The Tris(9-borabicyclo[3.3.1]nonyl)silylium Cation: A Suggestion for a Weakly Coordinated Silylium Cation in Solution

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The tris(9-borabicyclo[3.3.1]nonyl)silylium cation, Si(9-BBN)$_3^+$ (**3**), was investigated by ab initio quantum chemical methods, where, in particular, its coordination ability with benzene was studied. Dialkylboryl substitution leads to one of the thermodynamically most stable silylium ions investigated so far, which accordingly show a reduced tendency to coordinate with weakly nucleophilic solvents, such as benzene. The complex Si(9-BBN)$_3$−C$_6$H$_6^+$ (**6**) has a complex binding energy of just 4 kcal/mol and a Si−C bond length of 2.57 Å at HF/6-31G(d), which indicates that **6** is among the weakest silylium-cation−solvent complex ever investigated. Results suggest that silylium cations with bulky dialkylboryl substituents retain, to a large degree, their electronic character in solution and, therefore, should be interesting targets for experimental work. The nonpolar character of the 9-BBN substituents should enable usage of weakly coordinating hydrocarbon solvents, such as cyclohexane. If, in addition, weakly coordinating anions, such as the dodecamethylcarba-*closo*-dodecaborate anion, are utilized, it should be possible to synthesize silylium cations which are close to completely uncoordinated.

Introduction

The search for stable trivalent silylium cations (SiR$_3^+$)[1] in condensed phases has received much attention in the last years.[2−10] Despite considerable experimental efforts, there is no unambiguous proof for the existence of entirely free silylium ions in either solution phases or the solid state. Preparation of these cations is severely hampered by their extraordinarily large coordination ability, and even solvents such as sulfolane that resemle those that have been used successfully for the preparation of carbenium ions (CR$_3^+$)[11] coordinate to SiR$_3^+$.

Ab initio calculations for the model system SiR$_3^+$−methane show that even extremely weak nucleophilic solvents, such as pentane or cyclohexane, will interact with SiR$_3^+$ ions to a degree and that their silylium cation character is considerably reduced.[10] Schleyer and co-workers[1] have shown that the only solvent suited to preserve the silylium cation character of SiR$_3^+$ in solution would be liquid helium. Even Ne and Ar interact with SiR$_3^+$ in such a way that it is no longer justified to speak of nearly free silylium cations. Therefore, it is out of question that just by variation of the solvent and the counterion tetra- or pentacoordination of silylium cations in solution cannot be prevented. Clearly, other strategies have to be used to preserve the silylium cation character of SiR$_3^+$ in solution. Of these, we have recently probed[6,9,10] two, namely (a) internal

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(1) For an excellent state-of-the-art summary of the theoretical work on silylium cations, see: Maerker, C.; Kapp, J.; Schleyer, P.v.R. In *Organosilicon Chemistry II: From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1996; p 329.

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stabilization of SiR_3^+ so that its ability to coordinate with solvent molecules or counterions is reduced; and, (b) steric blocking of the Si^+ center. With regard to the first strategy, it is obvious that one cannot surround the Si^+ center by strong electron-donor groups (e.g., NR_2 groups), fill up the empty $3p\pi(Si^+)$ orbital with negative charge, and by this hinder strong interactions with solvent molecules or counterions. Clearly, such a strategy changes the character of SiR_3^+ from a silylium ion to an onium ion in the same way as this would happen by solvent coordination. As in the case of carbenium ions, one can stabilize SiR_3^+ only by rather moderate means, such as hyperconjugative or weak conjugative interactions with alkyl or aryl groups that leave its silylium cation character unchanged. Then, the question is whether such a weak internal stabilization together with steric blocking of the Si^+ center is sufficient to preserve the silylium cation character of SiR_3^+ in solution.

The stability of carbenium ions is increased by conjugative and hyperconjugative effects of aryl and alkyl substituents attached to the cationic center (C^+). For example, in $C(CH_3)_3^+$, orbital interactions between the pseudo-$\pi(CH_3)$ and $2p\pi(C^+)$ orbitals raise the energy of the $2p\pi$ LUMO and thereby reduce the electrophilicity of C^+. As a consequence, $C(CH_3)_3^+$ is more resistant against solvent coordination than a carbenium ion with less or no alkyl substituents.

In the case of silylium ions, the empty $3p\pi(Si^+)$ orbital overlaps less effectively with the $2p\pi$ or pseudo-π orbitals of an aryl or alkyl substituent and, therefore, reduces conjugative or hyperconjugative stabilization of SiR_3^+ that may prevent its coordination with a nucleophilic solvent molecule. On the contrary, alkyl and aryl groups withdraw σ-electronic charge from the electropositive Si atom, thus lowering the energy of the $3p\pi(Si^+)$ orbital. Therefore, aryl and alkyl substituents increase the electrophilicity of SiR_3^+ ions, which explains the high solvent complexation ability of alkyl-substituted silylium ions.

The electron-withdrawing effects of an alkyl or aryl group can be eliminated by using substituents R of lower electronegativity. For example, Lambert and co-workers investigated $Si(SiMe_3)_3^+$ (**1**) in aromatic solvents and observed a $\delta_{^{29}Si}$ value of 111 ppm for the cationic Si atom of **1**.[3a,c] Compared to the $\delta_{^{29}Si}$ values of alkyl-substituted silylium cations in solution, this value is significantly downfield shifted, which caused the authors of the experimental work to expect increased silylium cation character for **1**. However, Olah and co-workers,[5e] as well as Ottosson and Cremer,[9] provided convincing evidence based on ab initio calculations that the $\delta_{^{29}Si}$ value of 111 ppm[3a,c] measured for **1** in benzene solution results from a Wheland σ-complex of the form $Si(SiMe_3)_3{-}C_6H_6^+$, i.e., **1** reacts with solvent molecules and, thereby, looses its silylium cation character. According to IGLO (individual gauge for localized orbital) NMR chemical shift calculations, uncoordinated **1** possesses a $\delta_{^{29}Si}$ value of 920.6 ppm.[5e,9]

Even though $SiMe_3$ substituents only moderately affect the electrophilicity of **1** by inductive effects, the solvent coordination ability of **1** is still rather high since $SiMe_3$ provides little hyperconjugative stabilization for Si^+. This is a consequence of the relatively long Si−Si bond, which leads to relatively small $3p\pi(Si^+)$−pseudo-$\pi(SiC_3)$ overlap and hyperconjugative interactions. Accordingly, $SiMe_3$ substituents are not sufficient to reduce the solvent coordination ability of silylium cations to a degree that the latter can be considered as nearly free cations in benzene solution. To reach this goal, one has to substitute SiR_3^+ by substituents that both inductively and hyperconjugatively (or conjugatively)[12] stabilize Si^+. A suitable substituent in this respect should be the dialkylboryl group (BR_2).

Normal Si−B bonds (1.98−2.03 Å)[13] are considerably shorter than Si−Si bonds (2.34−2.40 Å)[14] and, accordingly, should lead to the better $3p\pi(Si){-}2p\pi(B)$ overlap needed for any substantial conjugative stabilization of SiR_3^+. Since B has a lower electronegativity (2.01) than C (2.50), the interacting orbitals should be closer in energy than in the case of alkyl or aryl substituents, which also should enhance hyperconjugative (conjugative) stabilization. In short, dialkylboryl substituents should reduce the electrophilicity (coordination ability) of SiR_3^+ and by this enhance the silylium cation stability in solution.

Another way of stabilizing SiR_3^+ in solution is to sterically block the approach of a solvent molecule toward the cationic center. The $SiMe_3$ group partially fulfils this goal. However, as shown in our previous investigation on **1**,[9] a trialkylsilyl substituent still possesses sufficient flexibility to bend away from the cationic center upon a collision between **1** and a solvent molecule, thus making place for the solvent molecule to bind to the cationic center. More promising as sterically blocking groups are rigid substituents with a bicyclic or polycyclic structure.

Following the ideas outlined above, we investigate in this work dialkylboryl-substituted silylium ions, with special concern on their stability toward benzene coordination. In particular, we will focus on $Si(BMe_2)_3^+$ (**2**) and $Si(9\text{-}BBN)_3^+$ (**3**), where **2** can be considered as a simple model compound for larger dialkylboryl-substituted silylium cations while **3** is our actual candidate for a stable silylium cation in solution. Cation **3** combines the inductive and hyperconjugative properties of a boryl substituent with the blocking ability of the 9-borabicyclo[3.3.1]nonyl (9-BBN) group and, therefore, may resist more than any other previously investigated silylium cation[2−7] in aromatic solutions the attack of a solvent molecule such as benzene.

Computational Methods

Geometry optimizations were performed at the Hartree−Fock (HF) level using Pople's 3-21G and 6-31G(d) basis sets.[15] The nature of each calculated stationary point was tested by HF/3-21G harmonic frequencies. Although HF provides a reasonable description of silylium cations, correlation corrected

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[12] Of course, a conjugative stabilization of SiX_3^+ by X = OR, NR_2, etc. can easily be achieved; however, this is not the goal of the search for stable silylium cations in solution because SiX_3^+ retains little silylium cation character.

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methods, such as second-order Møller–Plesset (MP2) perturbation theory or density functional theory (DFT), are preferable. In the present study DFT calculations were performed in order to improve the HF results. DFT covers large parts of unspecified correlation effects, which in the case of hybrid functionals of the B3LYP type,[16] lead to results of MP2 or even better quality.

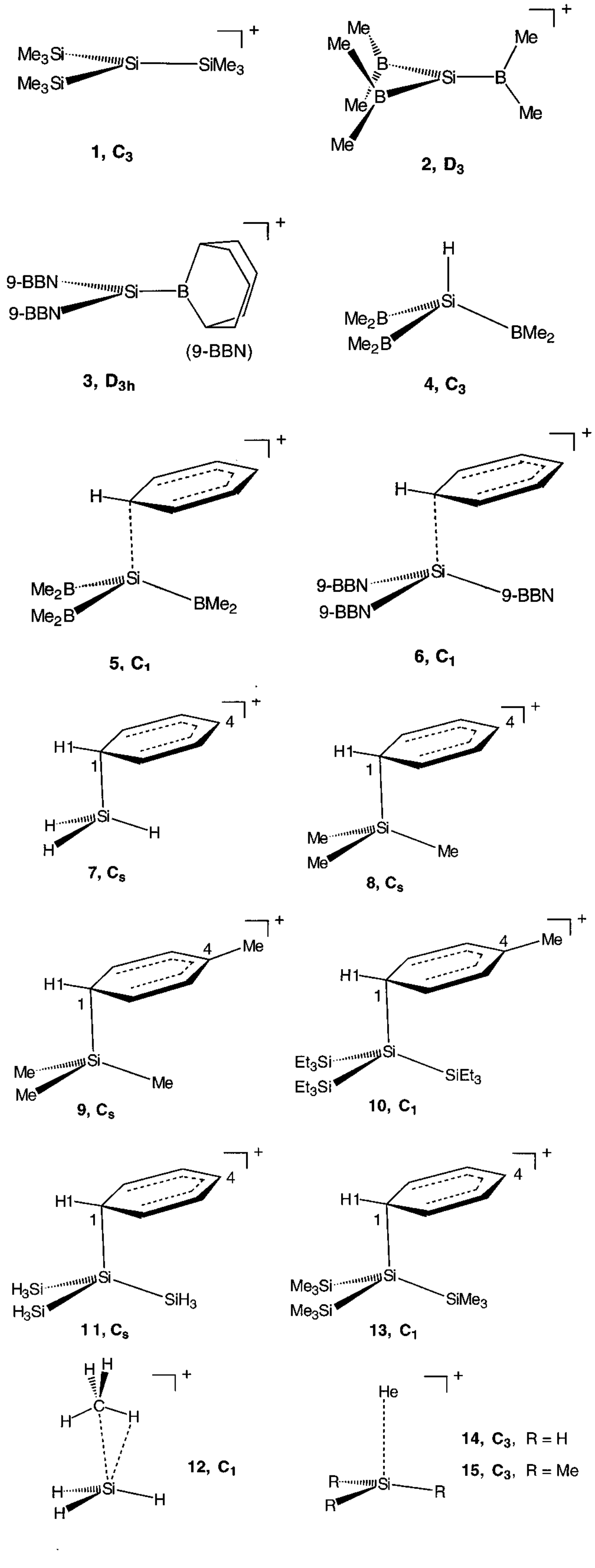
Successive calculations of NMR chemical shifts were carried out at HF/6-31G(d)-optimized geometries employing the IGLO method by Kutzelnigg and Schindler[17] in a form that makes routine calculation within standard ab initio packages possible.[18] In addition, electron correlation in the NMR chemical shift calculations was included with the GIAO (Gauge Invariance of Atomic Orbitals) method[19] in an implementation that works with the B3LYP hybrid functional. For the NMR chemical shift calculations, the [7s6p2d/5s4p1d/3s1p] basis set of Kutzelnigg and co-workers[17c] was used, which is of TZ+P quality and is known to lead to reasonable relative ^{13}C and ^{29}Si chemical shifts.

Calculations were performed with the ab initio packages COLOGNE94[20] and GAUSSIAN94.[21]

Results and Discussion

In Chart 1, molecules **1**–**15** are shown, which are discussed in this work. Perspective drawings of the geometries of cations **1**, **3**, **5**, and **6** together with some important geometrical parameters are given in Figures 1–4. Calculated geometrical parameters of the target compound **6** are shown in Table 1. A complete account of the optimized geometries and energies is given in the Supporting Information. Table 2 lists calculated IGLO-HF and GIAO-DFT NMR chemical shifts. The discussion of geometries and energies refer to B3LYP/6-31G(d) calculations where otherwise not noted.

Chart 1



Tris(trimethylsilyl)silylium Cation (1). Since this molecule has been discussed elsewhere,[5e,9] just some basic features of its geometry are pointed out here. In its equilibrium geometry, the cation possesses C_3 symmetry. The C atom of one of the three methyl groups at a Si atom is located approximately in the plane of the Si atoms while the other two adopt positions above and below this plane (SiSiSiC dihedral angle of about |60°|). In this way, steric interactions between the methyl groups of different Si atoms are largely avoided. Cation **1** has two different faces as a consequence of the arrangement of the methyl groups. For a nucleophilic solvent molecule approaching **1** from the top side, close contacts with H1, H2, and H3 (indicated by black balls in Figure 1) result. The three H atoms define the diameter of an opening (2.8 Å, see insert in Figure 1) that allows the direct approach of a solvent molecule toward the central Si atom. On the bottom side, there is a similar opening (atoms H4, H5, H6, see Figure 1) with a somewhat smaller diameter of 2.5 Å. Hence, the top side approach should be slightly preferred.

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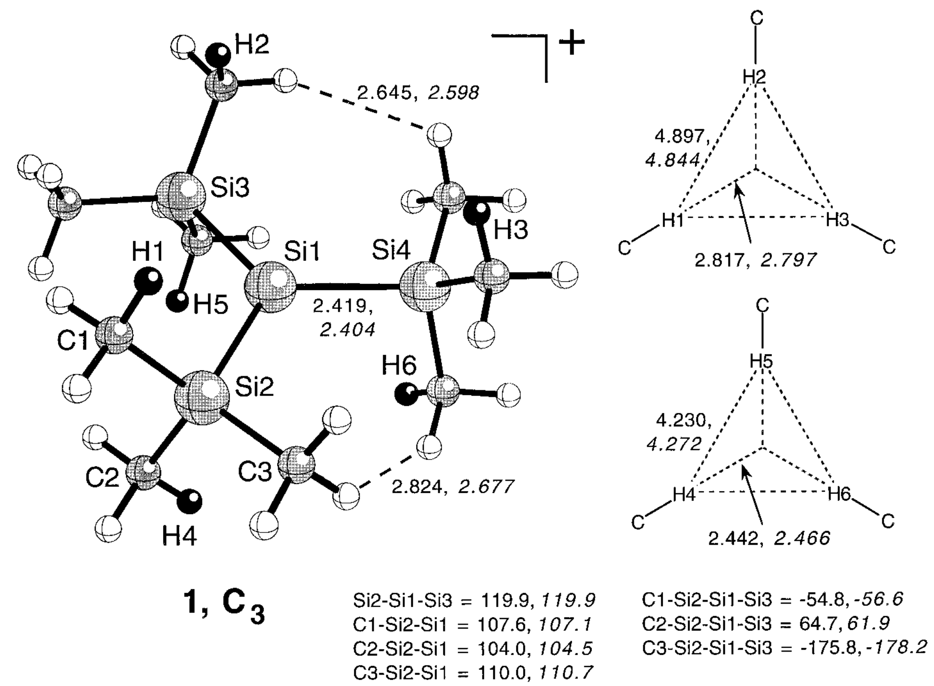
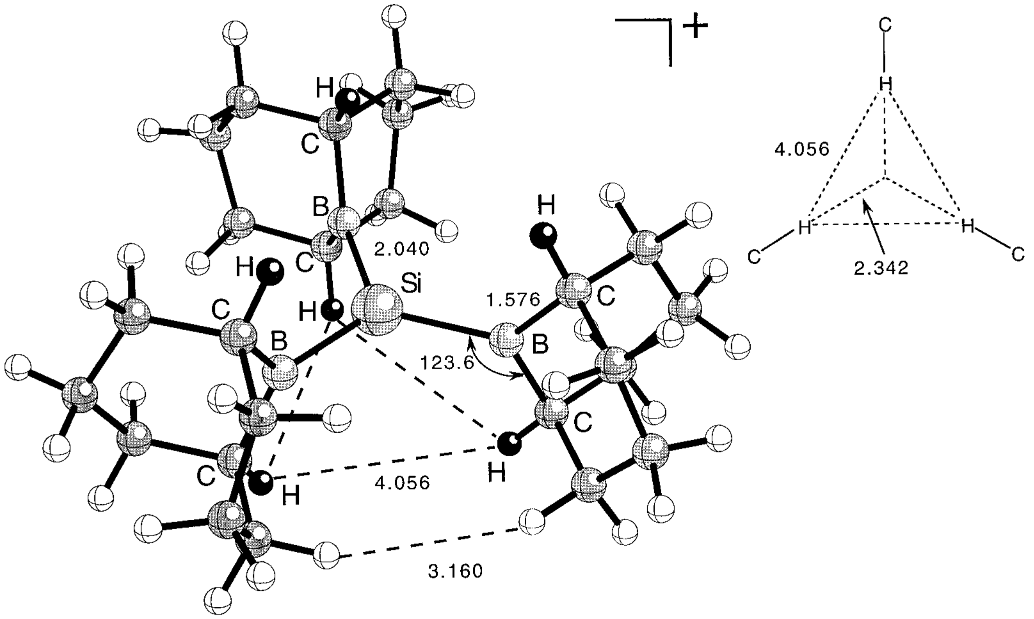


1, C_3

Figure 1. HF/6-31G(d) and B3LYP/6-31G(d) (values in italics) geometry of $Si(SiMe_3)_3^+$ (**1**). Parameters describing the geometry at the central Si atom and close contacts are given in Angstroms (bond lengths) and degrees (angles). The two inserts on the right side indicate the dimensions of the opening above the central Si atom formed by atoms H1, H2, H3 (black atoms) and below the central Si atom H4, H5, H6 (black atoms). The center of these openings is defined by a point above and below the central Si atom (see text).

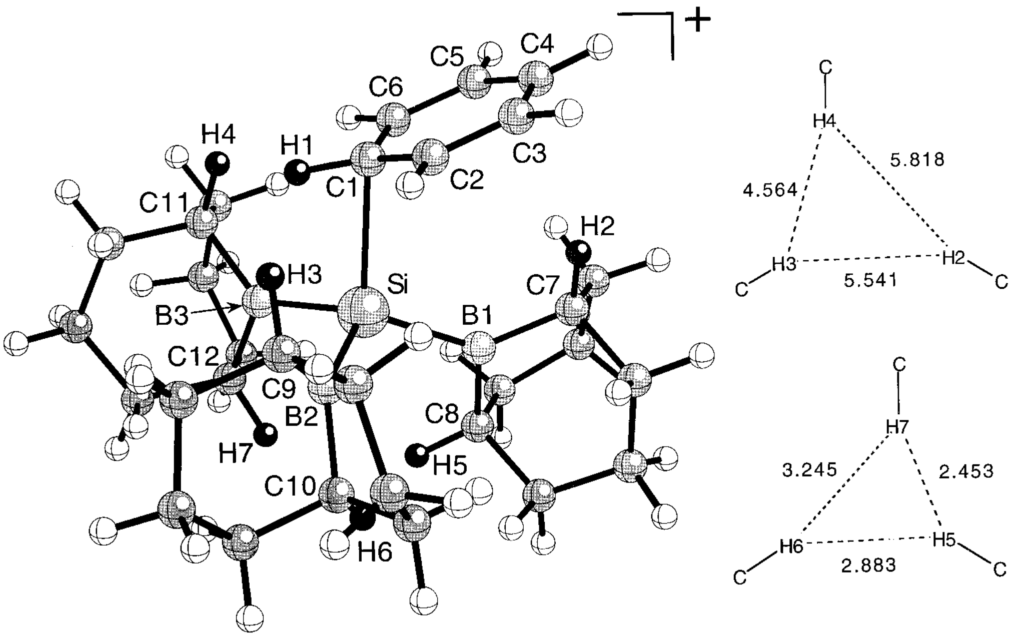


3, D_{3h}

Figure 2. HF/6-31G(d) geometry of $Si(9\text{-}BBN)_3^+$ (**3**). Parameters describing the geometry at the central Si atom and close contacts are given in Angstroms (bond lengths) and degrees (angles). The insert on the right side indicates the dimensions of the equivalent openings above and below the central Si atom formed by the black H atoms. The center of these openings is defined by a point above and below the central Si atom (see text).

Tris(dimethylboryl)silylium Cation (2). Cation **2** adopts a D_3 symmetrical geometry with the BC bonds rotated by 86° (rather than 90°, D_{3h} symmetry) out of the plane of Si and the three B atoms, as checked by a frequency calculation at the B3LYP/6-31G(d) level. In this way, steric repulsion between the Me groups is minimized. The SiB bond length is 2.03 Å, which is slightly smaller than the SiB single bonds in the corresponding hydride **2** (2.04 Å) because of hyperconjugative interactions between the central Si atom and the BMe_2 substituents.

According to the isodesmic reaction (eq 1), BMe_2 substitution stabilizes **2** by 61.9 kcal/mol at the B3LYP/6-31G(d) level, where SiH_3^+ is used as a reference. The corresponding stabilization energy caused by three methyl groups in $SiMe_3^+$ is 43.2 kcal/mol (eq 2), HF/6-



6, C_1

Figure 3. HF/6-31G(d) geometry of the complex $Si(9\text{-}BBN)_3{-}C_6H_6^+$ (**6**). The two inserts on the right side indicate the dimensions of the opening above the central Si atom formed by atoms H2, H3, H4 (black atoms) and below the central Si atom H5, H6, H7 (black atoms). Distances between these atoms are given in Angstroms (see text).

31G(d) energies are given in parentheses.

$$SiH_3^+ + SiH(BMe_2)_3 \rightarrow SiH_4 + Si(BMe_2)_3^+ \quad \Delta E = 61.9\ (54.4) \quad (1)$$

$$SiH_3^+ + SiHMe_3 \rightarrow SiH_4 + SiMe_3^+ \quad \Delta E = 43.2\ (36.0) \quad (2)$$

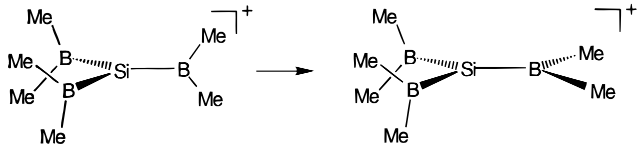
From reactions 3 and 4, we find that **1** is stabilized by 57.6 kcal/mol relative to SiH_3^+ and that the *tert*-butyl cation is stabilized by 83.7 kcal/mol relative to CH_3^+. Hence, the internal stability of silylium ions

$$SiH_3^+ + SiH(SiMe_3)_3 \rightarrow SiH_4 + Si(SiMe_3)_3^+ \quad \Delta E = 57.6\ (49.7) \quad (3)$$

$$CH_3^+ + CHMe_3 \rightarrow CH_4 + CMe_3^+ \quad \Delta E = 83.7\ (67.7) \quad (4)$$

slowly approaches that of trialkyl carbenium ions when replacing H in SiH_3^+ by Me, $SiMe_3$, and BMe_2. Our basic assumption, namely that boryl substituents are more stabilizing than trimethylsilyl substituents, is confirmed, although the extra stabilization is just 4 kcal/mol.

By rotation of one of the BMe_2 groups into the plane of the SiB_3 unit, hyperconjugative interactions between substituent orbitals and the $3p\pi(Si^+)$ orbital are suppressed for this group while steric repulsion is slightly enhanced. At B3LYP/6-31G(d), the increase in energy because of a 90° rotation of one group is 6.7 kcal/mol and that of all groups 23.2 kcal/mol. Assuming that the rotational barrier is predominantly due to a loss of hyperconjugative stabilization, the overall stabilization energy of the three BMe_2 groups in **2** can be partitioned into a hyperconjugative contribution of $3 \times 6.7 \approx 20$ kcal/mol and an inductive contribution of approximately 42 kcal/mol, where exact values are difficult to obtain because of steric and remaining hyperconjugative/conjugative delocalization effects in the planar form involving occupied pseudo-$\pi(CH_3)$, empty $2p\pi(B)$, and empty $3p\pi(Si^+)$ orbitals.[22] In any case, the energies obtained give some indication on the magnitude of inductive and hyperconjugative effects in **2**. In **1**, for which a similar partitioning is not possible, the former effect will be smaller while the latter will be of a comparable magnitude, considering the group electronegativities of $SiMe_3$ (1.990) and BMe_2 (BH_2 1.981).[23]



Tris(9-borabicyclo[3.3.1]nonyl)silylium Cation (3). The equilibrium geometry of **3** (Figure 2) possess D_{3h} rather than D_3 symmetry, which reflects the increased rigidity in the 9-BBN substituent. Above and below the central Si atom there are two equivalent openings in the spherical shape of cation **3**. Again, the diameter of these openings is determined by three H atoms (black balls in Figure 2), which will be the atoms of closest contact to any approaching solvent molecule. For **3**, the diameter (2.34 Å, Figure 2) is 0.5 Å smaller than that of the larger of the two openings in **1**, which indicates that three 9-BBN substituents should sterically block the central Si atom more effectively than three $SiMe_3$ substituents.

The volumes for $SiMe_3H$ and 9-borabicyclo[3.3.1]nonane are 79 and 114 cm^3/mol, respectively, where these values are based on the HF/6-31G(d) density. They correspond to spherical cavities with radii of 3.97 ($SiMe_3H$) and 4.42 Å (9-borabicyclo[3.3.1]nonane), which

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[22] Note that there is also a hyperconjugative interaction between the $Si{-}B_2$ unit and the empty $2p\pi(B)$ orbital, which by rotation is also eliminated.

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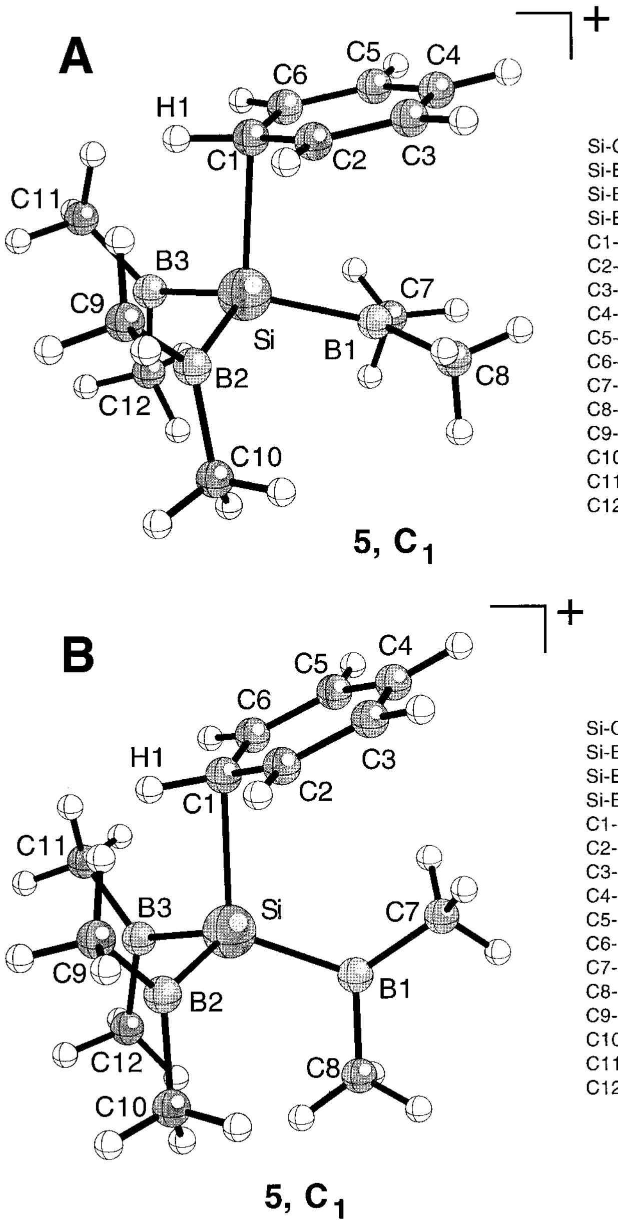

Si-C1 = 2.375
Si-B1 = 2.094
Si-B2 = 2.066
Si-B3 = 2.063
C1-C2 = 1.411
C2-C3 = 1.379
C3-C4 = 1.392
C4-C5 = 1.390
C5-C6 = 1.382
C6-C1 = 1.410
C7-B1 = 1.578
C8-B1 = 1.577
C9-B2 = 1.578
C10-B2 = 1.582
C11-B3 = 1.579
C12-B3 = 1.583

B1-Si-C1 = 104.0
B2-Si-C1 = 103.3
B3-Si-C1 = 103.1
H1-C1-Si = 88.7
C7-B1-Si = 118.7
C8-B1-Si = 120.5
C9-B2-Si = 125.4
C10-B2-Si = 115.3
C11-B3-Si = 125.9
C12-B3-Si = 115.0
B1-Si-C1-C4 = 4.3
C7-B1-Si-C1 = -99.9
C8-B1-Si-C1 = 87.5
C9-B2-Si-C1 24.5
C10-B2-Si-C1 = -158.9
C11-B3-Si-C1 = -17.4
C12-B3-Si-C1 = 166.5

5, C$_1$

Si-C1 = 2.346
Si-B1 = 2.046
Si-B2 = 2.057
Si-B3 = 2.053
C1-C2 = 1.421
C2-C3 = 1.390
C3-C4 = 1.401
C4-C5 = 1.401
C5-C6 = 1.390
C6-C1 = 1.420
C7-B1 = 1.565
C8-B1 = 1.572
C9-B2 = 1.568
C10-B2 = 1.572
C11-B3 = 1.569
C12-B3 = 1.572

B1-Si-C1 = 113.5
B2-Si-C1 = 101.3
B3-Si-C1 = 102.9
H1-C1-Si = 82.5
C7-B1-Si = 125.6
C8-B1-Si = 114.1
C9-B2-Si = 124.1
C10-B2-Si = 116.3
C11-B3-Si = 124.3
C12-B3-Si = 116.3
B1-Si-C1-C4 = 0.3
C7-B1-Si-C1 = -2.5
C8-B1-Si-C1 = 178.5
C9-B2-Si-C1 15.5
C10-B2-Si-C1 = -168.2
C11-B3-Si-C1 = -2.3
C12-B3-Si-C1 = 179.6

5, C$_1$

Figure 4. Geometry of the complex Si(BMe$_2$)$_3$-C$_6$H$_6^+$ (**5**) at (A) HF/6-31G(d) and (B) B3LYP/6-31G(d) levels. Distances are given in Angstroms and angles in degrees.

also indicates that the 9-BBN group is more bulky than the SiMe$_3$ group and, therefore, may effectively hinder a nucleophilic solvent molecule to approach the central Si atom.

The HF/6-31G(d) Si−B bond lengths in **3** are 2.040 Å, 0.02 Å shorter than those in **2**, which probably is due to increased hyperconjugative interactions.

Complexes Si(BMe$_2$)$_3$−C$_6$H$_6^+$ (5) and Si(9-BBN)$_3$−C$_6$H$_6^+$ (6). The HF/6-31G(d) equilibrium geometry of complex **6** is shown in Figure 3. It has no symmetry and a Si−C$_{\mathrm{benzene}}$ distance of 2.57 Å, which is 0.1−0.3 Å longer than any other Si−C$_{\mathrm{benzene}}$ distance reported for SiR$_3$−C$_6$H$_6^+$ complexes (compare with Table 3).[3−7] The degree of pyramidalization at the central Si atom is significantly reduced, which becomes obvious when comparing R−Si−R angles (Table 3). For **6**, the largest R−Si−R angle is 118°, while the corresponding angles for related benzene (toluene) complexes are close to 114°.

Electronic interactions between cation **3** and benzene are only possible if the opening above the central Si atom is enlarged, as is reflected by the dimension of the triangle H2,H3,H4 shown in Figure 3. The increase in the H−H distances is as large as 1.8 Å, where the 9-BBN substituent carrying H2 bends strongly backward, thus giving the benzene molecule the possibility to slide from the side of this substituent into the opening above the Si atom. Because of the bulk of the substituent directly below the benzene ring, the collision angle (as measured by the angle SiC1C4) is relatively large (114.6° as compared to 107.6° in the complex C$_6$H$_6$−SiMe$_3^+$, Table 3). The closest atom−atom contact calculated for **6** is that between H2 and C4 (2.74 Å), which is 0.26 Å smaller than the sum of the van der Waals radii (1.2 + 1.8 = 3 Å). In none of the other benzene/toluene−SiR$_3$ complexes investigated so far do such small contact distances occur (Table 3). Pyramidalization at the central Si atom of **6** leads to a narrowing of the opening in the back, where the H−H distances of the triangle H5H6H7 (Figure 3) decrease by as much as 1.5 Å (relative to cation **3**) to values which are equal to or larger than the sum of the van der Waals radii (2.4 Å). Hence, pyramidalization at the Si atom

Table 1. Selected Geometrical Parameters of 6[a]

bond distances		bond angles		dihedral angles	
Si−C1	2.568	Si−C1−C4	114.6	B1−Si−C1−C4	1.4
Si−B1	2.058	Si−C1−H1	78.4	B2−Si−C1−C4	120.3
Si−B2	2.066	B1−Si−C1	110.5	B3−Si−C1−C4	−126.9
Si−B3	2.064	B2−Si−C1	99.9	C7−B1−Si−C1	10.0
C1−H1	1.078	B3−Si−C1	98.4	C8−B1−Si−C1	−171.2
C7−B1	1.573	C7−B1−Si	130.6	C9−B2−Si−C1	15.2
C8−B1	1.585	C8−B1−Si	117.7	C10−B2−Si−C1	−166.6
C9−B2	1.578	C9−B2−Si	129.2	C11−B3−Si−C1	8.8
C10−B2	1.583	C10−B2−Si	119.4	C12−B3−Si−C1	−174.5
C11−B3	1.579	C11−B3−Si	129.2	C1−C2−C3−C4	0.9
C12−B3	1.584	C12−B3−Si	119.5	C2−C3−C4−C5	−1.1
C1−C2	1.403	H1−C1−C4	167.6	C3−C4−C5−C6	−1.3
C2−C3	1.381			C4−C5−C6−C1	1.3
C3−C4	1.390			C5−C6−C1−C2	1.1
C4−C5	1.388			C6−C1−C2−C3	−0.9
C5−C6	1.383				
C6−C1	1.402				
H1−H3	2.376				
H2−C3	2.923				
H2−C4	2.761				
H2−C5	3.026				

[a] Values calculated at the HF/6-31G(d) level. Distances are in Angstroms and angles in degrees.

Table 2. IGLO/[7s6p2d/5s4p1d/3s1p]//HF/6-31G(d) and GIAO-B3LYP/[7s6p2d/5s4p1d/3s1p]//B3LYP/6-31G(d) (Values in Italics) ^{29}Si NMR Chemical Shifts of the Central Si Atom[a]

molecule	sym	$\delta_{^{29}\mathrm{Si}}$
1 $Si(SiMe_3)_3^+$	C_3	920.6, *1029.1*
3 $Si(BMe_2)_3^+$	D_3	571.8, *587.3*
4 $SiH(BMe_2)_3$	C_3	−59.0, *−50.2*
5 $Si(BMe_2)_3C_6H_6^+$	C_1	116.4, *147.0*
6 $Si(9\text{-}BBN)_3C_6H_6^+$	C_1	(189.7)[b]

[a] Chemical shifts given in ppm relative to TMS. [b] Estimated value see text.

could actually be stronger; however, the SiC1 bonding interaction seems to be too weak to enforce the corresponding electron reorganization at the central Si atom.

Other descriptive parameters for the magnitude of interaction between benzene and SiR_3^+ are the geometrical parameters of the benzene ring. Compared to the other complexes listed in Table 3, the benzene ring of **6** is less distorted. Thus, the out-of-plane bending of H1 is just 13.4° while it is 19.1° in the case of $C_6H_6-SiMe_3^+$. Also, the degree of bond alternation is smaller for **6** than for any other complex of Table 3, thus indicating that the electronic structure of benzene is largely retained in **6**.

The calculated geometrical parameters of **6**, i.e. Si−C bond length, pyramidalization angles at Si, pyramidalization angle at C1 of benzene, contact distances between benzene ring and SiR_3^+, and bond alternation in benzene, clearly indicate that cation **3** interacts with benzene rather weakly because of hyperconjugative stabilization of **3** and the steric bulk of the 9-BBN substituents. This is confirmed by a complex binding energy of just 4.4 kcal/mol, calculated at the HF/6-31G(d) level, which is 50% smaller than the smallest value calculated for any other SiR_3^+−solvent complexes (Table 3).

Since a reliable calculation of $\delta_{^{29}\mathrm{Si}}$ NMR chemical shift was not possible for **6** because of computational limitations, the complex between cation **3** and benzene $C_6H_6-Si(BMe_2)_3^+$ (**5**), was investigated as a possible model for complex **6**. At the HF/6-31G(d) level, the BMe_2 group which has the strongest steric interactions with the

Table 3. Comparison of Calculated Properties of Complexes $R_3Si(S)^+$ (S = Solvent)[a]

	7 (SiH_3^+, benzene)	**8** ($SiMe_3^+$, benzene)	**9** ($SiMe_3^+$, toluene)	**10** ($SiEt_3^+$, benzene)	**11** ($Si(SiH_3)_3^+$, benzene)	**12** (SiH_3^+, methane)	**13** ($Si(SiMe_3)_3^+$, benzene)	**5** ($Si(BMe_2)_3^+$, benzene)	**6** ($Si(9\text{-}BBN)_3^+$, benzene)	**14** (SiH_3^+, He)	**15** ($SiMe_3^+$, He)
complexation energy	49.8	23.0	25.1	21.6	24.2	16.4	9.6	8.9	4.4	<1	<1
R(Si−C1)	2.078	2.213	2.140	2.186	2.239	2.391	2.452	2.375	2.568	2.773	3.224
$\delta_{^{29}\mathrm{Si}}$ $R_3Si(S)^+$	−23.8	83.1	60.4	79.3	55.6[b]	27.9	205.8	116.4	(189)	254	345
$\delta_{^{29}\mathrm{Si}}$ R_3Si^+	270.2	355.9	355.9	374.0	868.1	270.2	920.4	571.8		270.2	347
$\delta_{^{29}\mathrm{Si}}$ R_3SiH	−99.9	−16.6	−16.6		−139.2[b]	−99.9	−119.6	−59.0		−99.9	−16.6
silylium cation character[b]	20	27	21		19	34	31	28	(41)	96	99
averaged α(R−Si−R)	114.1	114.0	113.4	113.5	113.5		114.2	114.0	114.8	120	120
largest α(R−Si−R)	114.5	114.5	113.8	114.4	114.4		115.2	116.6	116.6	120	120
180−α(H1−C1−C4)	22.5	19.1	24.5	22.8	19.8		15.3	13.8	13.4		
α(Si−C1−C4)	105.4	107.6	111.1	111.2	107.2		110.5	103.7	114.6		
ΔR_{C-C}[c]	0.063	0.046	0.063	0.056	0.047		0.033	0.033	0.023		
closest C,H contact[d]	3.092	3.217		3.117	3.420		2.940	3.238	2.739		
reference	6a	6a	5e, 7	6e	10	1, 10	9	this work	this work	1	1
level of theory for geometry	HF/6-31G(d)	HF/6-31G(d)	HF/6-31G(d)	HF/6-31G(d)	HF/6-31G(d)	MP2(FC)/6-31G(d)	HF/6-31G(d)	HF/6-31G(d)	HF/6-31G(d)	MP2(FC)/6-31G(d)	MP2(FC)/6-31G(d)

[a] For numbering of atoms, see Charts 1 and 2. Geometries and energies calculated at the HF/6-31G(d) level and ^{29}Si IGLO NMR chemical shifts at the IGLO/[7s6p2d/5s4p1d/3s1p]//HF/6-31G(d) level. Complexation energies are given in kcal/mol, distances in Angstroms, angles in degrees, and δ^{29} Si values in ppm relative to TMS. [b] The silylium cation character is calculated by the expression $[\delta_{^{29}\mathrm{Si}}(R_3Si(S)^+) - \delta_{^{29}\mathrm{Si}}(R_3SiH)]/[\delta_{^{29}\mathrm{Si}}(R_3Si^+) - \delta_{^{29}\mathrm{Si}}(R_3SiH)]*100$ where S denotes the solvent. [c] ΔR_{C-C}: Longest minus shortest C−C bond lengths of the aromatic ring system in $R_3Si(S)^+$. [d] Closest contact distance between C atoms of the aromatic ring and H atoms of substituents R.

incoming benzene molecule rotates away from the perpendicular position it adopts in the equilibrium geometry of cation **2** into a planar position (Figure 4A). In this way, strong destabilizing steric interactions with the benzene ring are largely avoided at the cost of slightly increasing steric strain within cation **2**. Also, hyperconjugative interactions between BMe_2 groups and Si^+ are reduced, thus increasing the electrophilicity of **2** and leading to stronger cation−solvent interactions, as one would expect for cation **2**. This is confirmed by the calculated Si−C1 distance of **5** (2.375 Å, Figure 4, Table 3), which is smaller than that in $C_6H_6-Si(SiMe_3)_3^+$ (**13**, 2.452 Å, Table 3), the distortions of the benzene ring in **5**, as well as the calculated chemical shift values (Table 3). Also the complex binding energy (8.9 kcal/mol) is only moderately decreased compared to that of **13** (9.6 kcal/mol) at the HF/6-31G(d) level. However, at the B3LYP/6-31G(d) level, all BMe_2 groups are in perpendicular positions (Figure 4B). Accordingly, there should be an intricate interplay between intermolecular stabilization of Si^+ by a benzene molecule and intramolecular hyperconjugative stabilization by the third BMe_2 group. At the higher level of theory, the complex binding energy is also increased to 13.1 for **5**.

If we define the silylium cation character by the downfield shift of $\delta_{^{29}Si^+}$ calculated for the benzene complex in relationship to the total downfield shift $\delta_{^{29}Si^+}(SiR_3^+) - \delta_{^{29}Si^+}(SiR_3H)$, then we will obtain for **5** just 28% silylium cation character, which is smaller than that for complex **13** (31%, Table 3). For comparison, the complexes $He-SiMe_3^+$ and $He-SiH_3^+$ possess 96 and 99% silylium cation character while all $C_6H_6-SiR_3^+$ complexes investigated so far possess a remaining silylium cation character of ≤27% (Table 3).

To obtain a better model for complex **6**, the geometry of **5** was adjusted to that of **6** by freezing the $C_6H_6-Si(BC_2)_3$ unit at the equilibrium geometry of **6** and optimizing the positions of the 18 H atoms. In this way, hyperconjugative, inductive, and steric effects are similar to those of **6**, and an estimate of its silylium cation character can be determined by repetition of the NMR chemical shift calculations. A $\delta_{^{29}Si}(Si^+)$ value of 189 ppm (Table 3) was calculated, which suggests that **6** possesses a remaining silylium cation character of 41%. This is higher than for any other SiR_3^+−solvent complex investigated, however, it does not change the fact that despite hyperconjugative stabilization of **3**, steric blocking of its Si^+ center and a complex binding energy of just 4.4 kcal/mol, complex **6** is no longer a silylium cation. Although the estimated silylium cation character may change if the correct $\delta_{^{29}Si}$ value of **6** can be calculated, the description of **6** as a weakly bound silylium-cation−solvent complex rather than a nearly free silylium cation will not be changed.

Conclusions and Outlook

Silylium cations with dialkylboryl substituents in benzene solution interact weakly with the solvent and form a silylium−cation−benzene complex of reduced stability. In the case of three 9-BBN substituents, ab initio calculations predict a complexation energy of just 4 kcal/mol, which is the smallest ever found in any silylium-cation−benzene complex (Table 3). All other properties calculated for complex **6** are in line with this description. Although application of a higher level of theory (e.g., MP2/DZ+P) and the explicit consideration of a surrounding medium may change the description of **6**, our previous experience obtained for smaller $R_3Si-C_6H_6^+$ complexes[6,9] suggests that the general conclusion of this work should still be valid if refined ab initio data become available.

It is obvious that the results presented above do not suggest that cation **3** in benzene solution represents a nearly free silylium cation, although it comes closer to this state than any other silylium cation previously investigated. Apart from this, there are two other relevant aspects of using dialkylboryl substituents of considerable steric bulk that may stimulate new experimental efforts on generating nearly free silylium cations in solution. (1) The coordination ability of the silylium cation **3** investigated in this work could be further decreased by increasing the bulk of the boryl groups, e.g., by methylating the 9-BBN groups at strategic positions, or by replacing them with diadamantylboryl or dimesitylboryl substituents. Previous synthetic work on di- and even triadamantyl carbenium ions, as well as on dimesityl-substituted carbonyl compounds, clearly suggests that this should be possible.[24] (2) The nonpolar character of the 9-BBN groups should make it possible to work in alkane rather than aromatic solvents. It should be possible to use cyclohexane or pentane as the solvent, for which preliminary calculations indicate silylium-cation−solvent interactions which are considerably reduced to those taking place in benzene solution (compare complex binding energies of **7** and **12** in Table 3).

Furthermore, one should take advantaged of recent progress on weakly coordinating anions. Reed and coworkers found that the weakest coordination between hexahalo−carborane anions and trialkylsilylium cations takes place for hexachloro−carborane anions.[4f] However, it should be possible to obtain even weaker coordination if utilizing the dodecamethylcarba-*closo*-dodecaborate anion, recently developed by Michl and coworkers.[25] Salts of this anion were found to be stable to air, bases, and dilute acids and were found to be soluble in chloroform, carbon tetrachloride, and toluene.

Even though compounds with Si−B bonds are not considered as ordinary chemical substances, a number of synthetic procedures have been reported on the preparation of silaboranes.[13,26] Appropriate alkylboryl compounds, such as 9-borabicyclo[3.3.1]nonane, suitable for the synthesis of precursors to the silylium cation **3** are commercially available.[27] However, the Lewis acid nature of the 9-BBN substituents could lead to formation of borates, but under non-nucleophilic conditions this should be possible to avoid.

Thus, we believe that if **3** or some other silylium cations with bulky dialkylboryl substituents can be prepared, these species should be realistic candidates

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for uncoordinated silylium cations in condensed phases. They would under optimal experimental conditions, i.e., usage of alkane solvents and the carborane anion developed by Michl and co-workers,[25] press the limit toward completely free silylium ions. In such environments, it should be possible to observe a triboryl-substituted silyliym cation with a ^{29}Si NMR shift close 500 ppm, as calculated for **2**.

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Supporting Information Available: Figures and tables of Cartesian coordinates of **1**−**6** (9 pages). Ordering information is given on any current masthead page.

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