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The Nature of Protonated Decamethylsilicocene, $(Me_5C_5)_2Si^+H$

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Structure and bonding in several stereoisomers of the recently synthesized silyl cation $(Me_5C_5)_2Si^+H$ (**2**) and its hydrogen-substituted analogue $(C_5H_5)_2Si^+H$ (**3**) has been investigated by quantum-mechanical methods. DFT calculations at the B3LYP/6-311G(2d,p)//B3LYP/6-31G(d)+ΔZPVE level as well as coupled cluster calculations at the CCSD(T)/6-311G(d) level for the parent silyl cation **3** reveal that the $\eta^{1.5}$:$\eta^{1.5}$-coordinated isomer **3c** of C_2 symmetry is the most stable isomer. Two isomers of **3**, the η^2:η^3-bonded **3f** (C_s symmetry) and the η^2:η^2-coordinated **3e** (C_{2v} symmetry), are, however, very close in energy ($\Delta E < 1$ kcal mol^{-1}). This implies that **3** is a highly fluxional molecule which undergoes a series of effectively barrierless haptotropic shifts leading to a circumambulatory migration of the SiH group about the cyclopentadienyl ring. The positive charge in the silyl cation **3** is effectively transferred to the attached cyclopentadienyl substituent, leading to an exceptional thermodynamic stability: the secondary cation **3** is more stable than Me_3Si^+ by 18.7 kcal mol^{-1} (at B3LYP/6-311G(2d,p)//B3LYP/6-31G(d)+Δ*Z*PVE). Similarly, for the experimentally observed permethylated silyl cation **2**, three low-energy isomers with different hapticities for the silicon have been found to be very close in energy ($\Delta E < 1.5$ kcal mol^{-1} at B3LYP/6-311G(2d,p)//B3LYP/6-31G(d)), with the η^2:η^3 isomer **2f** only marginally favored. This clearly indicates that also **2** is a highly fluxional molecule. ^{29}Si NMR chemical shift calculations at the GIAO/B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) level suggest that the experimentally observed cation adopts the η^3:η^2-bonded structure **2f**. The unique intramolecular stabilization of the silyl cation **2** by the pentamethylcyclopentadienyl substituents and the additional steric protection of **2** by the methyl groups results in very low association energies A_E between the cation and solvent molecules (benzene, $A_E = -3.2$ kcal mol^{-1}; dimethyl ether, $A_E = -6.4$ kcal mol^{-1}). Although these interaction energies must be corrected by ca. −2 kcal mol^{-1} due to the neglect of intermolecular dispersion energy contributions by the applied DFT method, it can be concluded that **2** is best regarded as a free silyl cation even in solvents as nucleophilic as THF.

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Introduction

After a 50 year search, a series of free silylium ions[1] in the condensed phase have recently been synthesized and characterized.[2−4] The success of the syntheses of these silylium ions rests (i) on steric protection of the highly reactive, positively charged silicon[2] and/or (ii) on an efficient lowering of the electron deficiency of the silicon by either resonance effects[2] or integration of the silicon in aromatic[3] or homoaromatic[4] systems. Alternatively, the high electrophilicity of the positively charged silicon can be modified by intramolecular electron donation from remote donor substituents, leading to solvent-free ions with coordination numbers for silicon >3.[5−7] This interaction leads to a considerable

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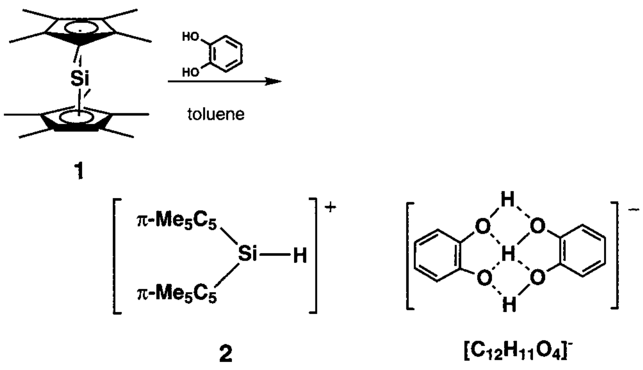
electron transfer from the donor group to silicon; thus, the silyl cation character of these positively charged species is disputable.[8,9] Similarly, in cationic species formed by the intermolecular reaction of transient silylium ions with solvent molecules in which silicon adopts coordination numbers 4 and higher, the positive charge is transferred to a large extent to the coordinated solvent molecule. Such stable cationic compounds are formed from silylium ions and solvents such as amines, nitriles, ethers, and even aromatic hydrocarbons and are identified as being silylated ammonium ions,[2a,10] nitrilium ions,[11] oxonium ions,[12] and arenium ions,[13] respectively. The structural, energetic, and electronic features of such silyl cation–solvent complexes have been accurately described on the basis of quantum-mechanical calculations,[8,9,13e–h] and in agreement with the experimental data,[2a,10–13] it has been shown that the silylium ion character in these species is lost.

A rather unusual type of silyl cation was recently obtained by Jutzi and Bunte by protonation of decamethylsilicocene (**1**) (Scheme 1).[14] The secondary silyl cation **2** is formed by reaction of **1** with 2 equiv of *o*-catechol. The ^{29}Si NMR chemical shift of −12.1 ppm for **2** measured in benzene is deshielded by 386 ppm in comparison with the signal for **1**, although this value is still more than 230 ppm less deshielded than that for Mes_3Si^+ (225 ppm).[2] Solvent effects on the ^{29}Si NMR chemical shift, a reliable tool for detecting solvent–cation interactions, are negligible; thus, for benzene as well as for nitrobenzene and even for THF solutions of **2** nearly the same ^{29}Si NMR chemical shifts ($\delta(^{29}Si)$ −12.1, −13.3, and −13.9, respectively) were found.[14b] The spectroscopic and analytic data suggest the formation of a solvent-free cationic species with a π-bonded ligand, and also its remarkable stability in nucleophilic solvents such as THF[14] hints at an unusual bonding situation in **2**. However, in the absence of any structural data only speculations about the bonding situation in **2** are possible. In this paper we report results of quantum-mechanical calculations for the model cation $(C_5H_5)_2Si^+H$ (**3**) and the experimentally observed $(C_5Me_5)_2Si^+H$ (**2**), which reveal that **2** is a highly fluxional molecule which is particularly stabilized by the intramolecular interaction between the pentamethylcyclopentadienyl ligand and the positively charged silicon.

Scheme 1



Computational Methods

Geometry optimizations[15] were performed initially at the ab initio SCF level of theory.[16] Refined geometries were obtained at the nonlocal DFT level of theory[17] using Becke's three-parameter hybrid functional and the LYP correlation functional (B3LYP)[18] and, for comparison, at the correlated ab initio MP2 level.[19] The standard 6-31G(d) basis set was used with all three methods. The DFT and the MP2 results for cations **3** are very similar; therefore, the computationally cheaper DFT method was employed for the larger systems and DFT results will be reported throughout the text. Stationary points were characterized by subsequent frequency calculations as minima, transition states, or higher order saddle points at the SCF/6-31G(d) and B3LYP/6-31G(d) level. Finally, relative energies have been calculated at the B3LYP/6-311G(2d,p) level using the B3LYP/6-31G(d) geometries (B3LYP/6-311G(2d,p)//B3LYP/6-31G(d)) and those energies have been further improved by adding zero-point vibration energy differences (ΔZPVE). Relative energies, reaction energies, and association energies, quoted in the text, are all computed at this level, if not stated otherwise. For the hydrogen-substituted cation **3**, the relative energy of the individual isomers was also evaluated using the highly accurate coupled cluster method at the

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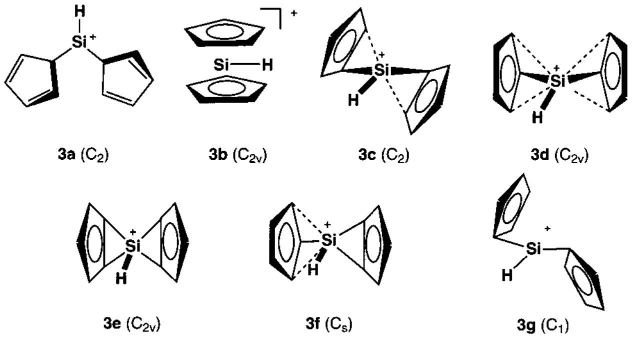
Table 1. Relative Energies of Silyl Cations $(C_5Me_5)_2Si^+H$ (2) and $(C_5H_5)_2Si^+H$ (3) in kcal mol^{-1} and the Number (in Brackets) and Size (in Parentheses) of Imaginary Frequencies

compd	point group	HF/6-31G(d)// HF/6-31G(d)	B3LYP/6-31G(d)// B3LYP/6-31G(d)	B3LYP/6-311G(2d,p)// B3LYP/6-31G(d) + ΔZPVE	MP2/6-31G(d)// MP2/6-31G(d)	CCSD(T)/6-311G(d)// B3LYP/6-31G(d)
3b	C_{2v}		56.6	55.8		57.0
3c	C_2	0.0 [1] (−148)	0.0 [0]	0.0	0.0	0.0
3d	C_{2v}	5.7 [2] (−99, −70)	5.7 [2] (−151, −93)	4.9	6.5	5.9
3e	C_{2v}	3.2 [2] (−228, −52)	0.2 [1] (−55)	0.3	0.0	0.6
3f	C_s	−1.4 [0]	0.5 [1] (−35)	0.3	1.8	0.4
3g	C_1	9.1	10.2 [0]	8.8	10.2	7.8
2c	C_2	0.0	0.0	0.0[a]		
2e	C_{2v}	5.9	1.3	1.4[a]		
2f	C_1	−2.0	0.1	−0.04[a]		
2g	C_s	6.5	9.3	10.3[a]		

[a] No ΔZPVE included.

Chart 1



CCSD(T)/6-311G(d) level[20] and B3LYP/6-31G(d) optimized geometries. CCSD(T) and DFT methods gave for the isomers of **3** practically identical relative energies, which indicates that the DFT results for the larger systems are reliable. The relative energies of isomers of cations **2** and **3** are summarized in Table 1. The electron distribution in cations **3** was analyzed using NBO[21] theory and a HF/6-311G(d) wave function. NMR chemical shifts have been calculated using the GIAO[22]/B3LYP method and the 6-311G(2d,p) basis set for all atoms. For comparison in some cases the larger 6-311+G(2df,p) basis set for silicon and a small 6-31G(d) basis set for C, H, O, and N was applied. Orbital plots were generated using a HF/6-311G(d) wave function and the Molden[23] program.

Results

(a) Structure and Energies of Isomers of Protonated Silicocene 3. Initially, seven possible isomers with the composition $[(C_5H_5)_2SiH]^+$, **3a**−**g**, have been considered in our study (Chart 1). The isomer **3a**, with both cyclopentadienyl rings σ-bonded to silicon which corresponds closely to a classical trivalent silylium ion, is not stable at the ab initio SCF and DFT/B3LYP level of theory but collapses during the optimization procedure to the C_2-symmetric isomer **3c**, the lowest energy isomer of **3** at the B3LYP/6-31G(d) level. The artificial structure corresponding to the η^5:η^5 isomer **3b**[24,25] is 55.8 kcal mol^{-1} higher in energy than **3c**, and free optimization in the point group C_{2v} results in the isomer **3d**. Therefore, the isomers **3a**,**b** were not further considered in our study.

The isomers **3c**−**g** are stationary points on the potential energy surface (PES) in their respective point groups. Their relative energies, together with the characterization of each stationary point in terms of the number and size of imaginary frequencies, are given in Table 1, and the calculated geometries are shown in Figure 1. At the DFT level, only the C_2-symmetric isomer **3c** and the unsymmetric **3g** correspond to local minima on the PES. In **3c**, the SiH group bridges unsymmetrically one CC bond of each cyclopentadienyl ring; the hapticity of the silicon can be therefore designated as being $\eta^{1.5}$:$\eta^{1.5}$.[27] In **3g**, which is 8.8 kcal mol^{-1} less stable than **3c**, one cyclopentadienyl ring is σ-bonded to the silicon while the second cyclopentadienyl ligand is coordinated in a $\eta^{1.5}$ fashion. Since for the transformation **3g** → **3c** only a rotation of the cyclopentadienyl rings around the Si−C bond is required, it is unlikely that in non-nucleophilic media **3g** is of any chemical significance. The highly symmetric η^3:η^3-bonded isomer **3d** is a second-order saddle point and lies 4.9 kcal mol^{-1} higher in energy than **3c**. The computed structure of the η^2:η^2 conformer **3e** is very similar to the experimentally determined structure of the isoelectronic $(\eta^2\text{-}C_5H_5)_2AlMe$.[28] **3e** is, however, the transition state for a synchronous, antisymmetric rotation of both cyclopentadienyl rings, while the η^3:η^2-bonded **3f** is the transition state for the rotation of only one cyclopentadienyl ligand. Thus, **3c** may undergo two degenerate transformations: one includes the synchronous rotation of both cyclopentadienyl ligands via **3e**, and the second rearrangement via **3f** includes only the rotation of one cyclopentadienyl ring. The PES in the

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[25] To ensure formal η^5:η^5-coordination all SiC distances in **3b** (point group C_{2v}) have been fixed to be equal during the optimization procedure. This results in a calculated structure for **3b** with SiC distances of 2.448 Å (at B3LYP/6-31G(d)).

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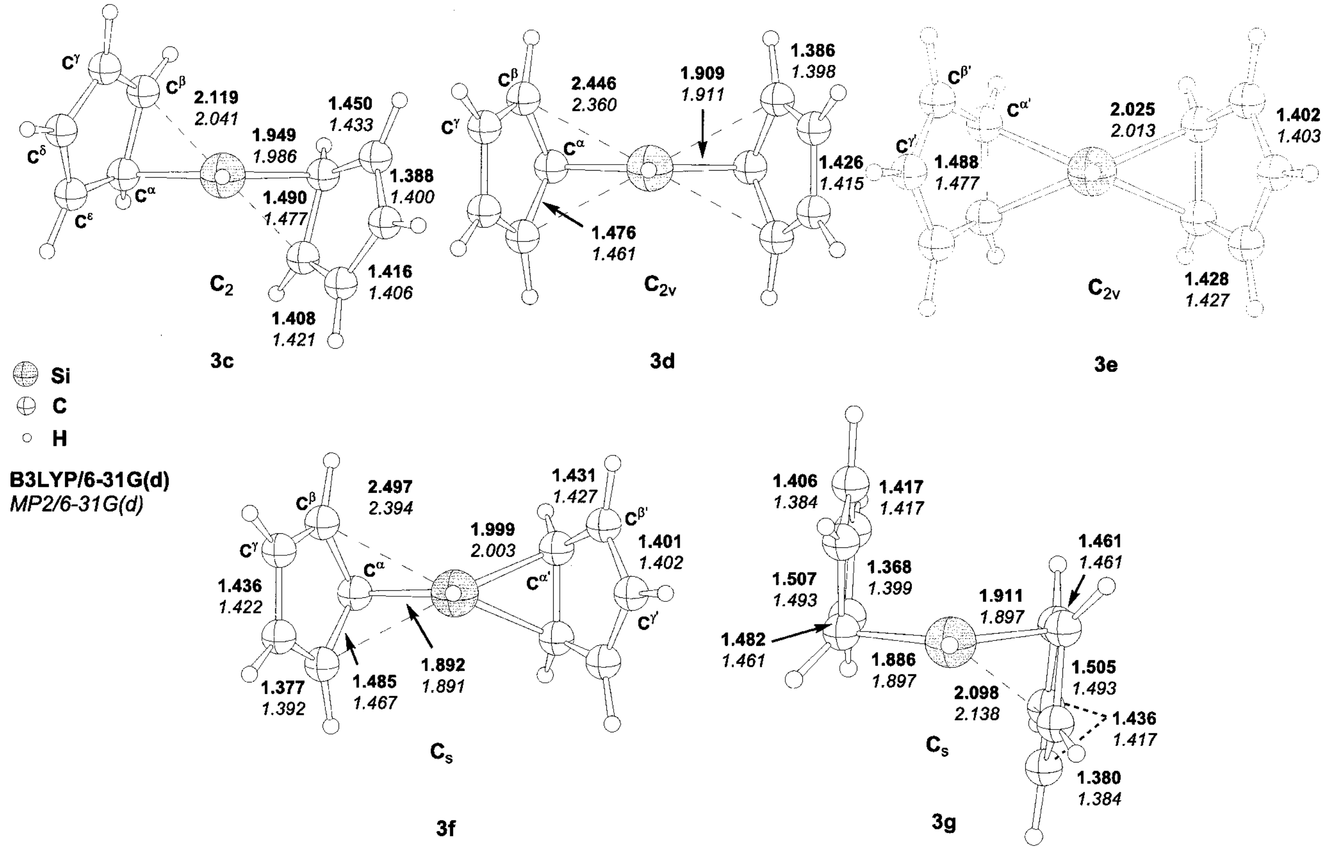

Figure 1. Calculated structures of $(C_5H_5)_2Si^+H$ isomers **3c**–**g** (at the B3LYP/6-31G(d) (boldface) and MP2/6-31G(d) levels (italics)). Bond lengths are given in Å.

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region of **3c**,**e**,**f** is extremely flat, as already indicated by the small imaginary frequencies of **3e**,**f** (-55 cm^{-1} (**3e**) and -35 cm^{-1} (**3f**)). Both transition states are only insignificantly higher in energy than **3c** (by 0.3 kcal mol^{-1} for both **3e** and **3f**). Clearly, it is impossible to assign on the basis of these relative energy differences a ground-state structure for the bis(cyclopentadienyl)silyl cation **3**, and even the characterization of the isomers as minima or as saddle points on the PES may vary with the applied method (see Table 1). Instead, the calculations predict that **3** is a highly fluxional molecule. A mechanism involving the circumambulatory migration of the SiH group about both cyclopentadienyl rings through a series of 1,2-silyl shifts along the sequence **3c** → **3e** → **3c** or **3c** → **3f** → **3c** is operative and pretends that there is, time-averaged, a highly symmetric molecule **3**. Similar negligible energy differences between different conformers with different hapticities has been recently reported for silicocene[29] and its higher homologues.[29c] For silicocene, the three lowest energy isomers (η^2:η^2, η^2:η^1, $\eta^{1.5}$:$\eta^{1.5}$)[29b] have computed energy differences of less than 0.4 kcal mol^{-1}.[29a] In general, the stereochemically nonrigid behavior of cyclopentadienyl compounds is well-documented,[30] and in particular, for compounds of main-group elements[28–32] the barriers for the haptotropic[32] rearrangements were found to be extremely small.

(b) Structures and Energetics of Isomers of Protonated Decamethylsilicocene (2). The steric requirements of the pentamethylcyclopentadienyl group are known to influence the actual hapticity of cyclopentadienyl compounds.[29c,30,31] Therefore, the energy differences between isomers of the permethylated **2** with different hapticities might be more pronounced than for the parent compound **3**. To test this hypothesis, the structures of the decamethyl analogues **2c**,**e**–**g** (Chart 2) of the respective isomers of **3** were optimized and the computed structures of the low-energy isomers **2c**,**e**,**f** are shown in Figure 2. The geometries of the permethylated **2c**,**e**,**f** are very similar to those of the parent compounds **3c**,**e**,**f**, with the major difference that Si–C distances are generally longer (by 0.002–0.054 Å). The isomer **2f** is slightly distorted from C_s symmetry, but the silicon is still best described as being η^2-bonded to one pentamethylcyclopentadienyl ligand and η^3-bonded to the second cyclopentadienyl group.[33] The energy differences between the individual isomers of **2** are again marginal (see Table 1); the isomers **2c**,**e**,**f** lie between an energy band of less than 1.5 kcal mol^{-1}, and only the isomer **2g** is energetically clearly separated, being 10.3 kcal mol^{-1} higher in energy than **2c**. In particular, **2c** and **2f** have practically the same energy.

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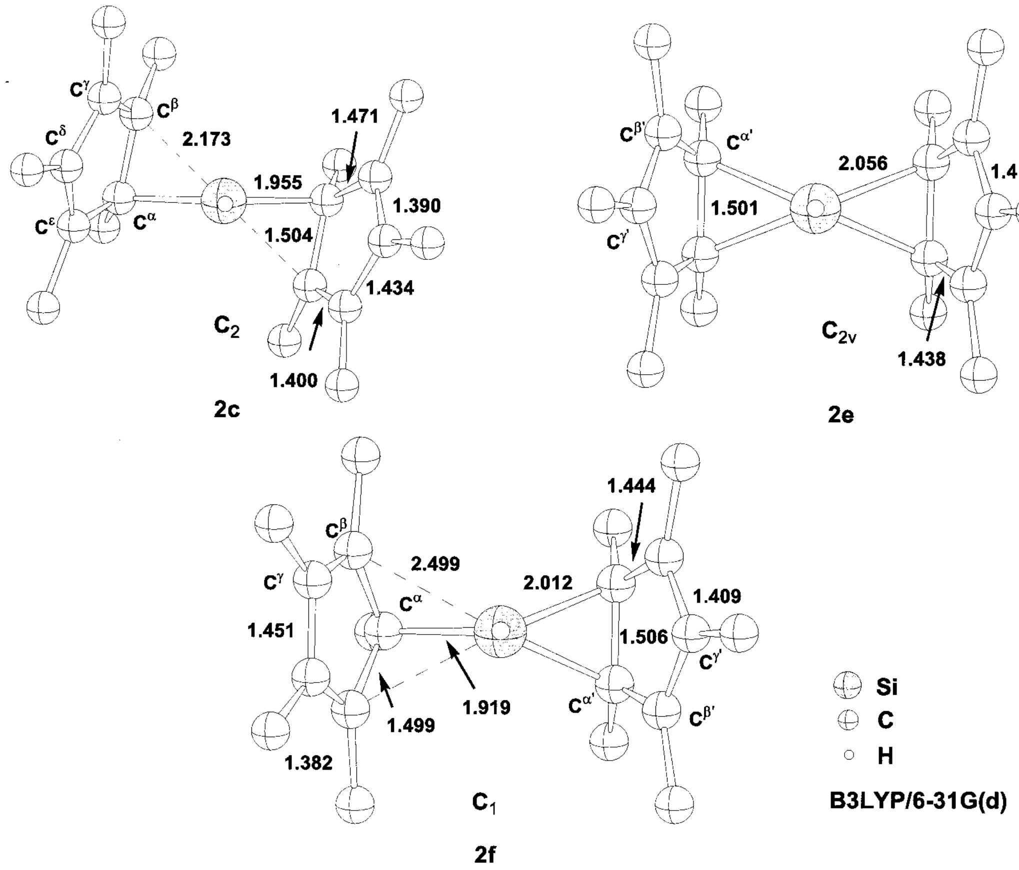

Figure 2. Calculated structures of $(C_5Me_5)_2Si^{+}H$ isomers **2c**,**e**,**f** at the B3LYP/6-31G(d) level. Bond lengths are given in Å, and all hydrogen atoms except the hydrogen atom attached to silicon are omitted for clarity.

Chart 2

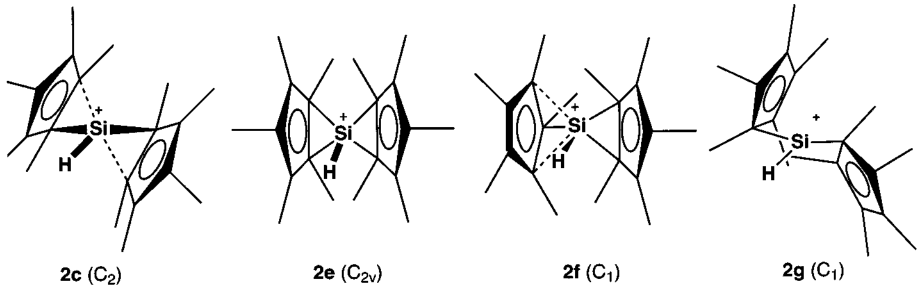

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Table 2. Calculated NBO Charges (in au, Charges Summed in Heavy Atoms) for Bis(cyclopentadienyl)silyl Cation Isomers and Related Compounds[a,b]

	Si	C^{α}	C^{β}	C^{γ}	C^{δ}	C^{ϵ}	$C^{\alpha'}$	$C^{\beta'}$	$C^{\gamma'}$
3c	1.40	−0.30	−0.17	0.16	−0.03	0.14			
3e	1.38						−0.23	0.15	−0.03
3f	1.43	−0.39	0.00	0.05			−0.26	0.21	0.05
4	0.92	−0.45	0.02	−0.02	−0.02	0.01			

[a] For the assignment see Figure 1. [b] Calculated at the HF/6-311G(d)/B3LYP/6-31G(d) level.

While at the level of the geometry optimization (B3LYP/6-31G(d)) **2c** is slightly more stable (by 0.1 kcal mol^{-1}), **2f** is favored by 0.04 kcal mol^{-1} at the higher B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) level. Therefore, also for the experimentally investigated decamethyl cyclopentadienyl silyl cation **2**, the barrier for a 1,2-shift of the SiH group is negligible, and a series of fast 1,2-shifts equilibrate all ring carbons and all methyl groups. In qualitative agreement with this predicted barrierless haptotropic rearrangement, **2** shows even at −80 °C in the ^{1}H NMR spectrum only one sharp signal for the methyl groups and in the ^{13}C NMR spectrum two signals corresponding to the ring carbons and the methyl groups.[14]

(c) Charge Distribution and Bonding in 3. An NBO analysis[21] of the HF/6-311G(d) wave functions of **3c**,**e**,**f** suggest highly delocalized structures (see Table 2 and Scheme 2). Comparison of the calculated NBO charges for **3c**,**e**,**f** with those calculated for the dihydride **4** (Chart 3) indicate that ca. 50% of the positive charge in the silyl cations **3c**,**e**,**f** is delocalized into the adjacent

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(33) Optimization of **2** in C_s symmetry, the point group of **3f**, results in the isomer **2h**, with a novel structure which has no counterpart in the bis(pentamethylcyclopentadienyl)silyl cation series. Both cyclopentadienyl ligands in **2h** are η^2-bonded to silicon, but one cyclopentadienyl ring has an an anti arrangement relative to the SiH vector while the second has a syn arrangement. **2h** is 5.7 kcal mol^{-1} higher in energy than **2c** (B3LYP/6-31G(d)), and the Si−C distances are as follows: syn C_5Me_5, 2.028 Å (SiC^{α}), 2.717 Å (SiC^{β}), 3.057 Å (SiC^{γ}); anti C_5Me_5, 2.040 Å ($SiC^{\alpha'}$), 2.856 Å ($SiC^{\beta'}$), 3.255 Å ($SiC^{\gamma'}$).

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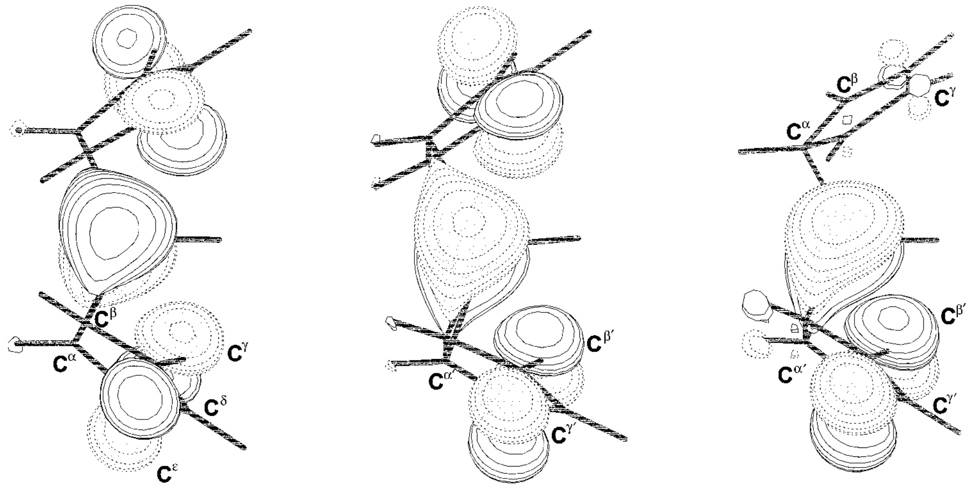


3c **3e** **3f**

Figure 3. Calculated shapes of the LUMOs of **3c**,**e**,**f**, at the HF/6-311G(d)//B3LYP/6-31G(d) level.

Scheme 2

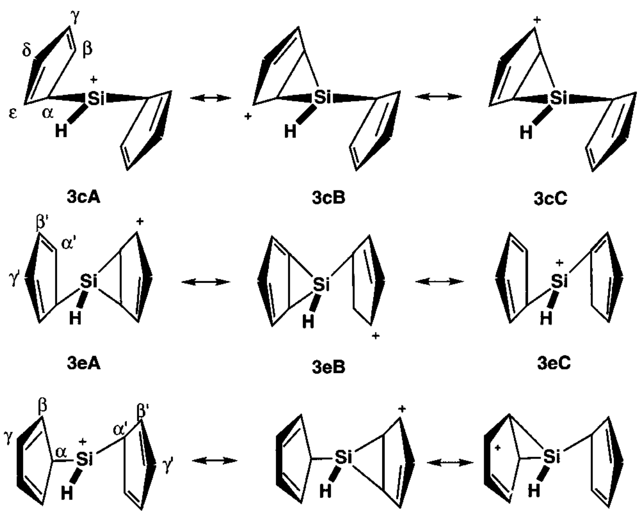
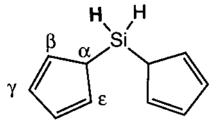


Chart 3



4

cyclopentadienyl rings. Obviously, allyl cation type resonance structures such as **3cB**, **3eB** and **3fB**, **3fC** are important for a description of the bonding in the bis(cyclopentadienyl)silyl cation isomers **3c**,**e**,**f**. This is in agreement with the calculated shape of the LUMO's, which for all three isomers **3c**,**e**,**f** are strongly delocalized with considerably large coefficients at C^{γ} and C^{ϵ} (**3c**), at $C^{\beta'}$ (**3e**), and at $C^{\beta'}$ and C^{γ} (**3f**) (see Figure 3).[23]

A detailed NBO analysis for **3c** reveals the intriguing bonding situation in this silyl cation. The occurrence of appreciable delocalization of charge is indicated by large second-order pertubative energy terms ΔE_{ij}[34] between the 3p(Si) and the π bonds of the cyclopentadienyl rings ($\Delta E_{ij} = 94.8$ kcal mol^{-1} between 3p(Si) and $\pi(C^{\beta}C^{\gamma})$ and $\Delta E_{ij} = 60.3$ kcal mol^{-1} between $\pi(C^{\delta}C^{\epsilon})$ and $\pi^*(C^{\beta}C^{\gamma})$). Consequently, the occupation of the formally empty 3p(Si) orbital in **3c** is 0.44e, while the π orbitals of the cyclopentadienyl ligands (1.68e and 1.73e for $\pi(C^{\beta}C^{\gamma})$ and $\pi(C^{\delta}C^{\epsilon})$, respectively) are significantly depleted with respect to their ideal value of 2e. Additional important delocalization modes are the interaction between the σ(SiC$^{\alpha}$) bond with the antibonding π^* bonds of the cyclopentadienyl rings (occupation σ(SiC$^{\alpha}$) 1.75 e, $\Delta E_{ij} = 36.7$ kcal mol^{-1} between σ(SiC$^{\alpha}$) and $\pi^*(C^{\beta}C^{\gamma})$ and $\Delta E_{ij} = 26.5$ kcal mol^{-1} between σ(SiC$^{\alpha}$) and $\pi^*(C^{\delta}C^{\epsilon})$) and the hyperconjugative interaction between the $C^{\alpha}-C^{\beta}$ σ bond and the 3p(Si) (occupation $\sigma(C^{\alpha}C^{\beta})$ 1.97e, $\Delta E_{ij} = 14.9$ kcal mol^{-1} between $\sigma(C^{\alpha}C^{\beta})$ and 3p(Si)). These orbital interactions are depicted schematically in Figure 4.

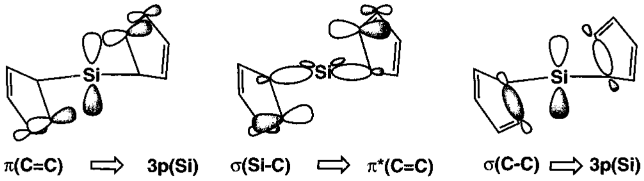


Figure 4. Main orbital interactions in the silyl cation **3c**, as derived from a NBO analysis.

These interactions between the cyclopentadienyl ligand and the Si−H group are also apparent in the calculated structures of **3c** and equally in the structure of the decamethyl-substituted **2c**. Most remarkably for the structure of **3c** is a long Si−C$^{\alpha}$ bond (1.949 Å) and a relatively short Si−C$^{\beta}$ separation (2.119 Å). In the neutral dihydride **4** the Si−C$^{\alpha}$ bond is calculated to be 0.025 Å shorter and the silicon and C$^{\beta}$ are separated by 2.780 Å. The formal C=C bonds in the cyclopentadienyl rings in the silyl cation **3c** (1.408 and 1.388 Å for $C^{\beta}{=}C^{\gamma}$ and $C^{\delta}{=}C^{\epsilon}$, respectively) are markedly longer than in the neutral **4** (1.359 Å). Similar bonding characteristics can be found for the permethylated **2c**: a long Si−C$^{\alpha}$ bond (1.955 Å), a relatively small Si−C$^{\beta}$ separation (2.173 Å), and comparatively long C=C bonds in the pentamethylcyclopentadienyl ligand (1.400 and 1.390 Å). The sum of the bond angles (Σ°Si) around

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(34) The second-order pertubative energy ΔE_{ij}, the stabilization energy associated with the interaction between orbital i and orbital j, is given by the following equation:[21b] $\Delta E_{ij} = -2F_{ij}^{2}/\Delta E_{ij}$, where $\Delta E_{ij} = \epsilon_j - \epsilon_i$. The Fock matrix element F_{ij} is roughly proportional to the corresponding overlap matrix element, S_{ij}, of the interacting orbitals, and ϵ_i and ϵ_j are the energies of the corresponding orbitals.

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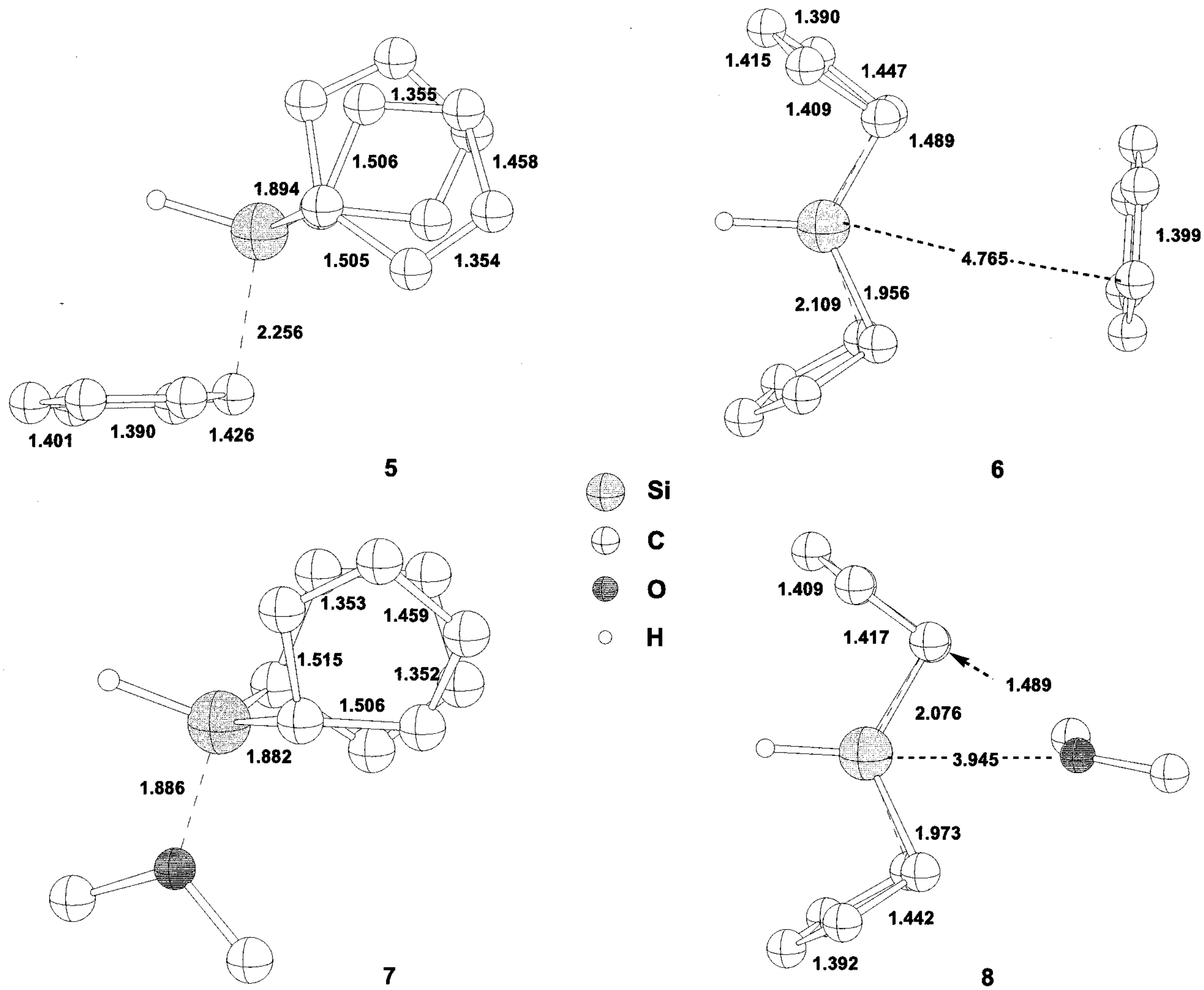

Figure 5. Calculated structures of benzenium and oxonium ions (**5**, **7**) deriving from $(C_5H_5)_2Si^+H$ (**3**) and the isomeric solvates with benzene (**6**) and Me_2O (**8**) at the B3LYP/G-31G(d) level. Bond lengths are given in Å, and all hydrogen atoms except the hydrogen atom attached to silicon are omitted for clarity.

silicon and its three closest neighbors is in both **2c** and **3c** exactly 360°.

The unique bonding situation in the silyl cations **2** and **3** results in an exceptional thermodynamic stability. According to the isodesmic equation (1) the cyclopen-

$$R_2SiH_2 + Me_3Si^+ \rightarrow Me_3SiH + R_2Si^+H \qquad (1)$$

tadienyl group in **3c** is more efficient in stabilizing a positively charged silicon than methyl and phenyl by 30.1 kcal mol^{-1} and by 7.9 kcal mol^{-1}, respectively (calculated reaction energies for (1): 11.4 kcal mol^{-1} for R = Me, −10.8 for R = Ph, and −18.7 kcal mol^{-1} for R = C_5H_5). Therefore, the secondary cation **3** (and similarly **2**) is among the thermodynamically most stabilized silylium ions such as Mes_3Si^+,[2b] $(Me_2B)_3Si^+$,[35] and $(Me_2N)_3Si^+$.[36]

Interestingly, bis(cyclopentadienyl)methylium, the carbon analogue of **3**, is only 13.8 kcal mol^{-1} more stable than the *tert*-butyl cation. Thus, the cyclopentadienyl ring is the only example so far for a substituent which stabilizes a silyl cation more efficiently than a carbocation.

(d) Interaction of 2 and 3 with Solvent Molecules. This unique intramolecular stabilization of the positively charged silicon by the cyclopentadienyl substituents in **2** and **3** reduces greatly its inherently high electrophilicity and weakens considerably its interaction with nucleophiles and therefore determines its fate in the condensed phase. For example, two different associates, **5** and **6**, between benzene and **3** are found computationally to be stable at the B3LYP/6-31G(d) level of theory (see Figure 5). In **5**, the silyl cation approaches the benzene at a distance of 2.256 Å. The significant bond length alternation in the benzene ring (1.426, 1.388, and 1.402 Å) and the nonplanar geometry around silicon identifies **5** as an arenium ion (Figure 5), similar to the complex between Et_3Si^+ and toluene.[13,37] Benzene coordination to **3**, computed for **6**, has virtually no impact on the geometries either of the benzene or of the silyl cation (see Figure 5). The benzene molecule in **6** is only loosely attached to the cation; in particular, no structure determinant interaction between the 3p(Si) and π orbitals of benzene is present. This is also reflected by the very small association energy (A_E) of merely −4.9 kcal mol^{-1}.[38] Due to the

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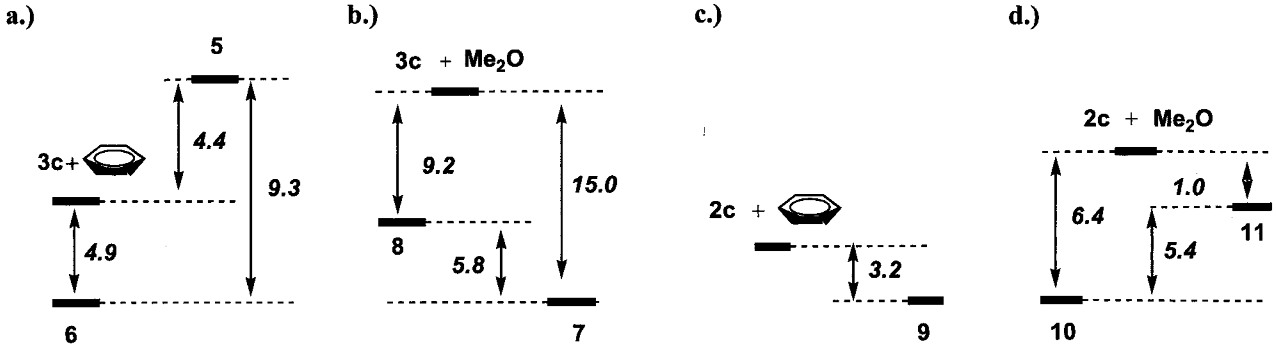

Figure 6. Relative energies of $(C_5H_5)_2Si^+H$ (**3**) and their complexes with (a) benzene and (b) dimethyl ether (in kcal mol^{-1}, at the B3LYP/6-311G(2d,p) + ΔZPVE level) and relative energies of $(C_5Me_5)_2Si^+H$ (**2**) and their complexes with (c) benzene and (d) dimethyl ether (in kcal mol^{-1}, at the B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) level).

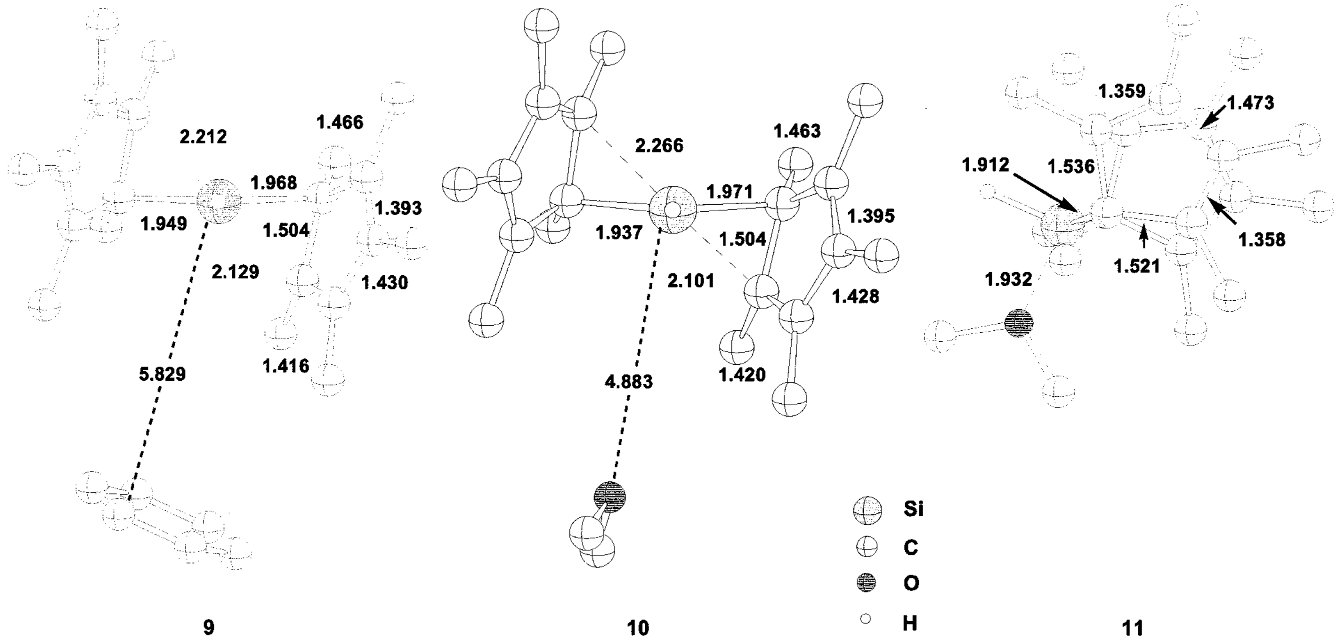

Figure 7. Calculated structures of solvate complexes of $(C_5Me_5)_2Si^+H$ with benzene (**9**) and Me_2O (**10**) and of the oxonium-type complex **11**, at the B3LYP/6-31G(d) level. Bond lengths are given in Å, and all hydrogen atoms except the hydrogen atom attached to silicon are omitted for clarity.

intermolecular interaction with the benzene molecule the favorable intramolecular stabilization of the silyl cation in **5** is widely repressed. As a consequence, the arenium ion **5** is *less stable* than isolated benzene and **3c** by 4.4 kcal mol^{-1} (see Figure 6a); therefore, **5** is metastable toward dissociation into **3c** and benzene. These results suggest that **3** forms in benzene only the weakly bonded associate **6**, in which the identity of **3** is largely preserved.

The situation is different, however, when more nucleophilic solvents, as for example dimethyl ether (which serves as a model for alkyl ether solvents in general), are considered. The oxonium ion **7** (see Figures 5 and 6b) is significantly more stable (by 5.8 kcal mol^{-1}) than the associate **8**, in which the silyl cation and the ether molecule are well separated by 3.945 Å. The calculated A_E for **3c** forming **7** is substantial (−15.0 kcal mol^{-1}) and indicates that bis(cyclopentadienyl)silyl cation **3** would not exist as a free ion in coordinating solvents such as ethers.

A benzenium ion formed from **2** and benzene, similar to **5**, is not a stationary point on the PES but collapses to the more stable solvate **9**. A_E for the experimentally investigated permethylated silyl cation **2** and benzene, calculated for **9**, is even smaller than predicted for **6** (−3.2 kcal mol^{-1}; see Figures 6c and 7). A weakly bonded associate such as **9** is not stable at ambient temperatures, and therefore, **2** is best described as a solvent-free silyl cation. Even in more nucleophilic ether solvents the formation of oxonium ions, i.e., **11**, is not to be expected (see Figures 6d and 7).[38] Instead, the solvate between **2** and dimethyl ether, **10**, is more stable than **11** by 5.4 kcal mol^{-1}. The small calculated A_E for **10** (−6.4 kcal mol^{-1}) implies that **2** is at ambient temperatures also in solvents as strongly nucleophilic as ethers

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(38) This value must be regarded as a lower boundary, since the dispersion energy term of the intermolecular forces is not covered by hybrid density functionals as the B3LYP functional applied here.[39] The dispersion energy term is, however, approximately one order of magnitude smaller than the ion−dipole interaction energy dominant here,[40] and its absolute value is usually less than 2 kcal mol^{-1}; i.e., for the benzene/CO complex, which is formed nearly exclusively due to dispersion forces, A_E = −1.75 kcal mol^{-1} was measured.[41] MP2 calculations account for the dispersion forces; however, they overestimate the A_E of ion−dipole complexes.[42] A test calculation for complex **6** at MP2/6-31+G(d,p) corrected for basis set superposition error predicts consequently the higher A_E = −8.4 kcal mol^{-1}. We are indebted to one of the reviewers for drawing our attention to this point.

Table 3. Calculated NMR Chemical Shifts for Cations 2 and Related Compounds (GIAO/B3LYP/6-311G(2d,p)//B3LYP/6-31G(d),[a,b] Experimental Values for 2 $[C_{12}H_{11}O_4]^-$ in Parentheses)

	$\delta(^{29}Si)$	$\Sigma/10\ (\delta(^{13}C)_{cyc})^c$	$\Sigma/10\ (\delta(^{13}C)_{Me})^d$	cor $\Sigma/10\ (\delta(^{13}C)_{cyc})^{c,f}$	cor $\Sigma/10\ (\delta(^{13}C)_{Me})^{d,f}$
2c	−41.9 −37.5[e]	137.3	13.1	131.4	8.8
2e	−66.6 −62.1[e]	137.7	13.3	131.8	9.0
2f	−15.6 −11.6[e]	138.5	13.0	132.6	8.7
9	−44.4	138.4	13.0	132.4	9.5
10	−37.5	138.3	12.9	132.3	9.4
11	98.5	131.1	12.9	125.3	9.4
2 $[C_{12}H_{11}O_4]^-$	(−12.1)[g]	(120.4)[g]	(10.8)[g]	(120.4)[g]	(10.8)[g]

[a] For the assignment see Figure 2. [b] Calculated values for TMS: σ(Si) 328.5, σ(C) 182.8. [c] Average $\delta(^{13}C)$ of all ring carbons. [d] Average $\delta(^{13}C)$ of all methyl carbons. [e] At GIAO/B3LYP/6-311+G (2df,p)(Si), 6-31G(d)(C, H, O)//B3LYP/6-31G(d); TMS $\sigma(Si) = 332.1$. [f] Calculated using the empirical correlation between calculated $\delta(^{13}C)_{calc}$ and the measured $\delta(^{13}C)_{exptl}$; $\delta(^{13}C)_{calcd} = 4.142 + 1.014[\delta(^{13}C)_{exptl}]$, derived for a set of 16 standard compounds using the B3LYP/GIAO/6-311G(2d,p)//B3LYP/6-31G(d) level of theory (for details see the Supporting Information). [g] In benzene-d_6.[14]

best regarded as a free ion. This is in perfect agreement with the experimentally found absence of any solvent-induced shift of the ^{29}Si NMR resonance when changing the solvent from aromatic hydrocarbons to THF.[14] The reversed relative stabilities of the oxonium ion/ether solvate pairs **7**/**8** and **11**/**10** reveal the decisive role which the methyl substituents play for the stability of **2** toward nucleophiles. Two effects are operative: (i) the +I effect of the methyl groups increases the donating ability of the cyclopentadienyl substituent, thus making intermolecular interactions with solvent molecules relatively less favored, and (ii) the steric requirements of the bulky pentamethylcyclopentadienyl substituent severely hamper the approach of nucleophiles.

(e) Chemical Shift Calculations. Calculations of NMR chemical shifts have been extensively applied in silyl cation chemistry. Optimized geometries obtained from quantum-mechanical computations in combination with accurate NMR chemical shift calculations have been used to differentiate between free silylium ions and complexes between the silyl cation and solvent molecules in which the silicon adopts a coordination number >3.[8,13e−k,43] Quantum-mechanical calculations of NMR chemical shifts could finally verify the characterization and identification of the first solvent-free silylium ion, Mes_3Si^+.[2b,d] NMR chemical shift calculations predict for silylium ions, R_3Si^+, a strongly low field shifted ^{29}Si NMR signal, with a chemical shift range from ca. 1000 ppm for tris(silyl)-substituted silylium ions[13k] to ca. 300−400 ppm for trialkylsilylium ions[13e−l] and 200−250 ppm for triarylsilylium ions.[2b] These theoretical predictions are in agreement with available experimental data; i.e., the silicon in Mes_3Si^+ resonates at 225.5 ppm.[2a] Intramolecular electron donation to the electron-deficient silicon by π-donor groups leads to a pronounced shielding of the silicon atom: silanorbornyl cations[6a,44] are characterized by ^{29}Si NMR chemical shifts of ca. 80 ppm, and for the elusive 7-silanorbornadienyl cation a very high field shifted silicon resonance at −147 ppm is predicted.[8,45] In agreement with that qualitative argument, NMR chemical shift calculations for the three low-energy isomers of decamethyl cyclopentadienyl silyl cation **2**, summarized in Table 3, predict for all three isomers **2c**,**e**,**f** an unusually shielded silicon, reminiscent of the particular bonding situation in these cations (see Table 3). While the ^{29}Si NMR chemical shift for the isomers **2c** and **2e** are predicted to be too shielded by 30 and 54 ppm, respectively, the good agreement between the calculated ^{29}Si NMR chemical shift for the η^2:η^3 isomer **2f** ($\delta(^{29}Si)$ −15.6) and the experimentally determined ^{29}Si NMR chemical shift of −12.1 ppm for **2** suggests that this isomer prevails in solution and is actually observed in the experiment, while the isomers **2c** and **2e** are short-lived intermediates or transition states for fast haptotropic shifts. This is also in agreement with the small energetic preference of **2f** over the C_2-symmetric isomer **2c** at the highest level of our calculations.

The small ^{29}Si NMR chemical shift differences calculated for the solvates **9** and **10** and the isolated silyl cation **2c** (see Table 3) confirm that the interaction between the cation and solvent are very small.[46] In addition, the extremely low field shifted ^{29}Si NMR resonance predicted for **11** ($\delta(^{29}Si)$ 98.5) definitely rule out the possibility that an oxonium ion such as **11** is formed from the silyl cation **2** in solvents such as THF.

The calculated average ^{13}C NMR chemical shifts for all three isomers **2c**,**e**,**f** are nearly identical ($\delta(^{13}C)_{av}$ 137.3−138.5 and 13.0−13.3; see Table 3). Interestingly, the ring carbon atoms are calculated by our method to be too deshielded by 16.9−18.1 ppm compared to the experiment. This unusually large deviation might be the result of (i) deficiencies of the applied method or (ii) systematic errors (as for example: (gas-phase calculation) − (measurement in the solution)). The use of an empirical correction, which is derived from a linear regression between experimental and calculated ^{13}C

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(46) The most stable isomer at B3LYP/6-31G(d) is **2c**, although at the higher B3LYP/6-311G(2d,p) level, **2f** is favored. Therefore, the free geometry optimization of the solvates **9** and **10** results in silyl cation structures which closely resemble **2c**. Consequently, the calculated chemical shifts of **9** and **10** have to be compared with those predicted for **2c**.

NMR chemical shifts for a set of 16 closely related compounds (for details, see the Supporting Information) accounts for some of these deficits and gives improved ^{13}C NMR chemical shifts for the ring carbon atoms, which are, however, still 11−12.4 ppm too deshielded.

Conclusion

Our computational study reveals that protonated decamethylsilicocene **2**[14] is a highly fluxional molecule which undergoes at temperatures as low as −80 °C a series of effectively barrierless haptotropic shifts leading to a circumambulatory migration of the SiH group about the cyclopentadienyl ring. ^{29}Si NMR chemical shift calculations suggest that the experimentally observed cation adopts the η^3:η^2-bonded structure **2f**, a bonding situation which is also found for the isoelectronic cation η^2:η^3-(C_5Me_5)As^+.[47] The topologically closely related isomers **2c** and **2e** are very near in energy ($\Delta E = 0.04$ and 1.4 kcal mol^{-1}, respectively). Therefore, all ring carbon atoms and all methyl groups of the pentamethylcyclopentadienyl ligands equilibrate even at very low temperatures. The positive charge in the hydrogen-substituted compound **3** (and similarly in **2**) is largely dispersed over the cyclopentadienyl substituents by interaction of the π orbitals of the C═C bonds with the formal empty 3p(Si), resulting in some carbocationic character for **3**. The same unique intramolecular stabilization of the silyl cation **2** by the cyclopentadienyl substituents and the additional steric protection of **2** by the methyl substituents results in very low association energies between the cation and solvent molecules;[38] therefore, **2** is even in solvents as nucleophilic as THF best regarded as a free silyl cation.

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Supporting Information Available: A table of total energies (hartrees) for all calculated compounds and a table and plot of calculated vs experimental ^{13}C NMR chemical shifts for a set of 16 compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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