# Study of Silyl Cations Bearing an Aryldiamine Pincer Ligand

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In this paper, we describe two routes to prepare silyl cations with at least one Si−H bond by using the bis-chelating ligand $C_6H_3(CH_2NMe_2)_2$-2,6. The first is the reaction between a pentacoordinate dihydrosilane $ArRSiH_2$ [Ar = $(C_6H_3(CH_2NMe_2)_2$-2,6] and an electrophile. The second is the reaction of the lithium derivative ArLi with a dichlorohydrosilane $RSiHCl_2$. These cations are 5-coordinated owing to intramolecular chelation by the two $NMe_2$ groups. By using the same bis-chelating ligand, the formation of silyl cations with Si−C bonds has also been investigated. We show that in an aprotic solvent with non-nucleophilic counteranions [$(3,5\text{-}(CF_3)_2C_6H_3]_4B^-$, $BPh_4^-$] there is also bis chelation of the two amino groups to the silicon atom giving 5-coordinated silyl cations while in the presence of nucleophilic anions ($Cl^-$, $Br^-$, $I^-$, $CF_3SO_3^-$) there is no bis chelation of the two $NMe_2$ groups but rather a fluxional coordination of these groups occurring at silicon.



## Introduction

Intensive investigations[1−4] into the generation of long-lived free tricoordinate silyl cations $R_3Si^+$ (also called silylium, silicenium, or silylenium cations) have shown that, although these species are stable in the gas phase,[5] they are always stabilized in solution or in the solid state, by coordinative interactions with either the counteranion or with the solvent.[6] Thus the most recent approach of Lambert et al.[7] to prepare a silylium cation with the non-nucleophilic anion tetrakis(pentafluorophenyl)borate (TPFPB) in toluene led to a silyl cation, the X-ray structure analysis of which has shown no bonding of the anion to the silicon but a distant coordination of a toluene molecule incorporated in the crystal lattice so that this species behaves as a silylium cation "protected" by $\eta^1$-$\pi$ coordination to toluene.[8−10] Another type of $R_3Si^+$ (compound **1**) (see Chart 1) in which $\pi$ ligands contribute to the stabilization of the cationic center was reported by Jutzi and Bunte.[11]

The formation of N→Si stabilized silylium cations has been investigated over many years. Thus early in 1963 West and Corey[12] reported the preparation of the stable 5-coordinate ion (siliconium ion) $[Ph_3Si(bipy)]^+$. In fact, few examples of structurally defined stabilized silylium cations are known. The X-ray analysis of the dimethylsilylium cation intermolecularly stabilized by two molecules of *N*-methylimidazole[13] (complex **2**) has revealed the pentacoordination of the silicon center with two Si−N distances of 2.034(3) and 2.005(3) Å. Recently, the X-ray structures of the silylium cations **3**[14] and **4**,[15] stabilized by two intramolecular N→Si coordinations and bearing one Si−H bond, have been published.

In a report predating the publication of structures **3** and **4**, we have provided evidence[16,17] for the formation of 5-coordinate silyl cations due to the bis chelation of two $NMe_2$ groups of the tridentate 2,6-bis[(dimethylamino)methyl]phenyl ligand **A**[18] (Chart 1). Interestingly, following this report, Willcott et al.[19] showed that compound **5** exists in $CD_3OD$ solution as a 4-coordinate silyl cation. This result prompted us to investigate further the conditions of existence of silyl cations using the ligand **A**. In this paper we describe the synthesis and characterization of a series of 5-coordinate silyl cations with at least one Si−H bond and a detailed study concerning the silyl cations with Si−C bonds.

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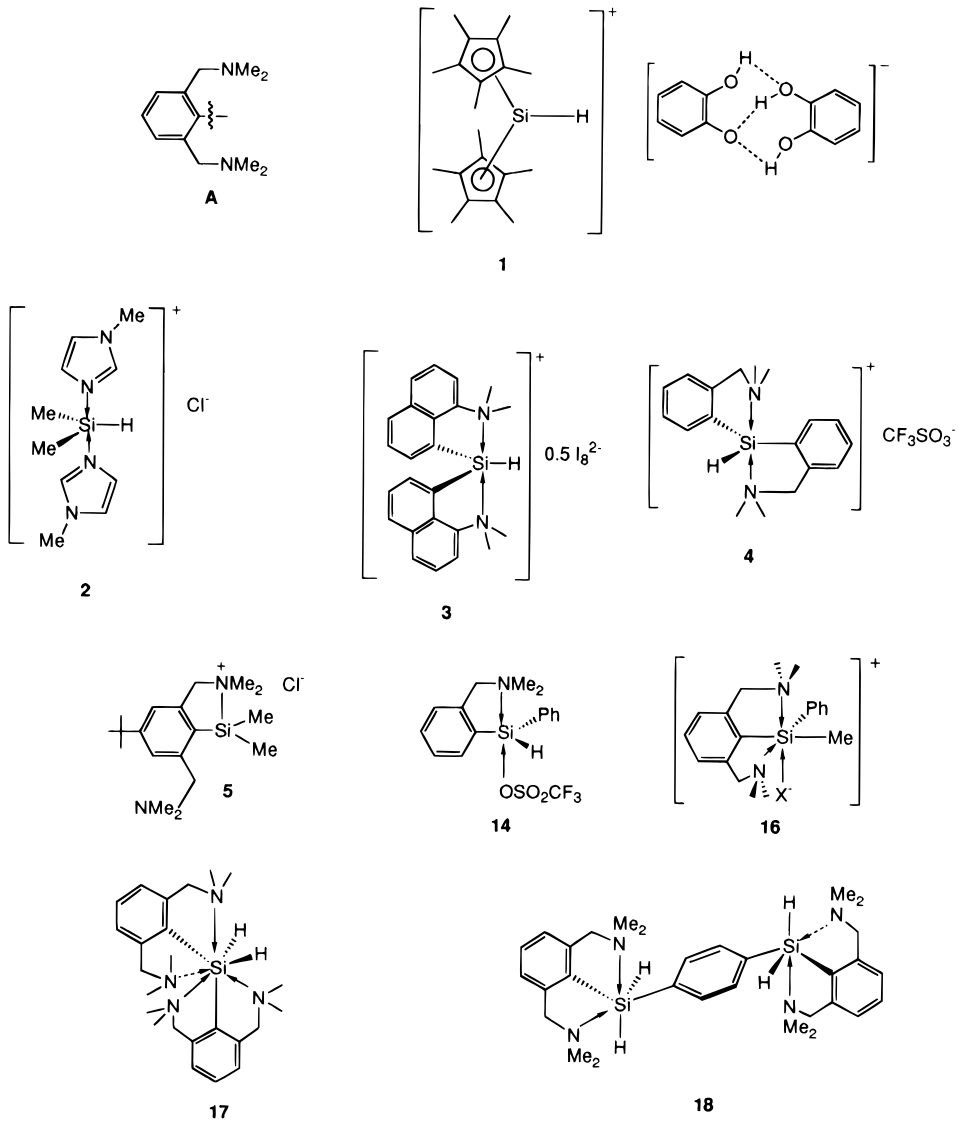
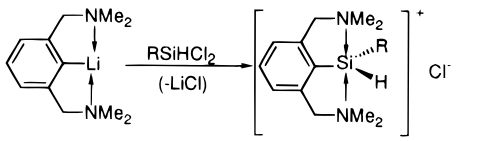
**Chart 1**




## Results and Discussion

**1. Five-Coordinate Silyl Cations with at Least One Si−H Bond.** In our earlier report[16] we described two routes leading to 5-coordinate silyl cations. The first (method A) is the reaction between a pentacoordinate dihydrosilane and an electrophile ($I_2$, PhCOCl, PhCOBr, $Ph_3C^+BF_4^-$, $CF_3SO_3SiMe_3$) (Scheme 1). The second (method B) is the reaction of the lithium derivative **9**[20] with a dichlorohydrosilane (eq 1). Since first




(1)

**6a** : R = Ph
**10** : R = CH=CH$_2$
**11** : R = Me
**12** : R = Cl

reported, these two methods have been further investigated and all the species prepared by one of these two routes are given in Scheme 1 (method A) and in eq 1 (method B). The compounds **6**−**8** and **10**−**12** were isolated as extremely air- and moisture-sensitive powders in contrast to compound **5** which is stable in air.[19] With the exception of **8** and **12** which will be described

**Scheme 1**

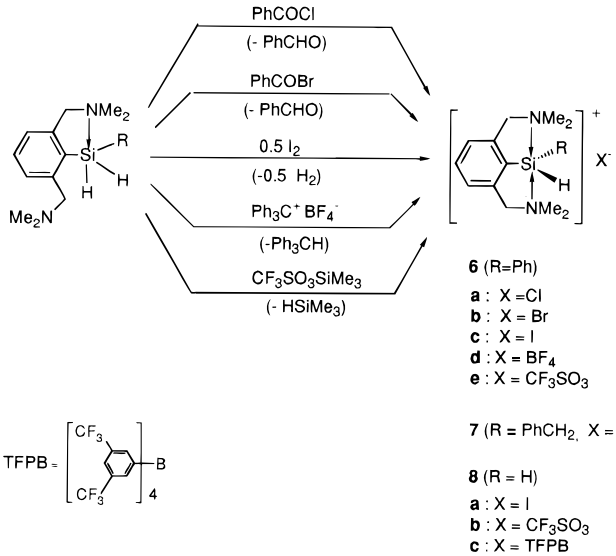



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**Table 1. Selected $^1$H and $^{29}$Si NMR[a] Data for Compounds 6a, 7, 10, and 11 at 293 K in $CD_2Cl_2$**

| | $^{29}$Si NMR | | $^1$H NMR | |
|---|---|---|---|---|
| compds | $\delta$ (ppm) | $J$(Si,H) (Hz) | $NCH_3$ | $NCH_2$ |
| **6a**[b] | −29.8 (d) (−51.5)[c] | 280 | 2.22 (s); 2.85 (s) | 4.01 (d, $^2J$(H,H) = 16 Hz), 4.39 (d, $^2J$(H,H) = 16 Hz) |
| **7** | −25.6 (d) (−42.6)[c] | 286 | 2.59 (s); 2.76 (s) | 3.87 (d, $^2J$(H,H) = 16 Hz), 4.05 (d, $^2J$(H,H) = 16 Hz) |
| **10** | −36.8 (d) | 280 | 2.57 (s); 2.61 (s) | 4.00 (d, $^2J$(H,H) = 15.4 Hz), 4.10 (d, $^2J$(H,H) = 15.4 Hz) |
| **11** | −27.7 (d) | 268 | 2.72 (s); 2.85 (s) | 4.10 (d, $^2J$(H,H) = 15 Hz), 4.24 (d, $^2J$(H,H) = 15 Hz) |

[a] $\delta$ in ppm relative to $Me_4Si$. [b] Reference 16. [c] $\delta$ ($^{29}$Si) in ppm for the starting silane $ArSiRH_2$.

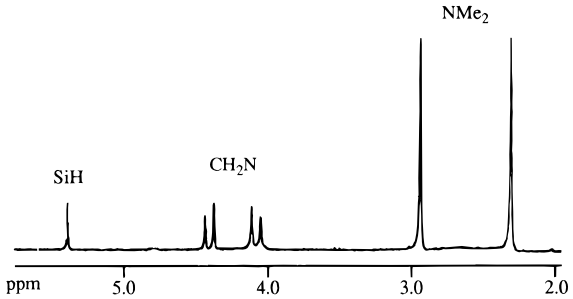
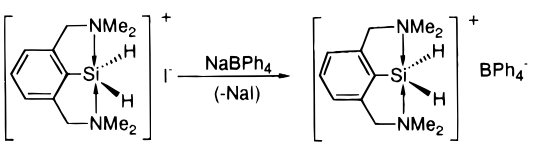



**Figure 1.** 250 MHz $^1$H NMR spectrum of **6a** in $CD_2Cl_2$ at 293 K.

subsequently, all the compounds exhibit very similar NMR data. Selected $^1$H and $^{29}$Si NMR data for compounds **6a**, **7**, **10,** and **11** are reported in Table 1. All the $^{29}$Si−$^1$H coupling constants (268−286 Hz) are significantly increased compared to those of the corresponding starting silanes (189−200 Hz). All these compounds display the same set of signals in their $^1$H NMR spectrum at room temperature in $CD_2Cl_2$ for the $CH_2NMe_2$ units, an AB system for the methylene protons and two signals of equal intensity for the $NMe_2$ groups. The two methyl resonances are due to the coordination of both nitrogen atoms to the silicon center, resulting in diastereotopy of the methyl groups of each $NMe_2$ unit, the two $NMe_2$ units being chemically equivalent. As an example, the $^1$H NMR spectrum of **6a** is reproduced in Figure 1. It is worth noting that these $^1$H NMR spectra are not temperature dependent within the range of temperatures studied (183−363 K). These data are consistent with a 5-coordinate silyl cation because of the chelation of both $NMe_2$ groups and not with a 4-coordinate silyl cation because of fluxional coordination of the $NMe_2$ groups (Scheme 2). Indeed, for such a structure, we should observe one signal for both the $NMe_2$ groups at room temperature because of the dynamic coordination−decoordination of the two $NMe_2$ units to the silicon center.[19] Furthermore the $^1$H NMR spectra should be temperature dependent and, at low temperature, when the coordination−decoordination process is slowed down (on the NMR time scale), we should observe a completely different set of signals.

Salts **8a**−**c** have very similar $^{29}$Si and $^1$H NMR spectra in $CD_2Cl_2$ (Table 2). Replacement of iodide in **8a** by tetraphenylborate affords the salt **8d** (X = $BPh_4$) (eq 2) which shows also the same $^1$H and $^{29}$Si chemical




(2)

shifts as **8a**−**c**. The $^1$H NMR spectra of **8a**−**d** in $CD_2Cl_2$ display at room temperature a single resonance for all

**Scheme 2**

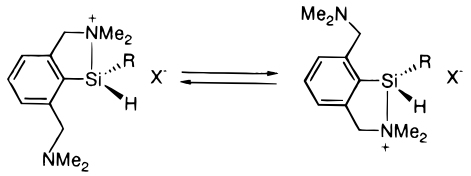



**Table 2. Selected $^1$H and $^{29}$Si NMR[a] Data for Compounds 8a−d**

| compds | $^{29}$Si NMR | | $^1$H NMR | |
|---|---|---|---|---|
| (anion) | $\delta$ (ppm) | $J$(Si,H) (Hz) | $NCH_3$ | $NCH_2$ |
| **8a**[b] ($I^-$) | −45.0 (t, $CDCl_3$), −43.0 (s, solid state) | 262 | 2.66 (s) | 4.12 (s) |
| **8b** ($CF_3SO_3^-$) | −44.9 (t, $CD_2Cl_2$) | 264 | 2.60 (s) | 4.00 (s) |
| **8c** (TFPB$^-$) | −44.9 (t, $CD_2Cl_2$) | 262 | 2.65 (s) | 4.05 (s) |
| **8d** ($BPh_4^-$) | −45.0 (t, $CD_2Cl_2$) | 263 | 2.51 (s) | 3.80 (s) |

[a] $\delta$ in ppm relative to $Me_4Si$. [b] Reference 16.

the methyl groups and a single resonance for all the methylene protons. A low-temperature $^1$H NMR study of **8a** showed no change down to 173 K except broadening of signals. The $^{29}$Si NMR spectra of **8a**−**d** ($CDCl_3$) each show a triplet ($\delta$ −44.9 to −45.0 ppm) with a large $^{29}$Si−$^1$H coupling constant (Table 2, $^1J$(Si,H) = 262−264 Hz) which is in the same range as those of **6**, **7**, **10**, and **11** (Table 1) and is significantly increased compared to that of the starting silane $ArSiH_3$ ($^1J$(Si,H) = 200 Hz). The IR spectrum of **8a** in KBr exhibits two Si−H stretches at $\nu$ = 2191 and 2209 $cm^{-1}$, close to that of **6a** ($\nu$ = 2202 $cm^{-1}$). Furthermore, it is worth noting that the salts **8a**−**d** react vigorously in MeOH solution giving rise to several unidentified products (observed by $^{29}$Si NMR spectroscopy). All these data suggest also the formation of a 5-coordinate silyl cation as a result of the coordination of both $NMe_2$ groups.

The $^{29}$Si NMR spectrum of the chlorinated compound **12** ($CDCl_3$) (eq 1) shows a doublet at $\delta$ = −40.3 ppm with a $^{29}$Si−$^1$H coupling constant of 334 Hz, larger than those observed in **6**−**8**, **10**, and **11** and for the structurally characterized silyl cations **1**,[11] **2**,[13] **3**,[14] and **4**.[15] The IR spectrum of **12** in KBr exhibits a Si−H stretch at $\nu$ = 2204 $cm^{-1}$, close to the Si−H absorbance for **6a** ($\nu$ = 2202 $cm^{-1}$). The $^1$H NMR spectrum of **12** at room temperature displays one signal for all the methyl groups at $\delta$ = 2.85 ppm and one signal for the methylene protons at $\delta$ = 4.28 ppm. Lowering the temperature of the NMR sample resulted in broadening and decoalescence of the $NMe_2$ and methylene signals (Figure 2). At 173 K (250 MHz, $CD_2Cl_2$) the $^1$H NMR spectrum of **12** exhibits two broad signals for the methyl groups and a badly resolved AB system for the benzylic protons, which corresponds to the same pattern as for **6**, **7**, **10,** and **11**. Finally, molar conductivity of **12** in $CH_2Cl_2$ was found to be 14.1 S $cm^2$ $mol^{-1}$. We assume that these overall $^1$H NMR data are consistent with a structure of the 5-coordinate silyl cation in which both $NMe_2$ groups

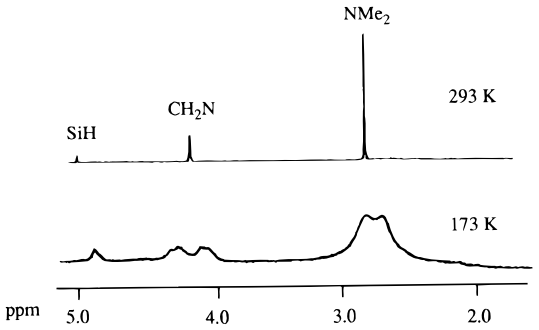



**Figure 2.** Variable-temperature 250 MHz $^1$H NMR spectra of **12** in $CD_2Cl_2$.

**Scheme 3**

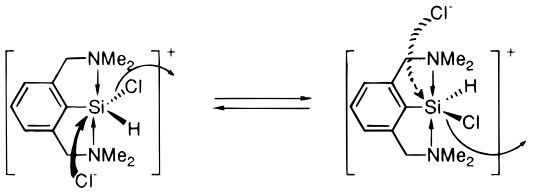


**Table 3. Selected $^1$H and $^{29}$Si NMR[a] Data in $CD_2Cl_2$ for Salts 13a−e and 15a−b**

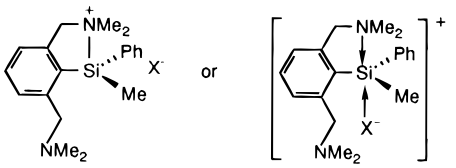
| | | $^1$H NMR | |
|---|---|---|---|
| compds | $^{29}$Si NMR | $NCH_3$ | $NCH_2$ |
| **13a** | −7.0 | 2.35 (s) | 3.97 (d, $^2J$(H,H) = 14 Hz), 4.10 (d, $^2J$(H,H) = 14 Hz) |
| **13b** | −7.2 | 2.25 (s) | 3.85 (d, $^2J$(H,H) = 11 Hz), 3.95 (d, $^2J$(H,H) = 11 Hz) |
| **13c** | −7.9 | 2.30 (s) | 3.94 (d, $^2J$(H,H) = 13 Hz), 4.45 (d, $^2J$(H,H) = 13 Hz) |
| **13d** | −7.1 | 2.35 (s) | 3.80 (d, $^2J$(H,H) = 15 Hz), 3.95 (d, $^2J$(H,H) = 15 Hz) |
| **13e** | −8.5 | 1.92 (s) | 3.40 (d, $^2J$(H,H) = 17 Hz), 3.69 (d, $^2J$(H,H) = 17 Hz) |
| **15a** | −14.5 | 1.75 (s); 2.35 (s) | 3.75 (d, $^2J$(H,H) = 15 Hz), 3.80 (d, $^2J$(H,H) = 15 Hz) |
| **15b** | −15.0 | 1.90 (s); 2.45 (s) | 3.86 (d, $^2J$(H,H) = 15 Hz), 3.95 (d, $^2J$(H,H) = 15 Hz) |

[a] $\delta$ in ppm relative to $Me_4Si$.

are coordinated to the silicon. The equivalence of the two methyl groups on each $NMe_2$ unit observed at room temperature is interpreted as the result of an intra- or intermolecular rearrangement process involving attack of $Cl^-$ at the silicon atom with inversion of configuration (Scheme 3). At low temperature this process is slowed (on the NMR time scale) so that the methyl groups on each $NMe_2$ unit and the methylene protons appear diastereotopic, both $CH_2NMe_2$ unit being equivalent.

In conclusion, silyl cations containing the aryldiamine ligand **A** are always 5-coordinated with a symmetrical chelation of both $NMe_2$ groups when there is at least one hydrogen bonded to the silicon atom.

**2. Silyl Cations with Si−C Bonds**. Following the NMR study of Willcott et al.[19] showing that compound **5** is a 4-coordinate silyl cation and not a 5-coordinate silyl cation in $CD_3OD$, we have examined in detail the nature of silyl cations bearing the ligand **A** and two further Si−C bonds. For this purpose we have chosen a model in which the silicon atom is surrounded by different substituents in order to obtain more information about the mode of coordination of donor groups to the chiral silicon center.




**13** **a**: X = Cl
**b**: X = Br
**c**: X = I
**d**: X = $CF_3SO_3$
**e**: X = $BF_4$
**f**: X = TFPB

**Figure 3.**

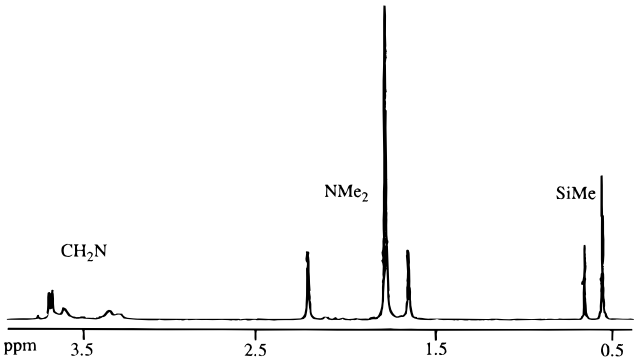
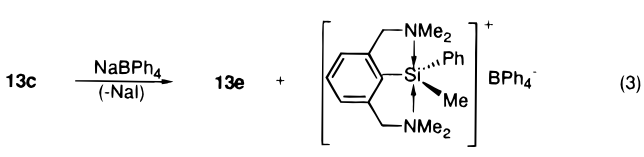



**Figure 4.** 250 MHz $^1$H NMR spectrum of **13e** and **15a** in $CD_2Cl_2$ at 293 K.

ArSiMePhH undergoes hydride abstraction by reaction with an electrophile such as PhCOBr, PhCOCl, $I_2$, or $CF_3SO_3SiMe_3$ to give hygroscopic salts **13a−d**, which show very similar $^1$H and $^{29}$Si NMR spectra (Table 3) in $CD_2Cl_2$. At ambient temperature the $^{29}$Si NMR spectra of all these compounds display a singlet lying between −7.0 and −7.9 ppm. The $^1$H NMR spectra at room temperature show the equivalence of the two $CH_2NMe_2$ units, each unit appearing as a singlet assigned to the $NMe_2$ protons and an AB pattern for the methylene protons. These data are not consistent with a structure in which the two $NMe_2$ groups are symmetrically coordinated to the silicon center. They are consistent with structures in which at room temperature fluxional coordination of the two $NMe_2$ groups occurs at silicon giving either a 4-coordinated silyl cation or a tight ion pair between an intramolecular coordinated silyl cation and a $X^-$ anion (compounds **13a−d**, Figure 3). Coordination of an anion to a silyl cation was previously observed by Belzner et al.[15] in the case of compound **14**.

Treatment of the iodide **13c** with $NaBPh_4$ (eq 3) gives

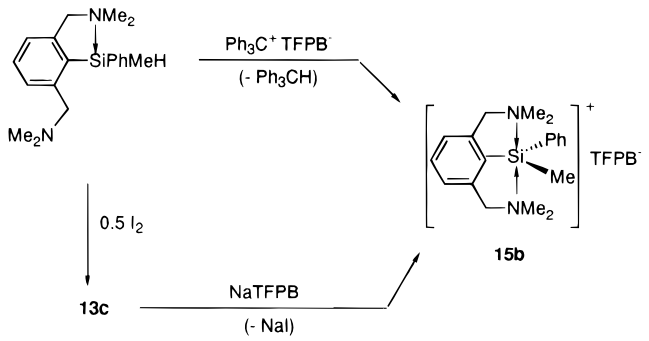



(3)

**15a**

rise to a mixture of two products as shown in the $^{29}$Si NMR spectrum ($\delta$ = −8.5 and −14.5 ppm). The signal at −8.5 ppm was assigned to **13e** (Figure 3), while the signal at −14.5 ppm was assigned to the species **15a** in which the two $NMe_2$ groups are coordinated to the silicon atom as it was proposed for **6a−e**, **7**, **8**,**10**, **11**, and **12**. The $^1$H NMR spectrum (Figure 4) exhibits the

**Scheme 4**




signals corresponding to the two species (cf. Experimental Section), with a **13e**/**15a** ratio of 3/1. It is to be noted that the $^1$H NMR spectrum of the mixture **13e**,**15a** changes as a function of time, the proportion of **15a** diminishing slowly while that of **13e** increases to give a 9/1 ratio after 3 days. Furthermore, when a drop of water is added to the solution containing this mixture, the signals assigned to **15a** disappear immediately leaving only signals which are close of those assigned to **13e**.

Hydride abstraction from ArSiMePhH by use of trityltetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB)[21] affords the salt **15b** which can also be prepared by anion exchange between iodide and TFPB from **13c** (Scheme 4). It is noteworthy that **15b** is very air and moisture sensitive. Furthermore the $^1$H and $^{29}$Si NMR data of **15b** are close of those of **15a.** The $^{29}$Si NMR spectrum shows one resonance at $\delta = -15.0$ ppm. The $^1$H NMR spectrum exhibits the same pattern as those of **6a**−**d**, **7**, **10**, and **11**, two signals assigned to the methyl groups of each $NMe_2$ unit and an AB pattern assigned to the methylene protons, both $CH_2NMe_2$ units being equivalent. Furthermore, though only one resonance was observed in the $^{29}$Si NMR spectrum, the $^1$H NMR spectrum exhibits additional signals corresponding to those of **13f** (less than 10% present). These data show the crucial role of the non-nucleophilic TFPB anion in promoting the formation of **15b**. Interestingly a low-temperature $^1$H NMR study of these TFPB salts in $CD_2Cl_2$ solution has shown no change concerning the signals attributed to **15b** down to 173 K. In contrast, the signals attributed to **13f** (the minor product in these conditions) change drastically as the temperature is decreased. There is first broadening and then decoalescence of the $NMe_2$ and methylene signals. At 203 K, the $^1$H NMR spectrum exhibits four broad single resonances for the $NMe_2$ groups. The methylene protons appear as an AB and an AX system. It is worth noting that the $^1$H NMR spectra of **13a**−**d** display the same pattern at low temperature but with a very poor resolution because of the low solubility of these ions in $CD_2Cl_2$ at low temperature. These data are not all consistent with a static arrangement in which only one $NMe_2$ group would be coordinated to the silicon center while the other would not. In such a situation, we should observe three $NMe_2$ signals, and two AX or AB systems for the methylene protons. We explain the changes in the $^1$H NMR spectrum of **13f** observed at low temperature in $CD_2Cl_2$ supposing that at this temperature there is a static arrangement of the two $NMe_2$ groups which should be coordinated to the silicon center in a cis arrangement, the anion occupying a site of coordination and forming a tight ion pair **16** approximating to a 6-coordinate silyl cation. It is to be noted that the coordination of the two $NMe_2$ groups in a cis position at silicon has been previously observed for the [4 + 4] coordinate silicon compound **17**[22] and the [4 + 2] bis(dihydrosilane) **18**.[23] These data suggest that species **13** are probably 5-coordinated rather than 4-coordinated silyl cations (Figure 3).

In conclusion, this study has shown that silyl cations bearing the ligand **A** and at least one Si−H bond are always siliconium ions with chelation of both $NMe_2$ groups to the silicon atom. That constitutes another example of the high ability of hydrosilanes to expand their coordination number.[22, 23] The structure of salts bearing the ligand **A** and two further Si−C bonds is a more complicated problem depending both on the counteranion and on the solvent. In aprotic solvent with non-nucleophilic anions ($TFPB^-$, $BPh_4^-$) there is also formation of 5-coordinate silyl cations by chelation of the two $NMe_2$ groups to the silicon atom, while with nucleophilic anions ($Cl^-$, $Br^-$, $I^-$, $CF_3SO_3^-$) fluxional coordination of both amino groups was observed at room temperature.

## Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk tube techniques. All solvents were purified by distillation ($CCl_4$, $CH_2Cl_2$, and $CH_3CN$ from $P_2O_5$; diethyl ether from sodium−benzophenone) prior to use and were stored under an argon atmosphere. All chlorosilanes were distilled over Mg under argon prior to use.

Trityltetrakis[3,5-bis(trifluoromethyl)phenyl]borate[21] and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate[21] were prepared by literature methods. Preparations of {2,6-bis[(dimethylamino)methyl]phenyl}phenylsilicon chloride (**6a**), {2,6-bis[(dimethylamino)methyl]phenyl}phenylsilicon iodide (**6c**), and {2,6-bis[(dimethylamino)methyl]phenyl}silicon iodide (**8a**) are described in ref 16.

IR spectra ($cm^{-1}$) were recorded on a Perkin-Elmer 1600 Fourier transform spectrometer. Mass spectra and FAB mass spectra (matrix, *o*-nitrophenyl octyl ether, NPOE, or *m*-nitrobenzyl alcohol, NBA) were registered on Jeol JMS-D100 and Jeol JMS-SX102 spectrometers. Brucker AM-300, 250-AC, and 200-SY spectrometers were used to obtain $^1$H, $^{13}$C, and $^{29}$Si NMR spectra, and their chemical shifts were referenced to $Me_4Si$. Elemental analysis were performed by the Centre de microanalyse du CNRS. Satisfactory elemental analysis could not be obtained on salts **6b**,**d**,**e**, **7**, **8b**,**c**,**d**, **10**, **12**, **13a**−**e**, and **15a**,**b** because they are extremely air and/or moisture sensitive.

**{2,6-Bis[(dimethylamino)methyl]phenyl}phenylsilicon Bromide (6b).** Benzoyl bromide (1.24 g, 6.7 mmol) was added dropwise at room temperature with the syringe to a solution of {2,6-bis[(dimethylamino)methyl]phenyl}phenylsilane (2.0 g, 6.7 mmol) in $CCl_4$ (25 mL). The reaction mixture was stirred at room temperature for 10 min. The solvent was then removed under vacuum, and the residue was taken up in ether (30 mL). The yellow precipitate was filtered off and washed with ether (3 × 10 mL) to give **6b** (2.30 g, 6.1 mmol, 91%). Mp: 127 °C (dec). $^{29}$Si NMR (39.76 MHz, $CDCl_3$): −29.7 (d, $^1J$(Si,H) = 280 Hz). $^1$H NMR (250 MHz, $CDCl_3$): 2.24 (s, 6H, $NCH_3$); 2.80 (s, 6H, $NCH_3$); 4.02 (d, $^2J$(H,H) = 16 Hz,

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2H, $CH_2N$); 4.40 (d, $^2J$(H,H) = 16 Hz, 2H, $CH_2N$); 5.20 (s, 1H, SiH); 7.20−7.93 (m, 8H, Ar). IR ($CH_2Cl_2$, $cm^{-1}$): 2215 (SiH). MS (FAB positive mode, NPOE): $m/z$ = 297 [$(M - Br)^+$, 100]. MS (FAB negative mode, NPOE): $m/z$ = 79−81 [$(Br^-)$, 100]. HRMS (FAB positive mode, NPOE): Calcd $m/z$ = 297.1675; found, $m/z$ = 297.1654.

**{2,6-Bis[(dimethylamino)methyl]phenyl}phenylsilicon Tetrafluoroborate (6d).** Trityl tetrafluoroborate (1.10 g, 3.35 mmol) in $CH_2Cl_2$ (20 mL) was added dropwise at room temperature to a solution of {2,6-bis[(dimethylamino)-methyl]-phenyl}phenylsilane (1.00 g, 3.35 mmol) in $CH_2Cl_2$ (30 mL). The reaction mixture was stirred at room temperature for 1 h. The solvent was then removed under vacuum and the residue washed with ether (4 × 15 mL) to eliminate $Ph_3CH$ yielding **6d** (1.10 g, 2.9 mmol, 86%). Mp: 157 °C (dec). $^{29}$Si NMR (39.76 MHz, $CDCl_3$): −29.8 (d, $^1J$(Si,H) = 282 Hz). $^1$H NMR (250 MHz, $CDCl_3$): 2.16 (s, 6H, $NCH_3$); 2.72 (s, 6H, $NCH_3$); 3.90 (d, $^2J$(H,H) = 16 Hz, 2H, $CH_2N$); 4.30 (d, $^2J$(H,H) = 16 Hz, 2H, $CH_2N$); 5.15 (s, 1H, SiH); 7.10−7.82 (m, 8H, Ar). IR ($CH_2Cl_2$, $cm^{-1}$): 2210 (SiH). MS (FAB positive mode, NPOE): $m/z$ = 297 [$(M - BF_4)^+$, 100]. MS (FAB negative mode, NPOE): $m/z$ = 87 [$(BF_4^-)$, 100]. HRMS (FAB positive mode, NPOE): Calcd, $m/z$ = 297.1675; found, $m/z$ = 297.1657.

**{2,6-Bis[(dimethylamino)methyl]phenyl}phenylsilicon Trifluoromethanesulfonate (6e).** Trimethylsilyl triflate (0.5 mL, 2.58 mmol) was added dropwise at room temperature with the syringe to a solution of silane $ArPhSiH_2$ (0.77 g, 2.58 mmol) in $CH_2Cl_2$ (10 mL). The reaction mixture was stirred at room temperature for 10 min. The solvent was removed under vacuum, and the residue was taken up in ether (30 mL). The white precipitate was then filtered out and washed with ether (3 × 10 mL) to give **6e** (1.05 g, 2.45 mmol, 91%). Mp: 135 °C (dec). $^{29}$Si NMR (39.76 MHz, $CDCl_3$): −29.7 (d, $^1J$(Si,H) = 281 Hz). $^1$H NMR (250 MHz, $CDCl_3$): 2.18 (s, 6H, $NCH_3$); 2.35 (s, 6H, $NCH_3$); 3.95 (d, $^2J$(H,H) = 16 Hz, 2H, $CH_2N$); 4.22 (d, $^2J$(H,H) = 16 Hz, 2H, $CH_2N$); 5.10 (s, 1H, SiH); 7.26−7.80 (m, 8H, Ar). IR ($CH_2Cl_2$, $cm^{-1}$): 2208 (SiH). MS (FAB positive mode, NPOE): $m/z$ = 297 [$(M - CF_3SO_3)^+$, 100]. MS (FAB negative mode, NPOE): $m/z$ = 149 [$(CF_3SO_3^-)$, 100]. HRMS (FAB positive mode, NPOE): Calcd, $m/z$ = 297.1675; found, $m/z$ = 297.1661.

**{2,6-Bis[(dimethylamino)methyl]phenyl}benzylsilane.** A 31.3 mmol amount of the {2,6-bis[(dimethylamino)-methyl]phenyl}lithium derivative **9**[20] in ether (30 mL) was added dropwise at 0 °C to 3.81 g (31.3 mmol) of benzylsilane in ether (30 mL). The reaction mixture was stirred overnight at room temperature. Distilled water (0.56 mL) was then added to the reaction mixture to hydrolyze LiH. After filtration of LiOH, the solution was dried over $MgSO_4$ and filtered. The solvent was then removed under vacuum to give a viscous oil which was distilled, and {2,6-bis[(dimethylamino)methyl]-phenyl}benzylsilane ($ArBzSiH_2$) was isolated as a colorless oil (7.3 g, 22.8 mmol, 73%). Bp: 118−119 °C (0.05 mmHg). $^{29}$Si NMR (39.76 MHz, $CDCl_3$): −42.6 (tt, $^1J$(Si,H) = 189 Hz, $^2J$(Si,H) = 9.5 Hz). $^1$H NMR (250 MHz, $CDCl_3$): 2.31 (s, 12H, $NCH_3$); 2.62 (t, 2H, $^3J$(H,H) = 3.6 Hz, $SiCH_2$); 3.60 (s, 4H, $CH_2N$); 4.28 (t, 2H, $^3J$(H,H) = 3.6 Hz, $SiH_2$); 7.22−7.43 (m, 8H, Ar). $^{13}$C NMR (62.89 MHz, $CDCl_3$, {H}): 22.8 ($SiCH_2$); 44.0 ($NCH_3$); 64.8 ($CH_2N$); 124.0, 127.6, 128.1, 128.3, 128.5, 134.3, 142.0, 147.6 (Ar). IR ($CCl_4$, $cm^{-1}$): 2121 ($SiH_2$). Anal. Calcd for $C_{19}H_{28}N_2Si$: C, 73.07; H, 8.97; N 8.97. Found: C, 72.67; H, 9.04; N, 8.87.

**{2,6-Bis[(dimethylamino)methyl]phenyl}benzylsilicon Iodide (7).** A solution of iodine (0.34 g, 1.34 mmol) in ether (20 mL) was added dropwise at 0 °C to a solution of {2,6-bis[(dimethylamino)methyl]phenyl}benzylsilane (0.85 g, 2.72 mmol) in ether (10 mL). The reaction mixture was stirred at room temperature for 5 h. The solid obtained was filtered out and was washed with ether (2 × 20 mL) to give **7** (1.05 g, 2.4 mmol, 88%) as a yellow brown solid. Mp: 145 °C (dec). $^{29}$Si NMR (39.76 MHz, $CDCl_3$): −25.6 (d, $^1J$(Si,H) = 286 Hz). $^1$H NMR (250 MHz, $CDCl_3$): 2.59 (s, 6H, $NCH_3$); 2.67 (s, 2H, $CH_2Si$); 2.76 (s, 6H, $N(CH_3)_2$); 3.87 (d, 2H, $^2J$(H,H) = 16 Hz, $CH_2N$); 4.05 (d, 2H, $^2J$(H,H) = 16 Hz, $CH_2N$); 4.7 (s, 1H, SiH); 6.62−7.50 (3m, 8H, Ar). $^{13}$C NMR (62.89 MHz, $CDCl_3$, {H}): 19.0 ($CH_2Si$); 46.7, 49.0 ($NCH_3$); 63.6 ($CH_2N$); 124.7, 125.0, 126.2, 126.8, 129.2, 134.4, 134.8, 142.9 (Ar). IR ($CHCl_3$, $cm^{-1}$): 2207 (SiH). MS (FAB positive mode, NPOE): $m/z$ = 311 [$(M - I)^+$, 100]. MS (FAB negative mode, NPOE): $m/z$ = 127 [$(I^-)$, 100]. HRMS (FAB positive mode, NPOE): Calcd, $m/z$ = 311.1944; found, $m/z$ = 311.1915.

**2,6-Bis[(dimethylamino)methyl]phenylsilane.** A 7.8 g (25 mmol) amount of {2,6-bis[(dimethylamino)methyl]phenyl}-trimethoxysilane[24] in ether (60 mL) was added dropwise at 0 °C to a suspension of $LiAlH_4$ in ether (60 mL). The reaction mixture was stirred at room temperature for 2 days and refluxed for 4 h. The solvent was then removed under vacuum. A 40 mL volume of pentane was added to the residue to precipitate the salts which were filtered off. After removal of the solvent the crude product was distilled under vacuum to give 5.4 g (23.8 mmol, 95%) of 2,6-bis[(dimethylamino)methyl]-phenylsilane. B.p.: 45−50 °C (0.1 mmHg). $^{29}$Si NMR (39.76 MHz, $CDCl_3$): −81.4 (t, $^1J$(Si,H) = 200 Hz). $^{15}$N NMR (20.28 MHz, $CDCl_3$, {H}, $CH_3NO_2$): −349 (s). $^1$H NMR (250 MHz, $CDCl_3$): 2.11 (s, 12H, $NCH_3$); 3.47 (s, 4H, $CH_2N$); 4.05 (s, 3H, $SiH_3$); 7.00−7.24 (m, 3H, Ar). $^{13}$C NMR (62.89 MHz, $CDCl_3$, {H}): 43.3 ($NCH_3$); 63.8 ($CH_2N$); 127.1, 129.0, 132.8, 147.9 (Ar). IR ($CCl_4$, $cm^{-1}$): 2099, 2122 and 2149 (SiH). MS (70 eV, EI): $m/z$ = 222 [$(M)^+$, 63]; 58 [$(H_2C{=}NMe_2)^+$, 100]. Anal. Calcd for $C_{12}H_{22}N_2Si$: C, 64.86; H, 9.90; N, 12.60. Found: C, 63.98; H, 9.20; N, 12.60.

**{2,6-Bis[(dimethylamino)methyl]phenyl}silicon Trifluoromethanesulfonate (8b).** Trimethylsilyl triflate (1.47 mL, 7.6 mmol) was added dropwise at 0 °C with the syringe to a solution of 2,6-bis[(dimethylamino)methyl]phenylsilane (1.68 g, 7.53 mmol) in 40 mL of ether. There is immediately formation of a white precipitate. The reaction mixture was stirred at room temperature for 4 h. The precipitate was then filtered out and washed with ether (3 × 10 mL) to give **8b** (2.72 g, 7.35 mmol, 97%). Mp: 122−124 °C. $^{29}$Si NMR (39.76 MHz, $CD_2Cl_2$): −44.9 (t $^1J$(Si,H) = 264 Hz). $^1$H NMR (250 MHz, $CD_2Cl_2$): 2.60 (s, 12H, $NCH_3$); 4.00 (s, 4H, $NCH_2$); 4.55 (s, 2H, SiH); 7.15 (d, 2H, Ar), 7.50 (t, 1H, Ar). $^{13}$C NMR (62.89 MHz, $CD_2Cl_2$): 49.3 ($NCH_3$); 66.7 ($NCH_2$); 123.0 (q $^1J$(C,F) = 316 Hz, $CF_3$); 125.3, 125.7, 136.3, 144.7 (Ar). MS (FAB positive mode, NPOE): $m/z$ = 221 ($(M - CF_3SO_3)^+$, 100). MS (FAB negative mode, NPOE): $m/z$ = 149 ($(CF_3SO_3)^-$, 100). HRMS (FAB positive mode, NPOE): Calcd, $m/z$ = 221.1474; Found, $m/z$ = 221.1379.

**{2,6-Bis[(dimethylamino)methyl]phenyl}silicon Tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (8c).** Trityl tetrakis[3,5-bis(trifluoromethyl)phenyl]borate[21] (1.10 g, 1 mmol) in $CH_2Cl_2$ (15 mL) was added dropwise at 0 °C to a solution of 2,6-bis[(dimethylamino)methyl]phenylsilane (0.22 g, 1 mmol) in $CH_2Cl_2$ (15 mL). The reaction mixture was stirred at room temperature for 7 h. The solvent was then removed under vacuum, and the residue was washed with pentane (4 × 20 mL) to eliminate $Ph_3CH$ yielding **8c** (1.02 g, 0.94 mmol, 95%). Mp: 139−140 °C. $^{29}$Si NMR (39.76 MHz, $CD_2Cl_2$): −44.9 (*t*, $^1J$(Si,H) = 262 Hz). $^1$H NMR (250 MHz, $CD_2Cl_2$): 2.65 (s, 12H, $NCH_3$); 4.05 (s, 4H, $NCH_2$); 4.60 (s, 2H, SiH); 7.11−7.80 (m, 15H, Ar). IR ($CH_2Cl_2$, $cm^{-1}$): 2361, 2338 (SiH). $^{13}$C NMR (50.32 MHz, $CD_2Cl_2$, {H}): 44.4 ($NCH_3$); 65.9 ($NCH_2$); 118.4, 125.5 (q, $^1J$(C,F) = 272 Hz), 125.6, 127.1, 129.7 (m), 135.7, 136.7, 143.3 (Ar, $CF_3$); 162.6 (q $^1J$(B,C) = 50 Hz, BC). MS (FAB positive mode, NBA): $m/z$ = 221 [$(M - B[C_6H_3(CF_3)_2]_4)^+$, 100]. MS (FAB negative mode, (NBA): $m/z$ = 862 [$(B[C_6H_3(CF_3)_2]_4)^-$, 100)] HRMS (FAB positive mode, NPOE): Calcd, $m/z$ = 221.1474; found, $m/z$ = 221.1378.

**{2,6-Bis[(dimethylamino)methyl]phenyl}silicon tetraphenylborate (8d).** Sodium tetraphenylborate (0.34 g, 1

(24) Carré, F.; Chuit, C.; Corriu, R. J. P.; Fanta, A.; Mehdi, A.; Reyé, C. *Organometallics* **1995**, *14*, 194.

mmol) in $CH_3CN$ (15 mL) was added dropwise at room temperature to a solution of {2,6-bis[(dimethylamino)methyl]-phenyl}silicon iodide[16] **(8a)** (0.35 g, 1 mmol) in $CH_3CN$ (15 mL). The reaction mixture was stirred at room temperature for 10 h. The solvent was removed under vacuum, and 10 mL of $CH_2Cl_2$ was added to the residue to precipitate NaI, which was filtered out. After removal of the solvent **8d** (0.458 g, 0.85 mmol, 85%) was obtained as a white powder. Mp: 133−134 °C. $^{29}$Si NMR (49.69 MHz, $CD_2Cl_2$): −45.0 (t, $^1J$(Si,H) = 263 Hz). $^1$H NMR (250 MHz, $CD_2Cl_2$): 2.51 (s, 12H, $NCH_3$); 3.80 (s, 4H, $NCH_2$); 4.45 (s, 2H, SiH); 6.80−7.70 (m, 23H, Ar). $^{13}$C NMR (62.89 MHz, $CD_2Cl_2$, {H}): 47.6 ($NCH_3$); 65.1 ($NCH_2$); 122.3, 124.9, 126.1, 127.1, 135.0, 136.3, 142.9 (Ar); 164.1 (q $^1J$(B,C) = 50 Hz, BC). IR ($CH_2Cl_2$, cm$^{-1}$): 2359, 2337 (SiH). MS (FAB positive mode, NPOE): *m/z* = 221 [(M − $BPh_4$)$^+$, 100]. MS (FAB negative mode, NPOE): *m/z* = 319 [($BPh_4$)$^-$, 100]. HRMS (FAB positive mode, NPOE): Calcd, *m/z* = 221.1474; found, *m/z* = 221.1378.

**{2,6-Bis[(dimethylamino)methyl]phenyl}vinylsilicon Chloride (10).** An 8.3 mmol amount of lithium derivative **9**[20] in ether (20 mL) was added dropwise at 0 °C to a solution of dichlorovinylsilane (0.95 mL, 8.3 mmol) in ether (10 mL). The reaction mixture was stirred at room temperature for 1 h. The solvent was then removed under vacuum, and the residue was taken up in $CH_2Cl_2$ (15 mL). LiCl was filtered on Celite, and the solvent was removed under vacuum. The residue was washed with (2 × 10 mL) of ether. After filtration, 1.6 g of **10** (5.7 mmol, 70%) was obtained as a white powder. Mp: 170 °C (dec). $^{29}$Si NMR (39.76 MHz, $CDCl_3$): −36.8 (dm, $^1J$(Si,H) = 280 Hz). $^1$H NMR (250 MHz, $CDCl_3$): 2.57 (s, 6H, $NCH_3$); 2.61 (s, 6H, $NCH_3$); 4.00 (d, 2H, $^2J$(H,H) = 15.4 Hz, $CH_2N$); 4.10 (d, 2H, $^2J$(H,H) = 15.4 Hz, $CH_2N$); 4.59 (d, 1H, $^2J$(H,H) = 2 Hz, SiH); 5.7−5.85 (m, 1H, CH=C); 6.19−6.30 (m, 2H, C=$CH_2$); 7.16−7.48 (m, 3H, Ar). MS (FAB positive mode, NPOE): *m/z* = 247 [(M − Cl)$^+$, 41]; 263 [(M − H+OH)$^+$, 100].

**{2,6-Bis[(dimethylamino)methyl]phenyl}methylsilicon Chloride (11).** A 10 mmol amount of lithium derivative **9**[20] in ether (20 mL) was added dropwise at −30 °C to a solution of methyldichlorosilane (1.04 mL, 10 mmol) in ether (20 mL). The reaction mixture was stirred at room temperature for 6 h, and the solvent was removed under vacuum. The white solid obtained was taken up in dry $CH_2Cl_2$ (20 mL). The precipitated LiCl was filtered out on Celite, and $CH_2Cl_2$ was removed under vacuum to give a white solid which was washed several times with ether. After filtration, 2.43 g of crude **11** (9 mmol, 90%) was obtained as a white powder. $^{29}$Si NMR (39.76 MHz, $CDCl_3$): −27.7 (d, $^1J$(Si,H) = 268 Hz). $^1$H NMR (250 MHz, $CDCl_3$): 0.71 (d, $^3J$(H,H) = 2.5 Hz, 3H, $SiCH_3$); 2.72 (s, 6H, $NCH_3$), 2.85 (s, 6H, $NCH_3$); 4.10 (d, $^2J$(H,H) = 15 Hz, 2H, $CH_2N$); 4.24 (d, $^2J$(H,H) = 15 Hz, 2H, $CH_2N$); 4.55 (broad signal, 1H, SiH); 7.15−7.50 (m, 3H, Ar). $^1$H NMR (250 MHz, $CDCl_3$, 313 K): 0.71 (d, $^3J$(H,H) = 2.6 Hz, 3H, $SiCH_3$); 2.73 (s, 6H, $NCH_3$), 2.81 (s, 6H, $NCH_3$); 4.09 (d, $^2J$(H,H) = 15 Hz, 2H, $CH_2N$); 4.25 (d, $^2J$(H,H) = 15 Hz, 2H, $CH_2N$); 4.55 (q, 1H, SiH); 7.15−7.50 (m, 3H, Ar). $^{13}$C NMR (62.89 MHz, $CDCl_3$, {H}): 3.4 ($SiCH_3$); 43.1 ($NCH_3$); 62.5 ($NCH_2$); 129.0, 129.4, 132.2, 139.3 (Ar). IR ($CH_2Cl_2$, cm$^{-1}$): 2361, 2342 (SiH). MS (FAB positive mode, NPOE): *m/z* = 235 [(M − Cl)$^+$, 100]. HRMS (FAB positive mode, NPOE): Calcd, *m/z* = 235.1631; found, *m/z* = 235.1627.

**{2,6-Bis[(dimethylamino)methyl]phenyl}chlorosilicon Chloride (12). 12** was prepared according to the method reported in the literature.[16] Mp: 140 °C (dec). $^{29}$Si NMR (49.69 MHz, $CD_2Cl_2$): −40.3 (d, $^1J$(Si,H) = 334 Hz). $^{29}$Si NMR (49.69 MHz, $CD_2Cl_2$, 173 K): −42.2 (d, $^1J$(Si,H) = 334 Hz). $^{29}$Si NMR (59.64 MHz, CP-MAS {H}): −40.8. $^{15}$N NMR (20.28 MHz, $CDCl_3$, {H}, $CH_3NO_2$): −333.8 (s). $^1$H NMR (250 MHz, $CD_2Cl_2$): 2.85 (s, 12H, $NCH_3$); 4.28 (s, 4H, $NCH_2$); 5.19 (s, 1H, SiH); 7.35 (d, $^3J$(H,H) = 7.5 Hz, 2H, Ar), 7.36 (t, $^3J$(H,H) = 7.5 Hz, 1H, Ar). IR (KBr, cm$^{-1}$): 2204 (SiH). MS (FAB positive mode, NPOE): *m/z* = 255 − 257 [(M − Cl)$^+$, 100].

**{2,6-Bis[(dimethylamino)methyl]phenyl}methylphenylsilane.** A 64.4 mmol amount of lithium derivative **9**[20] in ether (20 mL) was added dropwise at 0 °C to a solution of chloromethylphenylsilane (73.73 mmol, 11.54 g) in ether (50 mL). The reaction mixture was stirred at room temperature for 2 h. After filtration of LiCl on Celite, the solvent was removed under vacuum to give an oily residue, which was crystallized from pentane, giving 1.75 g of {2,6-bis[(dimethylamino)methyl]phenyl}methylphenylsilane (ArMePhSiH) (56.1 mmol, 76%) as colorless crystals. Mp: 53−56 °C. $^{29}$Si NMR (39.76 MHz, $CDCl_3$): −32.6 (dq, $^1J$(Si,H) = 189 Hz, $^2J$(Si,H) = 6 Hz). $^1$H NMR (250 MHz, $CDCl_3$): 0.55 (d, 3H, $^3J$(H,H) = 3.3 Hz, $SiCH_3$); 1.88 (s, 12H, $NCH_3$); 3.10 (d, 2H, $^2J$(H,H) = 12.9 Hz, $CH_2N$); 3.31 (d, 2H, $^2J$(H,H) = 12.9 Hz, $CH_2N$); 4.74 (q, 1H, $^3J$(H,H) = 3.3 Hz, SiH); 7.02−7.24 (m, 6H, Ar), 7.37−7.40 (m, 2H, Ar). $^{13}$C NMR (62.89 MHz, $CDCl_3$, {H}): −4.5 ($SiCH_3$); 44.3 ($NCH_3$); 65.0 ($CH_2N$); 127.4, 127.7, 128.0, 128.7, 134.1, 135.5, 140.5, 148.1 (Ar). IR ($CCl_4$, cm$^{-1}$): 2114 (SiH). MS (FAB positive mode, glycerol): *m/z* = 311 [(M − H)$^+$, 100]. Anal. Calcd for $C_{19}H_{28}N_2Si$: C, 73.07; H, 8.97; N, 8.97. Found: C, 73.37; H, 9.19; N, 8.90.

**{2,6-Bis[(dimethylamino)methyl]phenyl}methylphenylsilicon Chloride (13a).** Benzoyl chloride (0.12 mL, 1 mmol) was added dropwise with a syringe at room temperature to a solution of {2,6-bis[(dimethylamino)methyl]phenyl}-methyl-phenylsilane (0.312 g, 1 mmol) in $CCl_4$ (15 mL). The mixture was stirred at room temperature overnight. $CCl_4$ was then transferred to another Schlenk vessel leaving a sticky solid which was washed with ether (4 × 10 mL) giving 0.27 g of **13a** (0.77 mmol, 77%) as a white powder. Mp: 112.2−113.2 °C. $^{29}$Si NMR (39.76 MHz, $CD_2Cl_2$): −7.0 (s). $^1$H NMR (250 MHz, $CD_2Cl_2$): 0.75 (s, 3H, $SiCH_3$); 2.35 (s, 12H, $NCH_3$); 3.97 (d, $^2J$(H,H) = 14 Hz, 2H, $CH_2N$); 4.10 (d, $^2J$(H,H) = 14 Hz, 2H, $CH_2N$); 7.30−7.81 (m, 8H, Ar). $^1$H NMR (250 MHz, $CD_3CN$): 0.75 (s, 3H, $SiCH_3$); 2.30 (s, 12H, $NCH_3$); 3.91 (d, $^2J$(H,H) = 13 Hz, 2H, $CH_2N$); 4.20 (d, $^2J$(H,H) = 13 Hz, 2H, $CH_2N$); 7.35−7.62 (m, 8H, Ar). $^{13}$C NMR (62.89 MHz, $CDCl_3$, {H}): 1.9 ($SiCH_3$); 42.8 ($NCH_3$); 62.0 ($NCH_2$); 127.9, 128.3, 128.9, 130.1, 132.6, 134.3, 136.3, 139.3, 140.4 (Ar). MS (FAB positive mode, NPOE): *m/z* = 311 [(M − Cl)$^+$, 100]. HRMS (FAB positive mode, NBA): Calcd, *m/z* = 311.1944; found, *m/z* = 311.1897.

**{2,6-Bis[(dimethylamino)methyl]phenyl}methylphenylsilicon Bromide (13b).** Benzoyl bromide (0.26 mL, 2.24 mmol) was added dropwise with a syringe at 0 °C to a solution of {2,6-bis[(dimethylamino)methyl]phenyl}methylphenylsilane (0.70 g, 2.24 mmol) in $CCl_4$ (50 mL). The mixture was stirred at room temperature for 1 h. $CCl_4$ was then transferred to another Schlenk vessel leaving a sticky solid which was washed with ether (4 × 10 mL) giving **13b** (0.71 g, 1.81 mmol, 81%) as a white powder. Mp: 141−143 °C. $^{29}$Si NMR (39.76 MHz, $CD_2Cl_2$): −7.2 (s). $^1$H NMR (250 MHz, $CD_2Cl_2$): 0.68 (s, 3H, $SiCH_3$); 2.25 (s, 12H, $NCH_3$); 3.85 (d, $^2J$(H,H) = 11 Hz, 2H, $CH_2N$); 3.95 (d, $^2J$(H,H) = 11 Hz, 2H, $CH_2N$); 7.30−7.56 (m, 8H, Ar). $^{13}$C NMR (62.89 MHz, $CDCl_3$, {H}): 1.6 ($SiCH_3$); 42.9 ($NCH_3$); 62.3 ($NCH_2$); 128.0, 130.2, 132.4, 133.3, 134.2, 139.0, 139.9, 140.1 (Ar). MS (FAB positive mode, NPOE): *m/z* = 311 [(M − Br)$^+$, 100]. MS (FAB negative mode, NPOE): *m/z* = 79−81 [(Br)$^-$, 100]. HRMS (FAB positive mode, NBA): Calcd, *m/z* = 311.1944; found, *m/z* = 311.1897.

**{2,6-Bis[(dimethylamino)methyl]phenyl}methylphenylsilicon Iodide (13c).** A solution of iodine (0.127 g, 5 mmol) in $CH_3CN$ (15 mL) was added dropwise at −50 °C to a solution of {2,6-bis[(dimethylamino)methylphenyl}methylphenylsilane (0.312 g, 1 mmol) in $CH_3CN$ (15 mL). There is immediate decoloration of the iodine solution; the reaction mixture was warmed to room temperature and stirred for 8 h. The solvent was then removed, and the residue was washed with ether (2 × 15 mL) to give **13c** (0.39 g, 0.89 mmol, 89%) as a white powder. Mp: 53−54 °C. $^{29}$Si NMR (39.76 MHz, $CD_2Cl_2$): −7.9 (s). $^1$H NMR (250 MHz, $CD_2Cl_2$): 0.80 (s, 3H, $SiCH_3$); 2.30 (s, 12H, $NCH_3$); 3.94 (d, $^2J$(H,H) = 13 Hz, 2H,

$CH_2N$); 4.45 (d, $^2J$(H,H) = 13 Hz, 2H, $CH_2N$); 7.35−7.65 (m, 8H, Ar). $^1$H NMR (250 MHz, $CD_3CN$): 0.80 (s, 3H, $SiCH_3$); 2.25 (s, 12H, $NCH_3$); 3.75 (d, $^2J$(H,H) = 11 Hz, 2H, $CH_2N$); 3.95 (d, $^2J$(H,H) = 11 Hz, 2H, $CH_2N$); 7.35−7.60 (m, 8H, Ar). $^1$H NMR (250 MHz, $CD_3OD$): 0.80 (s, 3H, $SiCH_3$); 2.30 (broad signal, 12H, $NCH_3$); 3.90 (broad signal, 4H, $NCH_2$); 7.35−7.65 (m, 8H, Ar). $^{13}$C NMR (62.89 MHz, $CDCl_3$, {H}): 1.9 ($SiCH_3$); 43.9 ($NCH_3$); 63.7 ($NCH_2$); 128.9, 130.5, 133.4, 133.8, 134.2, 140.0, 140.7, 141.7 (Ar). MS (FAB positive mode, NPOE): *m/z* = 311 [$(M - I)^+$, 100]. MS (FAB negative mode, NPOE): *m/z* = 127 [$(I)^-$, 100]. HRMS (FAB positive mode, NBA): Calcd, *m/z* = 311.1944; found, *m/z* = 311.1897.

**{2,6-Bis[(dimethylamino)methyl]phenyl}methylphenylsilicon Trifluoromethanesulfonate (13d).** Trimethylsilyltriflate (0.21 mL, 1.1 mmol) was added dropwise at 0 °C to a solution of silane {2,6-bis[(dimethylamino)methyl]phenyl}methylphenylsilane (0.34 g, 1.1 mmol) in ether (40 mL). The solution was warmed to room temperature and stirred for 4 h. The solvent was then removed, and the residue was washed with ether (2 × 20 mL) to give **13d** (0.48 g, 1.04 mmol, 95%) as a white powder. Mp: 105−106 °C. $^{29}$Si NMR (49.69 MHz, $CD_2Cl_2$): −7.1 (s). $^1$H NMR (250 MHz, $CD_2Cl_2$): 0.80 (s, 3H, $SiCH_3$); 2.35 (s, 12H, $NCH_3$); 3.80 (d, $^2J$(H,H) = 15 Hz, 2H, $CH_2N$); 3.95 (d, $^2J$(H,H) = 15 Hz, 2H, $CH_2N$); 7.35−7.62 (m, 8H, Ar). $^1$H NMR (250 MHz, $CD_3OD$): 0.80 (s, 3H, $SiCH_3$); 2.35 (broad signal, 12H, $NCH_3$); 3.98 (broad signal, 4H, $NCH_2$); 7.35−7.70 (m, 8H, Ar). $^{13}$C NMR (62.89 MHz, $CD_2Cl_2$, {H}): 2.3 ($SiCH_3$); 45.1 ($NCH_3$); 65.3 ($NCH_2$); 122 (q $^1J$(C,F) = 315 Hz, $CF_3$); 130.0, 131.7, 132.2, 134.5, 135.0, 140.2, 141.3, 143.0 (Ar). MS (FAB positive mode, NPOE): *m/z* = 311 [$(M - CF_3SO_3)^+$, 100]. MS (FAB negative mode, NPOE): *m/z* = 149 [$(CF_3SO_3)^-$, 100]. HRMS (FAB positive mode, NBA): Calcd, *m/z* = 311.1944; found, *m/z* = 311.1897.

**{2,6-Bis[(dimethylamino)methyl]phenyl}methylphenylsilicon Tetraphenylborate (13e and 15a).** A solution of sodium tetraphenylborate (0.342 g, 1 mmol) in $CH_3CN$ (15 mL) was added dropwise at room temperature to a solution of **13c** (0.44 g, 1 mmol) in $CH_3CN$ (15 mL). The reaction mixture was stirred overnight, and the solvent was then removed. The residue was taken up in dry $CH_2Cl_2$, and after filtration of NaI and removal of the solvent, 0.535 g (0.85 mmol, 85%) of a mixture of **13e** and **15a** was obtained. Mp: 89−90 °C. $^{29}$Si NMR (39.76 MHz, $CD_3CN$): −8.5 (s, **13e**); −14.5 (s, **15a**). $^1$H NMR (250 MHz, $CD_2Cl_2$): 0.70 (s, 3H, $SiCH_3$ for **13e**); 0.80 (s, 3H, $SiCH_3$ for **15a**; 1.75 (s, 6H, $NCH_3$ for **15a)**; 1.92 (s, 12H, $NCH_3$ for **13e**); 2.35 (s, 6H, $NCH_3$ for **15a**); 3.40 (d, $^2J$(H,H) = 17 Hz, 2H, $CH_2N$ for **13e**); 3.69 (d, $^2J$(H,H) = 17 Hz, 2H, $CH_2N$ for **13e**); 3.75 (d, $^2J$(H,H) = 15 Hz, 2H, $CH_2N$ for **15a**); 3.80 (d, $^2J$(H,H) = 15 Hz, 2H, $CH_2N$ for **15a**; 6.80−7.65 (m, 56H, Ar for **13e** and **15a**). The ratio of **13e**:**15a** was 5:2. $^1$H NMR (250 MHz, $CD_3CN$): 0.75 (s, 3H, $SiCH_3$ for **13e**); 0.95 (s, 3H, $SiCH_3$ for **15a**); 1.80 (s, 6H, $NCH_3$ for **15a)**; 2.25 (s, 12H, $NCH_3$ for **13e**); 2.40 (s, 6H, $NCH_3$ for **15a**); 3.70 (d, $^2J$(H,H) = 14 Hz, 2H, $CH_2N$ for **13e**); 3.92 (broad signal, 4H, $NCH_2$ for **15a**); 3.95 (d, $^2J$(H,H) = 14 Hz, 2H, $CH_2N$ for **13e**); 6.75−7.70 (m, 56H, Ar for **13e** and **15a**). The ratio of **13e**:**15a** was 3:1. $^1$H NMR (250 MHz, $CD_3CN$ + $D_2O$): 0.75 (s, 3H, $SiCH_3$ for **13e**); 2.25 (s, 12H, $NCH_3$ for **13e**); 3.80 (broad signal, 4H, $NCH_2$ for **13e**); 6.70−7.60 (m, 28H, Ar for **13e**). $^{13}$C NMR (62.89 MHz, $CD_2Cl_2$, {H}): 0.61 ($SiCH_3$ for **13e**), 1.10 ($SiCH_3$ for (**15a**); 43.3 ($NCH_3$ for **13e**), 47.6 ($NCH_3$ for **15a**); 64.0 ($NCH_2$ for **13e**), 64.1 ($NCH_2$ for **15a**); 117.3, 118.1, 118.5, 122.3, 126.1, 128.4, 128.6, 129.2, 129.5 130.0, 130.7, 131.2, 132.7, 136.3, 138.3, 142.1 (Ar for **13e** and **15a**), 164.2 (q, $^1J$(B,C) = 49 Hz, BC). MS (FAB positive mode, NBA): *m/z* = 311 [$(M - BPh_4)^+$, 100]; (FAB negative mode, NBA): *m/z* = 319 [$(BPh_4^-)$, 100]. MS HRMS (FAB positive mode, NBA): Calcd, *m/z* = 311.1944; found, *m/z* = 311.1897.

**{2,6-Bis[(dimethylamino)methyl]phenyl}methylphenylsilicon Tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (15b). Method a.** A yellow solution of trityltetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (0.276 g, 0.25 mmol) in $CH_2Cl_2$ (15 mL) was added at 0 °C to a solution of {2,6-bis-[(dimethylamino)methyl]phenyl}methylphenylsilane (0.078 g, 0.25 mmol)) in $CH_2Cl_2$ (15 mL). The yellow color disappeared immediately. The reaction mixture was warmed to room temperature and was stirred for 8 h. The solvent was then removed under vacuum, and the residue was washed with pentane (4 × 15 mL) to eliminate $Ph_3CH$, giving **15b** (0.277 g, 0.23 mmol, 95%). Mp: 71−72 °C. $^{29}$Si NMR (39.76 MHz, $CD_2Cl_2$): −15.0 (s). $^1$H NMR (250 MHz, $CD_2Cl_2$, 293 K): 0.80 (s, 3H, $SiCH_3$ for **13f**); 0.94 (s, 3H, $SiCH_3$ for **15b**); 1.90 (s, 6H, $NCH_3$ for **15b**); 2.25 (broad signal, 12H, $NCH_3$ for **13f**); 2.45 (s, 6H, $NCH_3$ for **15b**); 3.69 (broad signal, 4H, $NCH_2$ for **13f**), 3.86 (d, $^2J$(H,H) = 15 Hz, 2H, $CH_2N$ for **15b**; 3.95 (d, $^2J$(H,H) = 15 Hz, 2H, $CH_2N$ for **15b**; 7.10−7.85 (m, 40H, Ar for **15b** and **13f**). $^1$H NMR (250 MHz, $CD_2Cl_2$, 183 K): 0.67 (s, 3H, $SiCH_3$ for **13f**); 0.82 (s, 3H, $SiCH_3$ for **15b**); 1.47 (s, 3H, $NCH_3$ for **13f**); 1.67 (s, 3H, $NCH_3$ for **13f**); 1.77 (s, 6H, $NCH_3$ for **15b**), 2.37 (s, 6H, $NCH_3$ for **15b**); 2.67 (s, 3H, $NCH_3$ for **13f**); 2.88 (s, 3H, $NCH_3$ for **13f**); 3.52 (d, $^2J$(H,H) = 17 Hz, 1H, $NCH_2$ for **13f**), 3.77 (broad signal, 2H, $NCH_2$ for **13f**); 3.97 (broad signal, 4H, $NCH_2$ for **15b**); 4.52 (d, $^2J$(H,H) = 17 Hz, 1H, $NCH_2$ for **13f**); 7.02−7.87 (m, 40H, Ar for **15b** and **13f**). $^{13}$C NMR (50.32 MHz, $CD_2Cl_2$, {H}): −5.7 ($SiCH_3$ for **13f**); 1.6 ($SiCH_3$ for **15b**); 44.1 ($NCH_3$ for **13f**); 48.2 ($NCH_3$ for **15b**); 64.9 ($NCH_2$ for **13f**); 65.1 ($NCH_2$ for **15b**); 117.4, 118.2, 118.4, 122.8, 126.2, 128.2, 128.7, 129.1, 129.4, 129.6, 130.1, 130.2, 130.8, 133.6, 135.0, 135.3 (Ar for **15b** and **13f**); 144.9 (Ar, $CF_3$); 162.6 (q, $^1J$(B,C) = 50 Hz, BC). MS (FAB positive mode, NBA): *m/z* = 311 [$(M - B[C_6H_3(CF_3)_2]_4)^+$, 100)]. MS (FAB negative mode, NBA): *m/z* = 862 [$(B[C_6H_3(CF_3)_2]_4)^-$, 100)]. HRMS (FAB positive mode, NBA): Calcd *m/z* = 311.1944; found, *m/z* = 311.1897.

**Method b.** Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate (0.442 g, 0.5 mmol) in 15 mL of $CH_3CN$ solution was added dropwise at ambient temperature to a solution of **13c** (0.219 g, 0.5 mmol) in $CH_3CN$ (15 mL). The reaction mixture was stirred for 8 h. The solvent was then removed under vacuum and the residue taken up in dry $CH_2Cl_2$ (20 mL). NaI insoluble in $CH_2Cl_2$ was removed by filtration, and after removal of the solvent, **15b** (0.557 g, 0.47 mmol, 95%) was obtained as a white powder. Mp: 71−72 °C.

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