

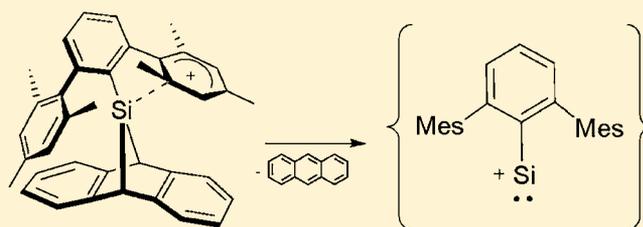
Dibenzosilanorbornadienyl Cations and Their Fragmentation into Silyliumylidenes

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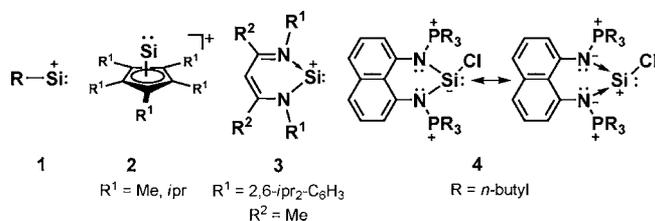
S Supporting Information

ABSTRACT: The terphenyl-substituted dibenzosilanorbornadienyl cation **11** was synthesized and isolated in the form of its $[B(C_6F_5)_4]^-$ salt. The salt was characterized by NMR spectroscopy supported by quantum mechanical computations and by an XRD analysis of a corresponding acetonitrilium salt. The thermal fragmentation of $11[B(C_6F_5)_4]$ in benzene results in the high-yield formation of diphenylterphenylsilylium borate $17[B(C_6F_5)_4]$. High-lying intermediates in this process are solvent-complexed terphenylsilyliumylidene **8** and the hydrogen- and phenyl-substituted silylium ion **20**. The formation of silylium ion **20** by reaction of silyliumylidene **8** with the solvent benzene demonstrates the high potential of this four valence electron species in C–H bond activation reactions. In addition, the instability of the hydrogen-substituted silylium ion **20** in benzene opens new mechanistic perspectives particular for dihydrogen activation by silyl cationic frustrated Lewis pairs and in general for the dihydrogen activation by strong Lewis acids.



INTRODUCTION

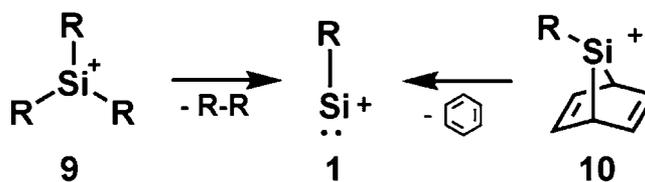
The extreme Lewis acidity of silylium ions R_3Si^+ , silicon cations with silicon in oxidation state IV,¹ recently found beneficial applications in catalysis,² in bond activation reactions,³ and in activation processes of small molecules.^{4,5} Already in 2004, Gaspar pointed out that the combination of the high Lewis acidity of silylium ions and the amphiphilic character of nonstabilized silylenes as accomplished in the shape of silyliumylidenes RSi^+ , **1**, creates silicon cations with an extraordinarily high reactivity and synthetic potential.⁶ Since then, several groups have reported the successful preparation and isolation of stabilized silyliumylidenes, such as cations **2–4**.^{7–9} For the synthesis of each of these highly electron deficient species, bulky and strongly electron donating substituents were applied, which also extend the coordination number of the silicon cation. Some of these compounds already show a distinct and highly interesting reactivity.^{7,8} The strongly stabilizing substituents which are needed to pacify the electron demand of the silicon atom however significantly influence the chemical behavior of the silicon(II) cation and mask its reactivity to a certain extent.



This prompted us to search for substituents R in silyliumylidenes **1** which extend their lifetime in the condensed

phase without spoiling their original reactivity. In this respect, the 1,3-diarylphenyl (terphenyl) substituents seemed to be a good compromise between the requirements for thermodynamic stabilization and steric protection on one hand and, on the other hand, for preserved reactivity of the silicon(II) cation.¹⁰ Isolobal neutral compounds of group 13 metals in oxidation state I, **5**, stabilized by terphenyl substituents exist,^{10b–d} and Power and co-workers reported on the synthesis of the toluene complex of terphenyl-substituted monocoordinated lead cation **6**.¹¹ In line with these experimental achievements, the results of quantum mechanical computations suggested that, in the case of silicon, the thermodynamic stabilities of terphenyl-substituted silyliumylidenes such as **7** and **8** approach those of cations **2** and **3**.¹² The same theoretical study suggested that in general α -elimination from silylium ions **9** (Scheme 1) is a suitable synthetic approach to silyliumylidenes. In particular, the elimination of benzene from 7-silanorbornadienyl cations **10** is particularly well suited for

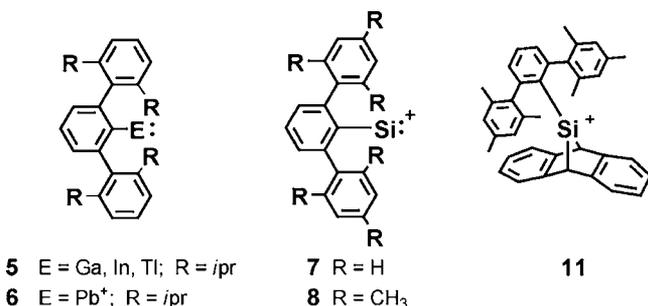
Scheme 1. Synthesis of Silyliumylidenes **1** from Silylium Ions **9** and **10** by α -Elimination



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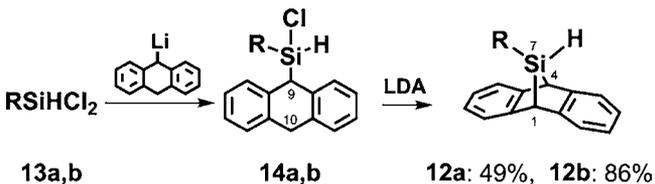
the generation of terphenyl-substituted silyliumylidenes **7** and **8** (Scheme 1).¹² Following these theoretical guidelines, we report here on the synthesis of a 7-terphenyl-substituted dibenzo-7-silanorbornadienyl cation **11** by hydride transfer from the corresponding silane **12a** and on the investigation of its thermal decomposition, which provides evidence for the intermediate formation of the terphenyl-substituted silyliumylidene **8**.



RESULTS AND DISCUSSION

Dibenzo-7-silanorbornadienes **12** were prepared according to a procedure published by Tokitoh and co-workers starting from dichlorosilanes **13**.¹³ The central step in this reaction sequence involves regioselective deprotonation of 9-silyldihydroanthracene **14** at carbon atom C¹⁰, followed by an intramolecular substitution reaction (Scheme 2). The regioselectivity of the

Scheme 2. Synthesis of Dibenzo-7-silanorbornadienes **12** from 9-Silyldihydroanthracene **14**^a



^aFor **12a**, **13a**, and **14a**, R = 2,6-bis(2,4,6-trimethylphenyl)phenyl (Ter). For **12b**, **13b**, and **14b**, R = 2,6-bis(2,4,6-tri-*iso*-propylphenyl)phenyl (Ter*). LDA = lithium di-*iso*-propylamide.

C¹⁰-deprotonation increases with the steric bulk of the applied base and of the substituent R at the silicon atom.¹³ Therefore, this route is particularly well suited for the synthesis of dibenzo-7-silanorbornadienes with bulky terphenyl substituents.¹⁴ Dibenzosilanorbornadienes **12** were obtained in satisfying isolated yields (Scheme 2) and were fully characterized by NMR spectroscopy and X-ray diffraction analysis of suitable crystals (see Figure 1, Table 1, and the Supporting Information). The relatively low field shifted resonances in the ²⁹Si NMR spectra ($\delta(^{29}\text{Si}) = 31.6$ (**12a**), 31.5 (**12b**)) are characteristic for 7-silanorbornadienes.^{14–16} From a structural point of view, the long endocyclic Si–C^{1/4} bonds ($d(\text{SiC}^{1/4}) = 192.7$ pm (**12a**), 192.4 pm (**12b**)) are noticeable. Both features, the deshielded ²⁹Si nuclei and the long endocyclic SiC bonds, are typical of the 7-silanorbornadiene subunit, and they are indications of the occurrence of $\sigma-\pi^*$ conjugation in these compounds.^{14,15}

Addition of benzene to an equimolar mixture of trityl tetrakis(pentafluorophenyl) borate ([Ph₃C][B(C₆F₅)₄]) and dibenzo-7-silanorbornadiene **12a** results in a biphasic reaction mixture, characteristic of benzene solutions of the [B(C₆F₅)₄][–]



Figure 1. Molecular structure of dibenzo-7-silanorbornadiene **12b** in the crystal (thermal ellipsoid presentation drawn at the 50% probability level; only one of two independent molecules in the crystal is shown). All hydrogen atoms but the SiH hydrogen atom (red) are omitted. Bond lengths (pm) and angles (deg): Si–C(1), 192.04(14); Si–C(4), 192.74(16); Si–C(ter), 189.09(16); C(1)–C(2), 151.73(23); C(2)–C(3), 140.09(22); C(1)–Si–C(4), 81.44(7).

salts. Monitoring of the reaction progress by ¹H NMR spectroscopy of the lighter nonpolar phase indicates a slow hydride transfer and selective formation of the terphenyl-substituted 7-silanorbornadienyl borate **11**[B(C₆F₅)₄][–], which was obtained as the sole product after 14 h at room temperature (Scheme 3, Figure 2a). In contrast, the bulkier Ter* substituent of dibenzosilanorbornadiene **12b** efficiently hampers the hydride transfer reaction, and its reaction with trityl cation yields after 24 h an intractable mixture of different compounds as judged from ²⁹Si NMR spectroscopy.

The 7-silanorbornadienyl borate **11**[B(C₆F₅)₄][–] was characterized by multinuclear NMR spectroscopy (Table 1). The ²⁹Si NMR resonance of cation **11** is practically independent of the solvent used ($\delta(^{29}\text{Si}) = 1.3$ (benzene-*d*₆) (Figure 2b), 1.2 (toluene-*d*₈), 2.2 (chlorobenzene-*d*₃)). This suggests only insignificant solvent cation interactions, and it discards the possibility of the formation of an arene complex. The ²⁹Si NMR signal for cation **11** is, however, detected at an unusually low frequency compared to that of triarylsilylium ions ($\delta(^{29}\text{Si}) = 215\text{--}230$)⁴ or even to that of the terphenyl-substituted dimethylsilylium ion **15** and closely related cations ($\delta(^{29}\text{Si}) = 59\text{--}80$).¹⁷ The silyl cation **15** greatly benefits from intramolecular π -donation from the flanking aryl groups, which is accompanied by a significant shielding of the silicon atom. Similar intramolecular interactions between the positively charged silicon atom and the flanking aryl groups, and consequently comparable shielding effects on the silicon nuclei, are expected to be operative in cation **11** (Scheme 4). In addition, homoconjugative effects between the π -system of the benzenorbornadiene part of cation **11** and the positively charged silicon atom add a second shielding influence on the ²⁹Si NMR chemical shift. This shielding effect, which accompanies homoconjugation, is well documented for 7-norbornadienyl cations¹⁸ and is predicted also for their silicon analogues.¹⁶ In summary, both shielding effects account for the unusually high field shifted ²⁹Si NMR resonance of the 7-silanorbornadienyl cation **11**.

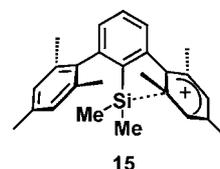
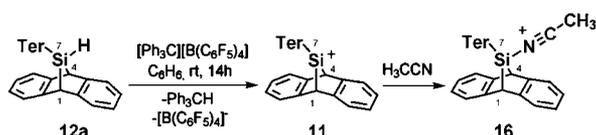


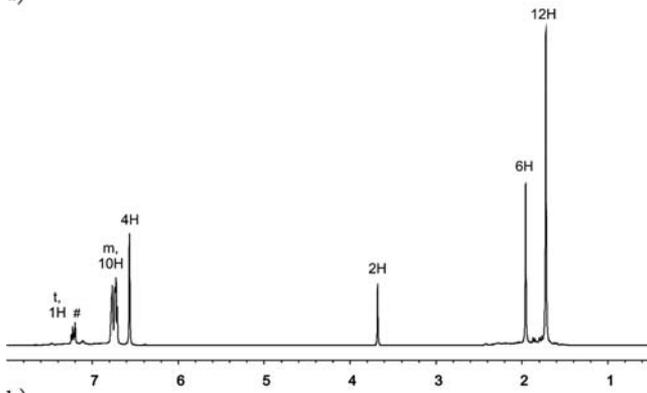
Table 1. Selected Experimental and Theoretical (Italic) NMR and Structural Parameters for Dibenzo-7-silanorbornadienes **12**, Dibenzo-7-silanorbornadienyl Cation **11**, Silyliumylidene **8**, and Related Compounds

compd	R	$\delta(^{29}\text{Si})$ ($^1\text{J}(\text{SiH})$, Hz) ^a	$\delta(^{13}\text{C}^{1/4})$ ^a	$\delta(^1\text{H}^{1/4})$ ^a	$d(\text{SiC}^1)$, $d(\text{SiC}^4)$ (pm)	$\alpha(\text{C}^1\text{SiC}^4)$ (deg)	ref
12a ^b	Ter ^c	31.6 (209.4)	44.3	2.82	192.75, 192.60	81.36	14
12b	Ter* ^d	31.5 (207.0)	44.4	2.70	192.04(14), 192.74(16)	81.44(7)	this work
11	Ter ^c	1.3 1.2 ^e 2.2 ^f -14.3 ^g	44.2	3.68	190.5, 189.5 ^h 190.28(44), 189.18(39) 191.0, 191.0 ^h	84.5 ^h 82.84(18) 83.2 ^h	this work
16	Ter ^c	6.4 -6.2 ^g	43.8	2.66			this work
17	Ter ^c	52.7 63.2 ^g					this work
8	Ter ^c	381 ^g					this work
24	Ter ^c	285 ^g					this work

^aIn benzene-*d*₆ at room temperature. ^bData from ref 14. ^cTer = 2,6-bis(2,4,6-trimethylphenyl)phenyl. ^dTer* = 2,6-bis(2,4,6-triisopropylphenyl)phenyl. ^eIn toluene-*d*₈ at room temperature. ^fIn chlorobenzene-*d*₅ at room temperature. ^g²⁹Si NMR chemical shifts calculated at GIAO/B3LYP/IGLOIII//PCM/M06-2X/6-311+G(d,p). ^hStructural parameter obtained at M06-2X/6-311+G(d,p).¹⁹

Scheme 3. Synthesis of Dibenzo-7-silanorbornadienyl Cation **11** and Nitrilium Ion **16**

a)



b)

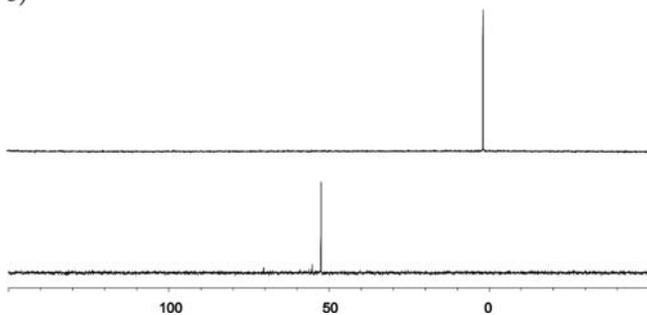
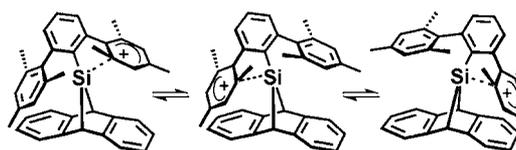


Figure 2. (a) ¹H NMR (500 MHz) spectrum of **11**[B(C₆F₅)₄] in benzene-*d*₆ (the pound sign indicates the residual proton signal of the solvent). (b) ²⁹Si{¹H} NMR (100 MHz) spectra of **11**[B(C₆F₅)₄] in benzene-*d*₆ at room temperature (upper trace) and after heating for 2 h to 70 °C (lower trace).

The ¹H and ¹³C NMR spectra obtained from **11**[B(C₆F₅)₄] are notable in that only one set of signals ($\delta(^1\text{H}) = 1.72, 1.96, 6.57$, Figure 2a) for the flanking mesityl groups of the terphenyl substituent in the ¹H NMR spectrum and only five resonances

Scheme 4. Intramolecular Interaction in Terphenyl-Substituted Dibenzo-7-silanorbornadienyl Cation **11** and the Degenerate Equilibrium between Different Equivalent Conformers of Cation **11**

of methine carbon atoms in the aromatic region of the ¹³C NMR spectra indicate a highly symmetric structure for cation **11** on the NMR time scale at room temperature. This time-averaged symmetry of cation **11** is rationalized by a degenerate equilibrium between equivalent conformers of cation **11** (Scheme 4). A similar dynamic behavior was established for the strongly related silyl cation **15** and was put forward as a reason for the isochronicity of the mesityl substituents in the NMR experiment.¹⁷ The computed molecular structure of cation **11** (at M06-2X/6-311+G(d,p); see Figure 4a)¹⁹ suggests intramolecular π -donation from the flanking mesityl group to the electron-deficient silicon atom. The most significant features are (i) the short distance between the *ortho* carbon atom C(*o*) and the silicon atom ($d(\text{SiC}(\text{o})) = 238.0$ pm), which is markedly smaller than the sum of the van der Waals radii ($\sum(\text{vdW}) = 380$ pm),²⁰ and (ii) the notable pyramidalization of the silicon atom as judged from the sum of the bond angles around Si, $\sum\alpha(\text{Si})$, which deviates significantly from 360° ($\sum\alpha(\text{Si}) = 348^\circ$). GIAO ²⁹Si NMR chemical shift calculations predict for cation **11** in benzene solution a ²⁹Si NMR resonance at somewhat higher field than observed experimentally ($\delta(^{29}\text{Si}(\text{calcd})) = -14$).¹⁹

In solution the salts **11**[B(C₆F₅)₄] and **11**[HCB₁₁H₅Br₆] are only of limited stability, which severely hampered all attempts to grow crystals suitable for X-ray diffraction analysis. Previously, it was shown that the formation of complexes with solvents of higher donicity increases the thermal stability of 7-silanorbornadienyl cations.¹⁶ Addition of acetonitrile to a benzene solution of the borate **11**[B(C₆F₅)₄] results in the formation of the nitrilium salt **16**[B(C₆F₅)₄] as indicated by NMR spectroscopy (Scheme 3, Table 1). In particular, $\delta(^{29}\text{Si}) = 6.4$ is very close to the ²⁹Si NMR chemical shift of a strongly

related silanorbornadienylnitrilium borate reported previously ($\delta(^{29}\text{Si}) = 8.9$).¹⁶ Moreover, the increased thermal stability of the nitrilium borate allowed its crystallization from hexafluorobenzene/pentane as its hexafluorobenzene solvate. The small size of the needle-shaped crystals prevents a structure determination to high accuracy; the overall molecular structure and the topology of cation **16** are however secured (see Figure 3). In addition, DFT calculations at the M06-2X/6-311+G(d,p)

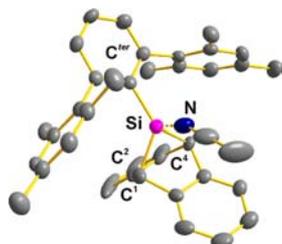


Figure 3. Molecular structure of nitrilium ion **16** in the crystal of $16[\text{B}(\text{C}_6\text{F}_5)_4] \cdot 2\text{C}_6\text{F}_6$ (thermal ellipsoid presentation drawn at the 50% probability level). All hydrogen atoms are omitted. Bond lengths (pm) and angles (deg): Si–C(1), 190.28(44); Si–C(4), 189.18(39); Si–C(ter), 185.89(40); C(1)–C(2), 152.49(75); C(2)–C(3), 139.23(66); C(1)–Si–C(4), 82.840(18); Si–C(2), 254.52(50); Si–C(3), 253.85(57); Si–N, 184.80(35).

level of theory predict for nitrilium ion **16** a molecular structure (Figure 4b) which is in all significant parameters very close to the experimental solid-state structure.¹⁹ Therefore, the isolation of nitrilium borate $16[\text{B}(\text{C}_6\text{F}_5)_4]$ provides further clear evidence of the molecular structure and the identity of cation **11**.

Upon heating of the biphasic benzene solution of borate **11** $[\text{B}(\text{C}_6\text{F}_5)_4]$ to 70 °C for 2 h, the complete degradation of cation **11** was observed. Anthracene was detected in the nonpolar phase by ^1H NMR spectroscopy and GC/MS, while in the ionic phase a new silicon-containing compound was formed in 70–80% yield (see Figure 2b). This new compound was characterized by one single ^{29}Si resonance at $\delta(^{29}\text{Si}) = 52.7$. The presence of the intact $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ anion was confirmed by ^{19}F NMR and ^{13}C NMR spectroscopy. ^1H and ^{13}C NMR spectra obtained from the reaction product at room temperature indicated a symmetric terphenyl-substituted species. In addition, a set of three signals in the ^1H NMR spectra were detected ($\delta(^1\text{H}) = 6.66, 6.91, \text{ and } 7.14$), which are typical of

phenyl protons.^{21,22} These signals were not found when the thermal fragmentation of cation **11** was performed in deuterated benzene. In this case, the ^{29}Si NMR chemical shift of the fragmentation product was $\delta(^{29}\text{Si}) = 53.0$. In addition, degradation of cation **11** in toluene- d_8 gave rise to a mixture of three isomeric silicon compounds as indicated by their very similar ^{29}Si NMR chemical shifts of $\delta(^{29}\text{Si}) = 56.8, 57.8, \text{ and } 58.7$. The identity of the cationic species **17** formed by the thermal degradation of cation **11** in benzene was finally established by its conversion into a neutral compound by reaction with $n\text{-Bu}_3\text{SnH}$ (Scheme 5). Addition of the tin hydride to the polar phase again gave a biphasic reaction mixture. The ionic product was identified as $[\text{n-Bu}_3\text{Sn}(\text{C}_6\text{D}_6)]\text{-}[\text{B}(\text{C}_6\text{F}_5)_4]$ by the ^{119}Sn NMR chemical shift of $\delta(^{119}\text{Sn}) = 262$ and its comparison with literature data.²³ The newly formed neutral product was unequivocally characterized as silane **18** by NMR spectroscopy ($\delta(^{29}\text{Si}) = -22.4, \delta(^1\text{H}(\text{SiH})) = 5.14, ^1J(\text{SiH}) = 203 \text{ Hz}$) and mass spectrometry ($m/z = 496.3$) and finally by its independent synthesis (see Scheme 5 and the Supporting Information). This result clearly indicates that the cationic species formed by thermal degradation of the dibenzo-7-silanorbornadienyl cation **11** in benzene is terphenyldiphenylsilylium ion **17**. Similarly, in toluene as solvent, a mixture of at least three tolyl-substituted silyl cations **19** is formed (see Scheme 6). This conclusion is suggested from ^{29}Si NMR investigations of the reaction mixture and from GC/MS analysis of the product mixture after derivatization with $n\text{-Bu}_3\text{SnH}$ (see the Supporting Information). Final evidence for the formation of silylium borate **17** $[\text{B}(\text{C}_6\text{F}_5)_4]$ came from its independent synthesis along the standard synthetic route by reaction of silane **18** with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (see Scheme 5).²⁴ The detected ^{29}Si NMR chemical shift for silyl cation **17** ($\delta(^{29}\text{Si}) = 52.7$) can be related to that reported for terphenyl-substituted silyl cation **15** ($\delta(^{29}\text{Si}) = 79.1$)¹⁷ in particular when the shielding influence on the ^{29}Si NMR chemical shift of the phenyl substituents in **17** compared to methyl groups in cation **15** is taken into account.²⁵ As indicated by the high-field ^{29}Si NMR resonance and similar to the situation found for terphenyl-substituted silyl cation **15**,¹⁷ cation **17** is stabilized by intramolecular interaction between the positively charged silicon atom and the flanking aryl groups of the terphenyl substituent. This is also shown by the results of computations at the M06-2X/6-311+G(d,p) level.¹⁹ The predicted molecular structure for silyl cation **17** (Figure 4c) is dominated by

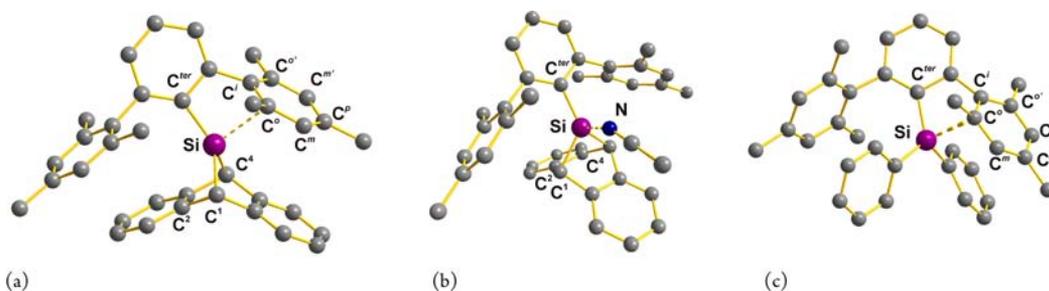
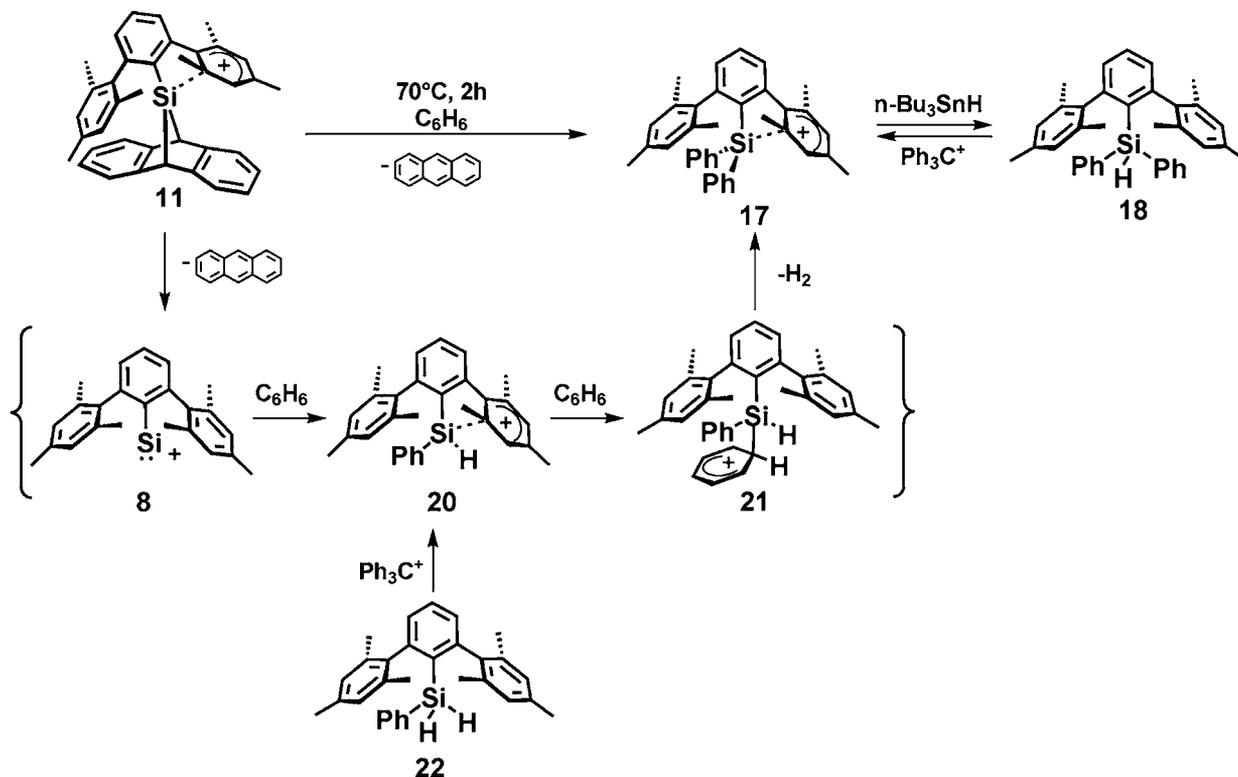
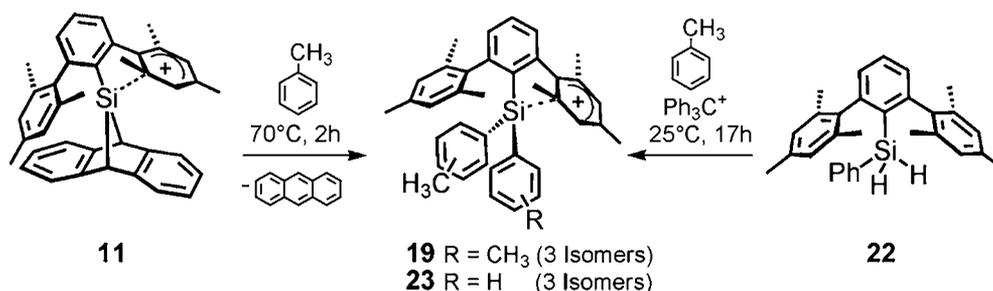
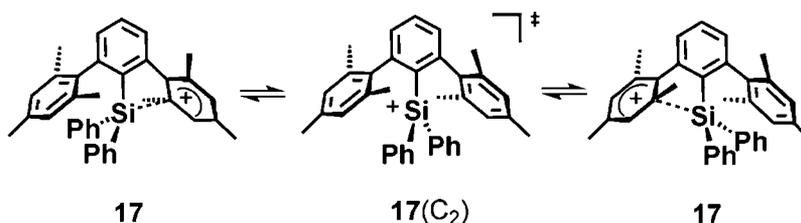


Figure 4. Calculated molecular structures of terphenyl-substituted dibenzo-7-silanorbornadienyl cation **11** (a), nitrilium ion **16** (b), and triarylsilylium ion **17** (c) (M06-2X/6-311+G(d,p)) Structural parameters pertinent for the discussion (bond lengths, pm; bond angles, deg): (cation **11**) Si–C(1), 190.5; Si–C(4), 189.5; Si–C(ter), 185.0; C(1)–C(2), 151.9; C(2)–C(3), 141.0; C(1)–Si–C(4), 84.5; Si–C(2), 235.4; Si–C(3), 236.2; Si–C(o), 238.0; C(o)–C(m), 141.2; C(m)–C(p), 138.3; C(p)–C(m'), 140.4; C(m')–C(o'), 138.7; C(o')–C(i), 141.1; C(i)–C(o), 142.6; (cation **16**) Si–C(1), 191.0; Si–C(4), 191.0; Si–C(ter), 185.7; C(1)–C(2), 152.1; C(2)–C(3), 140.7; C(1)–Si–C(4), 83.2; Si–C(2), 248.2; Si–C(3), 248.2; Si–N, 189.4; (cation **17**) Si–C(o), 230.4; Si–C(ter), 185.8; C(o)–C(m), 141.6; C(m)–C(p), 138.2; C(p)–C(m'), 140.3; C(m')–C(o'), 139.1; C(o')–C(i), 140.5; C(i)–C(o), 143.7.

Scheme 5. Thermal Decomposition of Dibenzo-7-silanorbornadienyl Cation 11 and Formation of Triarylsilyl Cation 17

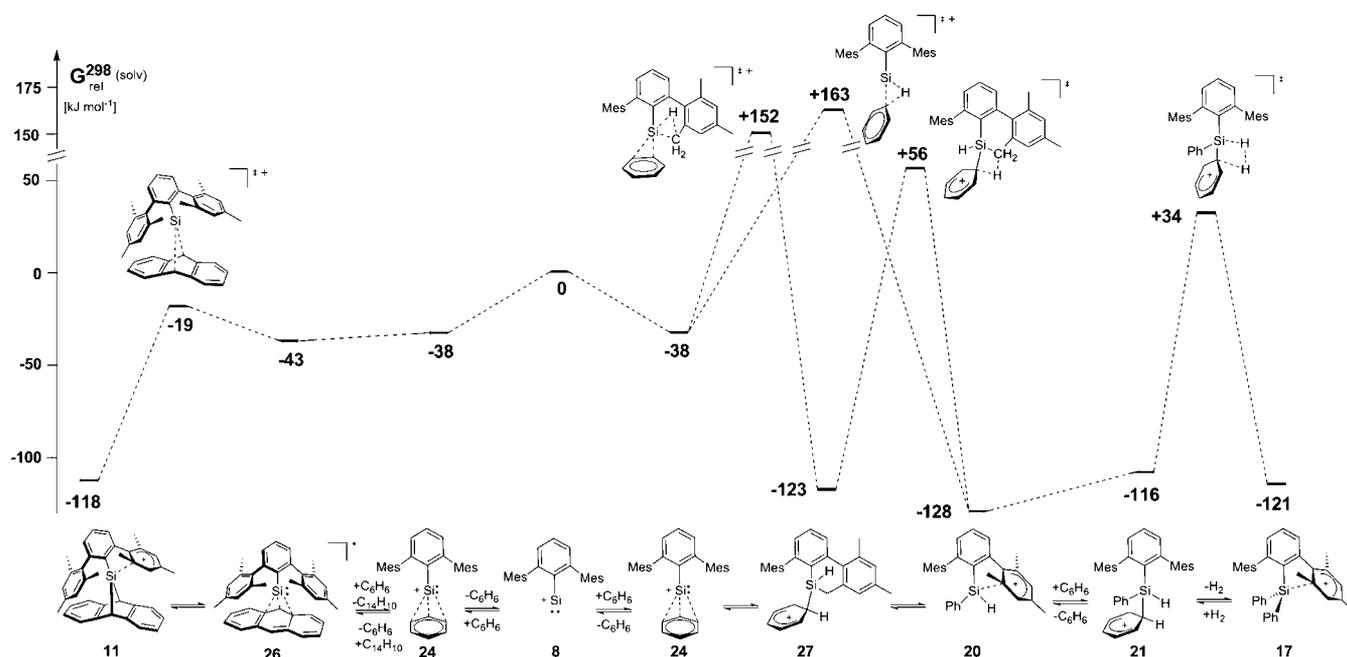


Scheme 6. Formation of Triarylsilyl Cations 19 and 23 in Toluene

Scheme 7. Equilibration of Different Isomers of Cation 17 via Transition State 17(C₂)

intramolecular electron donation from the flanking aryl group to the positively charged silicon atom, as revealed by the relatively small Si–C(*o*) distance ($d(\text{SiC}(\text{o})) = 230.4 \text{ pm}$; see Figure 4c) and the trigonal pyramidal coordination environment for the silicon atom as indicated by the sum of the bond angles around silicon: $\sum \alpha(\text{Si}) = 352^\circ$. These structural features characterize cation 17 as a silylarenium ion. The computationally predicted NMR chemical shift for cation 17 in benzene solution is $\delta(^{29}\text{Si}) = 63.2$ (GAO/B3LYP/IGLOIII//PCM/M06-2X/6-311+G(d,p)),¹⁹ in reasonable agreement with the experimental value. At ambient conditions cation 17 is a highly

dynamic molecule. The C₂ symmetric transition state for the interconversion of two equivalent structures of cation 17, 17(C₂), is found to be only 21 kJ mol⁻¹ higher in energy. This computational result suggests that the high symmetry of cation 17 in solution as indicated by ¹H and ¹³C NMR spectroscopy is only time averaged and can be explained by a degenerated equilibrium between equivalent silylarenium structures of cation 17 which is fast on the NMR time scale (Scheme 7). Similar equilibria are operative in cation 15 and related silyl cations.¹⁷

Scheme 8. Computed Reaction Path for the Decomposition of Dibenzo-7-silanorbornadienyl Cation 11 and Its Subsequent Reaction To Give Terphenylsilylium 17^a

^aRelative free Gibbs energy, $G_{\text{rel}}^{298}(\text{sol})$, in benzene at $T = 298.15$ K, $p = 27.93$ MPa (277 atm) computed at M06-2X/6-311+G(d,p) using the PCM model for inclusion of solvent effects.

A mechanistic scenario which accounts for the somewhat surprising formation of silyl cation 17 in the course of the thermal degradation of dibenzo-7-silanorbornadienyl cation 11 is detailed in Scheme 5. The detection of anthracene suggests the intended formation of terphenyl-substituted silyliumylidene 8 by thermal fragmentation of cation 11. Reaction of silyliumylidene 8 with the solvent benzene to give the silyl cation 20 follows. Conceding that complexation of the extremely electron deficient silyliumylidene 8 with benzene is expected on the basis of the results of previous quantum mechanical calculations,^{12,26,27} the formal insertion of the silyliumylidene 8 into the C–H bond of benzene to give silyl cation 20 is surprising. Although the terphenylsilyl cation 20 is stabilized by intramolecular π -electron donation from the flanking phenyl substituent, the formation of an intermolecular arenium ion 21 can be envisaged. The occurrence of two hydrogen atoms of different polarities in cation 21, the hydridic Si–H atom and the arenium proton, suggests facile dihydrogen elimination from cation 21 to give terphenyldiphenylsilyl cation 17.^{28,29}

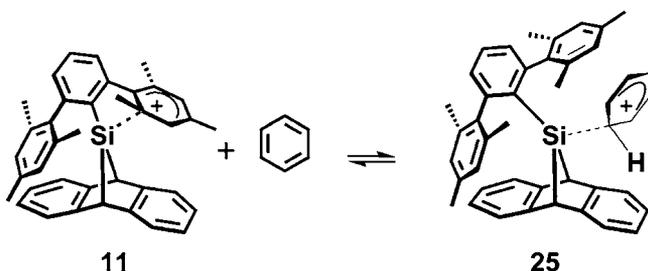
Support for this mechanistic proposal came from the following experimental observations: (i) When toluene is applied as the solvent for the thermal fragmentation of dibenzosilanorbornadienyl cation 11, tolyl groups instead of phenyl substituents are found in the obtained product mixture 19 (see above and Scheme 6). (ii) The ionization of dihydrosilane 22 by 1 equiv of trityl cation at room temperature in benzene results in the quantitative formation of silyl cation 17 (Scheme 5). The expected primary product silyl cation 20 was not detected. With toluene as the solvent, three different isomers of the tolyl- and phenyl-substituted silyl cation 23 were detected (Scheme 6). These results suggest that hydrido-substituted silyl cations such as 20 are not stable in arene solvents. Remarkably, under the applied reaction conditions, the hydrido substituent in cation 20 is replaced

by an aryl group to give either cation 17 or cation 23 depending on the arene solvent used.

All attempts to directly detect cation 8, or its complex with benzene, 24 (Scheme 8), by spectroscopic methods failed. For example, while ²⁹Si NMR chemical shift calculations predict a characteristic extremely low field resonance of the silicon nuclei in intermediate 8 at $\delta(^{29}\text{Si}(\text{calcd})) = 381$ and likewise a ²⁹Si NMR resonance for the benzene complex 24 at $\delta(^{29}\text{Si}(\text{calcd})) = 285$ (see Table 1), no ²⁹Si NMR signal in the low-field region from $\delta(^{29}\text{Si}) = 600$ to $\delta(^{29}\text{Si}) = 100$ was detected during the thermal fragmentation of dibenzosilanorbornadienyl cation 11. In addition, all attempts to intercept silyliumylidene 8 directly with reagents such as hydrosilanes or alkynes used in the past³⁰ for quenching silicon(II) compounds were unsuccessful due to the high reactivity of the starting compound 11[B(C₆F₅)₄] versus these reagents. Similarly, all attempts to stabilize cation 8 either by N-heterocyclic carbenes (NHCs)³¹ with different steric requirements or by crown ethers³² only led to inconclusive results.

Computations at the M06-2X/6-311+G(d,p) level of theory were applied to give insight into the generation of silyliumylidene 8 from dibenzo-7-silanorbornadienyl cation 11 and its fate in benzene solution.¹⁹ The intramolecular π -electron donation from the flanking aryl groups to the positively charged silicon atom in cation 11 prevents the formation of intermolecular complexes with arene solvents. In particular, the reaction of dibenzo-7-silanorbornadienyl cation 11 with benzene to give the intermolecular arenium ion 25 is computed to be endergonic at ambient conditions ($\Delta G^{298} = 37$ kJ mol⁻¹; see Scheme 9). This is in agreement with the experimentally observed absence of solvent effects on the ²⁹Si NMR chemical shift of cation 11 in arene solvents (see Table 1), and it excludes the formation of arene complexes such as 25 in the experiment. This computational result also suggests that the decomposition of cation 11 is not triggered by benzene

Scheme 9. Reaction of Dibenzo-7-silanorbornadienyl Cation **11** with Benzene To Give the Intermolecular Arenium Ion **25**



complexation. The thermal decomposition of cation **11** is predicted to be connected with a free energy barrier of 99 kJ mol⁻¹, and it results in the formation of the anthracene complex **26** of silyliumylidene **8** (Scheme 8). The subsequent replacement of anthracene by the solvent benzene to give the complex cation **24** is an essential thermoneutral process (see Scheme 8). The computations indicate, in agreement with previous theoretical investigations,^{12,26} that at no point along the reaction coordinate of the thermal decomposition of cation **11** in benzene a noncoordinated silyliumylidene **8** is formed; instead at ambient conditions the monocoordinated cation **8** is always bonded to solvent and/or reactant, for example, to benzene with 38 kJ mol⁻¹ or to anthracene with 43 kJ mol⁻¹.

The results of this computational study also suggest a possible mechanistic scenario for the formation of diphenyl-substituted silyl cation **17** from the benzene complex **24** of silyliumylidene **8** (see Scheme 8). In general, the overall reaction of cation **8** with 2 equiv of benzene to give terphenylsilylium ion **17** and dihydrogen is predicted by the calculations to be strongly exergonic ($\Delta G^{298} = -121$ kJ mol⁻¹). The direct insertion reaction of silyliumylidene **8** into the C–H bond of benzene to give silylium ion **20** is connected with a substantial barrier of $\Delta G^{298,\ddagger} = 163$ kJ mol⁻¹ relative to silyliumylidene **8** + C₆H₆ (Scheme 8, **24** → **20**). Interestingly, an alternative multistep process involves a smaller overall barrier (Scheme 8, **24** → **27** → **20**). Intramolecular insertion of the silicon cation into a benzylic C–H bond in an *ortho* position of one of the flanking mesityl groups leads to the formation of the cyclic silyl cation **27**. In the second step, intramolecular protonation of the newly formed Si–C bond is accompanied by ring-opening and formation of the silyl cation **20** in a slightly exergonic process ($\Delta G^{298} = -5$ kJ mol⁻¹).³³ The C–H activation process **24** → **27** is the rate-determining step in that alternative sequence, and its free Gibbs energy of activation is 11 kJ mol⁻¹ smaller than predicted for the direct process **24** → **20** (see Scheme 8). Therefore, the results of the computations favor the two-step process for the formal oxidative addition of benzene to silyliumylidene **8**. In the course of the substitution reaction of the hydrogen atom in cation **20** by a phenyl group in arenium ion **17**, a third cation, **21**, is suggested as an intermediate (see Scheme 5). The intramolecular coordination of the silyl cation by the flanking mesityl group in cation **20** is replaced in benzenium ion **21** by an intermolecular complexation with the solvent benzene. In agreement with the ad hoc assumption based on the relative electronegativities that the vicinal hydrogen atoms at the Si–C arenium bond in cation **21** show different polarities, a natural bond (NBO) analysis¹⁹ predicts a significantly different charge distribution for the Si–H and the arenium C^{ipso}–H hydrogen

atoms (calculated NBO charges: SiH, -0.17 au; arenium C^{ipso}H, +0.30 au). This antagonistic charge distribution seems to propose facile dihydrogen elimination from cation **21**. The calculated free Gibbs energy of activation for synchronous elimination of dihydrogen from **21** is however still appreciable ($\Delta G^{298,\ddagger} = 150$ kJ mol⁻¹). Nevertheless, this is the smallest barrier along the complete reaction sequence shown in Scheme 8. In addition, dihydrogen elimination from silylated arenium ions is not without precedence. Allen and Lampe report on the formation of silabenzyl cation in the ion–molecule reaction of SiH₃⁺ with benzene by dihydrogen elimination from the intermediate silylbenzenium ion.^{34–36} The overall substitution reaction **20** → **17** is predicted by the calculations to be slightly endergonic ($\Delta G^{298} = 7$ kJ mol⁻¹; see Scheme 8). All three cationic intermediates involved in this reaction sequence, **20**, **21**, and **17**, are, however, all very close in energy, and in view of the approximations regarding the contributions of thermal and entropy contributions (see the Supporting Information), a clear decision about the thermodynamic driving force is not justified. Nevertheless, in view of the computed positive ΔG^{298} value, the evolution of gaseous dihydrogen is certainly an important factor which drives the reaction toward the formation of silyl cation **17**.

CONCLUSION

The synthesis and NMR characterization of a terphenyl-substituted dibenzosilanorbornadienyl borate **11**[B(C₆F₅)₄] is reported. The analysis of the experimental NMR parameters of cation **11**, in particular the ²⁹Si NMR chemical shift, in combination with the results of quantum mechanical calculations reveals the intramolecular interaction with the flanking aryl groups of the terphenyl substituent. The identity of cation **11** is finally confirmed by a single-crystal X-ray diffraction analysis of the closely related dibenzosilanorbornadienyl nitrilium borate **16**[B(C₆F₅)₄]. Dibenzosilanorbornadienyl borate **11**[B(C₆F₅)₄] is thermally unstable and undergoes in aromatic solvents a fragmentation reaction upon heating. In this reaction, anthracene is formed and the terphenyl-substituted silyliumylidene **8** is obtained as a reactive intermediate in the form of its solvent complexes. The benzene complex of silyliumylidene **8** is transformed under the applied reaction conditions into the diphenylterphenylsilylium ion **17**. It can be demonstrated experimentally and it is supported by the results of computations that this reaction proceeds via a second silylium intermediate, the hydrogen-substituted silyl cation **20**. The surprising formation of silylium ion **17** illustrates the extreme reactivity of aryl-substituted silyliumylidenes, such as **8**, in C–H activation reactions. Moreover, it reveals a surprising instability of hydrogen-substituted silylium ions, such as **20**, in arene solvents. The density functional study disclosed a concerted elimination of dihydrogen from cation **21** as a feasible reaction path for the formation of the isolated silyl cation **17**. In view of the predicted almost thermoneutral course of the reaction, the reverse reaction, dihydrogen activation by silylium ions, seems feasible under certain conditions. Clearly, this result influences the mechanistic conceptions for dihydrogen activation by silyl cationic frustrated Lewis Pairs, and it might open a new approach for reversible dihydrogen activation.

■ ASSOCIATED CONTENT

■ Supporting Information

All experimental details, characterization data, and relevant NMR spectra, X-ray crystallographic information for compounds **12b**, **14b**, **16**[B(C₆F₅)₄], **18**, and **22**, all computational details, and tables of absolute energies and Cartesian coordinates. 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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