlClF_2$ (III) can be isolated as a by-product. The relative ease with which LiF or LiCl is eliminated is dependent on the reaction conditions, such as temperature, solvent, and reagent concentrations. At room temperature, and with a 4:1 mole ratio of lithium salt in THF to $Al_2Cl_6$ in $Et_2O$, LiCl elimination is preferred, and III is the main product (eq. 4). III is a colourless crystalline solid, soluble in the common organic solvents. It is moisture sensitive.



(4)

(III)

The unit cell of crystalline III contains two independent molecules, each with the Al–Cl bond lying along a crystallographic two-fold rotation axis. Differences between the two molecules are slight: a least-squares fit of the $(NSiF)_2AlCl$ skeletons gives a r.m.s. deviation of 0.045 Å for the fitted atoms; deviations for the carbon atoms are 0.039–0.231 Å, presumably because of small differences in torsion angles about the Si–C and N–C bonds in the two molecules.

The molecular structure, with bridging fluorine atoms, supports the interpretation of the molecule as a 2:1 adduct of the silicenium ylid with $AlClF_2$; this is also in agreement with the low-field $^{29}Si$ NMR chemical shift of 27.6 ppm, indicative of electropositive silicon, as in the 1:1 adducts I and II. Coordination of the nitrogen atoms is planar (sum of the bond angles around N(1) and N(2) 359.4 and 359.0°, respectively). Double-bond character is evident both in the short Si–N bonds (1.697(4) Å) and in the Al–N bonds (1.858(3) Å, cf. 1.770(2) and 1.963(2) for the probably double and single Al–N bonds in a molecule containing both [15] and 1.936(4) Å for the single bond in IV).

## Acknowledgements

We thank the Verband der Chemischen Industrie and the State of Niedersachsen for financial support. All computer programs were written by WC and GMS.

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