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Intramolecularly Stabilized Phenylsilyl and Anthrylsilyl Cations

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Phenyl-substituted silylium cations with two $-CH_2Z$ substituents in the ortho positions ($(R_2SiC_6H_3(CH_2Z)_2^+$, **I**) first synthesized by Corriu and co-workers provide useful model systems to investigate solvent coordination of silylium cations R_2HSi^+ (H is equivalent to the C_6H_5 group) in solution. By rotation of the side chains, group Z can be positioned in such a way that Si^+-Z interactions lead to an internal solvation of the silylium cation thus competing for or even preventing external solvation of $-R_2Si^+$ in solution. For $Z = NR_2$, the properties of type **I** cations resemble those of the strongly coordinated silylium cation−solvent complexes $R'_2HSi(NR_3)_2^+$ as is reflected by complexation energies, interaction distances, and δ^{29}Si NMR chemical shift values typical of pentacoordinated Si. Weakly coordinating solvents such as alkanes can be mimicked by using for type **I** cations the side chain $-C(CH_3)_3$. A $-SiH_2^+$ group interacts with the closest H atoms of the two adjacent methyl groups and, despite the fact that interactions are just electrostatic, **I** largely loses its silylium cation character as indicated by the calculated δ^{29}Si value. More silylium cation character is retained when a 1,8-dimethyl-substituted anthryl ring rather than the phenyl ring is used as a template for simulating solvent coordination of silylium cations in solution. The silyl cation $Me_2SiC_{14}H_7(CH_3)_2^+$ (**18**) with the $-SiMe_2^+$ group at position 9 framed between the two methyl substituents has a δ^{29}Si IGLO value of 187 ppm, which is just 150 ppm upfield from the corresponding value for Me_2HSi^+ in the gas phase (334 ppm). The synthesis of **18** and related cations should be an interesting target for experimental work on silylium cations in solution.

1. Introduction

The investigation of trivalent silicon cations R_3Si^+ (silylium or silicenium ions)[1] in solution has been intensified in the last years,[2] and several promising attempts to synthesize weakly coordinated silylium cations have been made lately.[3,4] Free ("naked") silylium ions are only possible if all interactions between cation and counterion or cation and solvent molecules are hindered in some way. In view of the "voracious appetite"[5] of R_3Si^+ for nucleophiles, the naked silylium cation in solution is a fiction that probably can never be realized. On the other hand, there are various strategies to realize weakly coordinated ("nearly free") silylium cations in solution, where it is somewhat arbitrarily handled by various authors when to call a silylium cation as being nearly free. We suggest in this connection four molecular properties to indicate silylium ion character, namely (a) the coordination or complex binding energy ΔE, (b) the coordination distance between Si^+ and the nearest atom of solvent S or counter ion X^-, (c) the electron population of the 3pπ orbital of Si^+, and (d) the electron density distribution between Si^+ and the closest S (X^-) molecule.

In addition, one can use the degree of pyramidalization at the Si^+ center, the distortion of the solvent molecule weakly coordinated to R_3Si^+, etc., to describe interactions between R_3Si^+ and S (or X^-) and, thereby, the degree of silylium cation character retained in solution.

Unfortunately, for none of the descriptive parameters listed above is it guaranteed that their changes are linearly related to the silylium cation character of a weakly coordinated complex $R_3Si(S)^+$. For example, recent ab initio investigations indicate that the complexation energy decreases quickly to a value (<5 kcal/mol) typical of van der Waals complexes, while the Si−S distance is still considerably smaller than the sum of the van der Waals radii or the $\delta^{29}Si^+$ chemical shift value does not suggest more than 30 or 40% silylium cation character.[6] Depending on which of these parameters has been calculated or measured, one author will consider a silylium cation to be nearly free, while another author will describe it as weakly bonded.

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[1] We use the term silylium cation for R_3Si^+ rather than silicenium ion, silylenium ion, or silyl cation, thus following recent IUPAC recommendations. See: *Nomenclature of Inorganic Chemistry*; Leigh, G. J., Ed.; Blackwell: Oxford, U.K., 1990; p 106.

[2] For recent reviews on the work on R_3Si^+ in solution see: (a) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191. (b) Chojnowski, J.; Stanczyk W. *Main Group Chem. News* **1994**, *2*, 6. (c) Lickiss, P. *J. Chem. Soc., Dalton Trans.* **1992**, 1333. (d) Chojnowski, J.; Stanczyk W. *Adv. Organomet. Chem.* **1990**, *30*, 243. (e) Strauss, S. H. *Chemtracts: Inorg. Chem.* **1993**, *5*, 119. (f) Houk, K. N. *Chemtracts: Org. Chem.* **1993**, *6*, 360.

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According to calculated δ^{29}Si values of $H_3Si(Ng)^+$ and $Me_3Si(Ng)^+$ complexes (Ng: noble gas element), the only solvent that would guarantee the best approximation to a free silylium cation would be liquid helium, while the other noble gases such as Ne or Ar already decrease the silylium cation character by considerable complexation with R_3Si^+.[5]

Despite the inherent problems of defining a nearly free silylium cation with the help of selected molecular properties, measurement or calculation of properties a–d helps to set up strategies to approximate the ideal case of a free silylium cation in solution as much as possible. In previous work,[6] we have considered the following possibilities of stabilizing a silylium cation R_3-Si^+ by (1) inductive, hyperconjugative, or weakly conjugative effects (internal stabilization), (2) steric blocking of the Si^+ center by bulky substituents R, and (3) reducing the coordination ability of S (e.g., by use of weakly nucleophilic solvents).

Clearly, an internally stabilized silylium cation is less prone to interact with solvent molecules S or a counterion X^-. However, internal stabilization must not lead to a loss of the silylium cation character. It is not appropriate to define the latter, as is normally done, by the positive charge of the Si atom and its trivalent character. Clearly, the silylium cation character is defined by the availability of the empty 3pπ-orbital at Si that dominates the character of the LUMO of R_3Si^+ and, therefore its reactive (electrophilic) behavior. The occupation of the 3pπ(Si^+) AO is not necessarily parallel to the total charge at Si^+. For example, it is possible to have strongly σ-electron-donating substituents Y attached to Si that decrease its positive charge but, however, do not alter the availability and population of the 3pπ(Si^+) orbital. Y_3Si^+ would be still a silylium cation despite reduced positive charge at Si. Alternatively, σ-withdrawing groups might increase the positive charge at Si while adjacent π-donor substituents Y fill up the 3pπ-orbital and, thereby, reduce its availability in the coordination process with a solvent molecule. Correctly, one would have to describe Y_3Si^+ to possess a (partial) SiY double bond. Although Y_3Si^+ might still possess a full positive charge at Si its silylium cation character (trivalent character at Si, availability of 3pπ(Si^+) AO) would be lost.

Clearly, *the objective is not to find a strongly stabilized* Y_3Si^+ *cation* ($Y = NR_2, OR, PR_2, SR$, *etc.*) *but to have an analogue to normal alkyl- and arylcarbenium ions* that are known to be just weakly coordinated cations in solutions. Hyperconjugative effects of an alkyl group or weak π-conjugative effects of an aryl group will also lead to a partial population of the 3pπ(Si^+) orbital; however, these effects will be smaller than in the corresponding carbenium ions and, therefore, will guarantee that the silylium cation character of these ions is not lost.

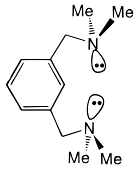
Our previous investigations have clearly shown that application of just one of the three strategies (internal stabilization, steric blocking, weak nucleophilic solvents) will be insufficient to realize a nearly free silylium cation; however, combination of all three of them may be successful in so far as some silylium cation character can be retained. This is confirmed by experimental investigations pushed ahead with considerable success by Lambert[2a,3] and, independently, by Reed.[4]

These authors made use of bulky and weakly coordinating anions, such as tetrakis(pentafluorophenyl) borate ($TPFPB^-$), to hinder interactions of R_3Si^+ with the counterion.[3,4] In addition, weakly nucleophilic solvents such as benzene and toluene were used to keep solvent coordination limited. However, it was shown by several groups that the experimental facts published by Lambert and co-workers speak against the formation of nearly free silylium ions and for the formation of Wheland σ-complexes between R_3Si^+ and aromatic solvents.[6–9]

In order to find systems that better realize a nearly free silylium cation one must proceed in two directions. First, one has to investigate R_3Si^+–solvent interactions to better understand how these interactions could be reduced. Second, one has to combine the three strategies listed above to a new strategy that more effectively prevents silylium cations from coordination with solvent/counterion molecules. In this connection, we have been stimulated by the recent work of Corriu and co-workers[10] that helps us to follow both directions of present silylium cation research.

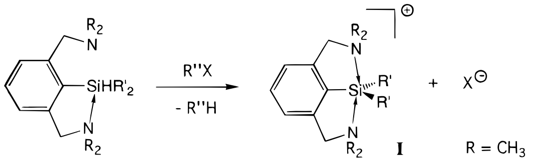
2. Internally Solvated Silylium Cations

Recently, Corriu and co-workers synthesized a series of compounds that can be described as internally solvated silylium cations.[10] Corriu and co-workers utilized the bidentated ligand **A**, developed by van Koten,[11] to



A

generate pentacoordinated siliconium ions according to reaction 1.



(1)

Experimentally, it is difficult to determine whether the Si–N interactions present in cation **I** are covalent or electrostatic, and therefore, the cationic species

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generated in reaction 1 were regarded as base-stabilized trivalent silylium ions.[10] The presence of silyl cations was verified by conductiometry and NMR chemical shift measurements. From the conductivity of the solutions it was possible to observe an increase of ionic character upon addition of oxidation agent R″X until 1 equiv had been added.

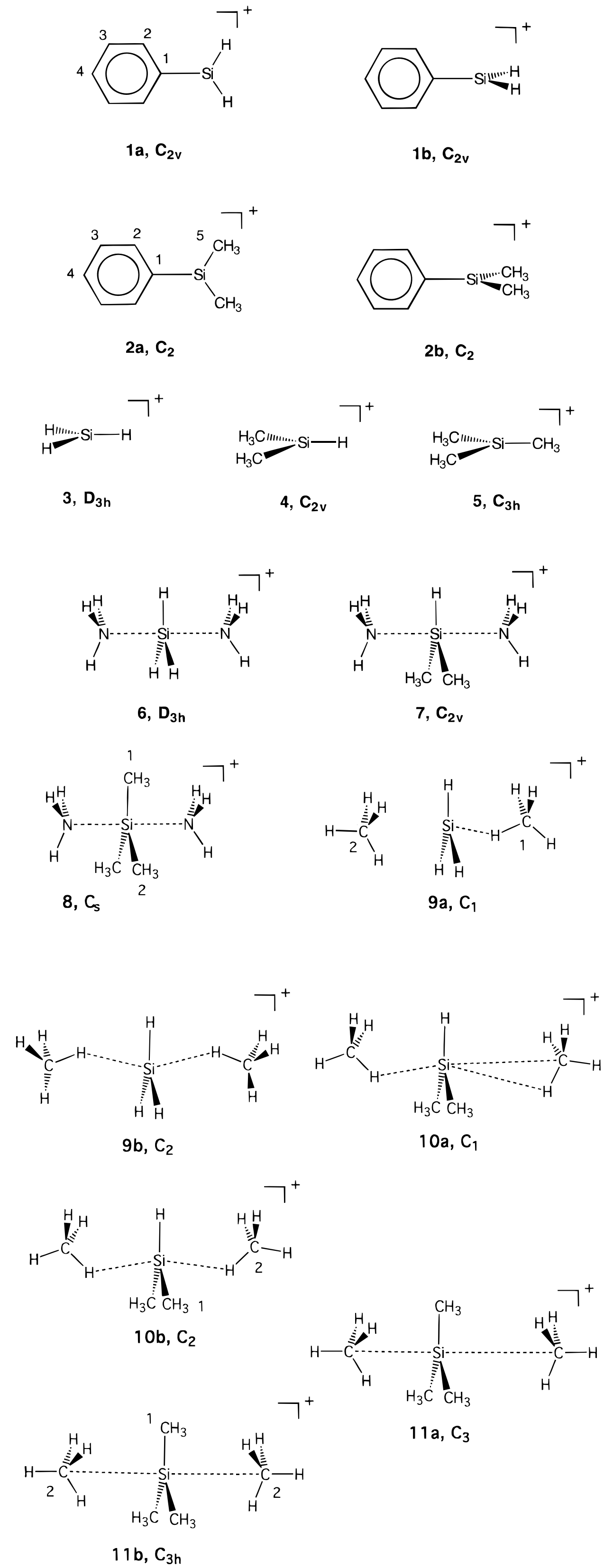
Cremer and co-workers showed by ab initio investigations for the H analogue of **I** (i.e., R = R′ = H) that **I** probably possesses covalent Si−N bonds and, therefore, is best described as a cation with pentacoordinated Si.[12,13] In line with this, X-ray crystallographic measurements performed on bidentated cationic compounds similar to **I** reveal that their Si−N distances (2.05−2.08 Å)[14,15] are just 0.30−0.40 Å longer than those of normal covalent Si−N bonds.[16] They resemble those calculated in the ab initio study of the H analogue of **I** (2.09 Å)[12] or those observed for the crystal structure of $Me_2HSi(N\text{-methylimidazole})_2^+$ (2.01−2.03 Å).[17] In other words, cation **I** is similar to a solvent-coordinated silylium cation in solution and, because of this, represents an easy to control model for (strongly and weakly) solvated silylium cations.

The investigation of cations **I** based on bidentated structures such as **A** should lead to a better understanding of silylium ions in solution. By varying **A** one can simulate $R_3Si^+{-}S$ interactions for a range of different solvents. Of special interest are those solvents that coordinate to Si^+ less strongly than N-containing solvents. This can be realized by replacing the NMe_2 groups in **A** by OR, COOR, SR, Cl, or R. In this way, the bidentated compounds can be used as models for silylium cation solvation in solvents as weakly nucleophilic as alkanes.

Another important aspect of internally solvated silylium cations such as **I** is that steric blocking of the Si^+ center can be accomplished easier than in normal silylium cations. Steric factors could suppress intermolecular coordination of solvent and/or counterion effectively, thus reducing any coordination to the available side groups of **A**. If interactions with the bidentated functionalities are weak, such systems would represent silylium cations locked inside a "cage".

The present work provides an ab initio description of internally solvated silylium cations **I** and investigates the question to what extent a weakly coordinated silylium cation locked in a cage can be realized. Energies, geometries, charge distributions, bonding properties, and NMR chemical shifts for molecules **1**−**18** shown in Charts 1 and 2 were calculated to describe coordination at Si in the bidentated species **12**−**18**.

Chart 1



3. Computational Methods

Geometries of compounds **1**−**18** (Charts 1 and 2) were fully optimized at the Hartree−Fock (HF) level using the 6-31G(d) basis set,[18] which is of DZ+P quality in the valence shell. Frequency calculations were performed, in order to verify that the calculated stationary points correspond to equilibrium

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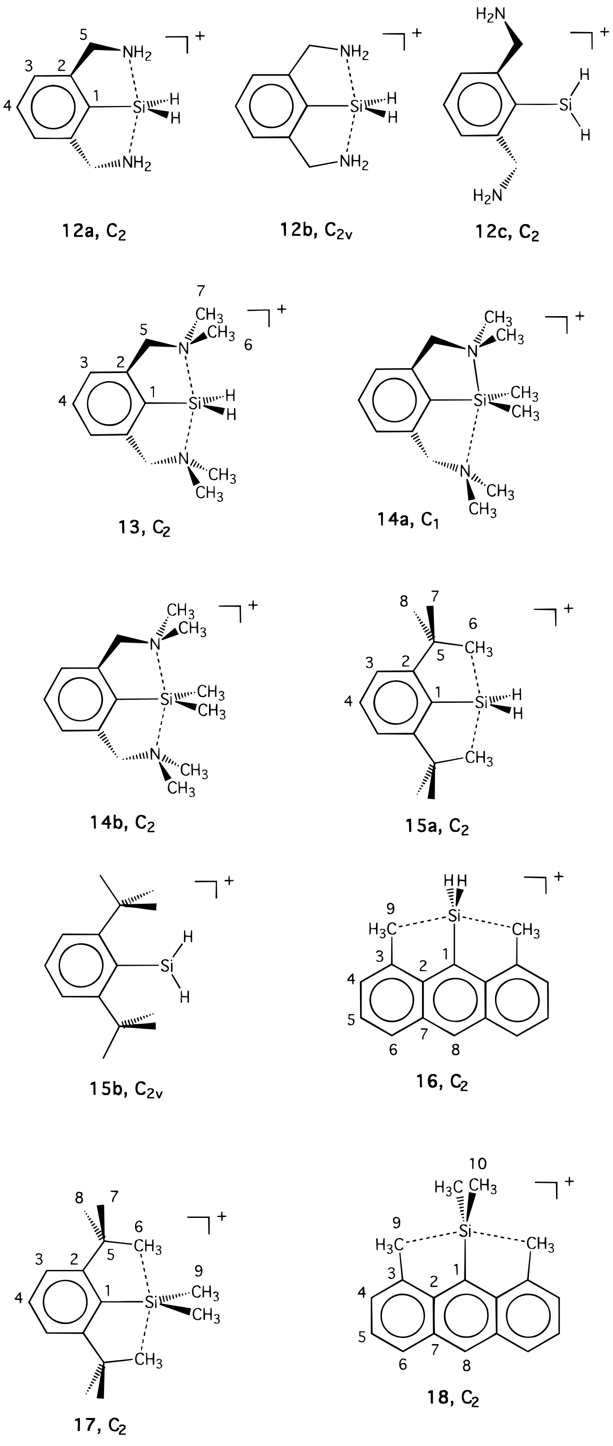
Chart 2



12a, C_2 12b, C_{2v} 12c, C_2

13, C_2 14a, C_1

14b, C_2 15a, C_2

15b, C_{2v} 16, C_2

17, C_2 18, C_2

geometries. Although HF provides a reasonable description of silylium cations, correlation corrected methods such as second-order Møller−Plesset (MP2) perturbation theory[19] or density functional theory (DFT) were also used in selected cases to improve HF results. DFT covers large parts of (unspecified) correlation effects, which in the case of hybrid functionals of the B3LYP type[20] lead to results of MP2 or even better quality. This was confirmed in the present study.

Apart from including correlation effects in the calculations, we also considered possible solvent effects using the self-consistent isodensity polarized continuum (SCIPCM) approach,[21] which in a simplified form provides insight into electrostatic solvent effects.

NMR chemical shift calculations were carried out with the IGLO method (individual gauge for localized orbitals) method of Kutzelnigg and Schindler,[22] using a (11s7p2d/9s5p1d/5s1p)-[7s6p2d/5s4p1d/3s1p] basis set, recommended for ^{29}Si and ^{13}C NMR chemical shift calculations.[23]

To investigate interactions between Si^+ and coordination partner, the calculated electron density distribution $\rho(\mathbf{r})$, its associated Laplace concentration $-\nabla^2\rho(\mathbf{r})$, and the energy density distribution $H(\mathbf{r})$ were analyzed using the virial partitioning method by Bader and co-workers.[24] Covalent and noncovalent bonding between Si and some atom A of the solvent molecule S is described according to criteria given by Cremer and Kraka:[25,26]

(1) In the case of covalent bonding between Si and A, there must be a path of maximum electron density (MED path) connecting the nuclei of Si and A. The existence of such a path implies a (3,−1) saddle point $\mathbf{r}_b$ of the electron density distribution $\rho(\mathbf{r})$ as well as a zero-flux surface between atoms Si and A (necessary condition).

(2) The local energy density $H(\mathbf{r}_b)$ must be stabilizing, i.e., smaller than zero (sufficient condition).

Calculations have been performed on a CRAY-YMP/416 and a Silicon Graphics Power Challenge using the COLOGNE96[27] and GAUSSIAN92[28] program packages.

4. Results and Discussion

A listing of calculated absolute and relative HF/6-31G(d) and B3LYP/6-31G(d) energies is given in Table 1. Relevant geometrical parameters of cations **1**−**11** are given in Figure 1 while those of cations **12**−**18** are shown in Figures 2−8. Optimized geometries of all molecules calculated in this work are listed in the suppporting information. IGLO/[7s6p2d/5s4p1d/3s1p]//HF/6−31G(d) ^{29}Si chemical shifts for the molecules investigated are summarized in Table 2, whereas Tables 3 and 4 contain calculated Si charges and results of the bond density analysis, respectively.

Phenyl-Substituted Silylium Cations. A phenyl ring stabilizes a silylium cation by inductive, conjugative, and (under certain circumstances) hyperconjugative effects. For example, inductive stabilization of a phenyl ring by a SiH_3 relative to that caused by a CH_3 group can be estimated from the isodesmic reaction (2)

$$C_6H_5CH_3 + SiH_4 \rightarrow C_6H_5SiH_3 + CH_4 \qquad (2)$$

($\Delta E = -6.4$ kcal/mol, HF/6-31G(d)) to be larger than 6.4

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Table 1. Calculated Absolute and Relative Energies[a]

molecule		sym	absolute energies HF/6-31G(d)	absolute energies B3LYP/6-31G(d)	rel energies HF/6-31G(d)	rel energies B3LYP/6-31G(d)	ref
1a	SiH_2Ph^+	C_{2v}	−519.934 36		0		12
1b	SiH_2Ph^+	C_{2v}	−519.910 34		15.1		12
2a	$SiMe_2Ph^+$	C_2	−598.054 76		0		this work
2b	$SiMe_2Ph^+$	C_2	−598.037 89		10.6		this work
3	SiH_3^+	D_{3h}	−290.328 91				6b
4	$SiHMe_2^+$	C_{2v}	−368.464 66				this work
5	$SiMe_3^+$	C_{3h}	−407.527 82				6b
6	$SiH_3(NH_3)_2^+$	D_{3h}	−402.871 53		105.0		6b
7	$SiHMe_2(NH_3)_2^+$	C_2	−480.966 60		83.6		this work
8	$SiMe_3(NH_3)_2^+$	C_s	−520.011 59		72.2		this work
9a	$SiH_3(CH_4)_2^+$	C_1	−370.739 71		12.8		this work
9b	$SiH_3(CH_4)_2^+$	C_2	−370.739 63	−372.026 78[c]	12.8	26.1	this work
10a	$SiHMe_2(CH_4)_2^+$	C_1		−450.712 97[c]		10.2	this work
10b	$SiHMe_2(CH_4)_2^+$	C_2	−448.862 53	−450.712 45[c]	4.7	9.9	this work
11a	$SiMe_3(CH_4)_2^+$	C_3		−490.054 14[c]		5.1	this work
11b	$SiMe_3(CH_4)_2^+$	C_{3h}	−487.923 51	−490.053 93[c]	3.3	5.0	this work
12a	$SiH_2C_6H_3(CH_2NH_2)_2^+$	C_2	−708.179 94		0		12
12b	$SiH_2C_6H_3(CH_2NH_2)_2^+$	C_{2v}	−708.178 93		0.7		12
12c	$SiH_2C_6H_3(CH_2NH_2)_2^+$	C_2	−708.042 16		86.5		12
13	$SiH_2C_6H_3(CH_2NMe_2)_2^+$	C_2	−864.292 31	−868.739 42			this work
14a	$SiMe_2C_6H_3(CH_2NMe_2)_2^+$	C_1	−942.374 61		0		this work
14b	$SiMe_2C_6H_3(CH_2NMe_2)_2^+$	C_2	−942.373 77	−947.384 12	0.5	0	this work
14c	$SiMe_2C_6H_3(CH_2NMe_2)_2^+$	C_1	−942.361 81	−947.367 52	8.0	10.4	this work
15a	$SiH_2C_6H_3(CMe_3)_2^+$	C_2	−832.203 41	−836.573 42	0		this work
15b	$SiH_2C_6H_3(CMe_3)_2^+$	C_{2v}	−832.174 79		18.0		this work
16	$SiH_2C_{14}H_7Me_2^+$	C_2	−903.297 93	−907.975 78			this work
17	$SiMe_2C_6H_3(CMe_3)_2^+$	C_2	−910.308 07	−915.238 73			this work
18	$SiMe_2C_{14}H_7Me_2^+$	C_2	−981.404 95	−986.643 62			this work

[a] Absolute energies in Hartree, relative energies in kcal/mol. [b] In case of solvent complexes $R_3Si(S)_n^+$ the relative energy gives the complexation energy obtained by the reaction $R_3Si(S)_n^+ \rightarrow R_3Si^+ + nS$, where S designates a solvent molecule. Relative energies not equal to zero are always given with regard to the most stable structure. [c] B3LYP/6-31G(d,p) values.

kcal/mol because the reaction energy of reaction 2 is a result of increased inductive stabilization (relative to CH_3) and decreased hyperconjugative stabilization where the hyperconjugative stabilization in toluene is about 5 kcal/mol.[29]

In silylium cation **1a** both inductive and conjugative stabilization should take place, which can be estimated in total by the energy of the isodesmic reaction (3) to be

$$SiH_3^+ + SiH_{4-n}R_n \rightarrow SiH_4 + R_nH_{3-n}Si^+ \quad (n = 1, 2, 3) \quad (3)$$

31.5 kcal/mol,[12] which is considerably larger than the stabilization of a silylium cation by a methyl group (13.9 kcal/mol, HF/6−31G(d)), however, less than the energy gain due to trimethyl substitution (36.0 kcal/mol).[6b] By rotating the phenyl ring by 90° into form **1b**, π-conjugation involving the SiH_2^+ group is suppressed. Form **1b**, which is located at the top of the rotational barrier, is 15.1 kcal/mol higher in energy, suggesting that the π-conjugation effect is similar in magnitude. For comparison, the rotational barrier for the benzyl cation $C_6H_5CH_2^+$ is 45.9 kcal/mol (HF/6-31G(d) value; HF/3-21G: 45.4[30]) since π-conjugation in the planar molecule involving overlap between the phenyl π-orbitals and a $2p\pi(C^+)$ AO is more effective than π-conjugation involving a $3p\pi(Si^+)$ orbital. The remaining $31.5 - 15.1 = 16.4$ kcal/mol are predominantly due to the inductive effect of a positively charged SiH_2 group and some hyperconjugative effects between the pseudo-π-orbitals of the SiH_2 group and the π-orbitals of the phenyl ring.

The two methyl groups in **2a** stabilize Si^+ by 25.9 kcal/mol. The rotational barrier of **2** is just 11.0 kcal/mol, indicating that the hyperconjugative interactions between the pseudo-π orbitals of the CH_3 groups and the $3p\pi(Si^+)$ orbital lead to about 5 kcal/mol stabilization, thus reducing π-conjugative stabilization from 15 to about 11 kcal/mol. The inductive effect of about 15−16 kcal/mol remains largely unaltered by dimethyl substitution.

In summary, one can predict that if rotation of the SiH_2 or $SiMe_2$ group is enforced because of steric reasons, the energy increase of 15 and 11 kcal/mol, respectively, has to be compensated by other stabilizing electronic effects.

The IGLO ^{29}Si shifts for the planar equilibrium geometries **1a** and **2a** are 200 and 268 ppm (Table 2), while those of the perpendicular forms are 266 and 321 ppm. The shift differences between planar and perpendicular forms can be understood from the calculated Mulliken charges of the Si atom, which are smaller in **1a** (0.826, Table 3) and **2a** (1.050) than in **1b** (0.945) and **2b** (1.098) because of π-delocalization in the planar forms. The ^{29}Si shifts of **1b** and **2b** resemble those of **3** and **4** (270 and 334 ppm, Table 2), thus indicating similar electronic structures at the corresponding Si^+ atoms. Hence, cations **1** and **2** in their perpendicular form represent typical silylium cations that are stabilized simply by hyperconjugative interactions.

Solvated Silylium Cations. The solvent prototypes NH_3 and CH_4 were used to simulate strong and weak nucleophilic solvents. Interactions between **3** and two NH_3 molecules lead to the pentacoordinated complex **6**. A HF/6-31G(d) coordination energy of 109 kcal/mol and an IGLO ^{29}Si shift of −128 ppm are calculated, where the latter value is about 400 ppm upfield from the shift

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(29) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd Ed.; Chapman and Hall: New York, 1986.

(30) Dorigo, A. E.; Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1989**, *111*, 6942.

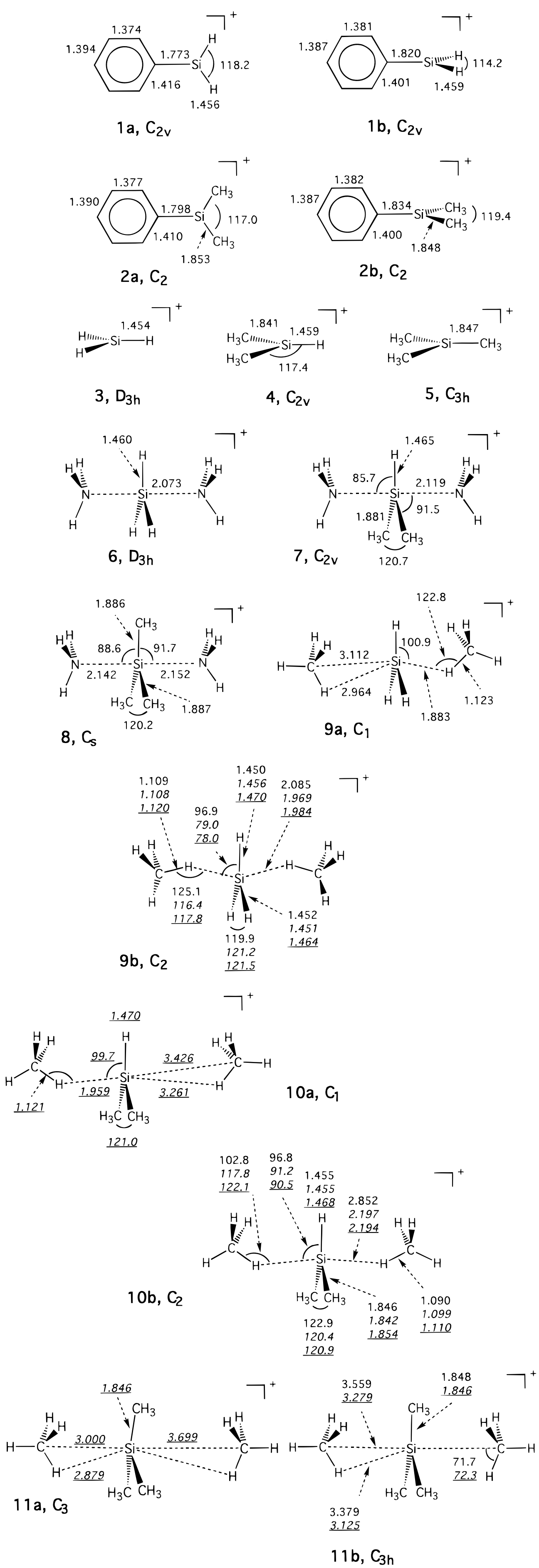

Figure 1. Calculated geometrical parameters of cations **1**−**11**. Bond lengths are in Å, angles in deg. HF/6-31G(d) values are in normal print, MP/6-31G(d,p) values in italics, and B3LYP/6-31G(d,p) values in underlined italics.

value of the free cation **3**. This indicates formation of covalent Si−N bonds as confirmed by the electron density analysis (Table 4). Weaker Si−N coordinations (83.6 and 72.2 kcal/mol, Table 1) together with more downfield shifted δ^{29}Si values of −69.4 and −44.0 ppm are calculated for NH_3 complexes **7** and **8** of cations **4** and **5**. Clearly, these data are a result of the increased internal stability of **4** and **5** as compared to that of **3**.

Complex **9** formed between **3** and two CH_4 molecules possesses an unsymmetrical equilibrium geometry at the HF/6-31G(d) level (**9a**, Chart 1 and Figure 1) where one H-atom of the closest CH_4 molecule approaches Si^+ by 1.883 Å. The second CH_4 molecule has the closest Si,H contact at 2.964 Å. However, the C_2 symmetrical geometry **9b**, in which the two methane molecules are located at the same distance from the Si^+ atom (Figure 1), is just 0.06 kcal/mol above **9a**. At the MP2/6-31G(d,p) and the B3LYP/6-31G(d,p) levels of theory, this difference vanishes and only **9b** is found to represent a stable complex with a complexation energy of 23.2 (MP2) and 26.1 kcal/mol (B3LYP, Table 1), respectively. MP2 and B3LYP suggest a Si^+,H interaction distance of 1.969 and 1.984 Å accompanied by a lengthening of the corresponding CH bond (1.108 and 1.120, Figure 1) by 0.02−0.03 Å. The IGLO ^{29}Si NMR chemical shift of **9** is sensitive to the calculated geometry. For **9a** (HF geometry), 64.3 ppm are obtained while for **9b** (MP2 geometry) a value of −3.7 ppm results, which means that despite the relatively weak complexation energy **9** cannot be considered as a silylium cation.

It has to be mentioned that similar Si,H−C interactions were found by Schleyer and co-workers[5] and Apeloig and co-workers who independently investigated the coordination complex $SiH_3(CH_4)^+$.[31] Eaborn and co-workers also reported that Me-groups are able to bridge to positive Si-atoms,[32] and this bridging should involve Si,H−C interactions that resemble those calculated for complex **9**.

Coordination of two CH_4 molecules to **4** and **5** (complexes **10** and **11**) is weaker than in **9** as reflected by B3LYP/6-31G(d,p) complexation energies of 10.2 (MP2: 11.7) and 5.1 kcal/mol (Table 1). The most stable complex geometries are C_1 symmetrical **10a** and C_3 symmetrical **11a**, which are characterized by closest Si,H interaction distances of 1.96 Å (**10a**) and 2.88 Å (**11a**), respectively. Again, the PES of both **10** and **11** is rather flat so that the barriers for the degenerate rearrangements **10a** → **10a′** and **11a** → **11a′** (**10a′**, **11a′**: mirror images of **10a**, **11a**) are just 0.3 and 0.1 kcal/mol (Table 1); i.e., including zero point energy vibrations both **10** and **11** can be described as the C_2 or C_{3h} symmetrical geometries **10b** (B3LYP Si,H distance, 2.19 Å) and **11b** (B3LYP Si,H distance, 3.12 Å, Figure 1) carrying out a large amplitude vibration.

Clearly, alkanes such as methane interact only weakly with silylium cations. However, this is sufficient to reduce the silylium cation character of ions such as $R_3Si(R'H)^+$ considerably where larger alkanes R′H will exhibit stronger coordination abilities than methane because of higher lying electron donor orbitals.

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(31) Apeloig, Y.; Merin-Aharoni, O.; Danovich, D.; Ioffe, A.; Shaik, S. *Isr. J. Chem.* **1993**, *33*, 387.

(32) (a) Eaborn, C.; Happer, D. A. R.; Hopper, S. P.; Safa, K. D. *J. Organomet. Chem.* **1980**, *188*, 179. (b) Al-Shali, S. A. I; Eaborn, C.; Fattah, F. A.; Najim, S. T. *J. Chem. Soc., Chem. Commun.* **1984**, *5*, 318. (c) Ayoko, G. A.; Eaborn, C. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1289.

Table 2. IGLO/[7s6p2d/5s4p1d/3s1p]//HF/6-31G(d) NMR Chemical Shifts[a]

molecule		sym	chemical shifts					
			δ^{29}Si	δ^{13}C				
1a	SiH_2Ph^+[b]	C_{2v}	200.3	132.6 (C1)	155.7 (C2)	134.5 (C3)	164.6 (C4)	
1b	SiH_2Ph^+[b]	C_{2v}	265.6	113.5 (C1)	140.6 (C2)	138.0 (C3)	151.1 (C4)	
2a	$SiMe_2Ph^+$	C_2	268.0	128.0 (C1)	151.5 (C2)	135.0 (C3)	159.4 (C4)	0.6(C5)
2b	$SiMe_2Ph^+$	C_2	320.6	124.4 (C1)	139.7 (C2)	137.7 (C3)	148.4 (C4)	12.1(C5)
3	SiH_3^+[b]	D_{3h}	270.2					
4	$SiHMe_2^+$	C_{2v}	334.1	9.8				
5	$SiMe_3^+$[b]	C_{3h}	355.9	9.0				
6	$SiH_3(NH_3)_2^+$[b]	D_{3h}	−127.7					
7	$SiHMe_2(NH_3)_2^+$	C_2	−69.4	−0.6				
8	$SiMe_3(NH_3)_2^+$	C_s	−44.0	2.0 (C1)	2.6 (C2)			
9a	$SiH_3(CH_4)_2^+$	C_1	64.3	15.5 (C1)	−5.3 (C2)			
9b	$SiH_3(CH_4)_2^+$[c]	C_2	−3.7[d]	10.2				
10b	$SiHMe_2(CH_4)_2^+$	C_2	288.1	6.5 (C1)	−2.0 (C2)			
	$SiHMe_2(CH_4)_2^+$[c]	C_2	175.9[d]	1.6 (C1)	7.7 (C2)			
11b	$SiMe_3(CH_4)_2^+$	C_{3h}	338.6	8.7 (C1)	−2.2 (C2)			
12a	$SiH_2C_6H_3(CH_2NH_2)_2^+$[b]	C_2	−80.5[e]	123.7 (C1)	147.3 (C2)	130.2 (C3)	142.1 (C4)	40.6 (C5)
13	$SiH_2C_6H_3(CH_2NMe_2)_2^+$	C_{2v}	−43.1[d,f]	122.6 (C1)	152.7 (C2)	131.1 (C3)	147.0 (C4)	61.0 (C5)
				45.4 (C6)	45.5 (C7)			
15a	$SiH_2C_6H_3(CMe_3)_2^+$	C_2	25.1[d]	106.6 (C1)	172.4 (C2)	131.2 (C3)	149.0 (C4)	37.0 (C5)
				37.6 (C6)	33.1 (C7)	29.3 (C8)		
16	$SiH_2C_{14}H_7Me_2^+$	C_2	63.9	97.1 (C1)	153.3 (C2)	128.1 (C3)	143.6 (C4)	130.6 (C5)
				141.0 (C6)	135.5 (C7)	155.1 (C8)	23.6 (C9)	
17	$SiMe_2C_6H_3(CMe_3)_2^+$	C_2	146.2	117.9 (C1)	170.9 (C2)	131.3 (C3)	147.4 (C4)	36.1 (C5)
				33.7 (C6)	37.9 (C7)	30.5 (C8)	7.6 (C9)	
18	$SiMe_2C_{14}H_7Me_2^+$	C_2	186.7	109.3 (C1)	151.6 (C2)	128.8 (C3)	142.9 (C4)	130.6 (C5)
				140.9 (C6)	135.9 (C7)	154.6 (C8)	24.2 (C9)	11.4 (C10)

[a] All shifts in ppm relative to TMS. For the numbering of atoms, see Schemes 1 and 2. [b] Values have been reported in ref 12. [c] Calculated at the IGLO/[7s6p2d/5s4p1d/3s1p]//MP2/6-31G(d,p) level. [d] The corresponding IGLO/[7s6p2d/5s4p1d/3s1p]//B3LYP/6-31G(d) values are −3.1 (**9b**), 173.5 (**10a**), 6.0 (**15a**), and −44.2 ppm (**13**). [e] Calculated at the IGLO/6-31G(d)//HF/6-31G(d) level. [f] Experimental δ^{29}Si value from ref 10a.

Strong Intramolecular Coordination. A previous investigation of **12** has shown[12] that this compound is most stable in the C_2-symmetrical form **12a** with the SiH_2 group rotated by 82° (Figure 2) out of the plane of the phenyl ring and the CH_2NH_2 groups slightly bent in opposite directions out-of-plane. However, the planar C_{2v} symmetric cation **12b** is just 0.7 kcal/mol higher in energy than **12a** so that **12** is probably characterized by a large amplitude vibration leading to effective C_{2v} symmetry.

Cation **12a** is 86.5 kcal/mol more stable than cation **12c** (Chart 2) with uncoordinated SiH_2^+. It was estimated that the coordination of SiH_2^+ by two NH_2 groups stabilizes **12a** by at least 100 kcal/mol, thus easily compensating the loss of π-conjugative stabilization of about 15 kcal/mol.[12] In **12a**, there are weak covalent bonds connecting Si and the N atoms (Table 4). The $3p\pi(Si^+)$ orbital is largely filled up with negative charge (Table 3) and, accordingly, the calculated chemical shift appears about 350 ppm upfield from the expected one (270 ppm for an uncomplexed cation) at −80 ppm (Table 2).

Compounds **13** and **14** were investigated by Corriu and co-workers[10] while just **12** was described by theoretical means.[12] In the present study it was possible for the first time to calculate the NMR shifts of **13** using a direct IGLO method.[33] We obtain a δ^{29}Si value of −43.1 ppm, which is in good accordance with the measured shift value of −46.4 ppm. The B3LYP geometry of **13** differs slightly from the corresponding HF geometry (Figure 3) in such a way that all bond lengths are somewhat longer; for example, the Si,N distance is 2.124 Å compared to 2.113 Å calculated at the HF level. The IGLO//B3LYP value of δ^{29}Si is −44.2 ppm, which is closer to the measured shift value. To estimate possible solvent effects on geometry and shift values, the geometry of **13** was also optimized at the SCIPCM-B3LYP/6-31G(d) level of theory using the dielectric constant of $CHCl_3$ ($\epsilon = 4.3$) since $CHCl_3$ was used in the NMR measurement of Corriu and co-workers.[10] Calculated changes in the B3LYP geometry due to the solvent $CHCl_3$ are smaller than 0.003 Å and 0.2°,

Table 3. Calculated Mulliken Charges at the HF/6-31G(d) Level

molecule		sym	q(Si)	$q(SiH_n)$
1a	$SiH_2C_6H_5^+$	C_{2v}	0.826	0.785
1b	$SiH_2C_6H_5^+$	C_{2v}	0.945	0.915
2a	$SiMe_2C_6H_5^+$	C_2	1.050	1.050
2b	$SiMe_2C_6H_5^+$	C_2	1.098	1.098
3	SiH_3^+	D_{3h}	0.932	1.000
4	$SiHMe_2^+$	C_{2v}	1.076	1.057
5	$SiMe_3^+$	C_{3h}	1.161	1.161
6	$SiH_3(NH_3)_2^+$	D_{3h}	0.883	0.555
7	$SiHMe_2(NH_3)_2^+$	C_{2v}	1.143	1.015
8	$SiMe_3(NH_3)_2^+$	C_s	1.296	1.296
9a	$SiH_3(CH_4)_2^+$	C_1	0.837	0.811
9b	$SiH_3(CH_4)_2^+$	C_2	0.837	0.819
10b	$SiHMe_2(CH_4)_2^+$	C_2	1.069	1.033
11b	$SiMe_3(CH_4)_2^+$	C_{3h}	1.183	1.183
12a	$SiH_2C_6H_3(CH_2NH_2)_2^+$	C_2	0.948	0.701
12b	$SiH_2C_6H_3(CH_2NH_2)_2^+$	C_{2v}	0.951	0.695
12c	$SiH_2C_6H_3(CH_2NH_2)_2^+$	C_2	0.781	0.710
13	$SiH_2C_6H_3(CH_2NMe_2)_2^+$	C_2	0.989	0.719
14a	$SiMe_2C_6H_3(CH_2NMe_2)_2^+$	C_1	1.266	1.266
14b	$SiMe_2C_6H_3(CH_2NMe_2)_2^+$	C_2	1.301	1.301
14c	$SiMe_2C_6H_3(CH_2NMe_2)_2^+$	C_1	1.173	1.173
15a	$SiH_2C_6H_3(CMe_3)_2^+$	C_2	0.855	0.735
15b	$SiH_2C_6H_3(CMe_3)_2^+$	C_{2v}	0.839	0.732
16	$SiH_2C_{14}H_7Me_2^+$	C_2	0.872	0.756
17	$SiMe_2C_6H_3(CMe_3)_2^+$	C_2	1.105	1.105
18	$SiMe_2C_{14}H_7Me_2^+$	C_2	1.083	1.083

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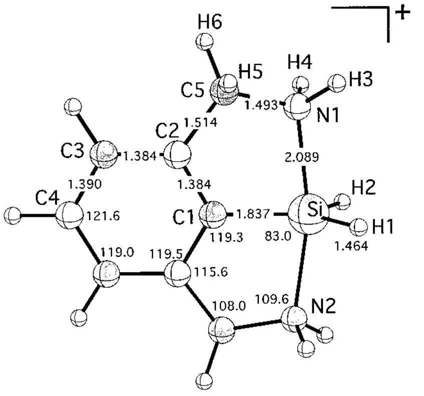
(33) Olsson, L.; Cremer, D. Unpublished work.

Table 4. Bond Density Analysis[a]

molecule		sym	atoms involved A,B	distance A,B	type of critical point	$\rho(\mathbf{r}_b)$	$H(\mathbf{r}_b)$	character of bond
6	$SiH_3(NH_3)_2^+$	D_{3h}	Si,N	2.073	(3,−1)	0.37	−0.09	weakly covalent
7	$SiHMe_2(NH_3)_2^+$	C_{2v}	Si,N	2.119	(3,−1)	0.34	−0.09	weakly covalent
8	$SiMe_3(NH_3)_2^+$	C_s	Si,N	2.142	(3,−1)	0.33	−0.09	weakly covalent
			Si,N	2.152	(3,−1)	0.32	−0.09	weakly covalent
9a	$SiH_3(CH_4)_2^+$	C_1	Si,H	1.883	(3,−1)	0.23	−0.07	weakly covalent
			Si,C	3.112	(3,−1)	0.05	−0.03	electrostatic
9b	$SiH_3(CH_4)_2^+$	C_2	Si,H	2.085	(3,−1)	0.15	−0.02	electrostatic
10b	$SiHMe_2(CH_4)_2^+$	C_2	Si,H	2.852	(3,−1)	0.16	−0.03	electrostatic
11b	$SiMe_3(CH_4)_2^+$	C_{3h}	Si,C	3.559	(3,−1)	0.02	0.00	electrostatic
12a	$SiH_2C_6H_3(CH_2NH_2)_2^+$	C_2	Si,N	2.089	(3,−1)	0.38	−0.11	weakly covalent
13	$SiH_2C_6H_3(CH_2NMe_2)_2^+$	C_2	Si,N	2.113	(3,−1)	0.38	−0.13	weakly covalent
14a	$SiMe_2C_6H_3(CH_2NMe_2)_2^+$	C_1	Si,N	2.015	(3,−1)	0.47	−0.15	weakly covalent
			Si,N	2.734	(3,−1)	0.14	−0.01	electrostatic
14b	$SiMe_2C_6H_3(CH_2NMe_2)_2^+$	C_2	Si,N	2.260	(3,−1)	0.30	−0.11	weakly covalent
15a	$SiH_2C_6H_3(CMe_3)_2^+$	C_2	Si,H	1.952	(3,−1)	0.21	−0.06	weakly covalent
16	$SiH_2C_{14}H_7Me_2^+$	C_2	Si,H	2.068	(3,−1)	0.17	−0.03	electrostatic
17	$SiMe_2C_6H_3(CMe_3)_2^+$	C_2	Si,H	2.040	(3,−1)	0.17	−0.03	electrostatic
18	$SiMe_2C_{14}H_7Me_2^+$	C_2	Si,H	2.200	(3,−1)	0.13	−0.01	electrostatic

[a] Distance in Å, $\rho(\mathbf{r}_b)$ in electron Å^{-3}, $H(\mathbf{r}_b)$ in hartree Å^{-3}. Each point $\mathbf{r}_b$ is characterized by (rank, signature). The character of the bond is given according to the criteria of Cremer and Kraka.[25,26] Calculations were performed at the HF/6-31G(d) level.



12a, C$_2$

H1-Si-C1 = 122.6
H1-Si-N1 = 94.2
H1-Si-N2 = 93.3
N1-Si-N2 = 166.1
H3-N1-Si = 113.7
H4-N1-Si = 107.3

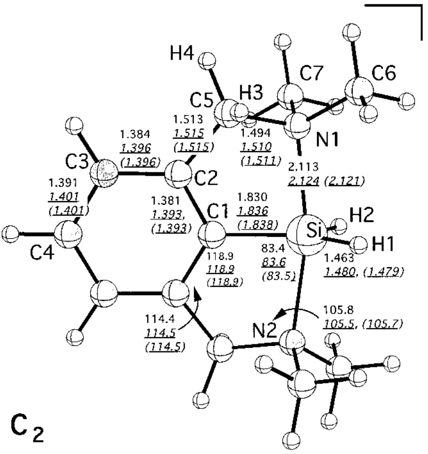
Si-C1-C2-C5 = -2.1
H1-Si-C1-C2 = 81.6
C1-C2-C5-N1 = 16.7
C2-C5-N1-Si = -21.9
C5-N1-Si-C1 = 17.7
N1-Si-C1-C2 = -8.9
H3-N1-Si-C1 = 142.2
H4-N1-Si-C1 = -101.2
H3-N1-C5-H5 = -28.7
H3-N1-Si-H1 = 19.9
H4-N1-Si-H1 = 136.5

Figure 2. HF/6-31G(d) geometrical parameters of cation **12**. Bond lengths are in Å, angles in deg.

suggesting almost no influence of the solvent on the geometry of **13**.

The δ^{29}Si value of **13** is shifted downfield by 34 ppm compared to the corresponding value for **12a** (−80.5 ppm, Table 2). The downfield shift is parallel to the difference in the positive charges of the SiH_2 group in **13** (0.719, Table 3) and **12** (0.701). It suggests that despite the stronger donor capacity of a NMe_2 group (**13**) compared to that of a NH_2 group (**12**), donation of negative charge to the empty 3pπSi$^+$ orbital and by this pentacoordination is smaller in **13**. This has to do with an increase in eclipsing strain between SiH_2, NR_2, and CH_2 groups in **13** as reflected by an elongation of the Si−N distances by 0.02 Å (2.089 in **12**, Figure 2, 2.113 Å in **13**, Figure 3), a larger N1−Si−C1−C2 dihedral angle (**12**, −8.9 and **13**, −21.5° (HF), −12.4° (B3LYP), Figures 2 and 3). To compensate for steric strain in **13** the NR_2 groups are more rotated than in **12**, and as a consequence, orbital overlap between the N lone pair orbitals and the 3pπ(Si$^+$) orbital is reduced.

Nevertheless, Si−N interactions are still rather strong due to the larger donor capacity of a NMe_2 group. They lead to covalent SiN bonding according to the electron density analysis (Table 4) with a stabilization of the pentacoordinated Si atom that should be similar to that in **6** or **12** (i.e., approximately 100−110 kcal/mol).



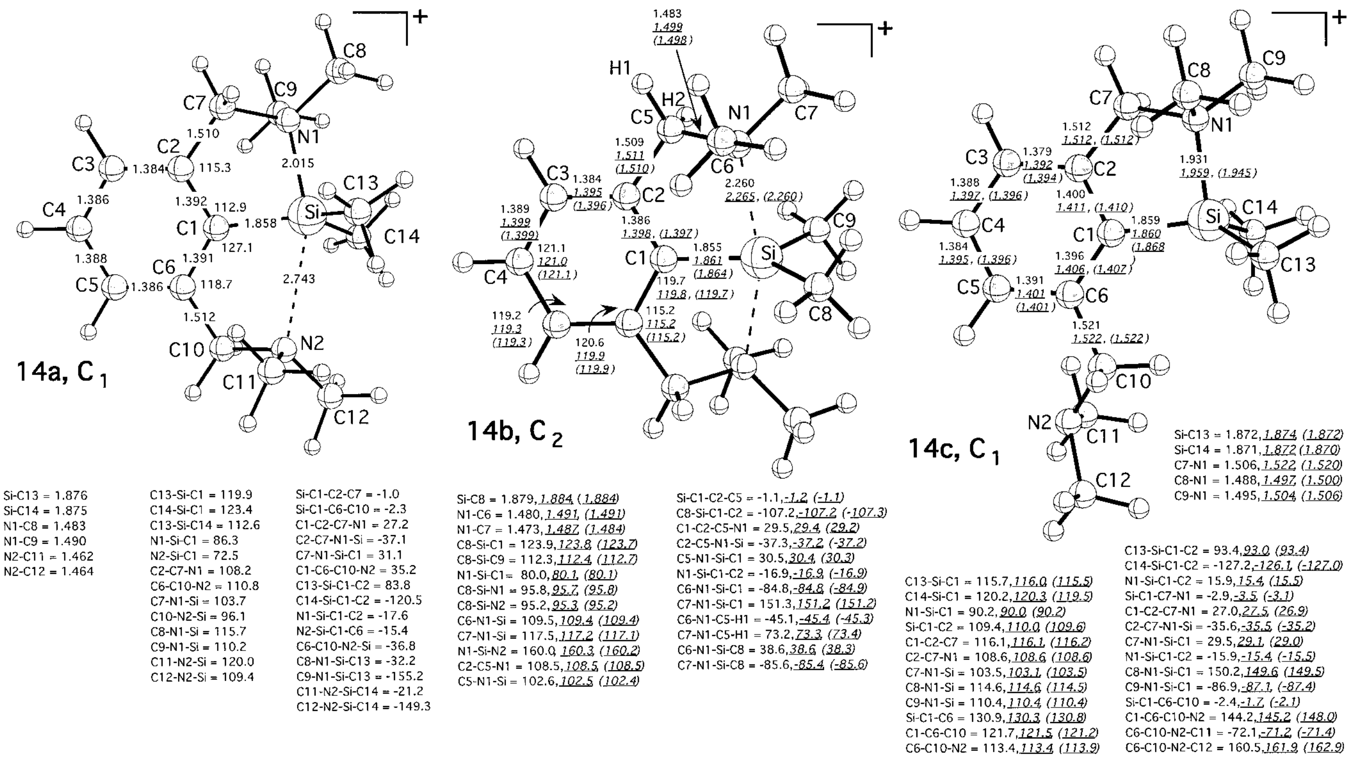
13, C$_2$

N1-C6 = 1.477, *1.488*, *(1.487)*
N1-C7 = 1.481, *1.493*, *(1.492)*
H1-Si-C1 = 122.6, *122.7*, *(122.6)*
H1-Si-N1 = 93.7, *93.6*, *(93.6)*
H1-Si-N2 = 93.5, *93.3*, *(93.3)*
N1-Si-N2 = 166.8, *167.2*, *(167.1)*
C6-N1-Si = 113.2, *113.2*, *(113.0)*
C7-N1-Si = 108.5, *108.4* *(108.3)*
C1-C2-C3 = 119.2, *119.1* *(119.0)*
C2-C3-C4 = 118.8, *118.9* *(118.9)*
C3-C4-C5 = 121.9, *121.8* *(121.8)*
C2-C5-N1 = 109.0, *109.1* *(109.0)*

Si-C1-C2-C5 = -2.6, *-2.7*, *(-2.6)*
H1-Si-C1-C2 = 77.6, *77.8*, *(77.8)*
C1-C2-C5-N1 = 23.4, *23.3*, *(23.1)*
C2-C5-N1-Si = -30.0, *-29.-8*, *(-29.6)*
C5-N1-Si-C1 = 24.0, *23.7*, *(23.6)*
N1-Si-C1-C2 = -21.5, *-12.4*, *(-12.3)*
C6-N1-Si-C1 = 145.6, *145.3*, *(145.2)*
C7-N1-Si-C1 = -93.2, *-93.2*, *(93.4)*
C6-N1-C5-H3 = -34.1, *-33.4*, *(-33.4)*
C7-N1-C5-H3 = -154.4, *-154.1*, *(-154.1)*
C6-N1-Si-H1 = 23.1, *22.7*, *(22.8)*
C7-N1-Si-H1 = 144.4, *144.2*, *(144.2)*

Figure 3. HF/6-31G(d) (normal print), B3LYP/6-31G(d) (underlined italics), and SCIPCM-B3LYP/6-31G(d) (ϵ($CHCl_3$) = 4.3; underlined italics in parantheses) geometrical parameters of cation **13**. Bond lengths are in Å, angles in deg.

In **14**, the silyl group is internally stabilized because of dimethyl substitution (approximately 25 kcal/mol). At equilibrium geometry (C_1-symmetrical **14a**, see Figure 4), there are two different Si,N interactions, namely one with a calculated distance of 2.01 Å and the other with 2.74 Å. However, the energy difference between **14a** and the C_2 symmetrical form **14b** with equal Si,N distances is just 0.5 kcal/mol (Table 1). At the B3LYP/6-31G(d) level, **14b** becomes more stable, thus indicating that a stable form **14a** does not exist. Because of computational limitations, it was not possible to calculate chemical shift values; however, it is noteworthy that different δ^{29}Si values have been reported for **14** in chloroform (−4.1 ppm) and methanol (6.4 ppm).[10a,34] The deviation of 10 ppm for the two solutions



Si-C13 = 1.876
Si-C14 = 1.875
N1-C8 = 1.483
N1-C9 = 1.490
N2-C11 = 1.462
N2-C12 = 1.464

C13-Si-C1 = 119.9
C14-Si-C1 = 123.4
C13-Si-C14 = 112.6
N1-Si-C1 = 86.3
N2-Si-C1 = 72.5
C2-C7-N1 = 108.2
C6-C10-N2 = 110.8
C7-N1-Si = 103.7
C10-N2-Si = 96.1
C8-N1-Si = 115.7
C9-N1-Si = 110.2
C11-N2-Si = 120.0
C12-N2-Si = 109.4

Si-C1-C2-C7 = -1.0
Si-C1-C6-C10 = -2.3
C1-C2-C7-N1 = 27.2
C2-C7-N1-Si = -37.1
C7-N1-Si-C1 = 31.1
C1-C6-C10-N2 = 35.2
C13-Si-C1-C2 = 83.8
C14-Si-C1-C2 = -120.5
N1-Si-C1-C2 = -17.6
N2-Si-C1-C6 = -15.4
C6-C10-N2-Si = -36.8
C8-N1-Si-C13 = -32.2
C9-N1-Si-C13 = -155.2
C11-N2-Si-C14 = -21.2
C12-N2-Si-C14 = -149.3

Si-C8 = 1.879, *1.884*, (*1.884*)
N1-C6 = 1.480, *1.491*, (*1.491*)
N1-C7 = 1.473, *1.487*, (*1.484*)
C8-Si-C1 = 123.9, *123.8*, (*123.7*)
C8-Si-C9 = 112.3, *112.4*, (*112.7*)
N1-Si-C1= 80.0, *80.1*, (*80.1*)
C8-Si-N1 = 95.8, *95.7*, (*95.8*)
C8-Si-N2 = 95.2, *95.3*, (*95.2*)
C6-N1-Si = 109.5, *109.4*, (*109.4*)
C7-N1-Si = 117.5, *117.2*, (*117.1*)
N1-Si-N2 = 160.0, *160.3*, (*160.2*)
C2-C5-N1 = 108.5, *108.5*, (*108.5*)
C5-N1-Si = 102.6, *102.5*, (*102.4*)

Si-C1-C2-C5 = -1.1, *-1.2*, (*-1.1*)
C8-Si-C1-C2 = -107.2, *-107.2*, (*-107.3*)
C1-C2-C5-N1 = 29.5, *29.4*, (*29.2*)
C2-C5-N1-Si = -37.3, *-37.2*, (*-37.2*)
C5-N1-Si-C1 = 30.5, *30.4*, (*30.3*)
N1-Si-C1-C2 = -16.9, *-16.9*, (*-16.9*)
C6-N1-Si-C1 = -84.8, *-84.8*, (*-84.9*)
C7-N1-Si-C1 = 151.3, *151.2*, (*151.2*)
C6-N1-C5-H1 = -45.1, *-45.4*, (*-45.3*)
C7-N1-C5-H1 = 73.2, *73.3*, (*73.4*)
C6-N1-Si-C8 = 38.6, *38.6*, (*38.3*)
C7-N1-Si-C8 = -85.6, *-85.4*, (*-85.6*)

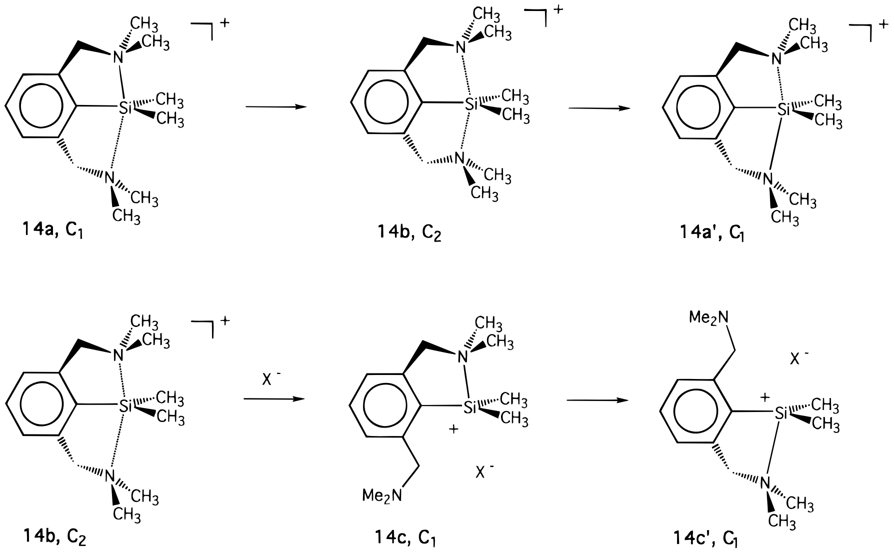
Si-C13 = 1.872, *1.874*, (*1.872*)
Si-C14 = 1.871, *1.872* (*1.870*)
C7-N1 = 1.506, *1.522*, (*1.520*)
C8-N1 = 1.488, *1.497*, (*1.500*)
C9-N1 = 1.495, *1.504*, (*1.506*)

C13-Si-C1 = 115.7, *116.0*, (*115.5*)
C14-Si-C1 = 120.2, *120.3*, (*119.5*)
N1-Si-C1 = 90.2, *90.0*, (*90.2*)
Si-C1-C2 = 109.4, *110.0*, (*109.6*)
C1-C2-C7 = 116.1, *116.1*, (*116.2*)
C2-C7-N1 = 108.6, *108.6*, (*108.6*)
C7-N1-Si = 103.5, *103.1*, (*103.5*)
C8-N1-Si = 114.6, *114.6*, (*114.5*)
C9-N1-Si = 110.4, *110.4*, (*110.4*)
Si-C1-C6 = 130.9, *130.3*, (*130.8*)
C1-C6-C10 = 121.7, *121.5*, (*121.2*)
C6-C10-N2 = 113.4, *113.4*, (*113.9*)

C13-Si-C1-C2 = 93.4, *93.0*, (*93.4*)
C14-Si-C1-C2 = -127.2, *-126.1*, (*-127.0*)
N1-Si-C1-C2 = 15.9, *15.4*, (*15.5*)
Si-C1-C7-N1 = -2.9, *-3.5*, (*-3.1*)
C1-C2-C7-N1 = 27.0, *27.5*, (*26.9*)
C2-C7-N1-Si = -35.6, *-35.5*, (*-35.2*)
C7-N1-Si-C1 = 29.5, *29.1*, (*29.0*)
N1-Si-C1-C2 = -15.9, *-15.4*, (*-15.5*)
C8-N1-Si-C1 = 150.2, *149.6*, (*149.5*)
C9-N1-Si-C1 = -86.9, *-87.1*, (*-87.4*)
Si-C1-C6-C10 = -2.4, *-1.7*, (*-2.1*)
C1-C6-C10-N2 = 144.2, *145.2*, (*148.0*)
C6-C10-N2-C11 = -72.1, *-71.2*, (*-71.4*)
C6-C10-N2-C12 = 160.5, *161.9*, (*162.9*)

Figure 4. HF/6-31G(d) (normal print), B3LYP/6-31G(d) (underlined italics), and SCIPCM-B3LYP/6-31G(d) ($\epsilon(CH_3OH) = 32.6$; underlined italics in parantheses) geometrical parameters of (a) **14a**, (b) **14b**, and (c) **14c**. Bond lengths are in Å, angles in deg.

Scheme 1



is remarkable and indicates structural differences for **14** in these two solvents. However, when the influence of the solvent on the equilibrium geometry of **14** was investigated by SCIPCM-B3LYP/6-31G(d) calculations, for dielectric constants up to $\epsilon(CH_3OH) = 32.6$ just **14b** and not **14a** was found.

Willcott and co-workers reported that **14** has a tetrahedral Si-atom and that a degenerate exchange between two equivalent conformations occurs.[34] It was concluded that the process involves a pentacoordinated transition state. The ΔG^* value for the exchange process was determined to be 10.1 kcal/mol in chloroform and 12.0 kcal/mol in methanol, which suggests that the stability of the tetracoordinated form increases in a polar solvent.[34] However, from our calculations we can exclude a degenerate exchange process of the type **14a** → {**14b**}$_{TS}$ → **14a′** (Scheme 1) since **14a** or **14a′** do not exist. It seems to us more likely that structure **14c** shown in Figure 4 is involved in the process.

In **14b**, there will be a large amplitude vibration of the amino groups that corresponds to a partial or, depending on solvent and counterion, full rotation of the side group leading from **14b** to **14c** and back to **14b**. In the presence of strongly coordinating counterions X^- one of the amino groups of **14b** could be replaced by X^- during rotation of the side chain to yield **14c**-X (Scheme 1). Experimental evidence for such a process has been provided by Corriu and co-workers.[10c] Closing of **14c-X** to **14b** + X^- and attack of a second X^- to replace the

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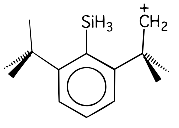
(34) Benin, V. A.; Martin, J. C.; Willcott, M. R. *Tetrahedron Lett.* **1994**, *35*, 2133.

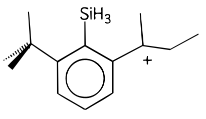
second amino group would lead to form **14c′**-X as shown in Scheme 1. The barrier of such a degenerate exchange process would be determined by the energy needed for the ring opening **14b** → **14c** since stabilization of **14c** in the form of **14c**-X is only possible after the opening step. At B3LYP/6-31G(d), **14c** is calculated to be 10.4 kcal/mol less stable than **14b** (Table 1), which is close to the ΔG^* value of 10.1 kcal/mol measured by Willcott and co-workers.[34] Nonspecific solvent interactions do not alter the stability of **14c** to any large extent, since the relative energy compared to **14b** was calculated as 6.9 kcal/mol at the SCIPCM-B3LYP/6-31G(d) level with $\epsilon(CH_3OH) = 32.6$.

Weak Intramolecular Coordination. Two *tert*-butyl substituents at a benzene ring in the position ortho to a SiH_2^+ group force the latter to rotate into an orthogonal form. The C_2-symmetrical equilibrium form **15a** is 18 kcal/mol more stable at HF/6-31G(d) than form **15b** with an in-plane arrangement of the SiH_2 group (Chart 2). Form **15b** represents the rotational transition state according to frequency calculations (one imaginary frequency of $162i$ cm^{-1} at HF/3-21G). Obviously, steric repulsion in **15b** is so large that conjugative interactions of SiH_2 with the phenyl ring (10−15 kcal/mol stabilization) cannot compensate this loss in energy. On the other hand, one cannot exclude that in a strongly coordinating solvent external coordination by S molecules will replace internal coordination and, thereby, enforce an equilibrium geometry with an in-plane arrangement of the SiR_2 group similar to **15b**. This also has to be considered for cations **16**, **17**, and **18** (Chart 1) discussed in this section, and therefore, the following discussion will be valid only for weakly coordinating solvents such as alkanes, halogenated hydrocarbons, or aromatic solvents.

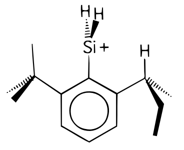
A second problem that has to be addressed before discussing cations **15**−**18** in detail is the possibility of an rearrangement of bidentated cations into carbocations or into other silylium ions. Normally, R_3Si^+ is more stable than R_3C^+ because of the larger electropositivity of Si compared to that of C. However, release in steric strain or enhanced aromatic stabilization could lead to more favorable isomeric forms. For example, in the case of **15a**, we also considered the cationic species **15c**−**15g**.



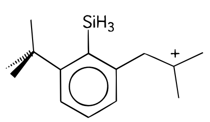
15c



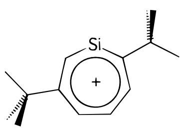
15d



15e



15f



15g

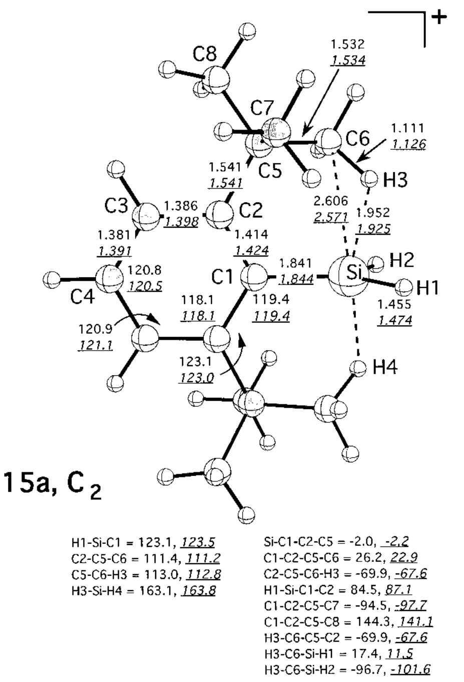


Figure 5. HF/6−31G(d) (normal print) and B3LYP/6−31G(d) (underlined italics) geometrical parameters of cation **15**. Bond lengths are in Å, angles in deg.

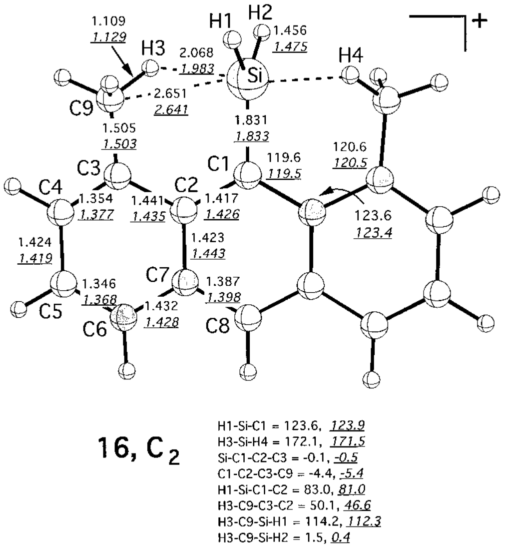
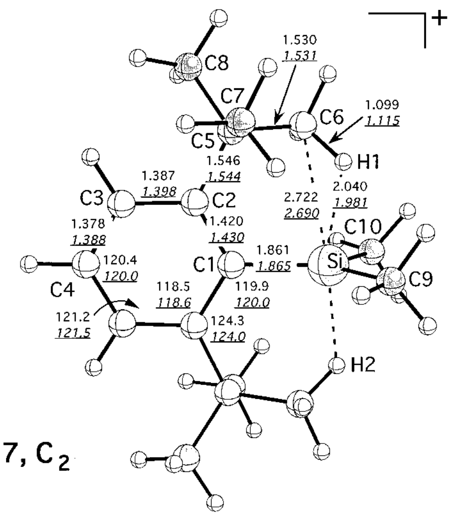


Figure 6. HF/6-31G(d) (normal print) and B3LYP/6-31G(d) (underlined italics) geometrical parameters of cation **16**. Bond lengths are in Å, angles in deg.

These cations possess energies similar to that of **15a**, where **15e** is the only cation that is more stable than **15a** ($\Delta E = -3.4$ kcal/mol at HF/6-31G(d)), while even a tertiary carbocation such as **15d** is 3.8 kcal/mol or silatropylium cation **15g** is 8.3 kcal/mol less stable. Since formation of ions **15d**, **15e**, and **15f** has to proceed via the rather unstable primary carbocation **15c** rearrangement of **15a** to one of these cations is rather unlikely even though one cannot fully exclude that strongly coordinating solvents might change somewhat the situation. Again, we have to emphasize that the following discussion is only valid for weakly coordinating solvents that only slightly change the structures of cations **15**−**18**.

The alkyl-substituted phenyl and anthryl ring in **15** (Figure 5) and **16** (Figure 6) represent templates that enforce internal solvation of a silylium cation by methyl groups. The methyl groups can rotate in such a position that steric repulsion is minimized while stabilizing SiH_2^+−methyl interactions are maximized. According to HF/6-31G(d) and B3LYP/6-31G(d) calculations, both **15a** and **16** are C_2-symmetrical (Figures 5 and 6) with the SiH_2 groups being essentially perpendicular to the aromatic rings (rotational angle for **15a**, 87.1, **16**, 81.0° (B3LYP/6-31G(d) values)). In **15a**, two methyl H atoms

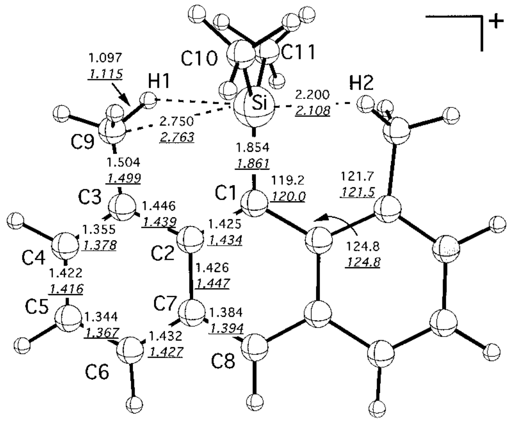


17, C_2

C9-Si = 1.871, *1.878*
C9-Si-C1 = 122.6, *122.7*
C2-C5-C6 = 111.8, *111.4*
H1-Si-H2 = 167.4, *168.0*

Si-C1-C2-C5 = -1.7, *-2.2*
C9-Si-C1-C2 = 83.5, *84.2*
C1-C2-C5-C6 = 29.0, *27.2*
C1-C2-C5-C7 = -92.2, *-93.7*
C1-C2-C5-C8 = 147.2, *145.5*
H1-C6-Si-C9 = 22.7, *19.0*
H1-C6-Si-C10 = -92.7, *-92.7*

Figure 7. HF/6-31G(d) (normal print) and B3LYP/6-31G(d) (underlined italics) geometrical parameters of cation **17**. Bond lengths are in Å, angles in deg.



18, C_2

Si-C10 = 1.869, *1.878*
C10-Si-C1 = 123.0, *123.1*
H1-Si-H2 = 175.5, *175.0*
C10-Si-C2-C3 = 84.3, *82.4*
Si-C1-C2-C3 = 0.0, *0.3*
C1-C2-C3-C9 = -4.9, *-6.0*
H1-C9-C3-C2 = 50.9, *47.3*
H1-C9-Si-C10 = 115.3, *110.8*
H1-C9-Si-C11 = 1.0 , *2.9*

Figure 8. HF/6-31G(d) (normal print) and B3LYP/6-31G(d) (underlined italics) geometrical parameters of cation **18**. Bond lengths are in Å, angles in deg.

are located at opposite sides of the Si-atom at a relatively short distance of 1.925 Å (B3LYP). The C−H bonds of these H-atoms are elongated by more than 0.04−1.13 Å (Figure 5). These geometrical data resemble distances calculated for **9** (1.984 and 1.12 Å; Figure 1) at the B3LYP/6-31G(d,p) level of theory, although interactions between Si^+ and H atom seem to be somewhat stronger in **15a**. Therefore, stabilization of the SiH_2^+ group in **15a** should be slightly larger than that calculated for complex **9** (26 kcal/mol, Table 1).

Through-space Si^+,H−C interactions can be explained as charge-induced dipole interactions between the Si^+ atom and the two interacting C−H bonds. However, interactions are not purely electrostatic since analysis of the electron density distribution reveals that there is some small build up of electron density between Si and H atoms although this is too weak to represent covalent interactions (Table 4). The positive charge at the SiH_2^+ group is considerably smaller (0.735; Table 3) compared to that calculated for **1b** (0.915). The calculated ^{29}Si shift for **15a** (25 ppm at IGLO//HF and 6.0 ppm at IGLO//B3LYP, Table 2) is upfield by 240−260 ppm compared to that of **1b** and, by this, suggests that silylium ion character is largely lost in **15a** similar to the situation in cation **9**.

Because the alkyl-substituted anthracene represents a more rigid template, Si^+,H−C interaction distances in **16** (1.983 Å at B3LYP, Figure 6) are longer than in **15a**. Less electron density is transferred in the region between Si and the closest H atom (Table 4) and, as a consequence, positive charge at SiH_2^+ (0.756, Table 3) is somewhat larger. In accord with this, the $\delta^{29}Si$ value is shifted downfield to 63.9 ppm.

Substitution of a silylium cation by two methyl groups increases its stability by 25 kcal/mol and, in addition, sterically hinders close contacts of a $-SiR_2^+$ group with bidentated functionalities. Therefore, the bidentated cations **17** and **18** should represent systems with very weak internal silylium cation coordination (Figures 7 and 8). This is confirmed by the calculated Si^+,H−C interaction distances of 1.981 Å (B3LYP, **17**) and 2.108 Å (B3LYP, **18**), which are longer than the corresponding distances in **15a** and **16**, respectively. The C−H bonds directed toward the $SiMe_2^+$ group (**17**, 1.115, **18**, 1.115 Å, B3LYP values) are less elongated and the charges at the Si^+ atom (**17**, 1.105, **18**, 1.083, Table 3) larger than the corresponding properties for the parent silylium cations **15a** and **16**.

The calculated ^{29}Si NMR chemical shifts of **17** (146.2 ppm) and **18** (186.7 ppm, Table 2) are about 120 ppm downfield shifted compared to those of **15a** and **16**. The $\delta^{29}Si$ value of **17** is just 175 ppm and that of **18** just 134 ppm smaller than that of the appropriate reference cation **2b** (321 ppm, Table 2). Hence, **17** and in particular **18** represent ions in which the silylium cation character is largely preserved. For comparison, coordination of an Ar atom to cation **5** would lead to an upfield shift of just 70 ppm [5] and that of a Cl or Br atom in YCH_3 to about 160 [6a] or 220 ppm.[5] Clearly, geometry, charge distributions, and chemical shifts suggest considerable silylium cation character for **18**, which accordingly is an attractive target for chemical synthesis.

5. Chemical Relevance of Investigations and Conclusions

Phenyl-substituted silylium cations with two $-CH_2Z$ substituents in the ortho positions (**I**) first synthesized by Corriu and co-workers[10] provide useful model systems to investigate solvent coordination of silylium cations R_2HSi^+ (phenyl is equivalent to H) in solution. By rotation of the side chains group Z can be positioned in such a way that Si^+−Z interactions lead to an internal solvation of the silylium cation, thus competing or even preventing external solvation of $-R_2Si^+$ in solution. Cations of type **I** have the advantage that, because of steric and electronic interactions with the side chains, the SiR_2^+ group is rotated into an orthogonal conformation with regard to the plane of the phenyl ring, thus electronically influenced by the latter just by inductive or weak hyperconjugative, but not conjugative, interactions. In this way, the silylium cation character of the SiR_2^+ group is retained as is documented by $\delta^{29}Si$

shift values almost identical with the parent R_2HSi^+ cations (Ph replaced by H).

By varying Z the situation in strongly and weakly coordinating solvents can be mimicked. Investigation of the silylium cations of type **I** with Z = NR_2 (cations **12**, **13**, and **14**) reveals that their properties closely resemble those of the strongly coordinated silylium cation–solvent complexes $R'_2HSi(NR_3)_2^+$. For example, cation **12** (Z = NH_2, $SiR_2^+ = SiH_2^+$) contains pentacoordinated Si as is reflected by covalent Si–N bonds with bond lengths of 2.09 Å ($R'_3Si(NR_3)_2^+$: 2.07 Å), a complexation energy close to 100 kcal/mol, and an upfield shift of δ^{29}Si by more than 340 ppm. Similar results are obtained for cation **13** (Z = NMe_2, $SiR_2^+ = SiH_2^+$) and confirmed by the available experimental results such as the δ^{29}Si value of −46 ppm (calculated −44 ppm).

In the case of cation **14** (Z = NMe_2, $SiR_2^+ = SiMe_2^+$), calculations suggest pentacoordination at Si (equilibrium geometry **14b**) in the presence of weakly coordinating counterions. However, strongly coordinating counterions X^- seem to be able to replace one of the amino groups, thus leading to **14c**-X (Scheme 1). The degenerate exchange process of the amino groups observed by Willcott and co-workers[34] should depend on the ring opening process **14b** → **14c**, for which we calculate an energy increase of 10.4 kcal/mol in line with experimental observations.

Weakly coordinating solvents such as alkanes can be mimicked by using for type **I** cations the side chain $-C(CH_3)_3$ (**15**, $SiR_2^+ = SiH_2^+$; **17**, $SiR_2^+ = SiMe_2^+$). In **15**, there are two Si^+,H–C interactions at 1.93 Å where the CH bonds are elongated to 1.13 Å similar as would also occur in a complex $H_3Si(CH_4)_2^+$ (**9b**, Figure 1), which is stabilized by 26 kcal/mol. The calculated δ^{29}Si value of 6 ppm is upfield by 260 ppm, thus indicating that even a weakly nucleophilic solvent such as methane does not guarantee preservation of the silylium cation character in solution.

If the Si^+ center is internally stabilized by two methyl groups, interactions with an alkane solvent are considerably reduced. For example, in cation **17**, the Si^+,H–C interaction distances are increased to 1.98 Å and the calculated δ^{29}Si value of 146 ppm is just 174 ppm upfield from the corresponding reference value calculated for cation **2b**. These values indicate considerable conservation of silylium cation character.

Even more silylium cation character is retained when a 1,8-dimethyl-substituted anthryl ring rather than the phenyl ring is used as a template for simulating solvent coordination of silylium cations in solution. In cations **16** and **18** (**16**, $SiR_2^+ = SiH_2^+$; **18**, $SiR_2^+ = SiMe_2^+$), R_2-Si^+ interactions with the two methyl groups in the peri positions are weak as is indicated by Si^+,H–C interaction distances of 1.98 and 2.11 Å, a small buildup of electron density in the interaction region that is typical of just electrostatic interactions, and δ^{29}Si values of 64 and 187 ppm, respectively. In the latter case, the δ^{29}Si value is just 134 ppm upfield from the reference value. Hence, cation **18** represents an internally solvated silylium cation, for which silylium cation character should be preserved to an extent not observed for any other silylium cation in solution.

In line with the pioneering synthetic work of Corriu and co-workers,[10] we suggest that anthryl-substituted silylium cations are synthesized and carry in the 1,8-position methyl groups for internal solvation of the silylium cation center. If these compounds are generated in weakly nucleophilic solvents in the presence of a weakly coordinating counterion, it should be possible to study the degree of methyl coordination with the help of ^{29}Si NMR spectroscopy and assistance by ab initio calculations within the NMR/ab initio/IGLO approach[35] that has been successfully used in several cases to determine geometries of solvated cations.[6] Use of stronger nucleophilic solvents will lead to external solvation of **18** by forcing the $-SiR_2^+$ group in the plane of the anthryl ring. This will be possible if the gain in complexation energy and conjugative stabilization (ca. 15 kcal/mol) is larger than the destabilizing steric interaction energy.

From our investigation we conclude that it will be impossible to generate nearly free silylium cations in solution unless the $-SiR_2^+$ group is placed in a cage of sterically blocking groups that prevent interactions of the Si^+ center with solvent or counterion molecules. Without sterical shielding of Si^+, even a weakly nucleophilic solvent such as an alkane will not prevent the formation of solvated R_3Si^+ cations that have largely lost their silylium cation character. Internal stabilization of the R_3Si^+ cation by hyperconjugative and inductive effects supports steric blocking of the Si^+ center. However, conjugative stabilization of Si^+ by π-donor substituents will also change the nature of the silylium cation to an extent that the question of the existence of R_3Si^+ cations in solution is no longer relevant.

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Supporting Information Available: A listing of Cartesian coordinates and absolute energies of all optimized geometries calculated in this work (16 pages). Ordering information is given on any current masthead page.

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(35) For a description of the NMR/ab initio/IGLO method see, e.g.: Cremer, D.; Olsson, L.; Reichel, F.; Kraka, E. *Isr. J. Chem.* **1993**, *33*, 369.