Persistent Bissilylated Arenium Ions

Rita Meyer, Karla Werner, and Thomas Müller*[a]

Abstract: A series of bissilylated arenium ions **1** with different substitution patterns on the aryl ring have been synthesized by hydride abstraction from 2-aryl-substituted 2,6-dimethyl-2,6-disilaheptanes (**2**) via transient silylium ions. The arenium ions have been identified by their characteristic NMR chemical shifts, ($\delta^{29}Si = 19.1 - 25.6$, $\delta^{13}C^{ipso} = 89.0 - 102.4$, $\delta^{13}C^{ortho} = 160.9 - 182.0$, $\delta^{13}C^{meta} = 132.5 - 146.9$, $\delta^{13}C^{para} = 150.2 - 169.9$) supported by quantum mechanical calculations of structures, energies, and magnetic properties at the B3LYP/6-311G(d,p)//B3LYP/6-31G(d) + ΔZPVE level of theory. The calculations clearly reveal the charge dispersing and stabilizing effect of the silyl substituents in arenium ions **1**. The bissilylated benzenium ion **1a** is more stable than the parent benzenium ion ($C_6H_7^+$) by 37.6 kcal mol^{-1}. The synthesized arenium ions **1** are stable in solution at room temperature for periods ranging from a few hours to days. This unusual stability is attributed to: 1) the thermodynamic stabilization of the arenium ion by two β-silyl substituents and 2) the essentially non-nucleophilic reaction conditions (the use of the weakly coordinating $[B(C_6F_5)_4]^-$ anion and aromatic hydrocarbons as solvents). Addition of stronger nucleophiles than aromatic hydrocarbons (for example, acetonitrile) results in desilylation of the arenium ion **1** and recovery of the 2-aryl-2,6-disilaheptane moiety.

Keywords: carbocations • density functional calculations • NMR spectroscopy • silicon • silyl effects

Introduction

Arenium ions,[1] formed by the protonation or alkylation of arenes, are key intermediates in electrophilic aromatic substitution reactions and in rearrangements in acidic solutions and the gas phase.[2–7] The history of stable arenium ions dates back to pioneering work by the groups of Olah,[8, 9] McLean,[10, 11] Doering,[12] and Gillespie[13] in the late 1950s to early 1960s. ^{13}C and ^{1}H NMR spectroscopic investigations in superacidic media by Olah and co-workers greatly elaborated this early work,[14–18] and recently even the eigenvalues of the ^{13}C chemical shift tensors of simple arenium ions have been determined on solid metal halide superacids.[19] Mechanisms and rates of gas-phase reactions involving arenium ions have been extensively studied by mass spectroscopy, ICR, and related methods.[20–28] Although the isolation of tetrafluoroborate salts of simple alkylbenzenium ions was achieved by Olah and Kuhn[8] in the mid-1950s and the structural characterization of the heptamethyl benzenium ion as the tetrachloroaluminate salt[29] dates back to the late 1960s, only the recent progress in experimental techniques has allowed the isolation of a silylarenium ion,[30] chloroarenium ions,[31] and even protonated arenes[32] as crystalline materials and their characterization by X-ray structure analysis.

Recent achievements in silyl cation chemistry[33] have cleared the way for a novel approach to stable, silyl-substituted carbocations[34] at ambient temperatures.[30, 35–37] The hydride-transfer reaction between trityl cations and trialkylsilanes in aromatic hydrocarbons, originally erroneously interpreted as resulting in stable silylium ions,[30, 39] yields persistent silylated arenium ions.[40] The high electrophilicity of these silylated arenium ions has been utilized in the synthesis of novel non-oxidizing superacids[32, 41] and stable silylium ions.[42] They are also suitable reagents for the transfer of R_3Si^+ equivalents to molecules with multiple bonds or lone pairs. This is highlighted by the synthesis of β-silyl-substituted carbocations,[35] which are persistent at room temperature and by the recent synthesis of persilylated phosphonium and arsonium ions.[43] Similarly, we have shown that intramolecular addition of transient silylium ions to C=C double and C≡C triple bonds yields silanorbornyl cations[37] and β-silyl-substituted vinyl cations,[36] respectively. The success of this approach to silyl-substituted carbocations over the traditional methods using magic acid or related superacidic media[44, 45] clearly rests on the reaction conditions. The omnipresence of fluorine- or oxygen-containing nucleophiles in those superacids results in the rapid decomposition of silyl-substituted carbocations by favorable cleavage of Si–C bonds even at temperatures as low as −100 °C.[44, 45] In contrast, the

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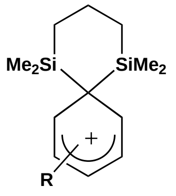
reaction conditions for the initial hydride transfer reaction, that is, involving weakly coordinating anions (e.g., the tetrakis(pentafluorophenylborate) anion) and aromatic hydrocarbons, exclude this type of successive reaction, thereby increasing the kinetic stability of the silylated cation. The advantages of these very weakly nucleophilic reaction conditions are highlighted by the recent synthesis of stable protonated arenes, including benzenium ($C_6H_7^+$), which were isolated as crystalline materials at ambient conditions with carborate or tetraarylborate anions[32] and protonated C_{60} fullerene.[41]

Following our previous work[36, 37] on the addition of transient silylium ions to C–C multiply bonded systems, we embarked on a systematic study on the intramolecular addition to aryl groups using 2-aryl-substituted 2,6-disilaheptanes **2** as precursors for the synthesis of bissilyl-substituted arenium ions **1**. The cyclic arenium ions **1** might be viewed as possible intermediates for a 1,5-aryl shift and thereby bear a close resemblance to the 1,3-bridged cations **3**, suggested by Eaborn and co-workers as intermediates in the solvolysis of silicon halides with the $\{(Me_2ArSi)(Me_3Si)_2C\}$ group.[46] We describe herein the synthesis of bissilylated arenium ions under experimental conditions that allow their NMR characterization in solution at ambient temperature. The results of quantum-mechanical investigations on structures, energies, and magnetic properties are reported; these not only corroborate the experimental findings but also give a detailed description of the bonding and charge distribution in arenium ions **1**.



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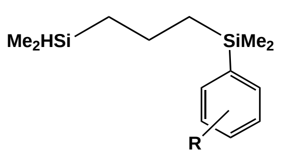

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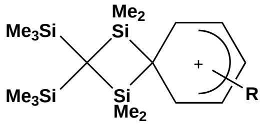

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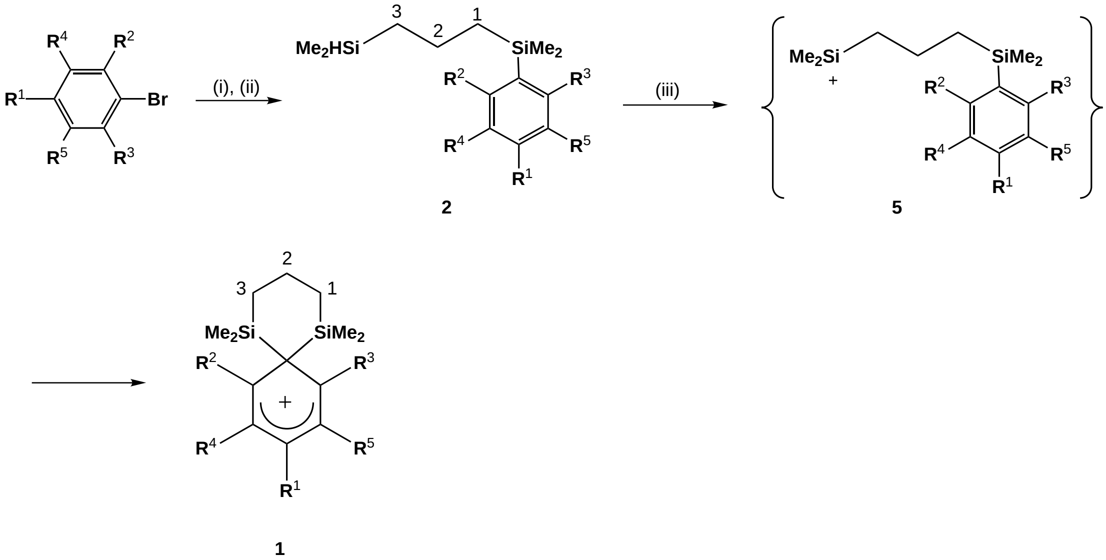
Results and Discussion

NMR studies: The starting materials for the synthesis of bissilylated arenium ions **1a–g**, that is, 2-aryl-2,6-disilaheptanes **2a–g**, were obtained from the silyl chlorides **4** by reactions summarized in Scheme 1. The structures of compounds **2** were verified by using standard one-dimensional ^{1}H, ^{13}C, ^{29}Si and two-dimensional ^{1}H/^{13}C NMR techniques. Characteristic for all disilaheptanes **2** are two ^{29}Si NMR signals, at $\delta^{29}\text{Si} = -14.1$ to -14.5 (SiH) and $\delta^{29}\text{Si} = -3.9$ to -4.6 (Si-aryl), and the multiplet ^{1}H NMR resonance for the SiH proton, at $\delta = 3.84-3.79$. Reactions of **2a–g** with one equivalent of trityltetrakis(pentafluorophenyl)borate (TPFPB) in [D$_6$]benzene at room temperature (RT) gave in the first step the silylium ions **5a–g** and triphenyl methane;[38] this last compound was unequivocally identified from its ^{1}H and ^{13}C NMR spectra.[47] The silylium ions **5a–g** are only transient species and undergo an intramolecular reaction yielding bissilylated arenium ions **1a–g** (Scheme 1).[38]

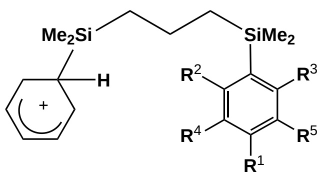
The arenium ions **1a–g** (Table 1) were identified by their characteristic NMR spectra (see Figure 1 for an example).[48] One single line in the ^{29}Si NMR spectra in [D$_6$]benzene at $\delta^{29}\text{Si} = 19.1-25.6$ indicates in each case the formation of a symmetric species (see Table 2). The observed chemical shift range is similar to the ^{29}Si NMR chemical shifts found for bis-β-silyl-substituted vinyl cations ($\delta^{29}\text{Si} = 22-24$)[36] and can be



Scheme 1. Synthesis of arenium ions **1** (see also Table 1): i) Mg, THF (**a–d**, **f**) or *n*BuLi, hexanes (**e**,**g**); ii) $Me_2HSi(CH_2)_3SiMe_2Cl$ (**4**),THF, reflux; iii) TPFPB, C_6D_6, RT.

Table 1. Substitution pattern of the aryl ring in substituted arenium ions **1a–g** (see Scheme 1).

	R^1	R^2	R^3	R^4	R^5
a	H	H	H	H	H
b	CH_3	H	H	H	H
c	CH_3	CH_3	H	H	H
d	H	CH_3	H	H	CH_3
e	H	CH_3	CH_3	H	H
f	H	H	H	CH_3	CH_3
g	CH_3	CH_3	CH_3	H	H



6a-g

clearly distinguished from the expected resonances of monosilylated benzenium ions, **6a–g**, at $\delta^{29}Si = 70-100$,[30b, 39] which might be formed by intermolecular reaction of the intermediate silylium ions **5a–g** with the solvent benzene. For the benzenium ion **1a**, nearly the same ^{29}Si NMR chemical shift is observed in $[D_8]$toluene as in $[D_6]$benzene ($\delta^{29}Si = 26.9$ and 25.6, respectively, see Table 2), indicating negligible solvent–cation interactions. This contrasts the behavior of cations of type **6** for which solvent effects on the ^{29}Si NMR chemical shift of more than 10 ppm are reported under the same conditions.[30b] The downfield shift of the ^{29}Si NMR signal, $\Delta\delta^{29}Si$, which occurs upon ionization of **2**, is significant (23–29 ppm and 33–40 ppm, for the Si–aryl and the Si–H resonance, respectively) and indicates an accumulation of positive charge at silicon. There is a clear dependence of $\Delta\delta^{29}Si$ on the

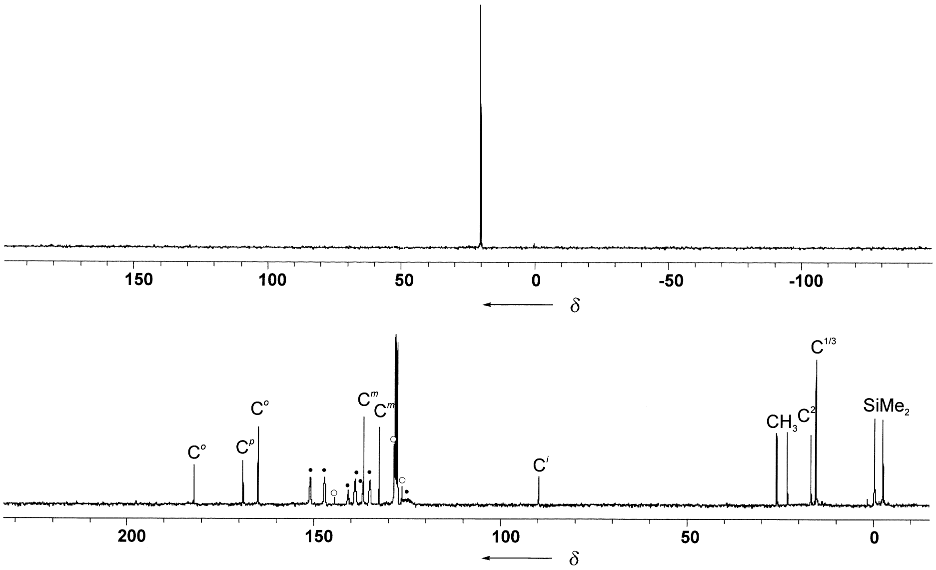


Figure 1. 49.7 MHz ^{29}Si {^1H} Inept NMR spectrum (upper trace) and 62.9 MHz ^{13}C {^1H} NMR spectrum of **1c** in $[D_6]$benzene (lower trace, ○ triphenylmethane, ● $[B(C_6F_5)_4]^-$).

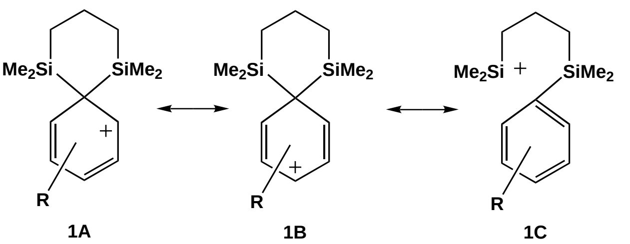
Table 2. Experimental,[a,d] calculated (at GIAO/B3LYP/6-311G(d,p)[b] in parenthesis), and corrected, theoretical NMR data[c] (in italics and parenthesis) of silylated arenium ions and related compounds.

	$\delta^{29}Si$	$\delta^{13}C^{ipso}$	$\delta^{13}C^{ortho}$	$\delta^{13}C^{meta}$	$\delta^{13}C^{para}$	$\delta^{13}C^{1/3}$	$\delta^{13}C^2$	$\delta^{13}CH_3$
1a	25.6	102.4	162.9	133.9	150.3	14.6	19.8	–2.9
1a[b]	(39.7)	(106.1)	(178.3)	(140.0)	(160.0)	(18.9)	(22.1)	(2.2)
1a[c]		*(101.3)*	*(171.9)*	*(134.5)*	*(154.0)*	*(16.3)*	*(19.4)*	*(0.0)*
1a[d]	26.9	102.6	163.0	133.2	150.3	14.6	19.9	–3.0
1b	22.1	93.3	165.8	135.6	169.9	14.4	17.1	23.5, –1.8
1b[b]	(34.9)	(98.8)	(176.3)	(141.2)	(180.2)	(18.7)	(22.2)	(27.3), (1.5)
1b[c]		*(94.3)*	*(170.0)*	*(135.7)*	*(173.8)*	*(16.1)*	*(19.5)*	*(24.5), (–0.7)*
1c	20.4	89.8	182.0, 165.1	136.7, 132.5	169.0	15.4	16.8	26.0, 23.1, –0.3, –2.6
1c[b]	(33.1)	(96.9)	(192.3),(174.7)	(143.9),(138.6)	(178.4)	(19.6)	(22.9)	(28.4), (26.4), (1.6), (0.8)
1c[c]		*(92.5)*	*(185.6), (167.8)*	*(138.3),(133.2)*	*(172.0)*	*(17.0)*	*(20.2)*	*(25.6), (23.6), (–0.6), (–1.4)*
1d	22.7	96.2	180.0, 164.2	142.4, 135.9	152.9	15.5	16.8	25.6, 19.5, –0.3, –2.3
1d[b]	(35.8)	(102.0)	(193.9),(173.5)	(150.7),(142.8)	(160.8)	(19.8)	(22.7)	(28.7), (23.0), (1.9), (1.2)
1d[c]		*(97.4)*	*(187.2), (158.2)*	*(145.0),(137.3)*	*(154.9)*	*(17.2)*	*(20.0)*	*(25.9), (20.3), (–0.3), (–1.0)*
1e	21.6	95.1	180.6	134.3	150.2	16.6	17.4	27.0, –0.1
1e[b]	(35.9)	(100.2)	(194.7)	(140.3)	(157.7)	(20.1)	(21.7)	(31.9), (2.3)
1e[c]		*(95.7)*	*(188.0)*	*(134.8)*	*(151.8)*	*(17.5)*	*(19.0)*	*(29.0), (0.1)*
1f	24.3	102.9	160.9	146.9	153.6	15.1	17.1	20.0, –1.4
1f[b]	(35.9)	(103.7)	(174.8)	(153.6)	(163.3)	(18.8)	(22.2)	(23.2), (2.0)
1f[c]		*(99.1)*	*(168.5)*	*(147.8)*	*(157.3)*	*(16.2)*	*(19.5)*	*(20.5), (–0.2)*
1g	19.1	89.0	179.7	135.7	167.3	16.7	16.8	27.8, 22.6, –0.5
1g[b]	(31.2)	(94.3)	(192.2)	(141.4)	(176.8)	(20.1)	(21.6)	(31.5), (26.3), (2.0)
1g[c]		*(89.9)*	*(185.5)*	*(135.9)*	*(170.5)*	*(17.5)*	*(18.9)*	*(28.6), (23.5), (–0.2)*
5a	(388.1),(–0.7)	(139.7)	(139.4),(137.1)	(135.5),(134.6)	(138.0)	(39.8),(27.1)	(21.0)	(12.8), (1.9)
6a	(115.5), (–3.7)	(141.2)	(138.5)	(134.5)	(136.9)	(37.0), (24.6)	(25.6)	(1.3), (–1.7)
10	35.0, –4.2	138.2	133.8	128.2	129.4	19.7, 17.2	18.0	0.0, –3.5, –3.7
11	(49.6), (32.7)	(107.2)	(177.5), (177.4)	(140.1), (139.0)	(158.9)	(19.9),(17.5)	(21.9)	(2.5), (1.7)

[a] In $[D_6]$benzene at RT, versus TMS. [b] Calculated using B3LYP/6-31G(d) geometries versus TMS; $\sigma^{29}Si(TMS) = 339.9$, $\sigma^{13}C(TMS) = 183.8$. [c] Calculated from theoretical data (see [b]) using the empirical correlation: $\delta^{calcd} = (2.234 \pm 1.158) + (1.019 \pm 0.008)\ \delta^{exptl}$, obtained from a set of 8 standard compounds; see Supporting Information for details. [d] In $[D_8]$toluene at RT.

electron donating ability of the aryl group, that is, $\Delta\delta^{29}Si$ is largest for the benzenium ion **1a** [$\Delta\delta^{29}Si = 29.7$ (Si–aryl) and 40.1 (Si–H)] and smallest for the mesitylenium ion **1g** [$\Delta\delta^{29}Si = 23.7$ (Si–aryl) and 33.5 (Si–H)].

Two multiplets in the ratio 1:2 in the ^{1}H NMR spectrum and two signals in the ^{13}C NMR spectrum at $\delta^{13}C = 19.8-16.8$ (C^2) and $\delta^{13}C = 14.4-16.7$ ($C^{1/3}$) for the three methylene groups of the carbon backbone (C^1–C^2–C^3) confirmed the formation of a symmetric cation in each case. The typical ^{13}C NMR chemical shift pattern for arenium ions[14–19] was found for each of the cations **1a–g** (see Table 2 and Figure 1). The *ortho* and *para* carbons of the aryl substituents in cations **1a–g** are strongly deshielded relative to the starting silanes ($\Delta\delta^{13}C^{ortho} = 39.6-28.9$ and $\Delta\delta^{13}C^{para} = 35.1-21.6$), while the *meta* carbons are only slightly affected by the ionization ($\Delta\delta^{13}C^{meta} = 9.9-6.3$). The ^{13}C NMR chemical shifts for the C^{ipso} are in the range 89.0–102.9 and are highly diagnostic of the structure of the ions. The strong high-field shifts of the C^{ipso} relative to the precursor silanes ($\Delta\delta^{13}C^{ipso} = -36.5$ to -49.4) are consistent with the rehybridization of C^{ipso} from sp^2 to sp^3, which occurs upon addition of the silyl cation to the aryl substituent. These characteristic changes in the ^{13}C NMR chemical shifts of the arene substituents gives evidence for the static nature of the ions **1a–g**, and, therefore, we can discard the possibility of a conceivable fast (on the NMR timescale) 1,5-aryl shift between two equivalent silylium ions **5a–g**. Furthermore, they indicate the delocalization of positive charge into the aryl substituent as rationalized by the dienyl cation-like representations **1A**,**B** (see Scheme 2).



Scheme 2. Schematic representation of the delocalization of positive charge in arenium ions **1**.

Comparison of the ^{13}C NMR data for the bissilylated arenium ions **1a**,**b**,**g** with reported data for non-silylated arenium ions, **7–9**,[15, 19] (Table 2, Figure 2), clearly reveal the influence of the two silyl substituents in cations **1**. The *ortho* and *para* positions of the aryl substituent in **1a**,**b**,**g** are less deshielded ($\delta^{13}C^{ortho} = 162.9-179.7$ and $\delta^{13}C^{para} = 150.3-169.9$) than found for the arenium cations **7–9** ($\delta^{13}C^{ortho} = 181.2-193.6$ and $\delta^{13}C^{para} = 178.1-201.9$), while the *ipso* carbons in **1a**,**b**,**g** are less shielded ($\delta^{13}C^{ipso} = 89.0-102.4$ (**1a**,**b**,**g**) and $\delta^{13}C^{ipso} = 49.5-52.2$ (**7–9**)). The changes of $\delta^{13}C^{ipso}$ and $\delta^{13}C^{ortho}$ can not be straightforwardly interpreted since the electronic effects are obscured by substituent effects of the silyl groups on $\delta^{13}C$; however, the remote $\delta^{13}C^{para}$ is a suitable probe for the charge distribution in arenium ions.[44c] The high-field shift of $\delta^{13}C^{para}$ for the pairs of equally substituted arenium ions **7/1a**, **8/1b**, and **9/1g** indicates that less positive charge is located in the aryl ring in cations **1a**,**b**,**g** than in the protonated arenes **7–9**, in accord with the well-established charge dispersing effect of β-silyl groups.[36, 49] Similar high-field shifts of the ^{13}C resonance of the positively charged carbons in carbocations upon β-silyl substitution have been reported for vinyl cations and related compounds.[34, 36, 43a,b]

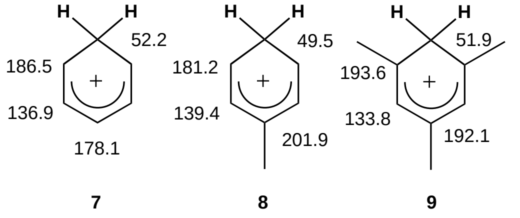
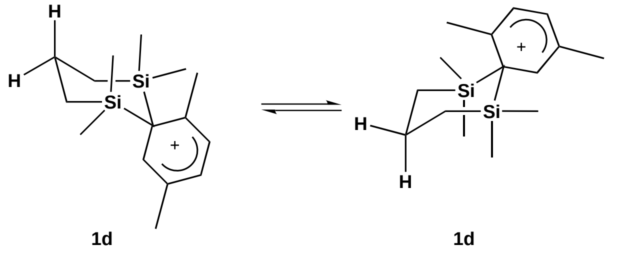


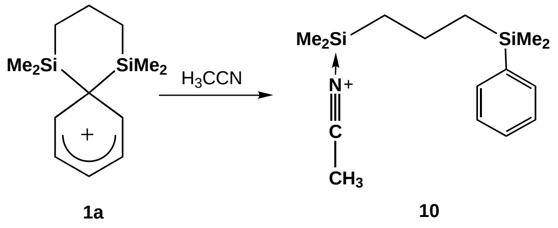
Figure 2. ^{13}C NMR chemical shifts of arenium ions **7–9**.[15, 19]

For the asymmetrically substituted 2,4-xylylenium ion **1c**, two clearly separated signals for the equatorial and axial methyl groups at silicon are observed in the ^{1}H and ^{13}C NMR spectra recorded at 303 K (see Figure 1 for ^{13}C NMR). The ^{1}H NMR signals for the equatorial and axial protons of the central methylene group (C^2H_2) of the 1,3-disilacyclohexane ring were also clearly separated. The signals have no kinetic line broadening, indicating that the ring-flip process of the 1,3-disilacyclohexane ring in **1c** is slow on the NMR timescale at RT. In contrast, for the 2,5-xylylenium ion **1d**, kinetic line broadening of the respective signals at 303 K was detected. Additional NMR measurements at 285 and 318 K allowed an approximate calculation of the enthalpy of activation for the ring-flip process (see Scheme 3), which amounts to (15.1 ± 2.9) kcal mol^{-1} (see Supporting Information for details).[50]



Scheme 3. Ring-flip process in xylylenium ion **1d**.

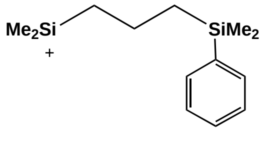
Arenium ions **1a–g** are stable at RT; however, there is a clear dependence of the stability of the ion on the number of substituents and the substitution pattern at the aryl ring. The benzenium ion **1a** gradually decomposes during a period of several hours in solution at RT, while the 2,4-xylylenium ion **1c** and the mesitylenium ion **1g** are stable for days under the same conditions. Addition of stronger coordinating solvents than aromatic hydrocarbons leads to the collapse of the intramolecular interaction, for example, the addition of acetonitrile to a solution of **1a** in benzene, instantaneously gives the acyclic silyl nitrilium species **10**, which is unequivocally identified by its characteristic ^{29}Si NMR spectra (see Scheme 4 and Table 2).[30b, 36, 51]



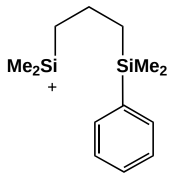
Scheme 4. Formation of the acyclic silyl nitrilium species **10**.

Theory: Calculations[52] of structures and energies of bissilylated arenium ions and related compounds were performed by using the nonlocal DFT level of theory and Becke's three parameter hybrid functional and the LYP correlation functional (B3LYP), along with the standard 6-31G(d) basis set (B3LYP/6-31G(d)).[53] Subsequent frequency calculations at the B3LYP/6-31G(d) level were carried out to verify the stationary points as minima.[54] Finally, relative energies were calculated at the B3LYP/6-311G(d,p) level with B3LYP/6-31G(d) geometries (B3LYP/6-311G(d,p)//B3LYP/6-31G(d)), and those energies were further improved by adding zero-point vibration energy differences (ΔZPVE). Relative energies, reaction energies, and association energies E_A quoted in the text are all computed at this level, unless otherwise stated. NMR chemical shifts were calculated by using the GIAO/B3LYP method[55] and the 6-311G(d,p) basis set for all atoms.

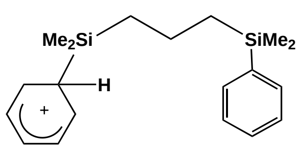
The results of calculations for isomeric $C_{13}H_{23}Si_2^+$ cations indicate that the silylium ion **5a** in its *anti*,*anti* conformation is a high-lying minimum on the potential energy surface (PES), while the *syn*,*syn* conformer is not a stationary point on the PES and collapses during the optimization procedure to the symmetrically bridged ion **1a**. The intramolecular stabilization of **5a** by the phenyl substituent, which is the energy difference between the arenium ion **1a** and the silylium ion **5a**, is 22.1 kcal mol^{-1}. Intermolecular interaction between the silylium ion **5a** and benzene, calculated for the ion **6a** ($E_A = -17.9$ kcal mol^{-1}), is smaller (by 4.2 kcal mol^{-1}). This suggests that even in benzene solution the intramolecular formation of the cyclic arenium ion **1a** is favored over the intermolecular reaction yielding the monosilylated arenium ion **6a**; this is in qualitative agreement with the experimental results. In addition, **1a** is further stabilized by weak interactions with the solvent. The interaction energy between benzene and **1a**, calculated for **11**, is, however, relatively small, $E_A = -2.6$ kcal mol^{-1}, suggesting that at room temperature no significant cation–solvent interactions are present.[56] This is in agreement with the negligible solvent effects on the ^{29}Si and ^{13}C NMR chemical shifts found experimentally for **1a** (see Table 2).



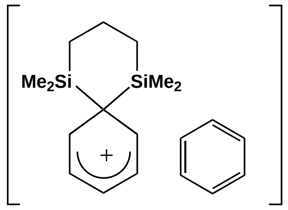
anti, anti **5a**



syn, syn **5a**



6a



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Quantum-mechanical methods for the calculation of NMR chemical shifts have been extensively applied in carbo-[57] and silyl-cation chemistry,[33a, 58] and the validity of theoretical structures is frequently established by comparing the computed NMR chemical shifts against the experimental data. The ^{29}Si and ^{13}C NMR chemical shifts calculated at GIAO/B3LYP/6-311G(d,p)//B3LYP/6-31G(d) for **1a**–**g** are summarized along with the experimental data in Table 2. The general trend of the experimental data is faithfully reproduced by the computations; however, the individual errors between the computed and experimental NMR chemical shift are large. In general all nuclei are predicted by the calculations to be too deshielded, for example, for **1a** by 2–15 ppm. In particular, the deviations for the unsaturated carbons are large: +9.6–15.4 for C^{ortho} and +7.7–10.3 for C^{para}. This is clearly due to deficiencies of the applied method and basis set. DFT-based methods like GIAO/DFT calculations are known to overestimate paramagnetic contributions to the chemical shielding, giving, in critical cases, overly deshielded chemical shifts.[58a, 59] In a series of papers Gauss, Siehl, and Schleyer and co-workers[60–63] have demonstrated the importance of including electron correlation in chemical shift calculations for unsaturated carbocations like vinyl,[61] allyl,[62] and arenium[14, 63] ions. For these cations, MP2[14, 19, 62, 63] or even higher correlated methods like CCSD(T)[61] must be applied. The size of the cations studied and the extent of our investigation prevent, however, the use of these highly accurate methods. Instead, an empirical correction, which is derived from a linear regression between experimental and calculated ^{13}C NMR chemical shifts for a set of eight closely related compounds (giving 34 data points, for details, see Supporting Information) was applied to account for some of the deficits of the less accurate GIAO/DFT method. This procedure gives improved theoretical ^{13}C NMR chemical shifts, for example, for **1a** deviations of −0.4–9 ppm are found. However, the overall agreement between these corrected theoretical and the experimental data is good (see Table 2); for example, the ^{13}C NMR chemical shift of the structural highly diagnostic C^{ipso} is nicely reproduced by the calculations (deviations from experimental δ^{13}C^{ipso} are −3.8–2.7). Thus, the NMR chemical shift calculations corroborate the validity of the computed structures.

The calculated structures of cations **1a**–**g** clearly identify them as arenium ions and the particular structural features can be straightforwardly discussed in terms of valence-bond formulas **1A**–**C** (see Scheme 2). The structure of **1a** is shown in Figure 3 and the important geometrical parameter of cations **1a**–**g** and **7**–**9** are summarized in Table 3. All cations

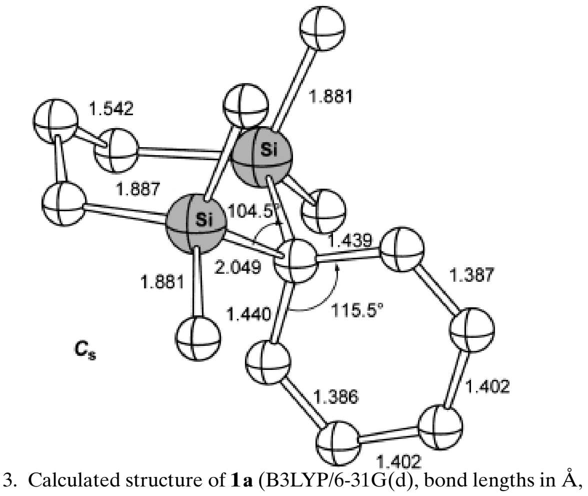


Figure 3. Calculated structure of **1a** (B3LYP/6-31G(d), bond lengths in Å, hydrogen atoms are omitted for clarity).

Table 3. Calculated geometrical parameters of arenium ions (at B3LYP/6-31G(d)).

	SiC^{ipso}	$C^{ipso}C^{ortho}$	$C^{ortho}C^{meta}$	$C^{meta}C^{para}$	A	$\alpha(SiC^{ipso}Si)$	$\beta(C^{ortho}C^{ipso}C^{ortho})$
1a	2.049, 2.049	1.439, 1.441	1.387, 1.386	1.402, 1.402	0.94	104.1	115.5
1b	2.038, 2.038	1.442, 1.442	1.381, 1.382	1.412, 1.409	0.93	104.6	114.7
1c	2.045, 2.045	1.457, 1.452	1.392, 1.377	1.404, 1.410	0.90	105.1	114.9
1d	2.049, 2.047	1.452, 1.450	1.399, 1.384	1.411, 1.391	0.92	104.6	115.9
1e	2.072, 2.055	1.466, 1.475	1.394, 1.389	1.390, 1.396	0.85	104.6	115.5
1f	2.041, 2.041	1.437, 1.438	1.392, 1.391	1.407, 1.407	0.96	104.4	115.9
1g	2.066, 2.049	1.476, 1.469	1.385, 1.389	1.404, 1.400	0.84	105.1	114.8
7		1.473	1.372	1.413	0.81	100.6[a]	116.9
8		1.475	1.366	1.425	0.77	101.3[a]	116.0
9		1.488	1.371	1.420	0.73	102.4[a]	117.9

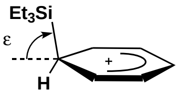
[a] $HC^{ipso}H$ angle.

1a–g are characterized by alternating C–C bond lengths in the six-membered carbocycle (long C^{ipso}–C^{ortho}, short C^{ortho}–C^{meta}, and long C^{meta}–C^{para} bonds). This bond length alternation in the six-membered ring can be quantified by using Julg's parameter A,[64] which is defined by the difference between the individual C–C bond length (r_i) and the average C–C bond length (r) of the n bonds in the six-membered ring [Eq. (1)].

$$A = 1 - (225/n)\Sigma(1 - r_i/r)^2 \qquad (1)$$

For benzene, $A = 1$ and the scaling factor 225 in Equation (1) is used to set $A = 0$ for Kekulé-benzene (r(C–C) = 1.520 and r(C=C) = 1.330).[64] For the arenium ions **1a–g**, A values of 0.96–0.84 are calculated (Table 3). The bond length alternation is in agreement with experimental structures for alkyl-substituted arenium ions[29–32] and can be rationalized by the dienyl cation resonance structures **1A** and **1B** (Scheme 2). The influence of the silyl substituents in **1a–g** is revealed by comparison of the calculated structures of **1a**,**b**,**g** with those of the non-silylated cations **7–9**. Qualitatively, the stabilizing β effect of the silyl groups favors the resonance structure **1A**, leading to an attenuation of the bond length alternation (i.e., larger A values) for the cations **1a**, **1b**, and **1g**, (A = 0.94, 0.93, and 0.84, respectively) relative to their non-silylated counterparts **7**, **8**, and **9** (A = 0.81, 0.77, and 0.73, respectively, see Table 3). The hyperconjugative effect of the silyl groups is also shown by the shorter C^{ipso}–C^{ortho} bonds in **1a**,**b**,**g** relative to the protonated arenes **7**, **8**, and **9** (1.441, 1.439 (**1a**), 1.473 (**7**); 1.442, 1.442 (**1b**), 1.475 (**8**); 1.476, 1.469 (**1g**) 1.488 Å (**9**)). Finally, the Si–C^{ipso} bonds in all arenium ions **1a–g** (2.038–2.066 Å) are strongly elongated [relative to the average r(Si–C^{aryl}) = 1.879 Å[65] in aryl silanes and to the average r(Si–C^{alkyl}) = 1.860 Å[65] in alkylsilanes or to r = 1.944 and 1.928 Å, calculated for the Si–C bonds in **1a(H)**] and is best described by the no-bond resonance structure **1C** (see Scheme 2).

The structures of silylated areniumions, for example, triethylsilyltoluenium (**12**),[30] have been discussed controversially. In particular, their formulation as σ complexes, that is, arenium ions, which is based mostly on the theoretical analysis of the structure and bonding in these cations,[40] has been severely questioned. Reed[66] and later Kochi[67] have alternatively put forward the idea of a continuum of structures between classical σ-complexes (arenium ions) and π complexes. A measure for the σ/π character is the angle ε between the electrophile, the C^{ipso}, and the plane of the arene ring. Pentamethylbenzenium, a typical σ complex has $\varepsilon = 50°$,[32, 67] while for π complexes, for example, arene/nitrosonium complexes, $\varepsilon \geq 90°$.[67] Thus, these authors assigned a rather high degree of π character to the monosilylated **12** ($\varepsilon = 76°$).[66, 67] In contrast, for the cations **1a–g**, ε = 52.1–52.6° were calculated. This is in agreement with the NMR results and with other structural parameters and these criteria clearly identify **1a–g** as σ complexes (arenium ions).



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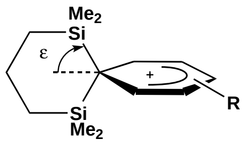
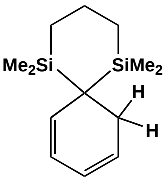
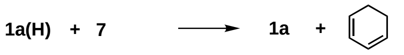


1a-g



1(H)

The structural and electronic differences between the silylated arenium ions and their non-silylated counterparts are accompanied by a strong stabilization of the silylated ions **1a–g**, that is, **1a** is more stable than the parent benzenium ion **7** by 37.6 kcal mol^{-1} as revealed by the isodesmic Equation (2); it is even more stable than trityl cation by 23.7 kcal mol^{-1} [Eq. (3)].



(2)

$$\mathbf{1a(H)} + Ph_3C^+ \longrightarrow \mathbf{1a} + Ph_3CH \qquad (3)$$

Conclusion

Bissilylated arenium ions **1** have been synthesized in benzene at RT by hydride-transfer reactions from 2-aryl-2,6-disilaheptanes (**2**) to trityl cation via transient silylium ions. The cations **1** have been characterized by NMR spectroscopy, which was supported by quantum-mechanical calculations of structures, energies, and NMR chemical shifts. The experimental data, as well as the theoretical results, reveal the arenium-type nature of the cations **1**. The unusual stability of the synthesized cations results from two factors: 1) an increased thermodynamic stability owing to the hyperconjugative effect of two silyl substituents in **1** and 2) an increased kinetic stability as a result of the use of essential non-nucleophilic reaction conditions, that is, weakly coordinating anions and hydrocarbon solvents.

Experimental Section

General: All reagents were obtained from commercial suppliers and were used without further purification. THF was distilled from sodium/potassium alloy/benzophenone. Benzene, $[\mathrm{D_6}]$benzene, toluene, and $[\mathrm{D_8}]$toluene were distilled from sodium. Acetonitrile was distilled from $\mathrm{P_4O_{10}}$. All reactions were carried out in oven-dried glassware under inert argon atmospheres. Reactions were monitored by thin-layer chromatography on 0.20 mm Machery-Nagel silica-coated aluminum plates. ICN silica 32–63, 60 Å silica gel was used for column chromatography. NMR spectra were recorded on Bruker AM-400 and DPX-250 instruments. ^{1}H NMR spectra were calibrated from residual non-deuterated solvents as internal reference; ^{13}C NMR spectra used the central line of the solvent signal. ^{29}Si NMR spectra were recorded by using the INEPT pulse sequence and were optimized on $\mathrm{Si(CH_3)_2}$ or SiH groups. The calibration was done by using external $\mathrm{(H_3C)_2SiHCl}$. ^{19}F NMR were calibrated against external $\mathrm{CF_2Cl_2}$. 2-Chloro-2,6-dimethyl-2,6-disilaheptane, (**4**) and TPFPB were prepared as described in the literature. [68, 69]

Synthesis of 2-aryl-2,6-disilaheptanes (2a–g): A 100 mL Schlenk flask was charged with of a solution of the metalated arene (1.1 equivalent, 22 mmol) in THF (50 mL), which was freshly prepared from the respective arene bromide and Mg (for the synthesis of **2a–d,f**) or *n*BuLi (in hexanes) (for the synthesis of **2e,g**). 2-Chloro-2,6-dimethyl-2,6-disilaheptane (**4**) (1.0 equivalent, 20 mmol) was then slowly added by syringe at 0 °C. The solution was heated to reflux for 3 hours. After hydrolysis ($\mathrm{NH_4Cl}$, ice, diethyl ether) the organic layer was separated, the volatile components were removed using a rotary evaporator, and the residue was distilled under reduced pressure (10^{-1} bar). All materials in the boiling point range from 40–140 °C were collected and then further purified on a silica gel column with hexanes as eluent.

Compound 2a:[70] Colorless oil; yield: 4.53 g (19.2 mmol, 96 %); ^{1}H NMR (250 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{1}\mathrm{H(CHCl_3)} = 7.24$): $\delta = 7.50$ (m, 2 H; $\mathrm{H}^{\mathrm{aryl}}$), 7.35 (m, 3 H; $\mathrm{H}^{\mathrm{aryl}}$), 3.83 (sept, $^{3}J(\mathrm{H,H}) = 3.6$ Hz, 1 H; SiH), 1.50–1.35 (m, 2 H; $\mathrm{C^1H_2}$), 0.90–0.80 (m, 2 H; $\mathrm{C^2H_2}$), 0.70–0.59 (m, 2 H; $\mathrm{C^3H_2}$), 0.25 (s, 6 H; $\mathrm{SiMe_2}$Aryl), 0.03, (d, $^{3}J(\mathrm{H,H}) = 3.6$ Hz, 6 H; $\mathrm{Si(CH_3)_2H}$); ^{13}C NMR (62.90 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{13}\mathrm{C(CDCl_3)} = 77.0$): $\delta = 139.7$ (C^{ipso}), 133.5 (C^{ortho}), 128.7 (C^{para}) 127.6 (C^{meta}), 19.8 ($\mathrm{C^1}$), 18.9 ($\mathrm{C^2}$), 18.6 ($\mathrm{C^3}$), −3.0 ($\mathrm{Si}(\mathit{C}\mathrm{H_3})_2$aryl), −4.4 ($\mathrm{SiH}(\mathit{C}\mathrm{H_3})_2$); ^{29}Si NMR (79.495 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{29}\mathrm{Si((H_3C)_2SiHCl)} = 11.1$, ext.): $\delta = -4.1$ (br s, $^{1}J(\mathrm{Si,C^{alkyl}}) = 52$ Hz; $\mathrm{Si(CH_3)_2}$Aryl), −14.5 (dm, $^{1}J(\mathrm{Si,H}) = 188.0$ Hz, $^{2}J(\mathrm{Si,H}) = 7$ Hz; $\mathrm{Si(CH_3)_2H}$).

Compound 2b: Colorless oil; yield: 4.25 g (17 mmol, 85 %); ^{1}H NMR (250 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{1}\mathrm{H(CHCl_3)} = 7.24$): $\delta = 7.45$ (m, 2 H; H^{ortho}), 7.10 (m, 2 H; H^{meta}), 3.80 (sept, $^{3}J(\mathrm{H,H}) = 3.6$ Hz, 1 H; SiH), 2.30 (s, 3 H; $\mathrm{CH_3}$), 1.48–1.29 (m, 2 H; $\mathrm{C^1H_2}$), 0.83–0.78 (m, 2 H; $\mathrm{C^2H_2}$), 0.65–0.53 (m, 2 H; $\mathrm{C^3H_2}$), 0.20 (s, 6 H; $\mathrm{SiMe_2}$aryl), 0.01 (d, $^{3}J(\mathrm{H,H}) = 3.6$ Hz, 6 H; $\mathrm{Si(CH_3)_2H}$); ^{13}C NMR (62.90 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{13}\mathrm{C(CDCl_3)} = 77.0$): $\delta = 142.2$ (C^{para}), 138.5 (C^{ipso}), 135.9 (C^{ortho}), 129.1 (C^{meta}), 21.4 ($\mathrm{CH_3}$), 19.8 ($\mathrm{C^1}$), 18.9 ($\mathrm{C^2}$), 18.7 ($\mathrm{C^3}$), −2.9 ($\mathrm{Si}(\mathit{C}\mathrm{H_3})_2$Aryl), −4.4 ($\mathrm{SiH(CH_3)_2}$); ^{29}Si NMR (79.495 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{29}\mathrm{Si((H_3C)_2SiHCl)} = 11.1$, ext.): $\delta = -4.3$ (br s; $\mathrm{Si(CH_3)_2}$Aryl), −14.4 (dm, $^{1}J(\mathrm{Si,H}) = 173.0$ Hz, $^{2}J(\mathrm{Si,H}) = 7$ Hz; $\mathrm{Si(CH_3)_2H}$).

Compound 2c: Colorless oil; yield: 2.66 g (10.1 mmol, 50 %); ^{1}H NMR (250 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{1}\mathrm{H(CHCl_3)} = 7.24$): $\delta = 7.29$ (m, 1 H; H^{ortho}), 6.94 (s, br, 2 H; H^{meta}), 3.79 (sept, $^{3}J(\mathrm{H,H}) = 3.6$ Hz, 1 H; SiH), 2.37 (s, 3 H; $\mathrm{CH_3}$), 2.26 (s, 3 H; $\mathrm{CH_3}$), 1.43–1.30 (m, 2 H; $\mathrm{C^1H_2}$), 0.87–0.81 (m, 2 H; $\mathrm{C^2H_2}$), 0.65–0.58 (m, 2 H; $\mathrm{C^3H_2}$), 0.25 (s, 6 H; $\mathrm{SiMe_2}$Aryl), −0.01 (d, $^{3}J(\mathrm{H,H}) = 3.6$ Hz, 6 H; $\mathrm{Si(CH_3)_2H}$); ^{13}C NMR (62.90 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{13}\mathrm{C(CDCl_3)} = 77.0$): $\delta = 143.5$ (C^{ortho}), 138.8 (C^{ipso}), 134.8 (C^{ortho}), 133.9 (C^{para}), 130.1 (C^{meta}), 125.7 (C^{meta}), 23.0 ($\mathrm{CH_3}$), 21.2 ($\mathrm{CH_3}$), 20.3 ($\mathrm{C^1}$), 19.1 ($\mathrm{C^2}$), 18.7 ($\mathrm{C^3}$), −1.71 ($\mathrm{Si}(\mathit{C}\mathrm{H_3})_2$Aryl), −4.37 ($\mathrm{SiH(CH_3)_2}$); ^{29}Si NMR (49.7 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{29}\mathrm{Si((H_3C)_2SiHCl)} = 11.1$, ext.): $\delta = -4.0$ (br s; $\mathrm{Si(CH_3)_2}$Aryl), −14.1 (dm, $^{1}J(\mathrm{Si,H}) = 173.1$Hz, $^{3}J(\mathrm{Si,H}) = 7.0$ Hz; $\mathrm{Si(CH_3)_2H}$).

Compound 2d: Colorless oil; yield: 4.28 g (16.2 mmol, 81 %); ^{1}H NMR (250 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{1}\mathrm{H(CHCl_3)} = 7.24$): $\delta = 7.20$ (br s, 1 H; $\mathrm{H}^{\mathrm{aryl}}$), 7.01 (br s, 2 H; $\mathrm{H}^{\mathrm{aryl}}$), 3.79 (sept, $^{3}J(\mathrm{H,H}) = 3.6$ Hz, 1 H; SiH), 2.35 (s, 3 H; $\mathrm{CH_3}$), 2.26 (s, 3 H; $\mathrm{CH_3}$), 1.41–1.30 (m, 2 H; $\mathrm{C^1H_2}$), 0.88–0.79 (m, 2 H; $\mathrm{C^2H_2}$), 0.65–0.58 (m, 2 H; $\mathrm{C^3H_2}$), 0.25 (s, 6 H; $\mathrm{SiMe_2}$Aryl), −0.01 (d, $^{3}J(\mathrm{H,H}) = 3.6$ Hz, 6 H; $\mathrm{Si(CH_3)_2H}$); ^{13}C NMR (62.90 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{13}\mathrm{C(CDCl_3)} = 77.0$): $\delta = 140.4$ (C^{ortho}), 137.4 (C^{ipso}), 135.3 (C^{ortho}), 133.8 (C^{meta}), 129.7 (C^{para}), 128.7 (C^{meta}), 22.5 ($\mathrm{CH_3}$), 21.1 ($\mathrm{CH_3}$), 20.2 ($\mathrm{C^1}$), 19.1 ($\mathrm{C^2}$), 18.7 ($\mathrm{C^3}$), −1.81 ($\mathrm{Si}(\mathit{C}\mathrm{H_3})_2$Aryl), −4.40 ($\mathrm{SiH(CH_3)_2}$); ^{29}Si NMR (49.7 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{29}\mathrm{Si((H_3C)_2SiHCl)} = 11.1$, ext.): $\delta = -3.9$ (br s, $^{1}J(\mathrm{Si,C^{aryl}}) = 64.9$ Hz, $^{1}J(\mathrm{Si,C^{alkyl}}) = 52.1$ Hz; $\mathrm{Si(CH_3)_2}$Aryl), −14.1 (dm, $^{1}J(\mathrm{Si,H}) = 173.2$ Hz, $^{3}J(\mathrm{Si,H}) = 7.0$ Hz, $^{1}J(\mathrm{Si,C}) = 50.3$ Hz; $\mathrm{Si(CH_3)_2H}$).

Compound 2e: Colorless oil; yield: 1.48 g (5.6 mmol, 28 %); ^{1}H NMR (250 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{1}\mathrm{H(CHCl_3)} = 7.24$): $\delta = 7.17$–7.09 (m, 1 H; H^{para}), 7.00–6.94 (m, 2 H; H^{meta}), 3.84 (sept, $^{3}J(\mathrm{H,H}) = 3.6$ Hz, $^{1}J(\mathrm{Si,H}) = 180.0$ Hz, 1 H; SiH), 2.46 (s, 6 H; $\mathrm{CH_3}$), 1.50–1.36 (m, 2 H; $\mathrm{C^1H_2}$), 1.00–0.88 (m, 2 H; $\mathrm{C^2H_2}$), 0.72–0.61 (m, 2 H; $\mathrm{C^3H_2}$), 0.42 (s, 6 H; $\mathrm{SiMe_2}$Aryl), 0.05 (d, $^{3}J(\mathrm{H,H}) = 3.8$ Hz, 6 H; $\mathrm{Si(CH_3)_2H}$); ^{13}C NMR (62.90 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{13}\mathrm{C(CDCl_3)} = 77.0$): $\delta = 144.2$ (C^{ortho}), 136.1 (C^{ipso}), 128.7 (C^{para}), 128.1 (C^{meta}), 24.9 ($\mathrm{CH_3}$), 22.2 ($\mathrm{C^1}$), 19.2 ($\mathrm{C^2}$), 18.6 ($\mathrm{C^3}$), 2.47 ($\mathrm{Si}(\mathit{C}\mathrm{H_3})_2$Aryl), −4.40 ($\mathrm{SiH(CH_3)_2}$); ^{29}Si NMR (49.7 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{29}\mathrm{Si((H_3C)_2SiHCl)} = 11.1$, ext.): $\delta = -4.2$ ($\mathrm{Si(CH_3)_2}$Aryl), −14.1 ($\mathrm{Si(CH_3)_2H}$).

Compound 2f: Colorless oil; yield: 4.78 g (18.1 mmol, 90.5 %); ^{1}H NMR (250 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{1}\mathrm{H(CHCl_3)} = 7.24$): $\delta = 7.14$ (br s, 2 H; H^{ortho}), 7.02 (br s, 2 H; H^{para}), 3.88 (sept, $^{3}J(\mathrm{H,H}) = 3.8$ Hz, $^{1}J(\mathrm{Si,H}) = 180.4$ Hz, 1 H; SiH), 2.35 (s, 6 H; $\mathrm{CH_3}$), 1.54–1.39 (m, 2 H; $\mathrm{C^1H_2}$), 0.91–0.80 (m, 2 H; $\mathrm{C^2H_2}$), 0.75–0.68 (m, 2 H; $\mathrm{C^3H_2}$), 0.27 (s, 6 H; $\mathrm{SiMe_2}$Aryl), 0.08 (d, $^{3}J(\mathrm{H,H}) = 3.6$ Hz, 6 H; $\mathrm{Si(CH_3)_2H}$); ^{13}C NMR (62.90 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{13}\mathrm{C(CDCl_3)} = 77.0$): $\delta = 139.4$ (C^{ortho}), 137.0 (C^{meta}), 131.3 (C^{ortho}), 130.5 (C^{para}), 21.4 ($\mathrm{CH_3}$), 19.8 ($\mathrm{C^1}$), 19.0 ($\mathrm{C^2}$), 18.7 ($\mathrm{C^3}$), −2.86 ($\mathrm{Si}(\mathit{C}\mathrm{H_3})_2$Aryl), −4.40 ($\mathrm{SiH(CH_3)_2}$); ^{29}Si NMR (49.7 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{29}\mathrm{Si((H_3C)_2SiHCl)} = 11.1$, ext.): $\delta = -4.1$ ($^{1}J(\mathrm{Si,C^{aryl}}) = 65$ Hz, $^{1}J(\mathrm{Si,C^{alkyl}}) = 53$ Hz; $\mathrm{Si(CH_3)_2}$Aryl), −14.1 ($^{1}J(\mathrm{Si,C}) = 50.4$ Hz; $\mathrm{Si(CH_3)_2H}$).

Compound 2g: Colorless oil; yield: 3.39 g (12.2 mmol, 61 %); ^{1}H NMR (250 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{1}\mathrm{H(CHCl_3)} = 7.24$): $\delta = 6.80$ (br s, 2 H; H^{meta}), 3.82 (sept, $^{3}J(\mathrm{H,H}) = 3.6$ Hz, 1 H; SiH), 2.40 (s, 6 H; $\mathrm{CH_3}$), 2.24 (s, 3 H; $\mathrm{CH_3}$), 1.53–1.35 (m, 2 H; $\mathrm{C^1H_2}$), 0.94–0.88 (m, 2 H; $\mathrm{C^2H_2}$), 0.68–0.61 (m, 2 H; $\mathrm{C^3H_2}$), 0.38 (s, 6 H; $\mathrm{SiMe_2}$Aryl), 0.04 (d, $^{3}J(\mathrm{H,H}) = 3.7$ Hz, 6 H; $\mathrm{Si(CH_3)_2H}$); ^{13}C NMR (62.90 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{13}\mathrm{C(CDCl_3)} = 77.0$): $\delta = 144.3$ (C^{ortho}), 138.4 (C^{ipso}), 132.5 (C^{para}), 132.5 (C^{meta}), 24.8 ($\mathrm{CH_3}$), 22.3 ($\mathrm{CH_3}$), 20.8 ($\mathrm{C^1}$), 19.3 ($\mathrm{C^2}$), 18.7 ($\mathrm{C^3}$), 2.4 ($\mathrm{Si}(\mathit{C}\mathrm{H_3})_2$Aryl), −4.4 ($\mathrm{SiH(CH_3)_2}$); ^{29}Si NMR (79.495 MHz, $[\mathrm{D_1}]$chloroform, 300 K, $\delta^{29}\mathrm{Si((H_3C)_2SiHCl)} = 11.1$, ext.): $\delta = -4.6$ (br s; $\mathrm{Si(CH_3)_2}$Aryl), −14.4 (dm, $^{1}J(\mathrm{SiH}) = 173.0$ Hz, $^{2}J(\mathrm{SiH}) = 7$ Hz; $\mathrm{Si(CH_3)_2H}$).

Synthesis of cations 1: Arylsilane **2** (0.5 mmol) was slowly added to a vigorously stirred solution of TPFPB (460 mg (0.5 mmol) in $[\mathrm{D_6}]$benzene (2 mL) at RT. The color (owing to the trityl cation) disappeared after the addition of one equivalent of silane. Stirring was stopped and the reaction mixture was allowed to separate into two layers, a yellow-brown highly viscous lower phase and a colorless upper phase. The upper phase, containing the byproduct triphenyl methane, was separated off and the lower layer was transferred by cannula into a NMR tube and was then investigated by NMR spectroscopy.

Compound 1a·$[B(C_6F_5)_4]^-$: ^{1}H NMR (400 MHz, [D_6]benzene, 300 K, δ^1H(C_6D_5H) = 7.20): δ = 8.01 (2H; H^{ortho}), 7.54 (1H; H^{para}), 7.20 (H^{meta}), 1.68 (br, 2H; H^2), 0.64 (m, 4H; $H^{1/3}$), −0.36 (12H; $Si(CH_3)_2$); ^{13}C NMR (100 MHz, [D_6]benzene, 300 K, δ^{13}C(C_6D_6) = 128.0): δ = 162.9 (C^{ortho}), 150.3 (C^{para}), 149.0 (d, ^1J(C,F) = 251.6 Hz; C^{meta} $[B(C_6F_5)_4]^-$), 138.7 (d, ^1J(C,F) = 241.5 Hz; C^{para} $[B(C_6F_5)_4]^-$), 136.9 (d, ^1J(C,F) = 251.5 Hz; C^{ortho} $[B(C_6F_5)_4]^-$), 133.9 (C^{meta}), 125.2 (br; C^{ipso} $[B(C_6F_5)_4]^-$), 19.8 (C^2), 102.4 (C^{ipso}) 14.6 ($C^{1/3}$), −2.9 ($Si(CH_3)_2$); ^{29}Si NMR (79.5 MHz, [D_6]benzene, 300 K, δ^{29}Si($(H_3C)_2SiHCl$) = 11.1, ext.): δ = 25.6; ^{19}F NMR (254 MHz, [D_6]benzene, 300 K, δ^{19}F(CF_2Cl_2) = 0): δ = −136.9 (d, J(F,F) = 8.4 Hz, 2F; F^{meta}), −167.7 (t, J(F,F) = 20.7 Hz, 1F; F^{para}), −171.5 (t, J(F,F) = 16.8 Hz, 2F; F^{ortho}).

Compound 1b·$[B(C_6F_5)_4]^-$: For NMR data of the $[B(C_6F_5)_4]^-$ anion see **1a**. ^{1}H NMR (400 MHz, [D_6]benzene, 300 K, δ^1H(C_6D_5H) = 7.20): δ = 7.95 (d, ^3J(H,H) = 8.1 Hz, 2H; H^{ortho}), 7.11 (^3J(H,H) = 8.1 Hz, 2H; H^{meta}), 2.08 (s, 3H; CH_3), 1.69 (br, 2H; H^2), 0.64 (m, 4H; $H^{1/3}$), −0.35 (12H; $Si(CH_3)_2$); ^{13}C NMR (100 MHz, [D_6]benzene, 300 K, δ^{13}C(C_6D_6) = 128.0): δ = 169.9 (C^{para}), 165.8 (C^{ortho}), 135.6 (C^{meta}), 93.3 (C^{ipso}), 23.5 (CH_3), 17.1 (C^2), 14.4 ($C^{1/3}$), −1.8 ($Si(CH_3)_2$); ^{29}Si NMR (79.5 MHz, [D_6]benzene, 300 K, δ^{29}Si($(H_3C)_2SiHCl$) = 11.1, ext.): δ = 22.1 (m, ^2J(SiH) = 5.6 Hz).

Compound 1c·$[B(C_6F_5)_4]^-$: For NMR data of the $[B(C_6F_5)_4]^-$ anion see **1a**. ^{1}H NMR (250 MHz, [D_6]benzene, 300 K, δ^1H(C_6D_5H) = 7.20): δ = 7.82 (d, ^3J(H,H) = 8.2 Hz, 1H; H^{ortho}), 6.90 (d, ^3J(H,H) = 8.2 Hz, 1H; H^{meta}), 6.69 (s, 1H; H^{meta}), 2.07 (s, 3H; CH_3), 2.00 (s, 3H; CH_3), 1.83 (br, 1H; $H^{e,2}$), 1.48 (br, 1H; $H^{a,2}$), 0.59 (m, 4H; $H^{1/3}$), −0.03, −0.64 (26H; $Si(CH_3)_2$); ^{13}C NMR (62.90 MHz, [D_6]benzene, 300 K, δ^{13}C(C_6D_6) = 128.0): δ = 182.0 (q, ^2J(C,H) = 5 Hz; C^{ortho}), 169.0 (q, ^2J(C,H) = 6 Hz; C^{para}), 165.1 (d, ^1J(C,H) = 164.8 Hz, C^{ortho}), 136.7 (d, ^1J(C,H) = 164.4 Hz; C^{meta}), 132.5 (d, ^1J(C,H) = 168.4 Hz; C^{meta}), 89.8 (s; C^{ipso}), 26.0 (q, ^1J(C,H) = 128.7 Hz; CH_3), 23.1 (q, ^1J(C,H) = 129.3 Hz; CH_3), 16.8 (t, ^1J(C,H) = 131 Hz; C^2), 15.4 (t, ^1J(C,H) = 121 Hz; $C^{1/3}$), −0.27 (q, ^1J(C,H) = 123 Hz; $Si(CH_3)_2$), −2.55 (q, ^1J(C,H) = 123.4 Hz; $Si(CH_3)_2$); ^{29}Si NMR (49.7 MHz, [D_6]benzene, 300 K, δ^{29}Si($(H_3C)_2SiHCl$) = 11.1, ext.): δ = 20.3 (^1J(SiC) = 55.1 Hz).

Compound 1d·$[B(C_6F_5)_4]^-$: For NMR data of the $[B(C_6F_5)_4]^-$ anion see **1a**. ^{1}H NMR (250 MHz, [D_6]benzene, 300 K, δ^1H(C_6D_5H) = 7.20): δ = 7.83 (s, 1H; H^{ortho}), 7.27 (d, ^3J(H,H) = 7.6 Hz, 1H; H^{para}), 6.69 (d, ^3J(H,H) = 7.6 Hz, 1H; H^{meta}), 2.09 (s, 3H; CH_3), 1.92 (s, 3H; CH_3), 1.68 (br; H^2), 0.62 (m, 4H; $H^{1/3}$), −0.10, −0.56 (br, 26H; $Si(CH_3)_2$); ^{13}C NMR (62.90 MHz, [D_6]benzene, 300 K, δ^{13}C(C_6D_6) = 128.0): δ = 179.9 (s; C^{ortho}), 164.2 (d, ^1J(C,H) = 162.8 Hz; C^{ortho}), 152.9 (d, ^1J(C,H) = 164.8 Hz; C^{para}), 142.4 (s; C^{meta}), 135.9 (d, ^1J(C,H) = 165.2 Hz; C^{meta}), 96.2 (s; C^{ipso}), 25.6 (q, ^1J(C,H) = 129.4 Hz; CH_3), 19.5 (q, ^1J(C,H) = 129.5 Hz; CH_3), 16.8 (t, ^1J(C,H) = 130.9 Hz; C^2), 15.5 (t, ^1J(C,H) = 119 Hz; $C^{1/3}$), −0.26 (br q, ^1J(C,H) = 120 Hz; $Si(CH_3)_2$), −2.28 (br q, ^1J(C,H) = 120 Hz; $Si(CH_3)_2$); ^{29}Si NMR (49.7 MHz, [D_6]benzene, 300 K, δ^{29}Si($(H_3C)_2SiHCl$) = 11.1, ext.): δ = 22.7.

Compound 1e·$[B(C_6F_5)_4]^-$: For NMR data of the $[B(C_6F_5)_4]^-$ anion see **1a**. ^{1}H NMR (250 MHz, [D_6]benzene, 300 K, δ^1H(C_6D_5H) = 7.20): δ = 7.19 (br; H^{arom}), 2.10 (br; CH_3), 1.76 (br; H^2), 0.62 (br; $H^{1/3}$), −0.37 (br; $Si(CH_3)_2$); ^{13}C NMR (62.90 MHz, [D_6]benzene, 300 K, δ^{13}C(C_6D_6) = 128.0): δ = 180.6 (C^{ortho}), 150.2 (C^{para}), 134.3 (C^{meta}), 95.1 (C^{ipso}), 27.9 (CH_3), 23.1 (CH_3), 17.4 (C^2), 16.6 ($C^{1/3}$), −0.1 ($Si(CH_3)_2$); ^{29}Si NMR (49.7 MHz, [D_6]benzene, 300 K, δ^{29}Si($(H_3C)_2SiHCl$) = 11.1, ext.): δ = 21.6.

Compound 1f·$[B(C_6F_5)_4]^-$: For NMR data of the $[B(C_6F_5)_4]^-$ anion see **1a**. ^{1}H NMR (250 MHz, [D_6]benzene, 300 K, δ^1H(C_6D_5H) = 7.20): δ = 7.86 (s, 2H; H^{ortho}), 7.23 (s, 1H; H^{para}), 1.97 (s, 6H; CH_3), 1.68 (br, 2H; H^2), 0.63 (m, 4H; $H^{1/3}$), −0.34 (12H; $Si(CH_3)_2$); ^{13}C NMR (62.90 MHz, [D_6]benzene, 300 K, δ^{13}C(C_6D_6) = 128.0): δ = 160.9 (d, ^1J(C,H) = 164.9 Hz; C^{ortho}), 153.6 (d, ^1J(C,H) = 158.3 Hz; C^{para}), 146.9 (s; C^{meta}), 102.9 (s; C^{ipso}), 20.0 (q, ^1J(C,H) = 129 Hz; CH_3), 17.1 (t, ^1J(C,H) = 135 Hz; C^2), 15.1 (t, ^1J(C,H) = 119.1 Hz; $C^{1/3}$), −1.4 (q, ^1J(C,H) = 122.3 Hz; $Si(CH_3)_2$); ^{29}Si NMR (49.7 MHz, [D_6]benzene, 300 K, δ^{29}Si($(H_3C)_2SiHCl$) = 11.1, ext.): δ = 24.3 (^1J(Si,C) = 54.8 Hz).

Compound 1g·$[B(C_6F_5)_4]^-$: For NMR data of the $[B(C_6F_5)_4]^-$ anion see **1a**. ^{1}H NMR (400 MHz, [D_6]benzene, 300 K, δ^1H(C_6D_5H) = 7.20): δ = 6.6 (s, 2H; H^{meta}), 2.05 (s, 6H; CH_3), 1.94 (s, 3H; CH_3) 1.68 (br, 2H; H^2), 0.67 (m, 4H; $H^{1/3}$), −0.35 (12H; $Si(CH_3)_2$); ^{13}C NMR (100 MHz, [D_6]benzene, 300 K, δ^{13}C(C_6D_6) = 128.0): δ = 179.7 (C^{ortho}), 167.3 (C^{para}), 135.7 (C^{meta}), 89.0 (C^{ipso}), 27.8 (CH_3), 22.6 (CH_3) 16.8 (C^2), 16.9 ($C^{1/3}$), −0.5 ($Si(CH_3)_2$); ^{29}Si NMR (79.5 MHz, [D_6]benzene, 300 K, δ^{29}Si($(H_3C)_2SiHCl$) = 11.1, ext.): δ = 19.1 (^2J(SiH) = 5.6 Hz).

Synthesis of the nitrilium salt 10·$[B(C_6F_5)_4]^-$: Dry acetonitrile (20 mg, 0.5 mmol) was added at to a solution of freshly prepared **1a**·$[B(C_6F_5)_4]^-$ (0.5 mmol) in [D_6]benzene at RT, and the resulting solution was investigated by NMR spectroscopy. **10**·$[B(C_6F_5)_4]^-$: for NMR data of the $[B(C_6F_5)_4]^-$ anion, see **1a**. ^{1}H NMR (400 MHz, [D_6]benzene, 300 K, δ^1H(C_6D_5H) = 7.20): δ = 7.5 (2H; H^{aryl}), 7.40–7.20 (3H; H^{aryl}), 1.30–1.20 (m, 2H; H^1), 1.12 (s; CH_3), 0.80–0.73 (m, 2H; H^2), 0.68–0.62 (m, 2H; H^3), 0.30 (6H; $Si(CH_3)_2$Aryl), 0.04 (6H, $Si(CH_3)_2N^+CCH_3$); ^{13}C NMR (100 MHz, [D_6]benzene, 300 K, δ^{13}C(C_6D_6) = 128.0): δ = 138.2 (C^{ipso}), 133.8 (C^{ortho}), 129.4 (C^{para}), 128.2 (C^{meta}), 19.7 (C^1), 18.0 (C^2), 17.2 (C^3), 0.0 (CH_3CN^+), −3.5 ($Si(CH_3)_2$), −3.7 ($Si(CH_3)_2$); ^{29}Si NMR (79.5 MHz, [D_6]benzene, 300 K, δ^{29}Si($(H_3C)_2SiHCl$) = 11.1, ext.): δ = 35.0 (m, ^2J(Si,H) = 7 Hz; $Si(CH_3)_2N^+CCH_3$), −4.2 (br s; $Si(CH_3)_2$Aryl).

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[1] Arenium ions are also known as σ complexes, Wheland or Pfeifer–Wizinger intermediates, and cyclohexadienyl ions. In this contribution, the nomenclature arenium ion is used throughout, reflecting the trivalent carbenium ion nature of these ions.

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