

Influence of the solvent and of the counteranion on the structure of silyl cations stabilized by a terdentate aryl diamine ligand

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Abstract

Solution NMR studies of silyl cations $[\text{ArSiMe}_2]^+ \text{X}^-$ ($\text{X} = \text{I}, \text{CF}_3\text{SO}_3$) incorporating the terdentate aryl diamine ligand $\text{Ar} = \text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{NMe}_2)_2$ have been carried out in a protic solvent (methanol- d_4) and in an aprotic solvent (CD_2Cl_2). This study has shown that the structure of these silyl cations is highly dependent on the solvent. In CD_2Cl_2 , the silyl cation is five-coordinated owing to the coordination of one NMe_2 group and of the anion to the silicon centre which gives rise to a dissymmetric structure. On the other hand, in CD_3OD there is no coordination of the anion, but the silyl cation is also probably five-coordinated due to the coordination of the solvent to the silicon atom which is supported by the X-ray analysis of the compound **9**. With the weakly nucleophilic anion BPh_4^- in CD_2Cl_2 , in addition to the silyl cation previously described, another five-coordinated silyl cation resulting from the coordination of both NMe_2 groups to the Si centre was postulated. © 1997 Elsevier Science S.A.

Keywords: Stabilized silyl cation; Terdentate aryl diamine ligand; Solvent effect

1. Introduction

We have recently been [1–3] investigating the problem of the stabilization of silylium ions by using the potentially terdentate aryl diamine ligand **A** ($\text{Ar} = \text{C}_6\text{H}_3\text{-}2,6\text{-(CH}_2\text{NMe}_2)_2$) [4]. We have shown by NMR spectroscopy that silyl cations **1** with at least one Si-H bond are five-coordinated due to the intramolecular coordination of both NMe_2 groups [1]. This result was supported by the X-ray structure determination of compounds **2** [5] and **3** [6] for which a trigonal bipyramidal geometry was found, both NMe_2 groups being in apical position. The structure of salts incorporating the ligand **A** and two further Si-C bonds (one methyl and one phenyl group) was also investigated by NMR spectroscopy [3]. With the weakly nucleophilic anion tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate (TFPB) in CD_2Cl_2 , the silyl cation is five-coordinated owing to intramolecular coordination of both NMe_2 groups to the silicon centre as observed in **1**. In contrast, in the case of a more nucleophilic anion such as Cl^- , Br^- , I^- , CF_3SO_3^- , there is no intramolecular coordination of

both NMe_2 groups at room temperature but rather a fluxional coordination of these groups. Furthermore, it was inferred from dynamic ^1H NMR studies that these silyl cations are also five-coordinated in CD_2Cl_2 at room temperature owing to the coordination of the anion to the silicon centre forming a tight ion pair **4a**. The low temperature (203 K) ^1H NMR spectrum of **4a** is consistent with a static cis arrangement of the two NMe_2 groups to the silicon centre giving rise to a six-coordinated silyl cation **4b**. The geometry of the silyl cations **4b** being dissymmetric even if $\text{R} = \text{R}'$, we decided to prepare silyl cations with $\text{R} = \text{R}' = \text{Me}$ in order to study their structure. In this paper, we report the role of the solvent as well as that of the counteranion in the structure of the silyl cations with $\text{R} = \text{R}' = \text{Me}$.

2. Results and discussion

In a previous paper [1] we described the reaction between a pentacoordinate hydrosilane and an electrophile giving rise to silyl cations. Following this route, treatment of the pentacoordinate hydrosilane **5** with iodine or $\text{CF}_3\text{SO}_3\text{SiMe}_3$ affords iodide or triflate salts

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$[\text{ArSiMe}_2]^+ \text{X}^-$ ($\text{X} = \text{I}, \text{CF}_3\text{SO}_3$) which were isolated as hygroscopic white powders in 86% and 90% yields respectively.

The NMR studies of these compounds were carried out in CD_2Cl_2 and in CD_3OD . Their ^{29}Si NMR spectra display one signal, the chemical shift of which depends on the solvent. In CD_2Cl_2 the ^{29}Si NMR chemical shifts are slightly different ($\delta = 3.4$ ppm for the iodide salt and 2.8 ppm for the triflate salt), whereas in CD_3OD these signals are shifted down field at a very similar value in both cases (7.4–7.5 ppm).

These differences observed on changing the solvent suggest that these cations have different structures following the nature of the solvent. This was confirmed from dynamic ^1H NMR studies of these salts in both solvents.

2.1. Dynamic ^1H NMR studies in CD_2Cl_2

At room temperature in CD_2Cl_2 the ^1H NMR spectra of these two salts are very similar and display a sharp singlet for the NCH_2 protons and a sharp singlet for the N-methyl protons. As the temperature is decreased there is first broadening of the N-methyl and the methylene protons signals and then decoalescence, giving, at 173 K for the iodide (Fig. 1) and at 193 K for the triflate salt, four signals for the N-methyl protons and two broad resonances for the methylene protons of the iodide salt, whereas for the triflate a badly resolved AB system and an AX system were observed for these protons. The single resonance observed for Si-methyl protons at room temperature is split into two resonances of equal intensity at 173 K for the iodide and at 193 K for the triflate. It is to be noted that the same solution behaviour was observed from salts **4a** ($\text{R} = \text{Me}, \text{R}' = \text{Ph}$) [3].

On the basis of the above observations, the following conclusions can be drawn.

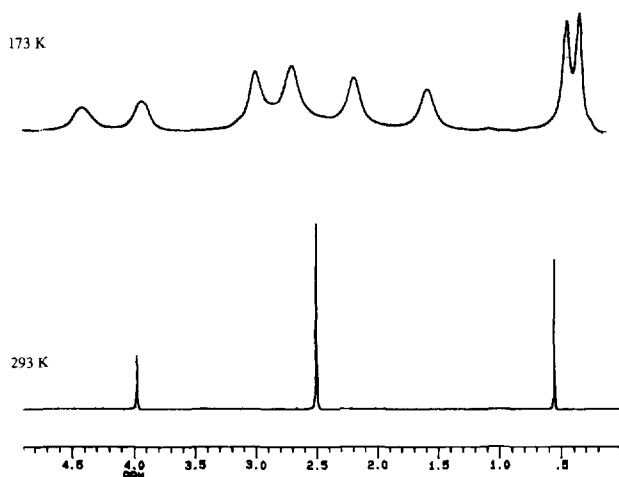


Fig. 1. Variable-temperature 250 MHz ^1H NMR spectra in CD_2Cl_2 for $[\text{ArSiMe}_2]^+ \text{I}^-$.

The low temperature ^1H NMR data for these salts indicate dissymmetric structures. They are not consistent with a static arrangement in which only one NMe_2 group would be coordinated to the silicon centre while the other one would not. In such a situation the ^1H NMR spectra would exhibit two N-methyl signals and two singlets for the N- CH_2 protons. To explain these data, we suppose that in these conditions the fluxional process is slowed down and that there is a static arrangement of the two NMe_2 groups coordinated to the silicon centre in a cis disposition, the anion occupying a site of coordination and forming a tight ion pair close to a six-coordinate silyl cation, as we have previously proposed for **4b** [3]. It is to be noted that the coordination of the two NMe_2 groups in a cis disposition at silicon has been observed for the (4 + 4)-coordinate silicon compounds **6** [7] and the (4 + 2) bis-dihydrosilane **7** [8]. Furthermore, the coordination of an anion to a silyl cation was also previously observed by Belzner et al. [6] and Jutzi and coworkers [9] respectively for compounds **8a** and **8b**.

At room temperature in CD_2Cl_2 the fluxional process should be fast (on the NMR time scale) so that these salts appear as five-coordinated silyl cations as **4a** [3], with only one NMe_2 group coordinated to the Si centre, the anion occupying the fifth coordination site. The equivalence of the NMe_2 groups should result from a dynamic coordination-decoordination process, the NMe_2 groups displacing each other rapidly on the ^1H NMR time scale. The ΔG^\ddagger value for the coordination-decoordination process was estimated to be 49.4 kJ mol^{-1} for the iodide and 46.1 kJ mol^{-1} for the triflate.

The coordination of the anion is consistent with the slight shift observed between the ^{29}Si NMR signals of the two salts. It is interesting to note that the chemical shift of compounds **4a** [3] also changes slightly as a function of the counteranion and that an upfield shift of 0.6 ppm had also been observed, on going from the iodide salt to the triflate salt **4a**, exactly as in the present case.

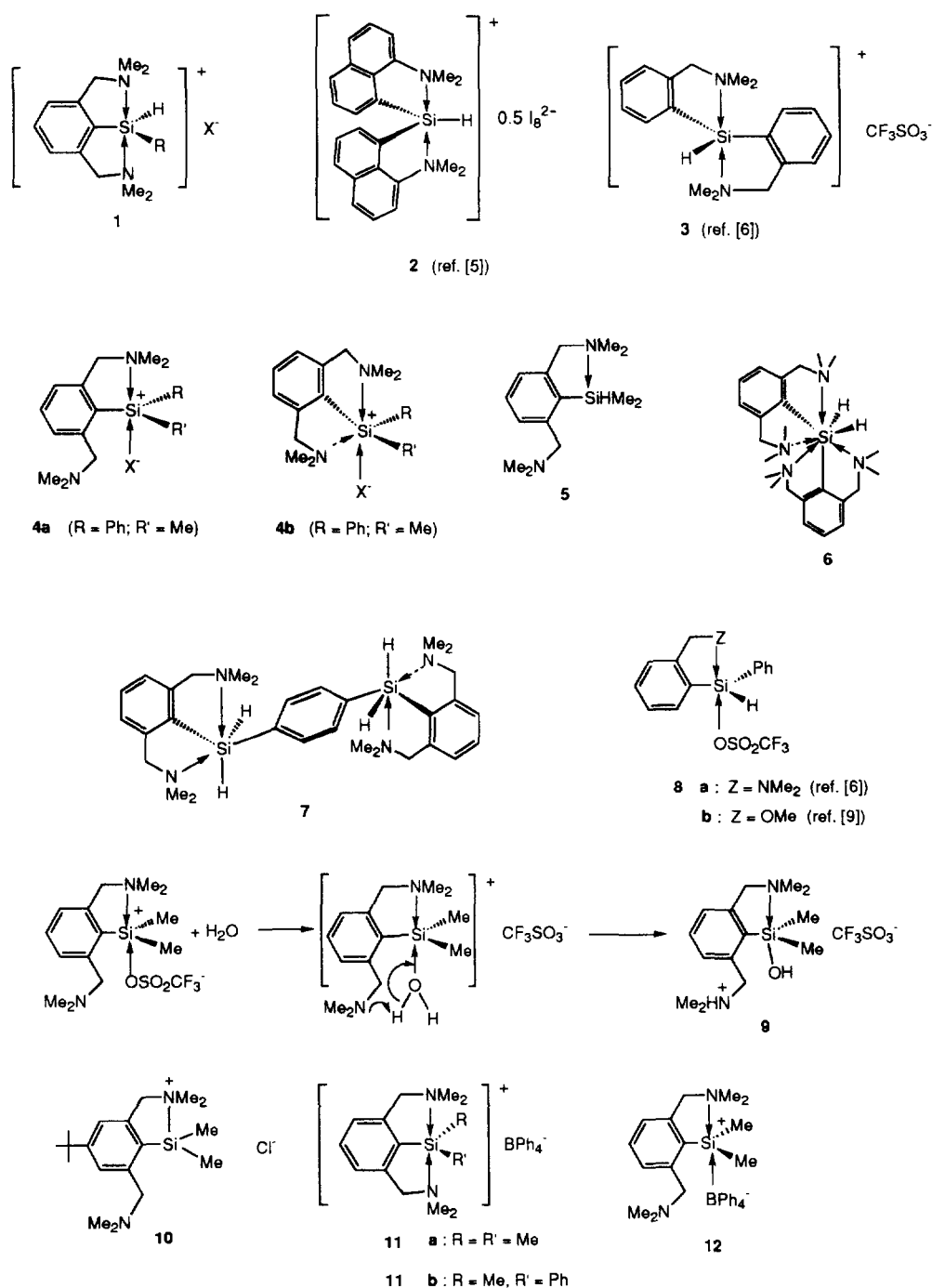
All attempts to obtain crystals of the iodide or of the triflate salts suitable for X-ray crystal structure determination were unsuccessful. However, during attempts to crystallize the triflate salt from a CH_2Cl_2 solution, some colourless crystals were obtained after about 1 month. The X-ray crystal structure determination of one of them has revealed that it corresponds to the salt **9** which results from the reaction of the triflate salt with traces of water (Scheme 1).

2.2. The X-ray structure of **9**

The ZORTEP drawing of **9** is displayed in Fig. 2. A summary of the crystallographic data is presented in Table 1 and the selected bond distances and angles are given respectively in Tables 2 and 3.

Structural features of interest are the following:
 the N(1)Me₂ group is coordinated to the silicon atom with an Si–N bond distance of 2.993(6) Å, which is shorter than the sum of the van der Waals radii of silicon and nitrogen atoms (3.6 Å) [10];
 the nitrogen atom N(2) is far from the silicon atom (3.737 Å) and is protonated. An OH group is σ -bonded to the silicon atom with an Si–O(1) covalent bond distance of 1.648 Å;
 the silicon atom adopts a slightly distorted tetrahe-

dral geometry, as shown by the following angle values: C(1)SiMe(1) 113.6°, C(1)SiMe(2) 116.6°, C(1)SiO(1) 102.7°, O(1)SiMe(1) 105.8°, O(1)SiMe(2) 103.4°, Me(1)SiMe(2) 112.9°. The N(1) atom is opposite the O(1)H(2) group, the N(1)SiO(1) angle being 170.9 (3)° so that the overall geometry of the molecule corresponds to a slightly distorted monocapped tetrahedron (theoretical angle values for a monocapped tetrahedron are of 109.4°, 180° and 70.5°);



Scheme 1.

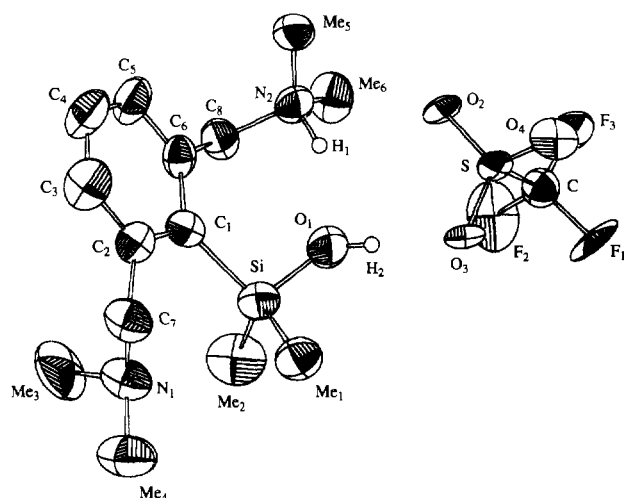


Fig. 2. ORTEP drawing of the molecule of compound **9** with the numbering of the atoms. Thermal ellipsoids are at the 50% probability level for the cation and 20% for the anion.

- there are hydrogen bonding interactions between H(1) and O(1) (1.84(6) Å) and between H(2) and the oxygen atom O(3) (2.005(6) Å) of the triflate anion, but there is no interaction between the anion and the silicon centre.

The formation of compound **9** can be explained by the reactions described in Scheme 1. In the presence of traces of water, the anion which occupied the fifth coordination site is displaced by a molecule of water with subsequent protonation of the free NMe₂ group.

Table 1
Summary of crystal data, intensity measurements, and refinement for compound **9**

Formula	C ₁₅ H ₂₇ F ₃ N ₂ O ₄ SSi
Crystal system	monoclinic
Space group	P2 ₁ /c
a (Å)	11.073(2)
b (Å)	11.625(2)
c (Å)	16.71(1)
β (deg)	99.04(3)
Volume (Å ³)	2124(1)
Mol. wt.	416.5
Z	4
d _{calcd} (g cm ⁻³)	1.302
Crystal size (mm ³)	0.70 × 0.25 × 0.10
Crystal colour	colourless
Recrystallization solvent	CH ₂ Cl ₂
Method of data collection	ω-θ
Radiation (graphite-monochromated)	Mo Kα
μ (cm ⁻¹)	2.45
2θ limits (deg)	4–52
No. of unique reflections	2758
No. of observed reflections	1199
Final no. of variables	178
R	0.048
R _w	0.049
Residual electron density (e ⁻ Å ⁻³)	0.22

Table 2
Interatomic distances (Å) for compound **9**

Si–C1	1.891(6)	C2–C7	1.511(9)
Si–Me1	1.837(7)	C7–N1	1.450(9)
Si–Me2	1.862(7)	N1–Me3	1.468(11)
Si–O1	1.648(5)	N1–Me4	1.465(10)
Si...N1	2.993(6)	C6–C8	1.523(9)
Si, N2	3.737(6)	C8–N2	1.500(8)
		N2–Me5	1.463(9)
		N2–Me6	1.491(9)
N2–H1	0.93(6)		
O1–H2	0.85(6)		
O1...H1	1.84(6)	S–C	1.793(9)
C1–C2	1.403(9)	S–O2	1.427(5)
C2–C3	1.400(9)	S–O3	1.415(6)
C3–C4	1.377(10)	S–O4	1.414(6)
C4–C5	1.379(10)	C–F1	1.327(11)
C5–C6	1.380(9)	C–F2	1.317(11)
C6–C1	1.414(8)	C–F3	1.262(11)

2.3. ¹H NMR studies in methanol-d₄

In CD₃OD the ¹H NMR spectra of these salts exhibit a sharp signal for the Si–Me protons and a broad signal for both the N–methyl and methylene protons, presumably due to the exchange process between the two NMe₂ groups at the silicon centre.

A variable-temperature ¹H NMR study was carried out for the iodide salt in methanol-d₄ (Fig. 3). As the temperature is decreased, each of the broad signals observed at room temperature coalesce first, then split into two resonances to give at 213 K two sets of broad singlets for both the methyl and methylene protons connected to the nitrogen atom.

The equivalence of the NMe₂ groups at room temperature should result from a dynamic coordination–decoordination process, as was observed in CD₂Cl₂. The ΔG[‡] for this process was estimated to be 50.1 kJ mol⁻¹, close to the value found for the very similar compound **10** (50.3 kJ mol⁻¹) [11].

At lower temperatures this process is slowed down (on the NMR time scale), so that at 213 K the two NMe₂ groups appear dissociated, one nitrogen atom

Table 3
Selected bond angles (deg) for compound **9**

C1–Si–Me1	113.6(3)	C1–C2–C7	122.0(6)
C1–Si–Me2	116.6(3)	C1–C2–C3	121.1(6)
C1–Si–O1	102.7(3)	C3–C2–C7	117.0(6)
C1–Si...N1	69.2(2)	C1–C6–C8	122.3(5)
O1–Si–Me1	105.8(3)	C1–C6–C5	121.8(6)
O1–Si–Me2	103.4(3)	C5–C6–C8	115.7(5)
O1–Si...N1	170.9(3)	C2–C7–N1	109.8(5)
Me1–Si–Me2	112.9(4)	C6–C8–N2	114.6(5)
Me1–Si...N1	81.7(3)	C8–N2–H1	101(4)
Me2–Si...N1	77.7(3)	N2–H1...O1	152(6)
Si–C1–C6	122.2(5)	Si–O1...H1	125(2)
C6–C1–C2	116.4(5)	Si–O1–H2	132(4)
Si–C1–C2	121.4(4)	H1...O1–H2	96(5)

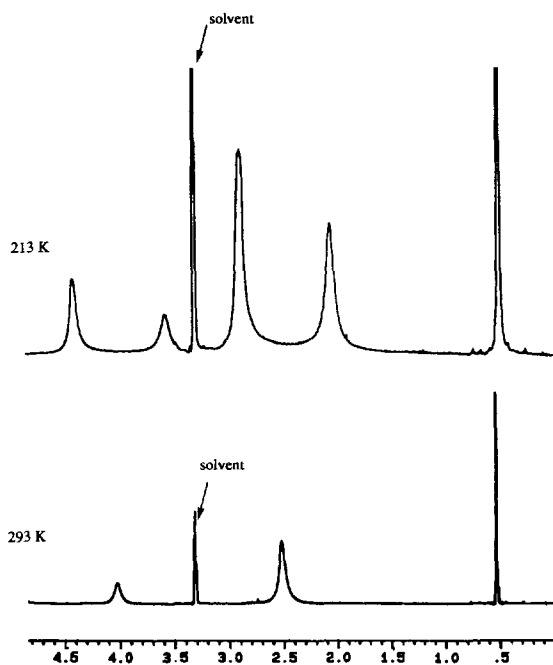


Fig. 3. Variable-temperature 250 MHz ^1H NMR spectra in CD_3OD for $[\text{ArSiMe}_2]^+ \text{I}^-$.

being coordinated to the silicon centre while the other is not. One set of singlets arises from the CH_2NMe_2 group coordinated to the silicon and the other from that uncoordinated to the silicon atom.

Indeed, two structures can be proposed for this silyl cation in methanol: in one the silicon centre is tetracoordinated, as was proposed for **10** by Willcott and coworkers [11]; in the other the silicon centre is five-coordinated, the fifth coordination site being occupied by a molecule of methanol- d_4 . This last hypothesis is supported overall by the results obtained on the silyl cations incorporating the terdentate aryl diamine ligand $\text{Ar} = \text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{NMe}_2)_2$ [1–3]. All of them are five-coordinated in CH_2Cl_2 . Thus, it is likely that in a nucleophilic solvent such as methanol, the fifth coordination site is no longer occupied by the anion but by the solvent.

2.4. Reaction of the iodide salt with NaBPh_4

In order to study the effect of a weakly nucleophilic anion, exchange of anion from the iodide salt was carried out with NaBPh_4 . The ^{29}Si NMR spectrum in CD_2Cl_2 of the reaction mixture shows two resonances, one at $\delta = 1.0$ ppm, which is just a little upfield compared to that of the starting salt ($\delta = 2.8$ ppm in CD_2Cl_2), and the other which is distinctly more upfield ($\delta = -5.6$ ppm). The formation of two species was confirmed by the ^1H NMR spectrum of the reaction mixture in CD_2Cl_2 , which at room temperature exhibits two distinct signals for the Si-Me protons, and two more for both the NMe_2 protons and the NCH_2 protons (Fig. 4).

Interestingly, as the temperature is decreased the signals attributed to one of the species in solution do not change at all, whereas signals attributed to the other species change drastically (Fig. 4). At 193 K one of the two Si-Me signals split into two signals, as was previously observed for the iodide and the triflate salts in CD_2Cl_2 . Unfortunately, the resolution of the NCH_2 and NMe protons corresponding to this second species is very poor at 193 K. Nevertheless, we assume that the species for which the ^1H NMR signals remain unchanged at low temperature is the five-coordinate silyl cation **11a** due to the coordination of both NMe_2 groups to the Si centre. We have assigned to this species the ^{29}Si NMR chemical shift at $\delta = -5.6$ ppm. The other species **12** (^{29}Si NMR, $\delta = 1$ ppm) should be the same as that previously described with I^- or CF_3SO_3^- as counteranion. Indeed, the ^{29}Si NMR chemical shift of **12** is slightly upfield compared to that of the iodide salt ($\delta = 3.4$ ppm) and to that of the triflate salt ($\delta = 2.8$ ppm), which is consistent with the coordination of the anion to the silicon centre. Furthermore, the ratio **11a**/**12** is not constant and changes as a function of time, the ratio of **11a** diminishing slowly while that of **12** increases to give a 1/6 ratio after 2 days. It is to be noted that the coexistence of two silyl cations had also been observed in the case of the silyl cation $[\text{ArSiPhMe}]^+ \text{BPh}_4^-$, the chemical shift of **11b** ($\delta = -14.5$ ppm) also being upfield compared to that of **4a** ($\text{X} = \text{BPh}_4$, $\delta = -8.5$ ppm) [3].

The ^1H NMR spectrum of this reaction mixture in CD_3OD at room temperature exhibits a single broad resonance for the NCH_3 protons, another for the NCH_2 protons and one singlet for the Si-Me protons, as observed for the iodide salt in the same conditions. Clearly there is only one species in methanol. Unfortunately, a variable-temperature ^1H NMR study as well as a ^{29}Si NMR study were not possible in CD_3OD because of the

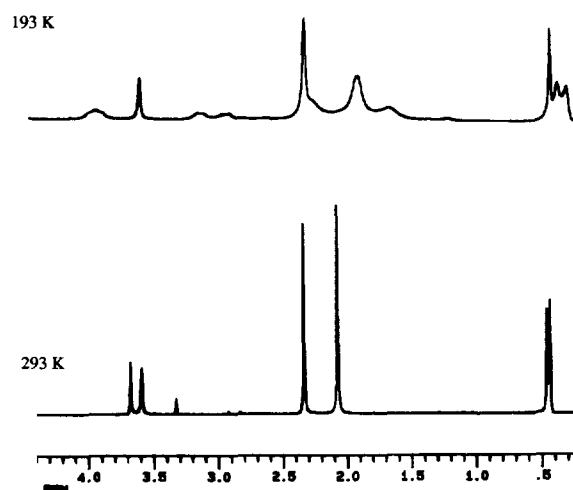


Fig. 4. Variable-temperature 250 MHz ^1H NMR spectra in CD_2Cl_2 for $[\text{ArSiMe}_2]^+ \text{BPh}_4^-$.

low solubility of the salt in this solvent. We assume that in methanol the silyl cation with BPh_4^- as counteranion has the same structure as that of the silyl cation with I^- or CF_3SO_3^- as counteranion. This result confirms that, whereas in CD_2Cl_2 the structure of the silyl cation changes with the nature of the anion, in methanol- d_4 it is independent of the anion.

2.5. Concluding remarks

Our study concerning the silyl cations incorporating the terdentate aryl diamine ligand $\text{Ar} = \text{C}_6\text{H}_3\text{-2,6-(CH}_2\text{NMe}_2)_2$ have shown that whatever the solvent and the counteranion they are always pentacoordinated. Two types of structure have been observed. In one structure both NMe_2 groups are coordinated to the silicon centre. This type of structure is always observed when the silyl cation has at least one Si-H bond. It is also observed when there are Si-C bonds and a weakly nucleophilic counteranion (TFPB). In the other structure one NMe_2 group is coordinated to the silicon centre, the fifth coordination site being occupied either by the nucleophilic anion or by the solvent when the latter is nucleophilic (e.g. methanol). Interestingly, these two types of cation with Si-C bonds coexist in CD_2Cl_2 solution when the counteranion is BPh_4^- .

3. Experimental section

All reactions were carried out under an argon atmosphere using Schlenk tube techniques. The solvents were dried by standard procedures prior to use and were stored under an argon atmosphere. Chlorosilanes were distilled over Mg under argon prior to use.

IR spectra (cm^{-1}) were recorded on a Perkin Elmer 1600 Fourier transform spectrometer. Mass spectra and FAB mass spectra (matrix, *o*-nitrophenyloctylether (NPOE), *m*-nitrobenzyl alcohol (NBA) or thioglycerol (GT) were registered on Jeol JMS-D100 or Jeol JMS-SX102 spectrometers. Bruker AM-300, 250-AC and 200-SY spectrometers were used to obtain ^1H , ^{13}C and ^{29}Si NMR spectra, and their chemical shifts were referenced to Me_4Si . Elemental analyses were performed by the Centre de microanalyse du CNRS. Satisfactory elemental analysis could not be obtained on salts, because they are extremely air- and moisture-sensitive.

3.1. {2,6-Bis[(dimethylamino)methyl]phenyl}dimethylsilane 5

36 mmol of 2,6-bis[(dimethylamino)methyl]phenyllithium [4] in ether (50 ml) were added at 0°C to a solution of chlorodimethylsilane (36 mmol, 4 ml) in ether (50 ml). The reaction mixture was stirred at room temperature for 5 h. After filtration

of LiCl on Celite the solvent was removed under vacuum. The oily residue was distilled to yield 7.2 g (81%) of **5** as a colourless oil. B.p. $120^\circ\text{C}/0.2\text{Torr}$. ^{29}Si NMR (40 MHz, CDCl_3): $\delta = -27.3$ (d, $^1J(\text{Si},\text{H}) = 200\text{ Hz}$). ^{15}N NMR (250 MHz, CDCl_3 , {H}, CH_3NO_2): -350.2 . ^1H NMR (250 MHz, CDCl_3): $\delta = 0.25$ (d, $^3J(\text{H},\text{H}) = 3.7\text{ Hz}$, 6H, $\text{Si}(\text{CH}_3)_2$); 2.05 (s, 12H, NCH_3); 3.41 (s, 4H, CH_2N); 4.3 (sept, $^3J(\text{H},\text{H}) = 3.7\text{ Hz}$, 1H, SiH); 6.95 to 7.1 (m, 3H, Ar). ^{13}C NMR (250 MHz, CDCl_3 , {H}): $\delta = -13$ ($\text{Si}(\text{CH}_3)_2$); 44.2 (NCH_3); 64.9 (CH_2N); 127.6, 127.7, 128, 137.5, 147 (Ar). IR (nujol): $\nu(\text{Si-H})$ 2111 cm^{-1} . MS (FAB positive mode, NBA): $m/z = 249$ (M-H^+) (100%). Anal. Found: C, 67.20; H, 10.80; N, 11.40. $\text{C}_{14}\text{H}_{26}\text{N}_2\text{Si}$. Calc.: C, 67.20; H, 10.40; N, 11.20%.

3.2. {2,6-Bis[(dimethylamino)methyl]phenyl}dimethylsilicon iodide

A solution of iodine (0.531 g, 2.1 mmol) in ether (20 ml) was added dropwise at 0°C to a solution of {2,6-bis[(dimethylamino)methyl]phenyl} dimethylsilane (1.06 g, 4.3 mmol) in ether (20 ml). There was immediate decoloration of the iodine solution and formation of a white solid. The reaction mixture was warmed to room temperature and stirred for 5 h. The white solid was filtered and then washed twice with 10 ml of ether to yield 1.3 g (86%) of the iodide salt. M.p. $113\text{-}114^\circ\text{C}$. ^{29}Si NMR (50 MHz, CD_2Cl_2): $\delta = 3.4$. ^{29}Si NMR (50 MHz, CD_3OD): $\delta = 7.4$. ^1H NMR (250 MHz, CD_2Cl_2): $\delta = 0.55$ (s, 6H, SiCH_3); 2.5 (s, 12H, NCH_3); 3.95 (s, 4H, NCH_2); 7.4 (s, 3H, Ar). ^1H NMR (250 MHz, CD_3CN): $\delta = 0.5$ (s, 6H, SiCH_3); 2.4 (s, 12H, NCH_3); 3.9 (s, 4H, NCH_2); 7.3 to 7.45 (m, 3H, Ar). ^1H NMR (250 MHz, CD_3OD): 0.5 (s, 6H, SiCH_3); 2.5 (broad signal, 12H, NCH_3); 4.0 (broad signal, 4H, NCH_2); 7.35 to 7.7 (m, 3H, Ar). ^1H NMR (250 MHz, CD_3OD , 213 K): $\delta = 0.5$ (s, 6H, SiCH_3), 2.1 (s, 6H, NCH_3), 2.8 (s, 6H, NCH_3); 3.6 (broad signal, 2H, NCH_2), 4.4 (broad signal, 2H, NCH_2); 7.3 to 7.75 (multiplet, 3H, Ar). ^{13}C NMR (62 MHz, CD_2Cl_2 , {H}): 4.1 (SiCH_3); 43.7 (NCH_3); 63.1 (NCH_2); 130.3, 133.7, 139.7 (Ar). ^{13}C NMR (62 MHz, CD_3OD , {H}): $\delta = -0.8$ (SiCH_3); 44.12 (NCH_3); 64.28 (NCH_2); 130.7, 133.3, 142.7 (Ar). ^{15}N NMR (20 MHz, CD_2Cl_2): $\delta = -334.27$. MS (FAB positive mode, NBA): $m/z = 249$ (M^+), 100%. FAB negative mode, GT: $m/z = 127$ (I^-) 50%. HRMS (FAB positive mode, NBA): found $m/z = 249.1780$ (M^+); calc. $m/z = 249.1787$ (M^+).

3.3. {2,6-Bis[(dimethylamino)methyl]phenyl}dimethylsilicon trifluoromethane-sulphonate

Trimethylsilyltriflate (0.418 ml, 2.17 mmol) was added dropwise by syringe at 0°C to a solution of **5** (0.544 g, 2.17 mmol) in ether (20 ml). After 30 min of stirring at

room temperature, the solvent was removed under vacuum and the residue was washed with ether (2×20 ml) to yield after filtration 0.77 g (90%) of the triflate salt as a white powder. M.p. 119–121 °C. ^{29}Si NMR (40 MHz, CD_2Cl_2): $\delta = 2.8$. ^{29}Si NMR (40 MHz, CD_3OD): $\delta = 7.5$. ^1H NMR (250 MHz, CD_2Cl_2): $\delta = 0.42$ (s, 6H, SiCH_3); 2.34 (s, 12H, NCH_3); 3.47 (s, 4H, NCH_2); 7.17 (d, $^3J(\text{HH}) = 6$ Hz, 2H, Ar), 7.2 (t, $^3J(\text{HH}) = 6$ Hz, 1H, Ar). ^1H NMR (250 MHz, CD_3OD): $\delta = 0.42$ (s, 6H, SiCH_3); 2.42 (broad signal, 12H, NCH_3); 3.92 (broad signal, 4H, NCH_2); 7.28 to 7.40 (m, 3H, Ar). ^{13}C NMR (62 MHz, CDCl_3 , {H}): $\delta = -4.2$ (SiMe_2); 47.1 (NCH_3); 64.5 (CH_2N); 125.1, 133.3, 143.8 (Ar). ^{19}F NMR (80 MHz, CDCl_3 , CFCl_3): $\delta = -80$ (s). IR (CHCl_3): $\nu(\text{C-F})$. 1256 cm^{-1} . MS (FAB positive mode NBA): $m/z = 249$ (M^+), 100%. FAB negative mode, NBA: $m/z = 149$ (CF_3SO_3^-), 100%. Anal. Found: C, 45.22; H, 6.28; N, 7.03. $\text{C}_{15}\text{H}_{25}\text{F}_3\text{N}_2\text{O}_3\text{Si}$. Calc.: C, 45.07; H, 6.41; N 6.96%.

3.4. {2,6-Bis[(dimethylamino)methyl]phenyl}dimethylsilicon tetraphenylborate

A solution of sodium tetraphenylborate (0.342 g, 1 mmol) in CH_3CN (10 ml) was added dropwise at room temperature to a solution of the iodide salt (0.376 g, 1 mmol) in CH_3CN (10 ml). The reaction mixture was stirred at room temperature for 8 h and the solvent was then removed. The residue was taken up in dry CH_2Cl_2 (15 ml) and after filtration of NaI and removal of the solvent, 0.482 g (85%) of a mixture of two tetraphenylborate salts was obtained. M.p. = 183–184 °C. ^{29}Si NMR (40 MHz, CD_2Cl_2): $\delta = -5.3$, 1.0. ^1H NMR (250 MHz, CD_2Cl_2): for **12**, 0.45 (s, 6H, SiCH_3); 2.0 (s, 12H, NCH_3); 3.55 (s, 4H, NCH_2); 6.9 to 7.6 (m, 23H, Ar). For **11a**, 0.46 (s, 6H, SiCH_3); 2.3 (s, 12H, NCH_3); 3.65 (s, 4H, CH_2N); 6.9 to 7.6 (m, 23H, Ar). The **12/11a** ratio was 2:1. ^1H NMR (250 MHz, CD_3OD): 0.5 (s, 6H, SiCH_3); 2.4 (broad signal, 12H, NCH_3); 3.9 (broad signal, 4H, NCH_2); 6.75 to 7.5 (m, 23H, Ar). ^{13}C NMR (62 MHz, CD_2Cl_2): for **12**, -4.1 (SiCH_3); 43.7 (NCH_3); 64.2 (NCH_2); 122.3, 126.1, 136.3 (Ar); 164.1 (q, $^1J(\text{BC}) = 50$ Hz, BC). For **11a**, 2.5 (SiCH_3); 47.1 (NCH_3); 64.5 (NCH_2); 122.3, 126.1, 136.3 (Ar); 164.1 (q, $^1J = 50$ Hz, BC). MS (FAB positive mode GT): $m/z = 249$ (M^+), 100%. FAB negative mode (GT): $m/z = 319$ (BPh_4^-), 95%. HRMS (FAB positive mode, GT): found $m/z = 249.1808$ (M^+); calc. $m/z = 249.1787$ (M^+); HRMS (FAB negative mode GT): found $m/z = 319.1662$ (BPh_4^-); calc. $m/z = 319.1658$ (BPh_4^-).

3.5. X-ray diffraction analysis of **9**

3.5.1. Crystal data

$\text{C}_{15}\text{H}_{27}\text{F}_3\text{N}_2\text{O}_4\text{SSi}$, $M = 416.5$ monoclinic, space group $P2_1/c$, $a = 11.073(2)$, $b = 11.625(2)$, $c =$

$16.71(1)$ Å, $\beta = 99.04(3)^\circ$, $Z = 4$, $D_c = 1.302$ g cm^{-3} , $F(000) = 880$, $\mu(\text{Mo K}\alpha) = 2.45$ cm^{-1} .

3.5.2. Data collection

Data were collected with a Nonius CAD-4 automated diffractometer in the θ range 2–26°. The size of the colourless crystal was approximately $0.70 \times 0.25 \times 0.10$ mm^3 . The method of data collection was ω - θ . Three reference reflections were measured at 60 min intervals and showed no significant changes in the intensities. The data were corrected for Lorentz and polarization factors and equivalent reflections were merged to give a total of 2758 unique data, of which 1199 were above background ($F > 4\sigma(F)$).

3.5.3. Structure solution and refinement

The direct methods (SHELXS 86) [12] revealed all the non-hydrogen atoms of the pincer ligand and silicon moiety and also all the atoms of the triflate anion. At this stage the conventional R factor was 0.13. Owing to the low number of observations, anisotropic thermal parameters were given only to fluorine, nitrogen, oxygen, silicon and sulphur atoms. The hydrogen atoms were included in the refinement in idealized positions (C-H 1.08 Å) SHELX-76 [13], excepted for H1 and later H2 which were revealed by difference Fourier syntheses. The hydrogen atoms and the carbon atoms were

Table 4
Fractional atomic coordinates ($\times 10^4$) with e.s.d.s in parentheses

Atom	x	y	z
Si	1800(2)	321(2)	2571(1)
C1	1209(6)	1216(5)	1647(3)
C2	-21(6)	1552(6)	1475(4)
C3	-414(7)	2357(6)	866(4)
C4	393(7)	2785(7)	392(4)
C5	1585(6)	2400(6)	505(4)
C6	1986(6)	1623(6)	1114(4)
Me1	1953(7)	-1214(6)	2349(5)
Me2	1084(7)	581(7)	3491(4)
C7	-986(6)	1045(6)	1917(4)
N1	-837(5)	-193(5)	1976(4)
Me3	-1046(9)	-742(7)	1176(5)
Me4	-1682(7)	-675(7)	2480(5)
C8	3278(6)	1165(6)	1130(4)
N2	4251(5)	1821(5)	1669(3)
Me5	4341(6)	3036(6)	1457(4)
Me6	5451(6)	1226(7)	1702(4)
H1	4056(57)	1641(55)	2173(38)
O1	3205(5)	806(5)	2833(3)
H2	3572(62)	1091(60)	3277(37)
C	6352(8)	1578(8)	4349(5)
F1	6477(5)	1240(6)	5116(3)
F2	6094(6)	667(5)	3885(4)
F3	7379(5)	1940(7)	4219(3)
S	5141(2)	2611(2)	4142(1)
O2	5139(5)	2891(5)	3310(3)
O3	4096(5)	1998(5)	4293(3)
O4	5545(7)	3500(5)	4697(3)

Table 5
Full list of bond angles

C1–Si–Me1	113.6(3)	Si...N1–C7	85.4(4)
C1–Si–Me2	116.6(3)	Si...N1–Me3	113.3(5)
C1–Si–O1	102.7(3)	Si...N1–Me4	124.3(5)
C1–Si...N1	69.2(2)	C6–C8–N2	114.6(5)
O1–Si–Me1	105.8(3)	C8–N2–Me5	114.5(5)
O1–Si–Me2	103.4(3)	C8–N2–Me6	109.7(5)
O1–Si...N1	170.9(3)	C8–N2–H1	101(4)
Me1–Si–Me2	112.9(4)	H1–N2–Me5	118(4)
Me1–Si...N1	81.7(3)	H1–N2–Me6	101(4)
Me2–Si...N1	77.7(3)	Me5–N2–Me6	111.3(5)
		N2–H1...O1	152(6)
Si–C1–C6	122.2(5)	Si–O1...H1	125(2)
Si–C1–C2	121.4(4)	Si–O1–H2	132(4)
C6–C1–C2	116.4(5)	H1...O1–H2	96(5)
C1–C2–C7	122.0(6)		
C7–C2–C3	117.0(6)	C–S–O2	103.1(4)
C1–C2–C3	121.1(6)	C–S–O3	103.6(4)
C2–C3–C4	120.3(7)	C–S–O4	102.3(4)
C3–C4–C5	119.9(7)	O2–S–O3	114.4(3)
C4–C5–C6	120.2(6)	O3–S–O4	115.8(4)
C5–C6–C8	115.7(5)	O4–S–O2	115.1(4)
C8–C6–C1	122.3(5)	S–C–F1	110.3(6)
C5–C6–C1	121.8(6)	S–C–F2	109.8(6)
C2–C7–N1	109.8(5)	S–C–F3	114.2(7)
C7–N1–Me3	111.7(6)	F1–C–F2	108.1(7)
C7–N1–Me4	110.1(6)	F2–C–F3	106.5(8)
Me3–N1–Me4	109.5(6)	F3–C–F1	107.7(7)

Table 6
Anisotropic Thermal parameters ($\times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si	56(1)	55(1)	56(1)	5(1)	16(1)	-2(1)
C1	49(5)	41(4)	44(4)	-11(3)	13(4)	-4(4)
C2	53(5)	50(5)	47(5)	-2(4)	11(4)	6(4)
C3	66(6)	89(6)	70(5)	3(6)	17(5)	17(5)
C4	84(6)	95(6)	51(5)	22(5)	3(5)	13(6)
C5	58(5)	96(6)	41(4)	8(5)	6(4)	6(5)
C6	45(4)	59(5)	38(4)	-9(4)	5(3)	3(4)
Me1	75(6)	69(6)	122(7)	9(5)	34(5)	24(5)
Me2	71(5)	84(6)	59(5)	2(4)	29(4)	-6(5)
C7	48(5)	58(6)	82(6)	-1(4)	19(4)	4(4)
N1	54(4)	50(4)	93(5)	0(4)	24(4)	1(4)
Me3	122(8)	88(7)	103(7)	-43(6)	7(6)	-39(6)
Me4	80(6)	68(6)	127(8)	29(6)	27(6)	-2(5)
C8	48(5)	70(5)	47(4)	-9(4)	15(4)	-8(4)
N2	52(4)	66(5)	39(3)	4(3)	17(3)	-4(4)
Me5	71(5)	68(6)	48(5)	2(4)	17(4)	-21(5)
Me6	48(5)	94(7)	71(5)	-4(5)	14(4)	11(5)
H1	80					
O1	65(4)	116(5)	53(3)	16(3)	9(3)	-27(3)
H2	80					
C	97(3)					
F1	142(5)	227(7)	116(4)	72(5)	3(4)	24(5)
F2	188(7)	127(5)	210(7)	-47(5)	8(5)	48(5)
F3	74(4)	323(9)	139(5)	52(6)	17(3)	-15(5)
S	99(2)	90(2)	44(1)	-5(1)	21(2)	-9(2)
O2	114(4)	119(5)	48(3)	11(3)	23(3)	-7(4)
O3	91(4)	149(6)	66(4)	15(4)	30(3)	-19(4)
O4	273(9)	98(5)	77(4)	-40(4)	36(5)	-39(5)

Table 7
Calculated hydrogen atom coordinates ($\times 10^4$)

H atom number	x	y	z	U
3	-1354	2642	767	105(13)
4	93	3422	-67	—
5	2208	2707	116	—
m1a	1049	-1587	2278	120(7)
m1b	2499	-1552	2891	—
m1c	2378	-1427	1829	—
m2a	252	100	3502	—
m2b	879	1490	3467	—
m2c	1726	395	4031	—
7a	-1882	1243	1588	56(9)
7b	-895	1409	2518	—
m3a	-343	-431	849	120(7)
m3b	-1921	-713	786	—
m3c	-843	-1618	1368	—
m4a	-1690	-1600	2537	—
m4b	-2550	-387	2162	—
m4c	-1517	-290	3075	—
8a	3487	1193	520	56(3)
8b	3301	284	1337	—
m5a	4502	3047	836	120(7)
m5b	5068	3492	1834	—
m5c	3478	3449	1495	—
m6a	5684	1274	1099	—
m6b	5417	336	1882	—
m6c	6135	1674	2120	—

refined isotropically. Three isotropic thermal parameters were attributed to the hydrogen atoms according to the group to which they were attached (methyl, methylene or phenyl) (Fig. 2). Refinement converged to an R (R_w) value of 0.048 (0.049) with $\rho = 0.22 \text{ e}^- \text{ \AA}^{-3}$. The final atomic coordinates are listed in Table 1, individual bond lengths in Table 2 and important bond angles in Table 3. Tables 4–7 are comprised of a list of anisotropic thermal parameters, a full table of bond angles and a list of the calculated hydrogen atom coordinates.

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