

# Evidence for the existence of silylium cations in condensed phases

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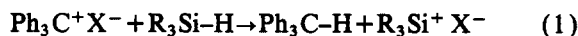
Ab initio geometry optimizations,  $^{29}\text{Si}$  NMR chemical shift calculations, and bond density investigations refute recent claims about the existence of silylium cations  $\text{R}_3\text{Si}^+$  ( $\text{R}=\text{Me}, \text{Et}$ ) in aromatic solvents. The alleged silylium cations react in these solutions by an electrophilic attack at the aromatic solvent molecule yielding a Wheland  $\sigma$  complex. However, ab initio calculations also indicate that it should be possible to generate fairly free silylium cations in aromatic solvents provided an electrophilic attack is sterically and/or electronically hindered.

## 1. Introduction

There is much dispute on the question whether triorganosilylium cations<sup>#1</sup>,  $\text{R}_3\text{Si}^+$ , can be generated in solution and whether some of the carbo cation chemistry can also be found for silicon [2–9]. Two of the protagonists of this dispute are Lambert and Olah. Lambert and co-workers [3–6] have presented results of conductance measurements, molecular weight determinations, and NMR investigations that can be interpreted as evidence for the formation of silylium ions in solution. However, Olah and co-workers have argued that Lambert's results may be best accounted for by assuming hydrolysis of  $\text{R}_3\text{SiX}$  by residual water in the solvents used [7,8]. Comparing calculated  $^{29}\text{Si}$ ,  $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts for the silylium cation,  $\text{SiH}_3^+$  (1), and the trimethylsilylium cation,  $\text{Si}(\text{CH}_3)_3^+$  (2), with observed chemical shifts, Olah and co-workers [8] concluded that no long-lived silylium ions exist in solution. These arguments were later criticized by Lambert, who, e.g., pointed out that water was present in the solvents used at a molarity one order of magnitude below that of the observed silylium cations [4].

In a recent publication, Lambert and Zhang [5]

have presented a promising new procedure for isolating silylium cations via



by using the weakly coordinating anion tetrakis(pentafluorophenyl)borate,  $(\text{C}_6\text{F}_5)_4\text{B}^-$  (TPFPB<sup>-</sup>), in aromatic solvents such as benzene. From measured  $^{29}\text{Si}$  NMR chemical shifts, they concluded that they had obtained  $\text{R}_3\text{Si}^+$  ( $\text{R}=\text{Me}, \text{Et}, \text{Pr}, \text{Me}_3\text{Si}$ ) ions with reduced electrophilic interactions with solvent or anion and, therefore, with a nearly free cationic structure. Lambert, Zhang, Stern, and Huffman (LZSH) [6] added further support to the postulated existence of silylium cations by investigating the crystal structure of  $\text{Et}_3\text{Si}^+(\text{C}_6\text{F}_5)_4\text{B}^-$  ( $3^+\text{TPFPB}^-$ ). The unit cell of the crystal contains four molecules of  $3^+\text{TPFPB}^-$  and eight molecules of the aromatic solvent toluene, which was used for recrystallizing  $3^+\text{TPFPB}^-$ . Each molecule of  $3^+\text{TPFPB}^-$  has one toluene molecule associated with the closest contact between Si and a toluene C atom being 2.18 Å [6]. The geometry at the Si atom is not planar as expected for a silylium cation but pyramidal, while the toluene ring is essentially planar and does not indicate any stronger interactions with 3 [6].

Lambert and co-workers interpreted the results of their structural and NMR spectroscopic investigation of  $3^+\text{TPFPB}^-$  as clear evidence for the exist-

<sup>#1</sup> We use the term silylium cation for  $\text{R}_3\text{Si}^+$  rather than silicenium ion, silylenium ion or silyl cation thus following recent IUPAC recommendations (see ref. [1]).

tence of silylium cation **3**. They based their conclusion on five arguments.

(1) Because of the low coordinating ability of the TPFPB anion and steric crowding around the negatively charged B atom, cation and anion are well separated in the crystal with the closest contact between Si and an atom of the anion (Si, F=4.04 Å) being significantly larger than the sum of the corresponding van der Waals radii (3.0 Å) [6].

(2) The closest Si, C contact distance between **3** and toluene is outside the range of normal SiC bond distances and indicates that, if covalent Si, C interactions are present at all, they are weak.

(3) The toluene molecule is essentially unperturbed, again indicating no or only small interactions between **3** and the solvent molecule.

(4) The pyramidalization at the Si atom is caused by steric effects, long-range orbital interactions and/or crystal-packing forces. It shows that silylium cations can easily be distorted from their planar equilibrium geometry.

(5) The measured  $\delta^{29}\text{Si}$  value of 94.3 ppm for  $3^+\text{TPFPB}^-$  results from enforced pyramidalization, but is still well above the corresponding value of  $\text{Et}_3\text{SiH}$  ( $\delta^{29}\text{Si}=0.2$ ) thus indicating considerable deshielding of the Si nucleus.

We have recently investigated a number of potential silylium cations in various environments by theoretical means [10] and have come to the conclusion that the probability of observing free silylium cations in condensed phases is small in the case of normal solvents such as sulfolane, etc., but cannot be excluded for aromatic solvents. From our experience, we claim that a SiC distance of 2.18 Å between **3** and toluene is not outside but well inside the range of covalent SiC bond distances and, accordingly, indicates the existence of a Wheland  $\sigma$  complex  $\text{Et}_3\text{SiC}_6\text{H}_5\text{CH}_3^+$ . To prove this description, we have carried out ab initio calculations for molecules 1–13 shown in fig. 1, namely silylium cations 1–3, reference compounds 4–9, and silylium–benzene interaction complexes 10–13. Calculated structures, stabilities, magnetic properties, and electron density distributions for these molecules reveal that almost all arguments given by LZSH to prove the silylium cation character of  $3^+\text{TPFPB}^-$  can be refuted. *The compound described by these authors is not the sily-*

*lium cation 3 but a covalently bonded complex between 3 and toluene.*

However, our ab initio investigation also reveals that the preparative method introduced by Lambert and Zhang [5] has a good chance of leading to nearly free silylium cations in condensed phases. We make suggestions how experiments have to be modified to achieve this goal and will prove that *free silylium cations can exist in condensed phases.*

## 2. Computational methods

Previous investigations [8,10,12] have shown that the geometries of silicon compounds are well described by Hartree–Fock (HF) calculations performed with an augmented basis set such as the 6-31G(d) basis [13]. Accordingly, we have carried out HF/6-31G(d) geometry optimizations for all compounds shown in fig. 1. For each of these molecules, we have calculated IGLO (individual gauge for localized orbitals) [14] NMR chemical shifts employing the [7s6p2d/5s4p1d/3s1p] basis set recommended by Kutzelnigg and Schindler [15] for  $\delta^{29}\text{Si}$  calculations.

In addition, we have analyzed the electron density distribution  $\rho(\mathbf{r})$  and the energy density distribution  $H(\mathbf{r})$  using the virial partitioning approach of Bader and co-workers [16]. In particular, we have investigated atom, atom interactions on the basis of the criteria given by Cremer and Kraka [17] to distinguish covalent from noncovalent (ionic) bonding. According to these authors, covalent bonding between atoms A and B requires the existence of a path of maximum electron density (MED) connecting the nuclei of A and B (necessary condition) as well as a negative (stabilizing) energy density at the saddle point  $r_b$  (bond critical point) of the MED path (sufficient condition). Since the existence of a MED path implies the existence of a bond critical point of rank 3 and signature  $-1$  ((3,  $-1$ ) point), covalent bonding is given if  $H(r_b) < 0$  for the (3,  $-1$ ) point  $r_b$  of  $\rho(\mathbf{r})$  between atoms A and B. The electron density analysis has helped to characterize bonding in many molecules with classical and nonclassical bonding situations [18]. In particular, it has proven useful to describe bent bonds and to distinguish three-mem-

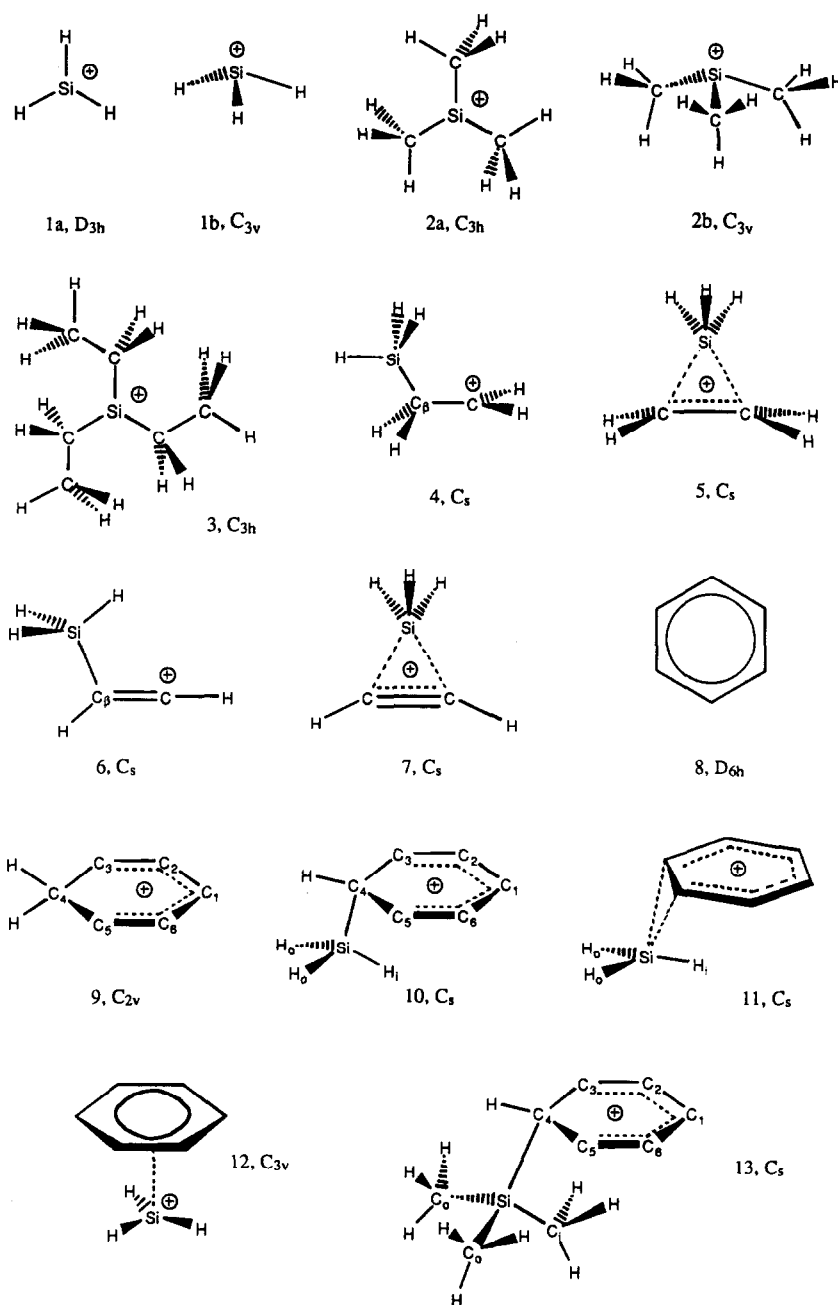


Fig. 1. Structure and equilibrium conformation of compounds 1-13.

bered rings from  $\pi$  complexes [19], which is of relevance for the present investigation.

Calculations have been performed on a CRAY XMP-416 using the COLOGNE ab initio package

[20], which includes an implementation of the IGLO method of Kutzelnigg and Schindler [14] and the bond analysis of Cremer and Kraka [17,18].

### 3. Results and discussion

Calculated energies are listed in table 1 while fig. 2 gives HF/6-31G(d) geometries of the target compounds **10** and **13**. Table 2 summarizes IGLO/[7s6p2d/5s4p1d/3s1p] NMR chemical shifts and table 3 contains relevant data of the bond density analysis.

Before we discuss the computational results for the target system **10**–**13**, we will establish some typical molecular features of silylium cations in the gas phase. Cations **1** (**1a**), **2** (**2a**), and **3** all possess a planar equilibrium geometry at the Si atom. Alkyl substitution of **1** leads to stabilization of the cation, which in the case of **2** is 36 kcal/mol (table 1). This is about half as large as the corresponding value for  $\text{CH}_3^+$  (65 kcal/mol, HF/6-31G(d) [21]; 85 kcal/mol, exp. estimate [22]). Alkyl substitution also leads to a downfield shift of  $\delta^{29}\text{Si}$  by 86 (**2**) and 107 ppm (**3**), which suggests that typical  $\delta^{29}\text{Si}$  values for silylium ions in the gas phase are at  $380 \pm 20$  ppm. Similar predictions have been made by Kutzelnigg and Schindler [15] and by Olah and co-workers

[7,8] who also investigated silylium cations with the IGLO method.

LZSH predict that steric or environmental effects can force silylium cations to adopt pyramidal geometries at the Si atom (argument (4)) [6]. Since this claim is essential for the rationalization of the crystal structure of  $3^+\text{TPFPB}^-$ , we have carried out HF/6-31G(d) calculations for the pyramidal geometries **1b** and **2b** (fig. 1) with tetrahedral bond angles at the Si atom. According to these calculations, **1b** and **2b** are destabilized in the gas phase by 24 and 21 kcal/mol (table 1), respectively, where even a relatively small distortion of the bond angles at Si already leads to a considerable energy increase. This is also true in noncoordinating solvents [10] and, therefore, we conclude, in contradiction to arguments given by LZSH [6], that *it is difficult to distort silylium cations from planarity, even in the presence of environmental effects*.

In this connection, we also have to reject another claim by LZSH, namely that pyramidalization at the Si atom in  $\text{R}_3\text{Si}^+$  leads to a strong highfield shift of  $\delta^{29}\text{Si}$  from about 380 ppm to 90 ppm (argument (5), see above) [6]. According to IGLO/[7s6p2d/

Table 1  
Calculated absolute and relative energies <sup>a)</sup>

Molecule	Sym.	Absolute energies I	Dissociation energies		Relative energies		
			I	II	I	II	
$\text{SiH}_3^+$	<b>1a</b>	$D_{3h}$	-290.32891			0	0
	<b>1b</b>	$C_{3v}$				23.9	23.7
$\text{Si}(\text{CH}_3)^+$	<b>2a</b>	$C_{3h}$	-407.52782			0	0
	<b>2b</b>	$C_{3v}$				21.1	21.1
$\text{Si}(\text{CH}_2\text{CH}_3)^+$	<b>3</b>	$C_{3h}$	-524.62670				
$\text{SiH}_3\text{CH}_2\text{CH}_2^+$	<b>4</b>	$C_s$	-368.42153	38.2	36.0	0	0
	<b>5</b>	$C_s$	-368.42755	42.0	38.9	-3.8	-2.9
$\text{SiH}_3\text{CHCH}^+$	<b>6</b>	$C_s$	-367.20198	34.7	30.8	0	0
	<b>7</b>	$C_{2v}$	-367.20591	37.1	33.0	-2.4	-2.2
$\text{SiH}_3\text{C}_6\text{H}_6^+$	<b>10</b>	$C_s$	-521.11145	49.8	46.4	0	0
	<b>11</b> <sup>b)</sup>	$C_s$	-521.10231	44.1	40.4	5.7	6.0
	<b>12</b> <sup>c)</sup>	$C_{3v}$	-521.06560	21.1	18.2	28.7	28.2
$\text{Si}(\text{CH}_3)_3\text{C}_6\text{H}_6^+$	<b>13</b>	$C_s$	-638.26763	23.0			

<sup>a)</sup> Absolute energies in hartree, relative energies in kcal/mol. Basis I corresponds to 6-31G(d) and basis II to the [5s4p1d/3s1p] basis of ref. [15]. Dissociation energies are given for the reaction:  $\text{R}_3\text{SiX}^+ \rightarrow \text{R}_3\text{Si}^+ + \text{X}$ . Relative energies unequal to zero are always given with regard to the energy of the molecule in the previous row.

<sup>b)</sup> The Hf/6-31G(d) optimized geometry has one imaginary frequency.

<sup>c)</sup> The Hf/6-31G(d) optimized geometry has two imaginary frequencies.

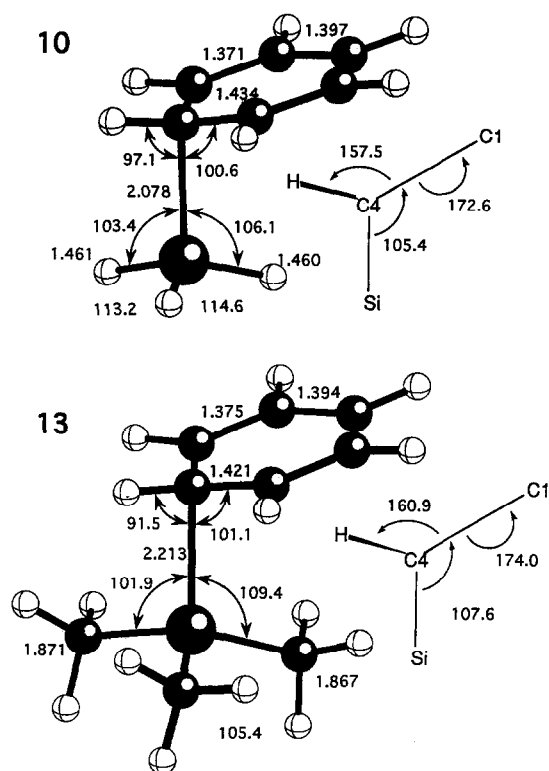


Fig. 2. HF/6-31G(d) geometry of **10** and **13**. Distances are given in Å, angles in deg.

5s4p1d/3s1p] calculations, pyramidalization of silylium cations causes a downfield shift of as much as 90 (**1**) and 40 (**2**) ppm (table 2) indicating strong deshielding rather than shielding of the Si nucleus. Similar shift changes are calculated for  $R_3Si^+$  ions in noncoordinating solvents<sup>#2</sup>, which means that for both gas phase and condensed phases pyramidal silylium cations possess a more positively charged Si atom. If pyramidalization is enforced, silylium cations will become even stronger electrophiles that can coordinate very weak nucleophiles. We conclude that *the pyramidal geometry and the  $\delta^{29}Si$  value found for the alleged cation **3** [5,6] are indicative of tetra-coordinated Si and a complete loss of the silylium ion character of  $3^+ TPFPB^-$ .*

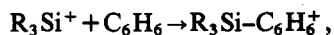
In line with this conclusion are the following observations.

<sup>#2</sup> For noncoordinating solvents with large dielectricity constants  $\epsilon$ , we find somewhat smaller downfield shifts ( $\epsilon=80$ ,  $\Delta\delta^{29}Si=78$  (**1**), 33 ppm (**2**), see ref. [10]).

(1) According to the reported crystal structure of  $3^+ TPFPB^-$  [6], there is a potential bonding partner for **3** in the form of a closely located toluene solvent molecule. Although the closest Si, C contact between **3** and toluene (2.18 Å [6]) is about 0.3 Å longer than a typical SiC bond distance of 1.88 Å found for alkylsilanes [10,23], it reminds one of SiC bond lengths of  $\beta$ -silyl substituted carbo cations such as **4** and **6** (fig. 1). Actually, these cations are stable in their nonclassical silyl-bridged forms **5** and **7** rather than in the classical forms **4** and **6** as has been shown by various authors [24]<sup>#3</sup> and is confirmed by our HF/6-31G(d) calculations. The classical structures **4** and **6** can only be enforced by freezing the CCSi angle at values of 109° and 120°, respectively. When this is done, bond lengths of 2.10 (**4**) and 2.03 Å (**6**) result while the nonclassical forms **5** and **7** possess SiC distances of 2.34 and 2.30 Å, respectively. Considering that alkyl substitution leads to further lengthening of the SiC bonds [10,23], then *the SiC contact distance of 2.18 Å observed by LZSH [6] should belong to a covalent SiC bond typical of  $\beta$ -silyl carbo cations.*

(2) The  $\delta^{29}Si$  values for the alleged  $R_3Si^+$  cations (80–110 ppm) reported by Lambert and Zhang [5] are by no means exceptional if one compares them with  $^{29}Si$  shift values calculated for cations **4**–**7** (table 2), which are –30 (**4**), –54 (**5**), –52 (**6**), and –32 ppm (**7**). Considering that replacement of the three H atoms of a  $SiH_3$  group by alkyl leads to downfield shifts of 90–110 ppm [10] (compare, e.g., with cations **1**, **2**, and **3**, table 2), then typical  $\delta^{29}Si$  shift values for  $\beta$ -silyl substituted carbo cations are in the region 40–80 ppm, close to the values found by Lambert and Zhang, but very different from the  $\delta^{29}Si$  values of silylium cations.

The only  $\beta$ -silyl substituted carbo cation structure, which could have been formed in the experiments of LZSH [6] is that of a Wheland  $\sigma$  complex as the result of an electrophilic attack of an intermediate silylium cation  $R_3Si^+$  with an aromatic solvent molecule such as benzene (**8**) or toluene,



$$R = H \text{ (10)}, CH_3 \text{ (13)}. \quad (2)$$

<sup>#3</sup> For an experimental verification of  $\beta$ -silyl substituted carbo cations, see ref. [25].

Table 2  
IGLO/[7s6p2d/5s4p1d/3s1p] NMR chemical shifts <sup>a)</sup>

Molecule	Sym.	Chemical shifts					
		$\delta^{29}\text{Si}$	$\delta^{13}\text{C}$				
$\text{SiH}_3^+$	1a	$D_{3h}$	270.2				
	1b	$C_{3v}$	363.1				
$\text{Si}(\text{CH}_3)_3^+$	2a	$C_{3h}$	355.9	9.0			
	2b	$C_{3v}$	397.1	23.5			
$\text{Si}(\text{CH}_2\text{CH}_3)_3^+$	3	$C_s$	376.9	16.5(C $\alpha$ )	7.5(C $\beta$ )		
$\text{SiH}_3\text{CH}_2\text{CH}_2^+$	4	$C_s$	-29.8	80.9(C $\alpha$ )	262.8(C $^+$ )		
	5	$C_s$	-54.1	139.5			
$\text{SiH}_3\text{CHCH}^+$	6	$C_s$	-51.7	63.6(C $\alpha$ )	288.3(C $^+$ )		
	7	$C_{2v}$	-31.9	89.1			
$\text{C}_6\text{H}_6$	8	$D_{6h}$		135.8			
$\text{C}_6\text{H}_7^+$	9	$C_{2v}$		205.2(C1)	134.2(C2)	199.9(C3)	43.8(C4)
$\text{SiH}_3\text{C}_6\text{H}_6^+$	10	$C_s$	-23.8	176.7(C1)	136.5(C2)	180.8(C3)	77.3(C4)
	11	$C_s$	10.5	152.1(C $\gamma$ )	145.0(C $\beta$ )	126.3(C $\alpha$ )	
$\text{Si}(\text{CH}_3)_3\text{C}_6\text{H}_6^+$	12	$C_{3v}$	201.9	138.3			
	13	$C_s$	83.1 (83.6) <sup>b)</sup>	166.2(C1)	137.1(C2)	163.1(C3)	91.7(C4) -4.4(Me $_t$ ) 4.5(Me $_o$ )

<sup>a)</sup> All shifts in ppm relative to TMS. For the numbering of atoms, see fig. 1. The IGLO calculations for 13 have been done with the 6-31G(d) basis set.

<sup>b)</sup> Experimental  $\delta^{29}\text{Si}$  value from ref. [4].

Table 3  
Bond density analysis <sup>a)</sup>

Molecule	Sym.	$R(\text{SiC})$	$r_b$	$\rho(r_b)$	$n$	$H(r_b)$	Character	Structure	
$\text{SiH}_3\text{CH}_2\text{CH}_2^+$	4	$C_s$	2.096	(3, -1)	0.44	0.49	-0.20	covalent	classical
	5	$C_s$	2.336					no bond	
			Si(CC)	(3, -1)	0.38	0.44	-0.20	covalent	$\pi$ complex
$\text{SiH}_3\text{CHCH}^+$	6	$C_s$	2.029	(3, -1)	0.49	0.54	-0.21	covalent	classical
	7	$C_{2v}$	2.295					no bond	
			Si(CC)	(3, -1)	0.36	0.42	-0.18	covalent	$\pi$ complex
$\text{SiH}_3\text{C}_6\text{H}_6^+$	10	$C_s$	2.078	(3, -1)	0.49	0.54	-0.24	covalent	classical
	11	$C_s$	2.354					no bond <sup>b)</sup>	
			Si(CC)	(3, -1)	0.34	0.41	-0.15	covalent	$\pi$ complex
12	$C_{3v}$	3.084	(3, +1)	0.07	0.0	0.0	no bond	electrostatic complex	
$\text{Si}(\text{CH}_3)_3\text{C}_6\text{H}_6^+$	13	$C_s$	2.213	(3, -1)	0.37	0.43	-0.17	covalent	classical

<sup>a)</sup> Distance in Å,  $\rho(r_b)$  in electron Å<sup>-3</sup>,  $H(r_b)$  in hartree Å<sup>-3</sup>. Each critical point  $r_b$  is characterized by (rank, signature). The character of the bond is given according to the criteria of Cremer and Kraka [17]. The bond order  $n$  has been calculated with the formula  $n = \exp\{A[\rho(r_b) - B]\}$  [17]. The structure denotes the topology of the bonds, namely between Si and C atom (classical) or in form of a T structure ( $\pi$  complex).

<sup>b)</sup> No bond critical point has been found, but there is a small amount of charge transfer (0.190  $e$ ), because of which 12 does not contain a free silylium cation.

To prove this rationalization of the observations made by Lambert and co-workers [5,6] we have calculated complexes 10–13.

Reaction of 1 with 8 may lead to the classical carbo cation 10 or the two nonclassical cations 11 and 12, which according to the relative stabilities of 4 and 5 (6 and 7) (table 1) should be more stable than 10. However, our calculations reveal that the  $\sigma$  complex 10 should be more stable by 6 and 28 kcal/mol (table 1) than the nonclassical  $\pi$  complexes 11 and 12, which possess one and two imaginary frequencies, respectively, at HF/6-31G(d). The HF/6-31G(d) equilibrium geometry of 10 shown in fig. 2 reveals a number of interesting structural features, which are indicative of a peculiar electronic structure of 10.

(a) Pyramidalization at the Si atom is slightly reduced ( $4^\circ$ – $7^\circ$ , fig. 2) compared to that of a normal  $\text{SiH}_3$  group. The C4SiH angle for the H atom sitting under the benzene ring is widened by  $3^\circ$  probably because of steric interactions.

(b) As predicted, the SiC bond is with 2.078 Å in the range of bond lengths typical of  $\beta$ -silyl substituted carbo cations.

(c) The silyl group forms an angle of  $105.4^\circ$  with the benzene ring, i.e. the  $\text{SiH}_3$  group sits on the  $\pi$ -orbital of ring atom C4.

(d) The benzene ring is only slightly distorted from planarity. The largest CCCC dihedral angle is  $8^\circ$  (corresponding to a folding angle of  $172.6^\circ$  between the planes C6C4C3 and C5C6C3C2, fig. 2) and the largest HCCH angle  $25.4^\circ$  (corresponding to HC4Si angle of  $97.1^\circ$  and a HC4C1 angle of  $157.5^\circ$ , fig. 2). In line with this is the fact that bond alternation in the ring caused by the  $\text{SiH}_3$  substituent is relatively small (1.434, 1.371, 1.397 Å, fig. 2).

All these features suggest a strong hyperconjugative effect of the SiC bond with the  $\pi$  system of the benzene ring, which is responsible for a complexation (dissociation) energy of almost 50 kcal/mol (table 1) measured by the (negative) energy of reaction (2). Similarly high hyperconjugative effects have been found for other  $\beta$ -silyl substituted cations [24,25] (for 4 and 6, dissociation energies are 38 and 35 kcal/mol, table 1) and have to do with the fact that the  $\sigma(\text{SiC})$  orbital is higher in energy than, for example, a  $\sigma(\text{CC})$  orbital and, therefore, can better interact with the empty  $p\pi$  orbital of a carbo cation. In 10, the hyperconjugative effect is enhanced

by the close vicinity of two rather than one positively charged  $\pi$  orbital (C3 and C5) and the admixture of  $3p\pi(\text{Si})$ -orbital character (reduction of pyramidal character at Si) to the SiC bonding orbital. In this way, the C4C3 and C4C5 bonds attain partial  $\pi$  character and become shorter while the SiC bond is weakened as is reflected by the bond lengths and the dissociation energy of 50 kcal/mol, which is more than 30 kcal/mol smaller than a normal SiC dissociation energy [26].

IGLO/[7s6p2d/5s4p1d/3s1p] NMR chemical shifts listed in table 2 confirm this description. The  $\delta^{29}\text{Si}$  shift value ( $-24$  ppm) and the  $\delta^{13}\text{C}$  shift of C4 (77 ppm) of 10 are similar to the corresponding values of 4 ( $-30$ , 81 ppm, table 2). The alternation of  $\delta^{13}\text{C}$  values in the ring is not as large as calculated for protonated benzene (9) also included in table 2.

It is surprising that the nonclassical  $\pi$  complex 11 is less stable than 10. This, however, becomes clear when realizing that due to the topology of the  $\sigma$  complex 10 Si interacts with three rather than one C atom. Beside the bonding interaction with C4, there are hyperconjugative interactions with atoms C3 and C5, which are just 2.73 Å away from Si. In 11, Si can only interact with two C atoms at a distance of 2.354 Å leading to an interaction energy of just 44 kcal/mol (table 1). Insofar, it is somewhat misleading to consider 10 as a classical  $\sigma$  complex. Interactions in molecule 10 are better considered as extension of nonclassical SiC bonding (compare with 5 and 7, fig. 1) to two dimensions and, therefore should be called a nonclassical C-centered  $\pi$  complex as opposed to the nonclassical double bond-centered and ring-centered  $\pi$  complexes 11 and 12. Common to these complexes is the interaction of the Si atom with the  $\pi$  system of the aromatic ring, which will be of relevance for the discussion in section 4.

C-centered and double-bond-centered  $\pi$  complexes can easily be distinguished by their NMR chemical shifts. The  $\delta^{29}\text{Si}$  value ( $-24$  ppm for 10, table 2) is shifted 34 ppm downfield and the  $\delta^{13}\text{C}$  values of the aromatic ring alternate in 11 much less than in 10. Both findings are in line with reduced interactions between 1 and 8 and, accordingly, a smaller perturbation of the aromatic ring.

Because of the lower stability of both 11 and 12 as compared to that of 10, we have calculated for  $\text{SiMe}_3\text{C}_6\text{H}_7^+$  just the analogue to 10, namely 13 (fig.

1). The HF/6-31G(d) geometry of **13** (fig. 2) is similar to that of **10**. Again, the benzene ring is almost planar exhibiting only moderate bond alternation (1.421, 1.375, 1.394 Å, fig. 2), which compares well with the bond alternation found by LZSH for  $\text{SiEt}_3\text{C}_6\text{H}_5\text{CH}_3^+$  (1.40, 1.37, 1.38 Å) [6]. Since the SiC bond is almost perpendicular to the ring plane ( $\text{SiC4C1} = 107.6^\circ$ ), **13** has to be described similar to **10** as the C-centered  $\pi$  complex that is characterized by hyperconjugative interactions between positively charged  $\pi$  system and SiC bond. However, the HF/6-31G(d) dissociation energy of **13** is almost 30 kcal/mol smaller than that of **10**. This is confirmed by mass spectrometric investigations of aromatic silylation reactions in the gas phase, which predict for **13** a dissociation energy of  $23.9 \pm 0.4$  kcal/mol [27] in good agreement with the calculated value of 23.0 kcal/mol (table 1). The lowering of the dissociation energy results from enhanced hyperconjugative interactions caused by an increase of the energy of  $\sigma(\text{SiC})$  ( $\text{CH}_3$  is more electronegative than H and, therefore, Si becomes more positive). As a consequence, the SiC bond length (2.213 Å, fig. 2) is longer than in **10** but close to the value (2.18 Å) observed by LZSH [6]. The calculated CSiC angles (fig. 2) indicate a pyramidalization at the Si atom similar to that found for  $\text{SiEt}_3\text{C}_6\text{H}_5\text{CH}_3^+$  [6]. All these features suggest that **13** is a reasonable model compound for  $\text{SiEt}_3\text{C}_6\text{H}_5\text{CH}_3^+$  and that conclusions with regard to its electronic structure can be generalized to the class of  $\text{R}_3\text{SiArH}^+$  TFPFB<sup>-</sup> compounds investigated by Lambert and co-workers [5,6].

A convincing proof that the crystal structure of  $\text{SiEt}_3\text{C}_6\text{H}_5\text{CH}_3^+$  can indeed be modelled by cation **13** is provided by the calculated IGLO NMR chemical shifts (table 2). The IGLO  $\delta^{29}\text{Si}$  value for **13** is 83.1 ppm, which is almost identical with the value found by Lambert and Zhang for the alleged cation **2** in benzene ( $\delta^{29}\text{Si} = 83.6$  ppm; 84.8 ppm in the solid state) [5]. Since IGLO NMR chemical shifts are very sensitive to calculated geometries [28,29] they can be used for an ab initio/IGLO/NMR determination of the geometry. In this sense, the identity of IGLO and experimental  $\delta^{29}\text{Si}$  values is (a) a striking verification of a C-centered  $\pi$  complex between **2** and an aromatic solvent molecule and (b) equivalent to an X-ray determination of the geometry of **13**. We quote in this connection from a recent paper by Onak

and co-workers [30]: "Structural assignments based on the ab initio/IGLO/NMR method are quickly approaching a confidence level that rivals modern day X-ray diffraction determinations of molecular structures."

Since the observed  $\delta^{29}\text{Si}$  value for  $\text{SiEt}_3\text{C}_6\text{H}_5\text{CH}_3^+$  TFPFB<sup>-</sup> (94.3 ppm [5]) is just 10 ppm downfield from that of **13** and since our calculations suggest an IGLO value of 94 ppm for this compound<sup>44</sup> we conclude that all relevant geometrical features calculated for **13** are also valid for  $\text{SiEt}_3\text{C}_6\text{H}_5\text{CH}_3^+$ . The alleged silylium cation **3** is best described as a covalently bonded complex between **3** and toluene, in which the silylium cation character is totally lost. This is fully confirmed by the calculated charge distributions. In **10** and **13**, Si has within 0.01 electron ( $e$ ) the same positive charge as in  $\text{SiH}_4$  or  $\text{Si}(\text{CH}_3)_4$ . Compared to the latter compounds, the ionic character of **10** and **13** is reflected by reduction of negative charges at H and  $\text{CH}_3$  and a transfer of positive charge to the benzene ring (**10** 0.47  $e$ ; **13** 0.36  $e$ ). When going from phenylsilane,  $\text{H}_3\text{SiC}_6\text{H}_6$ , to **10** the silyl group increases its positive charge by 0.33  $e$  while the benzene ring becomes more positive by 0.67  $e$ . This clearly suggests that the silylium cation character has been lost in **10**, **13**, and  $3\text{-C}_6\text{H}_5\text{CH}_3$ .

Although the calculated geometries and SiC dissociation energies suggest that in the case of **10** and **13** Si is covalently bonded to C4, this description has to be verified with the help of the electron density analysis in the SiC bonding region. For this purpose, we have also analyzed the electron density of silyl substituted carbo cations 4–7. We find covalent SiC bonds in the case of the classical ions **4** and **6** as documented by the existence of a (3, -1) bond critical point  $r_b$  between atoms Si and C, a negative (stabilizing) energy density  $H(r_b)$  and bond orders  $n$  of about 0.5 (table 3). However, the nonclassical cations **5** and **7**, although covalently bonded, do not possess SiC bonds. Instead, the Si atom is directly bonded to the midpoint of the CC bond, which is typical of the T structure of a  $\pi$  complex [19].

Covalent SiC bonds are also missing in complexes

<sup>44</sup> Replacement of Me by Et in **13** will lead to a downfield shift of 21 ppm for  $\delta^{29}\text{Si}$  (table 2, 2 and 3) while replacement of toluene by benzene will cause an upfield shift of 10 ppm thus yielding  $\delta^{29}\text{Si} = 94$  ppm as an estimate for  $\text{SiEt}_3\text{C}_6\text{H}_5\text{CH}_3^+$  [10].



**11 and 12.** The ring-centered complex **12** is predominantly stabilized by electrostatic interactions between Si atom and ring atoms as is revealed by a relatively low charge transfer from benzene ring to  $\text{SiMe}_3^+$  and the low  $\rho$  values calculated for the SiC internuclear region (table 3). In complex **11**, however, Si is covalently bonded to the midpoint of a CC ring bond, which again indicates the T structure of a  $\pi$  complex. The only covalent SiC bonds with similar density features and bond orders  $n$  as those calculated for cations **4** and **6** are detected for the C-centered  $\pi$  complexes **10** and **13** (table 3). Clearly, these complexes do no longer contain a silylium cation but a tetracoordinated covalently bonded Si atom<sup>#5</sup>. Because of these findings, arguments (2) and (3) (see section 1) of Lambert and co-workers have to be rejected.

All calculational results obtained in this work speak against the silylium cation character of  $\text{SiEt}_3\text{C}_6\text{H}_5\text{CH}_3^+\text{TPFPB}^-$ , which, because of arguments given above, is better described as a covalently bonded C-centered  $\pi$  complex between  $\text{SiEt}_3^+$  and toluene with tetracoordinated Si.

#### 4. Generation of silylium cations in condensed phases

Despite the fact that our ab initio investigation refutes most of the arguments and conclusions given by LZSH in their recent work on  $\text{SiEt}_3\text{C}_6\text{H}_5\text{CH}_3^+$  [6], we confirm that their major conclusion concerning the existence of almost free silylium cations in aromatic solvents is basically correct. In the following, we will prove this point and present suggestions for the experimental realization of free silylium cations in condensed phases.

As shown above, ions such as **13** represent  $\pi$  complexes with relatively weak covalent SiC bonding ( $\leq 23$  kcal/mol). By appropriate substitution at Si atom and aromatic ring, it should be possible to force the  $\text{SiR}_3^+$  group out of its position over a C atom and to push it into a central position over the ring. This

would have important electronic consequences as is revealed by the molecular properties of complex **12**.

The higher homologues of **12** can contain nearly free silylium cations contrary to the covalently bonded complexes **10** and **13**. For **12**, the SiC dissociation energy is almost 30 kcal/mol smaller than that for **10**, which means that in case of a trialkyl-substituted Si the dissociation energy is typical of a van der Waals complex ( $< 10$  kcal/mol). The silylium cation is almost planar with deviations from planarity of just  $8^\circ$  ( $\text{HSiH} = 118^\circ$  in **12**). The SiC distance is with 3.1 Å just 0.2 Å shorter than the van der Waals distance between  $\text{Si}^+$  and C<sup>#6</sup>. The  $\delta^{29}\text{Si}$  value of such a complex (202 ppm, table 2) is just 70 ppm upfield from a free silylium ion thus indicating that the Si nucleus is only slightly shielded in **12** by charge transfer from the aromatic ring. In **12**, the positive charge of the benzene ring has dropped from 0.47  $e$  (**10**) to 0.19  $e$ . According to our calculations we predict that the trimethyl and triethyl analogues of **12** will possess  $\delta^{29}\text{Si}$  shifts of about 310–320 ppm.

Synthetic realization of complexes such as **12** requires steric blocking of all positions over or under the ring C atoms and/or reduction of bonding effects. The first goal can be achieved by (a) substitution at the aromatic ring with bulky groups and (b) introduction of bulky Si substituents as for example  $\text{R} = \text{Me}_3\text{Si}$ . Lambert and Zhang have found a downfield shift of 228 ppm when going from the  $(\text{Me}_3\text{Si})_3\text{SiH}$  to  $(\text{Me}_3\text{Si})_3\text{SiC}_6\text{H}_6^+$  [5]. Since  $(\text{Me}_3\text{Si})_3\text{SiH}$  possesses a  $\delta^{29}\text{Si}$  of  $-117.4$  ppm for the central Si atom, which is about 25 ppm upfield from the  $\delta^{29}\text{Si}$  value of  $\text{SiH}_4$  [31], one can predict for free  $(\text{Me}_3\text{Si})_3\text{Si}^+$  a  $\delta^{29}\text{Si}$  value of about 245 ppm, for a C-centered  $\pi$  complex  $(\text{Me}_3\text{Si})_3\text{SiC}_6\text{H}_6^+$   $\delta^{29}\text{Si} = -50$  ppm, and for a ring-centered  $\pi$  complex  $(\text{Me}_3\text{Si})_3\text{SiC}_6\text{H}_6^+$   $\delta^{29}\text{Si} = 175$  ppm utilizing the shift data of table 2. The measured value for  $(\text{Me}_3\text{Si})_3\text{SiC}_6\text{H}_6^+$  is with 111 ppm [5] just 65 ppm upfield from that of a ring-centered  $\pi$  complex but 160 ppm downfield from the C-centered  $\pi$  complex, or in other words, the measured  $\delta^{29}\text{Si}$  reveals that a

<sup>#5</sup> We have to note that LZSH did not exclude the possibility of weak covalent bonding. However, in the context of their discussion of the interactions between  $\text{Et}_3\text{Si}^+$  and toluene weak covalent bonding was considered as a matter of a new kcal/mol rather than of 23 kcal/mol as found in the present work for **13**.

<sup>#6</sup> The van der Waals radius of C is 1.85, that of Si 2.0 Å. For  $\text{Si}^+$  a contraction of the van der Waals radius to 1.48 Å can be estimated from the ratio of covalent radii for Si and  $\text{Si}^+$  thus yielding a  $\text{Si}^+$ , C van der Waals distance of 3.33 Å.

nearly free silylium cation is realized up to 70% by  $(\text{Me}_3\text{Si})_3\text{SiC}_6\text{H}_5^+ \text{TPFPB}^-$  investigated by Lambert and Zhang [5]. We predict that there is a good chance to generate silylium cations by using highly substituted benzenes<sup>#7</sup> as aromatic solvents in connection with  $\text{Me}_3\text{Si}$  substituents at the Si atom.

## 5. Conclusions

There are three important conclusions resulting from our work.

(1) The recently postulated silylium cations are covalently bonded C-centered  $\pi$  complexes between  $\text{SiR}_3^+$  and aromatic solvents. Formally, they may be described as Wheland  $\sigma$  complexes, for which the silylium cation character is totally lost.

(2) Nevertheless, the use of the TFPFB anion in connection with aromatic solvents opens an intriguing route to nearly free silylium cations in the form of ring-centered  $\text{SiR}_3^+ - \text{C}_6\text{R}_6'$  van der Waals complexes with  $\delta^{29}\text{Si}$  values of about 310–320 ppm. These complexes can be best generated if both Si and the benzene ring are substituted by sterically demanding groups.

(3) The  $(\text{Me}_3\text{Si})_3\text{C}_6\text{H}_5^+ \text{TPFPB}^-$  compound investigated by Lambert and Zhang realizes by 70% the situation of a free tricovalent silylium cation in a condensed phase.

We suggest further experiments with properly substituted aromatic solvents and  $(\text{Me}_3\text{Si})_3\text{Si}^+ \text{TPFPB}^-$  to generate a free silylium cation in solution.

After this paper had been submitted, we learned about a similar study by Schleyer, Buzek, Müller, Apeloig, and Siehl [32] which comes to the same conclusion on the electronic nature of  $\text{Et}_3\text{Si}^+(\text{C}_6\text{F}_5)_4\text{B}^-$  (conclusion (1)). We thank Professor Apeloig for sending a preprint of their paper.

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<sup>#7</sup> Simple peralkylation of the benzene ring will probably not help because of the high melting point of the resulting compounds.

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