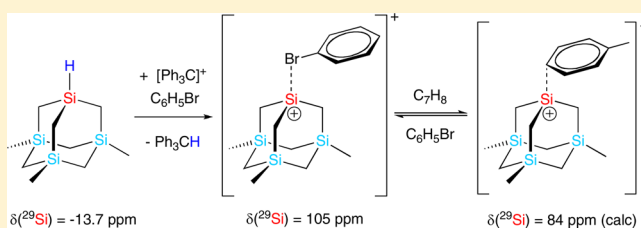


Synthesis and Structure of the First Bridgehead Silylium Ion

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Supporting Information

ABSTRACT: We report the first successful synthesis of the long-sought arene-solvated bridgehead silylium ion $[\text{Si}_4\text{Me}_3(\text{CH}_2)_6][\text{CHB}_{11}\text{Cl}_{11}]$ by hydride abstraction from the tetrasiladamantyl derivative $\text{HSi}_4\text{Me}_3(\text{CH}_2)_6$ with the trityl salt $[\text{Ph}_3\text{C}][\text{CHB}_{11}\text{Cl}_{11}]$ in toluene, benzene, or bromobenzene solution. The silylium...arene complex was characterized by X-ray diffraction analysis and by NMR spectroscopy and was studied computationally. NMR studies show that the silylium species undergoes a dynamic solvate exchange in BrPh/MePh mixed solvent.



The high Lewis acidity and reactivity of silylium ions $[\text{R}_3\text{Si}]^+$ are mainly responsible for the rather late (2002) first structural analysis of a donor-free silylium ion with a three-coordinate silicon center: namely, $[\text{Mes}_3\text{Si}][\text{HCB}_{11}\text{Me}_3\text{Br}_6]$ (Mes = 2,4,6-Me₃C₆H₂).¹ Silylium ions with smaller substituents have been isolated as solvent adducts or contact ion pairs such as $[\text{Et}_3\text{Si}\cdot\text{C}_7\text{H}_8][\text{B}(\text{C}_6\text{F}_5)_4]^{2,3}$ and $i\text{Pr}_3\text{Si}\cdot\text{Br}_6\text{B}_{11}\text{CH}_6$,⁴ respectively. Despite their high reactivity silylium ions have begun to be employed as catalysts or reagents in synthetic chemistry.^{5–9} Unlike carbon compounds, nucleophilic substitution at four-coordinate silicon centers takes place essentially exclusively through association mechanisms.¹⁰ This can result in a significant rate reduction for silane substrates in which the silicon center is the apex of a tricyclic species such as the tetrasiladamantanes $\text{XSi}_4\text{Me}_3(\text{CH}_2)_6$.¹¹

For example, the usually very labile Si–N bond is resistant to aqueous acidic hydrolysis in $\text{Et}_2\text{NSi}_4\text{Me}_3(\text{CH}_2)_6$, and the reduction of the Si–Cl unit in $\text{ClSi}_4\text{Me}_3(\text{CH}_2)_6$ to the hydrosilane $\text{HSi}_4\text{Me}_3(\text{CH}_2)_6$ (**1**) required prolonged reflux with LiAlH_4 .¹¹ On the basis of these findings, and in continuation of earlier studies by one of us on the synthesis of mono- and bis-triflates (**2** and **3**; Figure 1) and complexation studies with super Lewis acids¹² and a theoretical study (DFT and GIAO-NMR) of β -silyl-1-silaadamant-1-yl cations,¹³ we report the synthesis and characterization of an arene-solvated bridgehead silylium ion, $[\text{Si}_4\text{Me}_3(\text{CH}_2)_6\cdot\text{ArX}][\text{CHB}_{11}\text{Cl}_{11}]$ ($[\text{4}^+\cdot\text{ArX}][\text{CHB}_{11}\text{Cl}_{11}]$; ArX = C₇D₈, C₆D₃Br) derived from the bridgehead silane **1**.

The silylium ion $[\text{Si}_4\text{Me}_3(\text{CH}_2)_6][\text{CHB}_{11}\text{Cl}_{11}]$ ($[\text{4}^+][\text{CHB}_{11}\text{Cl}_{11}]$) was obtained through the classic reaction¹⁴ of the hydrosilane $\text{HSi}_4\text{Me}_3(\text{CH}_2)_6$ (**1**) with the trityl salt

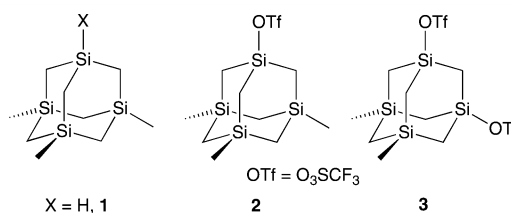


Figure 1. Previously synthesized silane derivative and the mono- and bis-triflates derived from tetrasiladamantane.

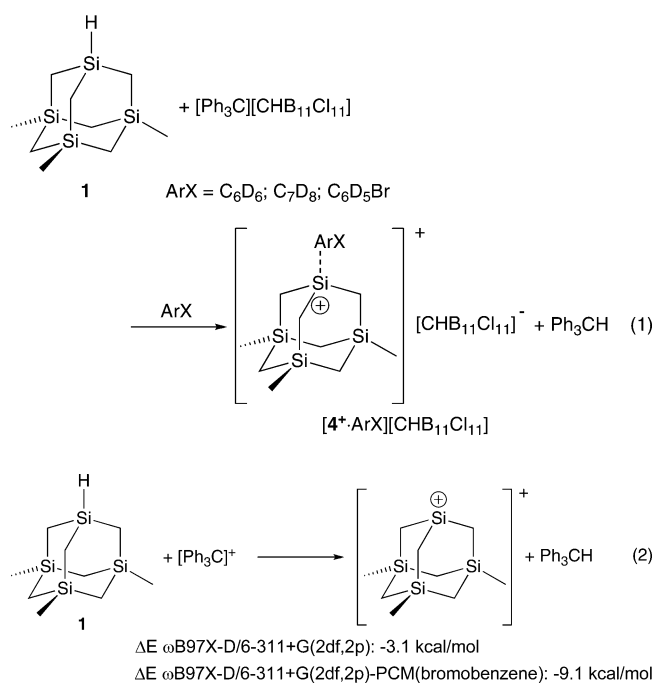
$[\text{Ph}_3\text{C}][\text{CHB}_{11}\text{Cl}_{11}]$ in benzene, toluene, or bromobenzene solution (eq 1).

The hydride abstraction process, studied computationally via the isodesmic reaction in eq 2, is found to be favorable toward the formation of the silylium ion and becomes more favorable by incorporating solvation effects (PCM).

In most cases, a brief heating at 80 °C is required to drive the reaction to completion. It is possible that this might be due to the intermediate formation of the hydride-bridged cationic species $[(\text{CH}_2)_6\text{Me}_3\text{Si}_4(\mu\text{-H})\text{Si}_4\text{Me}_3(\text{CH}_2)_6]^+$, which would be sufficiently stable to prevent or at least significantly slow down the hydride abstraction. This is supported by the observation that reaction mixtures still contain unreacted trityl salt but no hydrosilane **1** before heating. It has also been reported that such hydride-bridged compounds can be rather stable. In fact, the reaction of Et_3SiH with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in the absence of donor solvents affords solely $[\text{Et}_3\text{Si}(\mu\text{-H})\text{SiEt}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ and not the expected silylium species $[\text{Et}_3\text{Si}][\text{B}(\text{C}_6\text{F}_5)_4]$.^{15,16}

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$4^+[\text{CHB}_{11}\text{Cl}_{11}]$ is essentially insoluble in benzene or toluene but readily soluble in bromobenzene at room temperature. It possesses some solubility in hot (80 °C) benzene or toluene, and it can be crystallized from these solutions, resulting in microcrystals or X-ray-quality crystals, respectively. Although the silylium ion $4^+[\text{CHB}_{11}\text{Cl}_{11}]$ is thermally stable, it is very sensitive to minor impurities. This property and the limited availability of precursor **1** prevented us from obtaining pure samples of $4^+[\text{CHB}_{11}\text{Cl}_{11}]$ on a preparative scale. Reasonably pure samples have been obtained from NMR-scale experiments (ca. 50–60 μmol) in benzene solution, followed by removal of Ph_3CH , excess silane, and side products by repeated washing with benzene and dissolution in $\text{C}_6\text{D}_5\text{Br}$ for analysis.

For comparison and in an effort to obtain a toluene-soluble silylium salt, the synthesis of the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ salt of 4^+ was attempted in analogy to eq 1 above, using $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ as the hydride abstracting reagent. In contrast to reactions with the $[\text{CHB}_{11}\text{Cl}_{11}]^-$ salt, the reaction with the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion in toluene solution was complete within minutes at room temperature. We attribute this to the significantly higher solubility of the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ salts, even though these compounds tend to form dense oils in aromatic solvents,¹⁷ so-called liquid clathrates.¹⁸ The crude product initially separated as a dark yellow oil, which partially crystallized upon standing at room temperature for several days. Washing with toluene dissolved some of the crystalline material, and the ^1H NMR spectrum of the remaining partially dissolved crystalline material in C_7D_8 showed significant amounts of impurities or decomposition products. Brief (30 min) heating at 82 °C resulted in only minor changes to the ^1H NMR spectrum, but the ^{19}F NMR spectrum showed decomposition of the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion. The two new sets of signals are close to the values reported for $\text{B}(\text{C}_6\text{F}_5)_3$ ¹⁹ and $\text{Me}_3\text{SiC}_6\text{F}_5$,²⁰ suggesting C_6F_5 abstraction by a strong Lewis acid (4^+) as a likely decomposition pathway.²¹ The inability to obtain $[4^+\cdot\text{C}_7\text{H}_8][\text{B}(\text{C}_6\text{F}_5)_4]$ in a pure form was surprising, considering that the related trialkylsilylium-arene complexes $[\text{R}_3\text{Si}\cdot\text{ArH}][\text{B}(\text{C}_6\text{F}_5)_4]$ are readily accessible.¹⁷

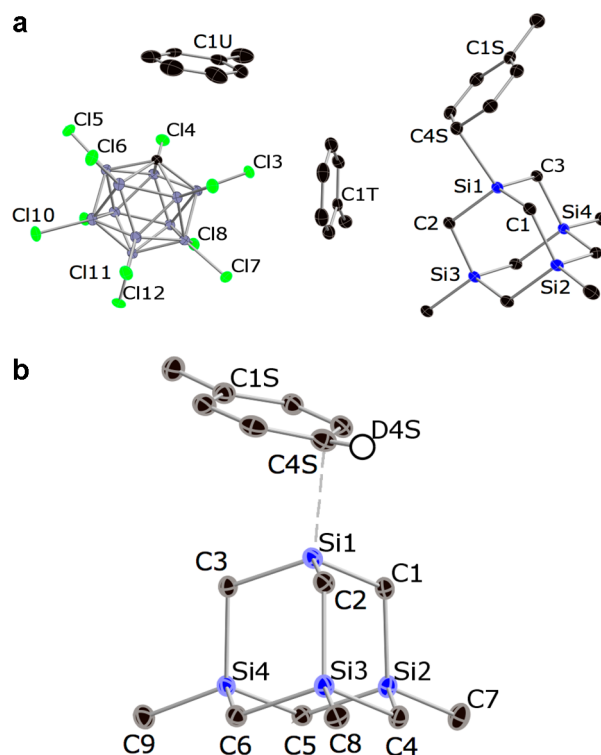


Figure 2. (a) X-ray crystal structure of $[4^+\cdot\text{C}_7\text{D}_8][\text{CHB}_{11}\text{Cl}_{11}]^-$ as a toluene adduct with solvent-separated cations and anions. (b) Thermal ellipsoid plot (30%) of the cation $[\text{Si}_4\text{Me}_3(\text{CH}_2)_6\cdot\text{C}_7\text{D}_8]^+$ ($4^+\cdot\text{C}_7\text{D}_8$). Hydrogen and deuterium atoms, with the exception of D4S, are omitted for clarity. Selected bond distances (Å) and angles (deg): Si(1)–C(1) 1.836(2), Si(1)–C(2) 1.839(2), Si(1)–C(3) 1.837(2), Si(1)⋯C(4S) 2.231(2); C(1)–Si(1)–C(2) 112.62(10), C(1)–Si(1)–C(3) 111.75(10), C(2)–Si(1)–C(3) 112.08(10), C(1S)–C(4S)–Si(1) 104.5.

The crystal structure analysis (Figure 2a) shows the silylium compound $[4^+\cdot\text{C}_7\text{D}_8][\text{CHB}_{11}\text{Cl}_{11}]^-$ as a toluene adduct with solvent-separated cations and anions. The cationic silicon center is closely coordinated to the para position of a toluene molecule with an Si(1)⋯C(4S) distance of 2.231(2) Å (Figure 2b).

The Si(1)–C bond distances within the cage average 1.837 Å, which is 0.036 Å shorter than the Si–C distances in the lower Si_3C_3 ring with an average value of 1.873 Å. The Si–C bonds that connect the lower ring with the cationic silicon center (e.g., Si(2)–C(1)) are slightly elongated with an average value of 1.901 Å, whereas the Si–CH₃ distances (1.864 Å) are close to the Si–CH₂ distances of the lower ring. The elongation of the Si(2)–C(1), Si(3)–C(2), and Si(4)–C(3) distances may be interpreted as a result of β -silyl hyperconjugation,¹³ but the expected concomitant shortening of the Si(1)–C distances is close to those reported for related trialkylsilylium ions (see below), which do not possess a β -silyl group. The C–Si(1)–C angles and the Si(1)–C–Si angles average 112.2 and 108.1°, respectively. The corresponding C–Si–C angles in the lower Si_3C_3 ring are clearly narrower (108.9°) and the Si–C–Si angles are significantly wider (113.5°). In comparison to the related neutral silanol $\text{HOSi}_4\text{Me}_3(\text{CH}_2)_6$ ¹² the main difference between its structure and the structure of $[4^+\cdot\text{C}_7\text{D}_8][\text{CHB}_{11}\text{Cl}_{11}]^-$ is the flattened geometry at the cationic silicon Si(1) in the latter species. In fact, the structural parameters of the cationic center of $[4^+\cdot\text{C}_7\text{D}_8][\text{CHB}_{11}\text{Cl}_{11}]^-$ closely resemble

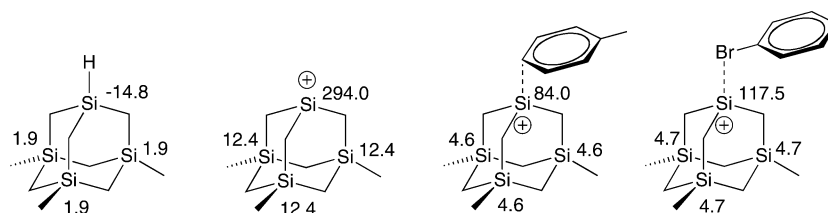


Figure 3. GIAO-²⁹Si NMR data at the ω B97X-D/6-311+G(2df,2p) level with solvation effects (PCM) for bromobenzene.

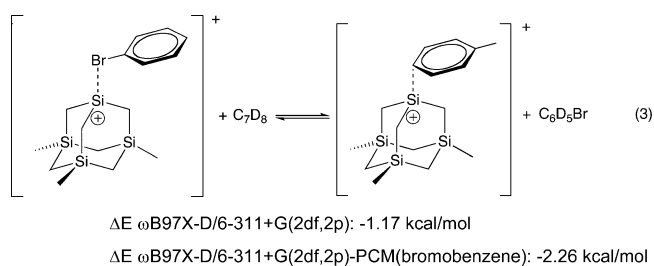
those of $[\text{Et}_3\text{Si}\cdot\text{C}_7\text{H}_8][\text{B}(\text{C}_6\text{F}_5)_4]$ (**5**), the first example of a toluene-coordinated silylium species,² and the more recently reported $[\text{Me}_3\text{Si}\cdot\text{C}_7\text{H}_8][\text{B}(\text{C}_6\text{F}_5)_4]$ (**6**).¹⁷ The Si–C distances and the C–Si–C angles average 1.84 Å and 114° and 1.833 Å and 113.7°, respectively. The Si···toluene distance in $[4^+\cdot\text{C}_7\text{D}_8][\text{CHB}_{11}\text{Cl}_{11}]^-$ is slightly longer than those in **5** and **6**, 2.231 Å versus 2.18 and 2.135 Å. The Si–C–C_{para} angles involving the cationic silicon centers and the coordinated toluene are very similar with values of 104.5, 104, and 106.1° for $[4^+\cdot\text{C}_7\text{D}_8][\text{CHB}_{11}\text{Cl}_{11}]^-$, **5**, and **6**, respectively, indicating a hybrid between a σ (Wheland type) or π complex.

Solution NMR data of $[4^+\cdot\text{C}_7\text{D}_8][\text{CHB}_{11}\text{Cl}_{11}]^-$ in $\text{C}_6\text{D}_5\text{Br}$ are in agreement with the formulation as the bromobenzene adduct $[4^+\cdot\text{C}_6\text{D}_5\text{Br}][\text{CHB}_{11}\text{Cl}_{11}]^-$ (eq 1). The ²⁹Si NMR chemical shift of the silylium ion was observed at 105 ppm. This value compares reasonably well with the computed value of 117.5 ppm for the bromobenzene complex by GIAO NMR calculations at the ω B97X-D/6-311+G(2df,2p) level with solvation effects (PCM) (Figure 3). The chemical shift for the corresponding toluene adduct was computed at 84.0 ppm, a value that is close to the 81.8 ppm observed for a toluene solution of **5**.³

The presence of the cationic silylium center is also reflected in the ¹H NMR and ¹³C NMR spectra of $[4^+\cdot\text{C}_7\text{D}_8]$, where the signal of the CH₂ groups next to the silylium center is shifted significantly downfield (0.56, 13.28 ppm) in comparison to the signal of the other CH₂ groups (−0.44, 3.86 ppm). These data may be compared to those for the triflate $\text{TfOSi}_4\text{Me}_3(\text{CH}_2)_6$, whose ¹H and ¹³C NMR chemical shifts for the two CH₂ sites were reported as 0.39, 7.81 ppm and −0.16, 4.56 ppm.¹²

During attempts to optimize the synthesis of $4^+[\text{CHB}_{11}\text{Cl}_{11}]^-$, the solution NMR spectrum of the crude product was recorded in a mixture of $\text{C}_6\text{D}_5\text{Br}$ and C_7D_8 . As this spectrum was substantially different from the spectrum in pure $\text{C}_6\text{D}_5\text{Br}$ (the ¹H NMR signal for the CH₂ groups next to the silylium center was broad and shifted upfield, and the signal of the other CH₂ groups displayed an AB pattern), measured amounts of toluene were added to a solution of $4^+[\text{CHB}_{11}\text{Cl}_{11}]^-$ in $\text{C}_6\text{D}_5\text{Br}$, and the NMR spectra of the resulting solutions were recorded. The addition of 2.1 equiv of toluene already results in a small upfield shift and slight broadening of the ¹H NMR signal for the CH₂ groups next to the silylium center. This signal continues to broaden and shift upfield to about 0.25 ppm upon the addition of 292 equiv of toluene (Figure S7, Supporting Information). The signal of the other CH₂ groups is less sensitive toward the toluene additions, but a slight broadening is observed upon the addition of 11 equiv of toluene, and the beginnings of the formation of an AB pattern can be seen upon the addition of 23 equiv of toluene. Interestingly, the ²⁹Si NMR signal of the cationic silicon center weakens already after the addition of 2.1 equiv of toluene and was not detected after the addition of more toluene. This may be a result of signal broadening due to the dynamic process in

addition to dilution by almost a factor of 2 and the partial separation of the substrate as an oil upon addition of 164 equiv of toluene. The ¹³C NMR signals are largely unaffected (see Figure S8, Supporting Information). We interpret these results as evidence of solvate exchange from bromobenzene to toluene at the cationic silicon center according to eq 3. This was also supported by calculation of the corresponding reaction, which shows this exchange to be slightly exothermic.



A similar competition between aryl halide and π -arene coordination (albeit intramolecularly) was observed for the *m*-terphenyl-substituted silylium species $[\{2-(2,6\text{-F}_2\text{C}_6\text{H}_3)-6\text{-}(\text{Me}_n\text{C}_6\text{H}_{5-n})\text{C}_6\text{H}_3\}\text{SiMe}_2]^+$.²²

The upfield shift of the ¹H NMR signal for the CH₂ groups next to the silylium center may be explained by the relatively close proximity of these hydrogen atoms to the center of the aromatic toluene ring (diamagnetic ring current,²³ $d(\text{center of toluene-H3A}) = 3.228$ Å in the structure of $4^+\cdot\text{C}_7\text{D}_8$), and the broadening is most likely due to the rotation of the toluene molecule around the Si···C axis. Similarly, the close contact of the toluene molecule and the cationic silicon center results in a greater chemical shift difference of the hydrogen atoms of the lower CH₂ groups, giving rise to an AB pattern.

In summary, the synthesis of the first arene-solvated bridgehead silylium ion, $[\text{Si}_4\text{Me}_3(\text{CH}_2)_6][\text{CHB}_{11}\text{Cl}_{11}]$ ($4^+[\text{CHB}_{11}\text{Cl}_{11}]$), by hydride abstraction from $\text{HSi}_4\text{Me}_3(\text{CH}_2)_6$ (**1**) with the trityl salt $[\text{Ph}_3\text{C}][\text{CHB}_{11}\text{Cl}_{11}]^-$ has been achieved in benzene, toluene, or bromobenzene solution. The silylium···arene complex was characterized by X-ray analysis and NMR spectroscopy and was also studied computationally. NMR studies in BrPh/MePh mixed solvent indicate a dynamic solvate exchange. This solvate exchange process is deemed favorable by computations.

■ ASSOCIATED CONTENT

📄 Supporting Information

Text, figures, a table, and CIF and xyz files giving experimental procedures, NMR spectra of $[4^+\cdot\text{C}_6\text{D}_5\text{Br}][\text{CHB}_{11}\text{Cl}_{11}]$, crystal data and structure refinement details for $[4^+\cdot\text{C}_7\text{D}_8][\text{CHB}_{11}\text{Cl}_{11}]\cdot 2\text{C}_7\text{D}_8$, additional figures of the structure and crystallographic data for $[4^+\cdot\text{C}_7\text{D}_8][\text{CHB}_{11}\text{Cl}_{11}]\cdot 2\text{C}_7\text{D}_8$, and Cartesian coordinates for the toluene and bromobenzene

complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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