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Dibenzosilanorbornadienyl cations and their Fragmentation into Silyliumylidenes

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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 a XRD analysis of a corresponding acetonitrilium salt. The thermal fragmentation of $\mathbf{11}[B(C_6F_5)_4]$ in benzene results in the high yield formation of diphenyl-terphenyl silylium borate $\mathbf{17}[B(C_6F_5)_4]$. High-lying intermediates in this process are solvent-complexed terphenylsilyliumylidene **8** and the hydrogen-phenyl substituted silyliumion **20**. The formation 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 silylcationic frustrated Lewis Pairs and in general for the dihydrogen activation by strong Lewis acids.

Introduction.

The extreme Lewis acidity of silvlium ions, R₂Si⁺, silicon cations with silicon in its 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 silvlium ions with the amphiphilic character of non-stabilized silvlenes as accomplished in the shape of silvliumvlidenes RSi:⁺, 1, creates silicon cations with an extraordinary high reactivity and synthetic potential.⁶ Since then several groups reported the successful preparation and isolation of stabilized silvliumylidenes, such as cations 2-4.79 For the synthesis of each of these highly electrondeficient species bulky and strongly electron donating substituents were applied, which also extent the coordination number of the silicon cation. Some of these compounds show already 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 behaviour of the silicon(II) cation and mask their reactivity to a certain extent.



This prompted us to search for substituents R in silvliumylidenes, 1, which extend their lifetime in 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 their oxidation state +I, 5, stabilized by terphenyl substituents exist^{10b-d} and Power and coworkers reported on the synthesis of the toluene complex of terphenyl substituted mono-coordinated lead cation, 6." In line with these experimental achievements, the results of quantum mechanical computations suggested, that in the case of silicon the thermodynamic stability of terphenyl-substituted silvliumylidenes such as 7 and 8, approaches those of cations 2 and 3^{12} The same theoretical study suggested that in general α elimination from silvlium ions, 9, (Scheme 1) is a suitable synthetic approach to silvliumylidenes. In particular, the elimination of benzene from dibenzo-7-silanorbornadienyl cations 10 is particularly well suited for the generation of terphenyl substituted silvliumylidenes 7 or 8 (Scheme 1).¹² Following these theoretical guidelines, we report here on the synthesis of a 7-terphenylsubstituted-dibenzo-7-silanorbornadienyl cation 11 by hydride transfer from the corresponding silane 12a and on the investigations of its thermal decomposition, which provides evidence for the intermediate formation of the terphenyl substituted silyliumylidene 8.



Scheme 1. Synthesis of silyliumylidenes, **1**, from silylium ions **9**, **10** by α -elimination.

Results and Discussion.

Dibenzo-7-silanorbornadienes 12 were prepared according a procedure published by Tokitoh and coworkers starting from Dichlorosilanes 13.13 The central step in this reaction sequence involves regioselective deprotonation of 9silylanthracene 14 at carbon atom C¹⁰, followed by an intramolecular substitution reaction (Scheme 2). The regioselectivity of the 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 Supplementary Material). The relatively low field shifted resonances in the ²⁹Si NMR spectra (δ^{29} Si=31.6 (12a); 31.5 (12b)) are characteristic for dibenzo-7-silanorbornadienes. $^{\rm 16}$ From a structural point of view the long endocyclic Si-C $^{\rm 1/4}$ bonds $(d(SiC^{1/4}) = 192.7 \text{ pm } (12a); 192.4 \text{ pm } (12b))$ are noticeable. Both features, the deshielded ²⁹Si nuclei and the long endocyclic SiC bonds are typical for the dibenzo-7silanorbornadiene subunit and they are indications for the occurrence of σ - π *-conjugation in these compounds.^{14,15}



Scheme 2. Synthesis of dibenzo-7-silanorbornadienes **12** from 9-dihydroanthracenylsilanes **14**. (a: R= 2,6-bis-(2,4,6-tri-methylphenyl)-phenyl (Ter); b: R=2,6-bis-(2,4,6-tri-*iso*-propylphenyl)-phenyl (Ter*), LDA Lithium-di-*iso*-propylamide).



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 in pm, angles in °). 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).

Addition of benzene to an equimolar mixture of trityl tetrakispentafluorophenyl borate ($[Ph_3C][B(C_6F_5)_4]$) and dibenzo-7-silanorbornadiene **12a** results in a biphasic reaction mixture, characteristic for benzene solutions of the $B(C_6F_5)_4$ salts. Monitoring of the reaction progress by ¹H NMR spectroscopy of the lighter non-polar phase indicates a slow hydride transfer and selective formation of the terphenylsubstituted 7-silanorbornadienyl borate $\mathbf{11}[B(C_6F_5)_4]$, which was obtained as the sole product after 14 h at r.t. (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 24h an intractable mixture of different compounds as judged from ²⁹Si NMR spectroscopy.



Scheme 3. Synthesis of 7-silanorbornadienyl cation 11 and nitriliumion 16.





Figure 2. a) 500 MHz ¹H NMR spectrum of $\mathbf{11}[B(C_6F_5)_4]$ in benzene-d₆ (# : residual proton signal of the solvent). b) 100 MHz ²⁹Si{¹H} NMR spectra of $\mathbf{11}[B(C_6F_5)_4]$ in benzene-d₆ at room temperature (upper trace) and after heating for 2h to 70°C (lower trace).



Figure 3. Molecular structure of nitrilium ion 16 in the crystal of $16[B(C_6F_5)_4] \cdot 2 \cdot C_6F_6$. (thermal ellipsoid presentation drawn at the 50% probability level). All hydrogen atoms are omitted (bond lengths in pm, angles in °). 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(176), Si-C(2) 254.52(50), Si-C(3) 253.85(57), Si-N 184.80(35).

The 7-silanorbornadienyl borate $\mathbf{11}[B(C_6F_5)_4]$ was characterized by multinuclear NMR spectroscopy (Table 1). The ²⁹Si NMR resonance of cation 11 is practically independent from the solvent used (δ^{29} Si= 1.3 (benzene-d₆) (Figure 2b), 1.2 (toluene-d₈), 2.2 (chlorobenzene-d₅)). 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 unusual low frequency compared to triarylsilylium ions $(\delta^{29}Si = 215-230)^4$ or even to the terphenyl substituted dimethylsilylium ion 15 and closely related cations (δ^{29} Si = 59-80).¹⁷ The silvl 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 benzonorbornadiene 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 unusual high field shifted ²⁹Si NMR resonance of the 7-silanorbornadienyl cation 11.



Scheme 4. Intramolecular interaction in terphenylsubstituted 7-silanorbornadienyl cation **11** and the degenerate equilibrium between different equivalent conformers of cation **11**.

The ¹H and ¹³C NMR spectra obtained from $\mathbf{11}[B(C_6F_5)_4]$ are notable in that respect that only one set of signals ($\delta^{1}H = 1.72$, 1.96, 6.57, Figure 2a) for the flanking mesityl groups of the terphenyl substituent in the ¹H NMR spectrum and only five resonances of methin 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 behaviour was established for the strongly related silvl cation 15 and was put forward as reason for the isochronicity of the mesityl substituents in the NMR experiment.¹⁷ The computed molecular structure of cation 11 (at Mo6-2X/6-311+G(d,p), see Figure $(4a)^{19}$ suggests intramolecular π -donation from the flanking mesityl group to the electron deficient silicon atom. Most significant features are (i) the short distance between the ortho carbon atom C(o) and the silicon atom d(SiC(o)) (d(SiC(o)) = 238.0 pm) which is markedly smaller than the sum of the van der Waals radii (Σ (vdW) = 380 pm)²⁰; and (ii) the notable pyramidalization of the silicon atom as judged from the sum of the bond angles around Si, $\Sigma\alpha(Si)$, which deviates significantly from $_{360^{\circ}}$ ($\Sigma\alpha$ (Si) = $_{348^{\circ}}$). GIAO $^{^{29}}$ Si NMR chemical shift calculations predict for cation 11 in benzene solution a ²⁹Si NMR resonance at somewhat higher field than observed experimentally $(\delta^{29}Si(calc) = -14)$.¹⁹

In solution the salts $\mathbf{n}[B(C_6F_5)_4]$ and $\mathbf{n}[HCB_nH_5Br_6]$ 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 $\mathbf{n}[B(C_6F_5)_4]$ results in the formation of the nitrilium salt $\mathbf{16}[B(C_6F_5)_4]$ as indicated by NMR spectroscopy (Scheme 3, Table 1). In particular, the ²⁹Si NMR chemical shift of $\delta^{29}Si = 6.4$ is very close to that of a strongly related silanorbornadienylnitrilium borate reported previously $(\delta^{29}Si = 8.9)$.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 is however secured (see Figure 3). In addition, DFT calculations at the Mo6-2X/6-311+G(d,p) level of theory predict for nitrilium ion 16 a molecular structure (Figure 4b), which is in all significant parameter very close to the experimental solid state structure.¹⁹ Therefore, the isolation of nitrilium borate, $\mathbf{16}[B(C_6F_5)_4]$, provides further clear evidence for the molecular structure and the identity of cation $\mathbf{11}$.

Upon heating of the biphasic benzene solution of borate $\mathbf{n}[B(C_6F_5)_4]$ to 70°C for 2h 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 ²⁹Si resonance at δ^{29} Si = 52.7. The presence of the intact $[B(C_6F_4)]^-$ anion was confirmed by ¹⁹F NMR and ¹³C NMR spectroscopy. ¹H and ¹³C 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 'H NMR spectra was detected (δ^{1} H = 6.66, 6.91 and 7.14), which are typical for 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 ²⁹Si NMR chemical shift of the fragmentation product was δ^{29} Si = 53.0. In addition, degradation of cation 11 in toluene-d₈ gave rise to a mixture of three isomeric silicon compounds as indicated by their very similar ²⁹Si NMR chemical shifts of δ^{29} Si = 56.8, 57.8 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-Bu₃SnH (Scheme 5). Addition of the tin hydride to the polar phase again gave a biphasic reaction mixture. The ionic product was identified as $[n-Bu_3Sn(C_6D_6)][B(C_6F_5)_4]$ by the ¹¹⁹Sn NMR chemical shift of δ^{119} Sn = 262 and its comparison with literature data.²³ The newly formed neutral product was unequivocally characterized as silane 18 by NMR spectroscopy $(\delta^{29}Si = -22.4, \delta^{1}H(SiH) = 5.14, {}^{1}J(SiH) = 203 Hz)$ and mass spectrometry (m/z = 496.3) and finally by its independent synthesis (see Scheme 5 and Supporting Information). This result clearly indicates that the cationic species formed by thermal degradation of the 7-silanorbornadienyl cation 11 in benzene is terphenyldiphenyl silvlium ion 17. Similarly, in toluene as solvent, a mixture of at least three tolylsubstituted silyl cations 19 is formed (see Scheme 6). This conclusion is suggested from ²⁹Si NMR investigations of the reaction mixture and from GC/MS analysis of the product mixture after derivatization with n-Bu₃SnH (see Supporting Information). Final evidence for the formation of silvlium borate $17[B(C_6F_5)_4]$ came from its independent synthesis along the standard synthetic route by reaction of silane 18 with $[Ph_3C][B(C_6F_5)_4]$ (see Scheme 5).²⁴ The detected ²⁹Si NMR chemical shift for silvl cation 17 (δ^{29} Si = 52.7) can be related to that reported for terphenyl substituted silyl cation **15** $(\delta^{29}Si = 79.1)^{17}$ in particular when the shielding influence on the ²⁹Si 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 ²⁹Si 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 Mo6-2X/6-311+G(d,p) level.¹⁹ The predicted molecular structure for silyl cation 17 (Figure 4c) is dominated by 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(SiC(o)) = 230.4 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: $\Sigma\alpha(Si) = 352^{\circ}$. These structural features characterize cation 17 as a silylarenium ion. The computationally predicted NMR chemical shift for cation 17 in benzene solution is $\delta^{29}Si = 63.2$ (GIAO/B3LYP/IGLOIII//PCM/Mo6-2X/6-311+G-(d,p)),¹⁹ in reasonable agreement with the experimental value. At ambient conditions cation 17 is a highly dynamic molecule. The C_2 symmetric transition state for the interconversion of two equivalent structures of cation 17, 17(C_2), is

found to be by 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 **Table 1**. Selected experimental, theoretical (italic) NMR and structural parameter for dibenzo-7-silanorbornadienes **12**, dibenzo-7-silanorbornadienyl cations **11**, silyliumylidenes **8** and related compounds.

Ср	R	δ ²⁹ Si (¹ J(SiH) [Hz])	$\delta^{13}C^{1/4}$	$\delta H^{1/4}$	$d(SiC^{1}), d(SiC^{2})$	$\alpha(C^{1}SiC^{4})$	ref.
d		[a]	[a]	[a]	[pm]	[°]	
12a [b]] Ter ^{lc}	31.6 (209.4)	44.3	2.82	192.75, 192.60	81.36	14
12 b	Ter*	31.5 (207.0)	44.4	2.70	192.74(16), 192.04(16)	81.44(7)	this work
11	Ter [c]	1.3	44.2	3.68			this work
		$1.2^{[e]}$ $2.2^{[f]}$ $-14.3^{[g]}$			190.5,189.5 ^[h]	84.5 ^[h]	
16] Ter ^{lc}	6.4	43.8	2.66	190.28(44), 189.18(38)	82.84(18)	this work
17] Ter ^{lc}	-0.2 ⁻²⁻⁵ 52.7			191.0, 191.0 ^{- 1}	83.2	this work
8] Ter ^{lc}	63.2 ¹⁸¹ 381 ^{lgl}					this work
24] Ter ^{lc}	285 ^{lgl}					this work

[a] In benzene-d₆ at room temperature. [b] Data from ref [14]. [c] Ter: 2,6-bis-(2,4,6-trimethylphenyl)-phenyl. [d] Ter*: 2,6-bis-(2,4,6-tri-*iso*-propylphenyl)-phenyl. [e] In toluene-d₈ at room temperature. [f] In chlorobenzene-d₅ at room temperature. [g] ²⁹Si NMR chemical shifts calculated at GIAO/B3LYP/IGLOIII//PCM/Mo6-2X/6-311+G(d,p). [h] Structural parameter obtained at Mo6-2X/6-311+G(d,p).¹⁹



Figure 4. Calculated molecular structures of terphenylsubstituted dibenzo-7-silanorbornadienyl cation **11** (a), nitrilium ion **16** (b) and triarylsilylium ion **17** (c). (Mo6-2X/6-311+G(d,p)) Structural parameter, pertinent for the discussion (bond lengths in pm, bond angles in [°]): 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(0) 238.0, C(0)-C(m) 141.2, C(m)-C(p) 138.3, C(p)-C(m') 140.4, C(m')-C(0') 138.7, C(0')-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(3) 248.2, Si-C(3) 248.2, Si-N 189.4. Cation **17**: Si-C(0) 230.4, Si-C(ter) 185.8, C(0)-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 8. Computed reaction path for the decomposition of dibenzo-7-silanorbornadienyl cation **11** and its subsequent reaction to give terphenylsilylium **17**. (Relative free Gibbs energy, $G_{rel}^{298}(solv)$ in benzene at T = 298.15 K; p = 27.93 MPa (277 atm) computed at Mo6-2X/6-311+G(d,p) using the PCM model for inclusion of solvent effects).

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A mechanistic scenario which accounts for the somewhat surprising formation of silyl cation 17 in 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 silyliumvlidene 8 by thermal fragmentation of cation 11. Reaction of silvliumylidene 8 with the solvent benzene to give the silvl cation 20 follows. Conceding that complexation of the extremely electron deficient silvliumylidene 8 with benzene is expected based on 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 silvl cation 20 is surprising. Although the terphenyl silyl 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 polarity in cation 21, the hydridic Si-H and the arenium proton, suggests facile dihydrogen elimination from cation 21 to give terphenyldiphenyl silyl cation 17.28, 29

Support for this mechanistic proposal came from the following experimental observations: (i) When toluene is applied as 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 dihydrido silane 22 by one equivalent of trityl cation at room temperature in benzene results in the quantitative formation of silvl cation 17 (Scheme 5). The expected primary product, silyl cation 20 was not detected. With toluene as solvent three different isomers of the tolyl-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 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 δ^{29} Si(calc) = 381 and likewise a ²⁹Si NMR resonance for the benzene complex 24 at δ^{29} Si(calc) = 285 (see Table 1), no ²⁹Si NMR signal in the low field region from δ^{29} Si = 600 – 100 was detected during the thermal fragmentation of dibenzosilanorbornadienyl cation 11. In addition, all attempts to intercept silyliumylidene 8 directly with reagents such as hydrido silanes or alkynes used in the past³⁰ for quenching silicon(II) compounds were unsuccessful due to the high reactivity of the starting compound $\mathbf{n}[B(C_6F_{\epsilon})_4]$ versus these reagents. Similarly, all attempts to stabilize cation 8 either by N-heterocyclic carbenes (NHC)³¹ with different steric requirements or by crown ethers³² only lead to inconclusive results.



Scheme 9. Reaction of dibenzo-7-silanorbornadienyl cation **11** with benzene to give the intermolecular arenium ion **25**.

Computations at the Mo6-2X/6-311+G(d,p) level of theory were applied to give insights 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 endogonic at ambient conditions $(\Delta G^{298} = 37 \text{ kJ mol}^{-1}$, 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 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 silvliumylidene 8 (Scheme 8). The subsequent replacement of anthracene by the solvent benzene to give the complex cation 24 is predicted to be an essential thermo neutral process (see Scheme 8). The computations indicate in agreement with previous theoretical investigations,^{12, 26} that at no point of the reaction coordinate of the thermal decomposition of cation 11 in benzene a noncoordinated silvliumylidene 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 suggest also a possible mechanistic scenario for the formation of diphenyl substituted silvl cation 17 from the benzene complex 24 of silvliumylidene 8 (see Scheme 8). In general, the overall reaction of cation 8 with 2 eq. benzene to give terphenyl silylium 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 silvliumylidene 8 into the C-H bond of benzene to give silvlium ion 20 is connected with a substantial barrier of $\Delta G^{298\ddagger} = 163 \text{ kJ mol}^{-1}$ relative to silyliumylidene 8 + C_6H_6 (Scheme 8, 24 \rightarrow 20). Interestingly, an alternative multi-step process involves a smaller overall barrier (Scheme 8; $24 \rightarrow 27 \rightarrow 20$). Intramolecular insertion of the silicon cation into a benzylic C-H bond in orthoposition 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 new formed Si-C bond is accompanied with ring opening and formation of the silyl cation 20 in a slightly exergonic process ($\Delta G^{298} = -5$ k]

57

58 59 60

mol⁻¹).³³ The C-H activation process $24 \rightarrow 27$ is the rate determining step in that alternative sequence and its free Gibbs energy of activation is by 11 kJ mol⁻¹ smaller than predicted for the direct process $24 \rightarrow 20$ (see Scheme 8). Therefore, the results of the computations favour the two step process for the formal oxidative addition of benzene to silyliumylidene 8. In 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 intermediate (see Scheme 5). The intramolecular coordination of the silvl 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 polarity, a natural bond (NBO) analysis¹⁹ predict a significantly different charge distribution for the Si-H- and the arenium- C^{ipso}-H- hydrogen atoms (calculated NBO charges: SiH: -0.17 a.u., arenium-C^{ipso}H: +0.30 a.u.). 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 silvlated 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 \rightarrow 17 is predicted by the calculations to be slightly endogonic $(\Delta G^{298} = 7 \text{ kJ mol}^{-1}, \text{ see Scheme 8})$. All three cationic intermediates involved in this reactions 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 SI Material), 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 towards the formation of silyl cation 17.

Conclusion.

The synthesis and NMR characterization of a terphenyl substituted dibenzosilanorbornadienyl borate $\mathbf{n}[B(C_6F_5)_4]$ is reported. The analysis of the experimental NMR parameter 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 $16[B(C_6F_5)_4]$. Dibenzosilanorbornadienyl borate $\mathbf{11}[B(C_6F_5)_4]$ is thermally unstable and undergoes in aromatic solvents a fragmentation reaction upon heating. In this reaction anthracene is formed and the terphenyl substituted silvliumylidene 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 diphenyl-terphenyl silylium ion 17. It could 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 as well as relevant NMR spectra. X-ray crystallographic information for compounds **12b**, **14b**, **16**[B(C_6F_5)_4], **18** and **22**. All computational details, 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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TOC Graphic:

