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The $C_5SiMe_7^+$ cation: pyramidal, bicyclic, or cyclohexadienyl?†

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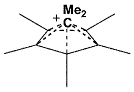
The monosila analogue of the $C_6Me_7^+$ cation can be accessed by hydride abstraction from (pentamethylcyclopentadienyl)dimethylsilane, Cp^*SiMe_2H. Treatment of this material with triphenylmethylium tetrakis(pentafluorophenyl)borate in dichloromethane at −50 °C produced a single cationic species stable for a day or longer. The presence of a single resonance for the ring methyls and a single resonance for the silyl methyls in both the ^1H and the ^{13}C spectra indicated either a static structure with fivefold symmetry or a dynamic structure in which the dimethylsilyl group equilibrates rapidly among positions. Density function theory calculations found a minimum whose structure had the unsymmetrical silabicyclo[3.1.0]hexenyl structure. Calculated ^1H, ^{13}C, and ^{29}Si chemical shifts for this structure were in good agreement with the observed values for this structure. Another calculated minimum was the silacyclohexadienyl structure, but its calculated chemical shifts were very different from those observed. We conclude that the cation has the bicyclic structure but rapidly interconverts the ring positions to produce the very simple NMR spectra.

Introduction

The $C_6Me_7^+$ energy surface comprises many interesting cations, including the pyramidal or nido cation **1**, the bicyclic structure **2**, and the cyclohexadienyl structure **3**.



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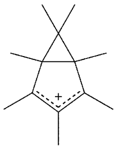

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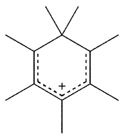
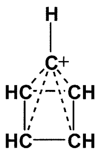


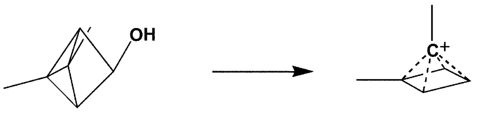
3

In 1958 Doering *et al.*[1] prepared **3**, then called the heptamethylbenzenonium ion and later the heptamethylbenzenium ion. Childs and Winstein[2] prepared the bicyclic cation **2** in 1968. Although the pyramidal cation **1** is unknown, similar materials have been prepared. In 1972, Stohrer and Hoffmann[3] suggested that the global energy minimum of the $C_5H_5^+$ energy surface is the pyramidal (C_{4v}) structure **4**, in which one CH entity hovers over the center of the square formed by the other four CH entities. The structure contains a hypervalent carbon at the apex and is dynamic, in that the CH entities can interchange their roles *via* other structures on the $(CH)_5^+$ surface. Masamune *et al.*[4] studied the dimethyl version of **4** both solvolytically and under stable ion conditions of magic acid. Their evidence was consistent either with the C_{4v}-like form **5** in eqn. 1, or with slightly less symmetrical equilibrating forms such as **6a**–**c** in eqn. 2.

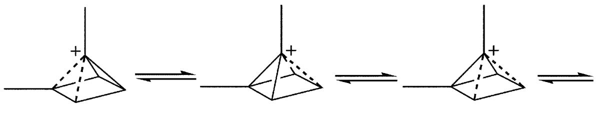


4

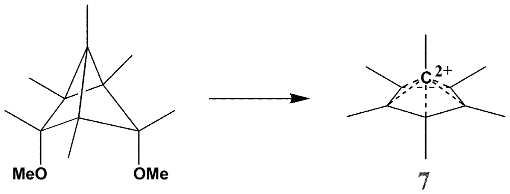
Hogeveen and co-workers[5] examined a related doubly charged system in which the apical group hovers over a pentagon (the $C_6Me_6^{2+}$ energy surface). They generated the hexamethyl derivative under stable ion, magic acid conditions according to eqn. 3 and discussed the results in terms of either the C_{5v} form **7** or equilibrating trihapto ions such as **8a**–**c** in eqn. 4. The doubly charged hexamethyl structure **7** should be more stable than the singly charged heptamethyl structure **1** because of pyramidal aromaticity.[4,5] Like Masamune, they favored the symmetrical form but concluded that the rapidly equilibrating forms of lower symmetry in eqn. 4 also were possible.



5 (1)



6a **6b** **6c** (2)



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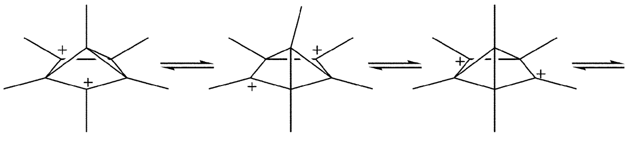

8a **8b** **8c** (4)

We have examined the monosila analogue of the $C_6Me_7^+$ cation, that is, the $C_5SiMe_7^+$ cation in which silicon carries two methyl groups. Silicon more readily accepts hypervalency, as in **1** and **5**, and its higher electropositivity should stabilize positive charge. Consequently, we have sought synthetic routes onto

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† Electronic supplementary information (ESI) available: ^1H, ^{13}C and ^{29}Si NMR spectra of $C_5SiMe_7^+$. See http://www.rsc.org/suppdata/ob/b3/b302921m/

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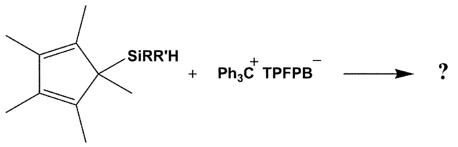
the $C_5SiMe_7^+$ surface. We report herein experimental and calculational results. The hypervalent silyl cation $(Me_5C_5)_2SiH^+$ (protonated decamethylsilicocene) superficially bears little resemblance to these cations, as its ^{29}Si shift is shielded (δ −12.1) rather than deshielded.[6] Recent calculations,[7] however, have indicated that it is relevant to the current study because the system is dynamic.

Results and discussion

Synthesis

Preparation of systems analogous to the polycyclic starting materials in eqns. 1 and 3, but with a single silicon atom replacing a single carbon, would be daunting. Consequently, we developed an alternative, more straightforward entry into the problem. We view the methyl groups as providing overall stabilization of positive charge by polarization and hyperconjugation. Our strategy to prepare the monosila analogue of **1**–**3** ($C_5SiMe_7^+$) involved using the double bonds of a cyclopentadiene ring **9** to trap internally a silylium ion generated on the periphery of the ring by removal of hydride, as illustrated in eqn. 5.



(5)

9

The illustrated entry system offers flexibility through variation of the substituents R and R′ on silicon. When R′ = H, treatment with triphenylmethylium (trityl or tritylium) can remove two hydride ions to generate the dication (that is, the $C_5SiMe_6^{2+}$ system when R = Me). When R and R′ are both alkyl or aryl, treatment with trityl can remove one hydride ion to generate the monocation. The $C_5SiMe_7^+$ cation is obtained when both R and R′ are methyl. The approach thus has the flexibility of potentially providing either mono- or dication. Moreover, a variety of systems are potentially accessible through variation of R and R′.

Even for the permethyl systems, there are numerous possible structures for both $C_5SiMe_6^{2+}$ and $C_5SiMe_7^+$. Many of these are displayed in Fig. 1 for the monocation. As for the carbon systems (**1** and **7**), the monosila pyramidal analogues are pyramidally antiaromatic for the monocation (**F** in Fig. 1) and pyramidally aromatic for the dication (**I** in Fig. 1).[4,5] Whereas dotted lines are used in the carbon systems (**1** and **7**), silicon is more easily hypervalent and permits use of solid lines (**F** and **I**).

The species generated initially by eqn. 5 would be a silylium cation of structure $Cp^*SiRR'^+$ for the monocation (**A** in Fig. 1 for R,R′ = Me) or Cp^*SiR^{2+} for the dication ("Cp*" represents the pentamethylcyclopentadienyl structure). The hydride abstraction method of eqn. 5 has been used widely for the attempted generation of silyl cations.[8] We amplified the method by the use of aromatic solvents[9] and anions of low nucleophilicity.[10] In the present case the anion is tetrakis(pentafluorophenyl)borate (TPFPB), which we utilized in the preparation of the first stable, tricoordinate silylium ion.[11] Such cations are extremely electron deficient and tend to react with even weak nucleophiles. The double bonds in the cyclopentadienyl ring of eqn. 5 offer the most convenient nucleophiles in the present case. Intramolecular trapping of the silylium ion by the double bonds will generate a cation with some degree of delocalization. Its possible structures are given in Fig. 1 and are discussed in the next section. The strategy of trapping a silylium ion by one double bond was used by Steinberger *et al.* to generate a silanorbornylium cation.[12]

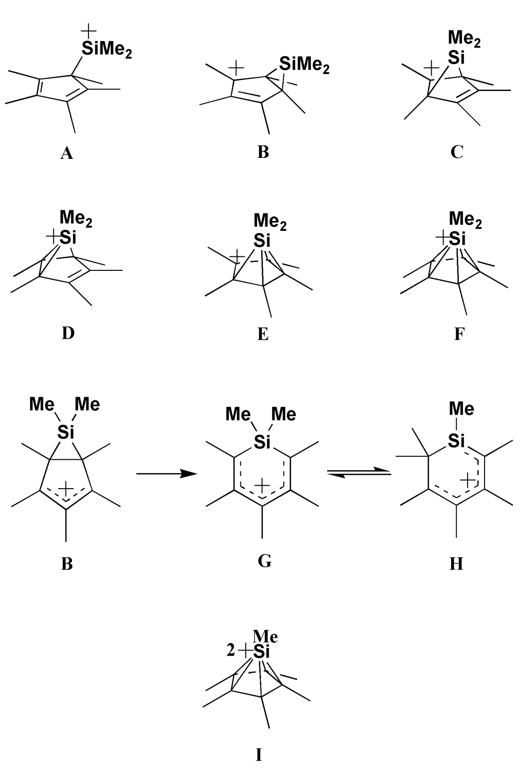
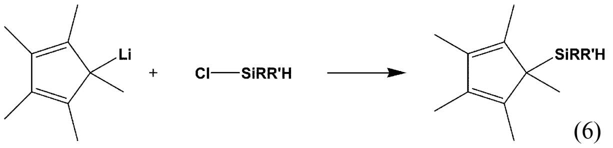


Fig. 1 Structures considered for the cation obtained by hydride abstraction from (pentamethylcyclopentadienyl)dimethylsilane.

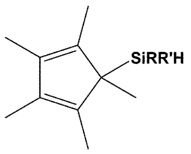
Silyl-substituted cyclopentadiene rings are readily prepared by the nucleophilic displacement of cyclopentadienyl anions on halo-substituted silanes (eqn. 6).



(6)

The illustrated example employs commercially available pentamethylcyclopentadienyl anion and a variety of chlorosilanes to form the products **10**. In addition, we prepared a single unmethylated example, cyclopentadienyldimethylsilane ($CpSiMe_2H$, **11**).

10a, R,R' = Me
10b, R,R' = Ph
10c, R = Me, R' = Ph
10d, R = Me, R' = Cl
10e, R = Me, R' = H



The neutral compounds **10** proved to have dynamic properties. We shall illustrate the fluxional properties with the observations from (pentamethylcyclopentadienyl)dimethylsilane (**10a**). Above 80 °C, the ^1H spectrum of **10a** contains only two methyl resonances (Fig. 2; note, these spectra are of the neutral starting material, **10a**, not the cation). The equivalent Me_2Si methyls resonate at δ −0.19, and all the ring methyls generate a single, slightly broadened peak at δ 1.67. The dynamic process of interconversion of the ring methyls has been characterized as a series of 1,5-sigmatropic shifts,[13] whereby the silyl substituent moves around the ring, eventually bonding to every ring carbon in turn and rendering all ring methyls equivalent. The methyls on silicon also interconvert through alternating between the *exo* and *endo* positions with respect to the five-membered ring during the rearrangements.

As the temperature is lowered, the ring-methyl resonance broadens, passes through coalescence at 40 °C, and reemerges

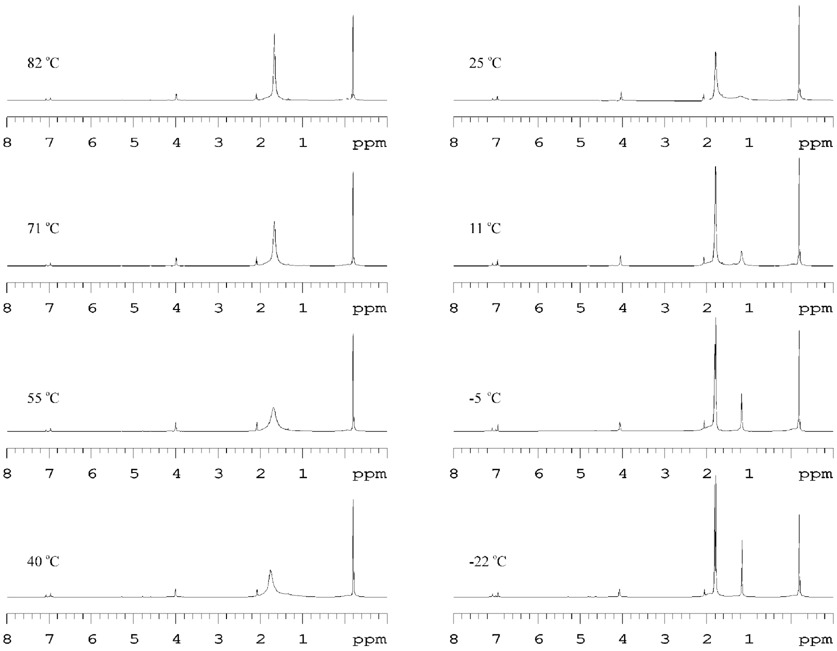


Fig. 2 The 500 ^{1}H MHz NMR spectrum of the neutral precursor (pentamethylcyclopentadienyl)dimethylsilane (**10a**) as a function of temperature.

as three peaks in the ratio 2 : 2 : 1, as expected for the static structure **10a**. The dimethylsilyl resonance remains a sharp singlet. The calculated $\Delta G^{\ddagger}$ is 14.3 kcal mol^{-1} at the coalescence temperature of 40 °C. All expected peaks are observable and sharp in the ^{13}C spectrum below -40 °C. Broadening begins above this temperature, so that at room temperature several of the peaks are invisible. The ^{13}C spectrum was not followed above room temperature for observation of full coalescence. Thus silylcyclopentadiene **10a** is a typically dynamic system, in which the silyl group moves around the ring *via* sigmatropic shifts. Observation of the NMR spectra at low temperatures provides data characteristic of the slow exchange structure.

Cation generation

Cations were generated in the same way as in many past studies that attempted to produce silylium ions, by abstraction of hydride from the silane by an electrophile according to eqn. 7 for **10a**.[8] The method takes advantage of the fact that the formed

$$\mathrm{Cp^*SiMe_2{-}H + Ph_3C^+\ TPFPB^- \longrightarrow Ph_3C{-}H + [Cp^*SiMe_2]^+} \quad (7)$$

C–H bond is stronger than the broken Si–H bond. The silanes in this study were allowed to react with trityl TPFPB,[14] prepared by the new method of Jordan *et al.*[15] Initial experiments in aromatic solvents at room temperature were unsuccessful, as the products decomposed on generation. Use of dichloromethane at -50 °C permitted formation of the product of hydride abstraction from Cp*SiMe$_2$H (eqn. 7) which is stable for a day or more. The ^{29}Si resonance at δ 107.8 occurs at a remarkably high frequency, indicative of considerable positive charge on silicon (the resonance for the starting material Cp*SiMe$_2$H, **10a**, is at δ -3.3). These numbers are comparable to those observed by us[10,16] for solvated silyl cations such as Et$_3$Si$^+$(C$_6$D$_6$) TPFPB$^-$ and by Reed[17] for anion-complexed silyl cations. Reed and we characterized these materials as possessing 30–50% silylium ion character, judging from the ^{29}Si chemical shift and the geometry around silicon in the X-ray structures.[16,17] The resonance is at a higher frequency than that of the silanorbornylium ion[12] (δ 80) but at a much lower frequency than what is expected for a fully tricoordinate silylium ion (**A** in Fig. 1). Thus it appears that the initially generated silylium ion was indeed trapped by the double bonds of the Cp* ring. Eqn. 7 implies no particular structure for this cation.

In dichloromethane only a single layer is formed in this reaction, whereas in aromatic solvents there are always two layers.[16] The product triphenylmethane migrates to the upper layer with aromatic solvents and can be syringed off to leave the pure cation in the lower layer. In dichloromethane, however, the two products remain together in the single layer along with some unreacted trityl TPFPB. The ^{1}H spectrum contains only two peaks, in addition to the peaks from triphenylmethane and excess trityl. The ring methyls generate a singlet at δ 2.11, and the dimethylsilyl group generates a singlet at δ 0.62. Similarly, the ^{13}C spectrum at -70 °C contains two singlets, other than resonances from triphenylmethane, excess trityl cation, the anion, and the solvent. The ring methyls resonate at δ 11.8 and the dimethylsilyl group at δ -3.3. The quaternary ring carbons give no visible peak, as discussed in the section Theoretical Calculations.

The product cation, according to both ^{1}H and ^{13}C spectra, either has fivefold symmetry or allows interconversion of the various methyl groups through a dynamic process, even at -70 °C. There are many structures that must be considered as possible candidates for the observed cation, as illustrated in Fig. 1. Structure **A** is the free silyl cation, depicted as a monohapto σ complex. Its expected ^{29}Si resonance should occur at extremely high field, probably greater than δ 300.[15] Given the observed value of δ 107.8, this structure may be eliminated. The alternative monohapto π complex differs from **A** only in slight movement of the dimethylsilyl group to a point directly over the ring carbon atom. It also should have an extremely high field ^{29}Si resonance and hence may be eliminated.

Structures **B**–**F** in Fig. 1 indicate possible σ complexes in which one or both double bonds are involved in bonding with silicon. Structures **B** (analogous to **2**) and **C** respectively are 1,2- and 1,3-dihapto variants; structure **D** is 1,2,3-trihapto; structure **E** is tetrahapto; and structure **F** is pentahapto. The π complex versions are diminishingly different. Structure **F** represents the symmetrical pyramidal cation (analogous to **1**). The NMR spectra could be explained either by structure **F** alone or by any of the other structures, in which sigmatropic shifts move the dimethylsilyl group rapidly around the ring. The equivalence of the dimethylsilyl methyls is equally well explained by either scenario. They are equivalent in the pyramidal cation.

Although nonequivalent in the various structures **B–E**, the methyls interconvert by rotation about the C–Si bond during the sigmatropic rearrangements.

The silabenzenium analogue of **3** is given by structure **G**, accessible from **B** by a simple ring-opening reaction. Childs and Winstein[2] found that the ring-opening process was rapid for the all-carbon case **2**. Methyl equilibration moreover is rapid in the carbon case.[2] For the sila analogue **G**, however, methyl shifts would lead to carbon–silicon double bonds, as in **H** (Fig. 1). Since silicon engages very weakly in double bonding, all structures like **H** should be unstable, thereby inhibiting methyl shifts in the silabenzenium ion **G**. Given the observed rapid equilibration of methyl groups in the product from eqn. 7, structure **G** with different C-methyl groupings is not a likely representation.

From the NMR spectra we come to the same conclusion that Hogeveen and Masamune did with their carbocations,[4,5] that the data are consistent with a symmetrical pyramidal structure **F** or with rapidly equilibrating unsymmetrical structures (**B–E**). We can provide a distinction between these two possibilities, however, by application of theory (next section). Theory also provides further information about the benzenium form **G**.

We carried out the reaction of eqn. 7 also with Cp*SiPh$_2$H, Cp*SiMePhH and CpMe$_2$H. In no case were stable cations formed, as no ^{29}Si resonances were observed at higher frequency than δ 35. Thus a stable cation is not observed when phenyl groups are present or when the ring lacks the five methyl groups. Treatment of Cp*SiMeH$_2$ with two moles of trityl TPFPB in an attempt to generate the silicon analogue of Hogeveen's carbodication **7** also was unsuccessful in generating a stable dication such as **I** in Fig. 1. All these attempts were made in both aromatic and chloro solvents and at both room temperature and −50 °C. The heptamethyl monocation thus provided a unique result.

Theoretical calculations

To elucidate the structure of the cation produced by hydride abstraction from (pentamethylcyclopentadienyl)dimethylsilane (**10a**), we adopted a two step calculational approach. First we determined the global minimum for [Cp*SiMe$_2$]$^+$ by density function theory at the B3LYP level[18,19] with the 6-31G(d,p) basis set. Then we calculated the ^{29}Si, ^{13}C and ^{1}H chemical shifts at the DFT/B3LYP/6-31G(d,p) level using GIAO and compared them with the observed values. This comparison permits conclusions to be drawn about the structure of the cation in solution.

We found only one polycyclic minimum, no matter what starting geometry from Fig. 1 was used. The monocyclic silyl cation **A** also was not a minimum. Wherever the silicon atom was placed originally, the resulting minimum, when unconstrained by symmetry, was the bicyclic structure **B**. The global minimum dihapto structure **B** (Fig. 3, Table 1) contains an allyl cation in the five-membered ring, which is fused to a silacyclopropane ring to form a silabicyclo[3.1.0]hexenyl structure analogous to **2**.

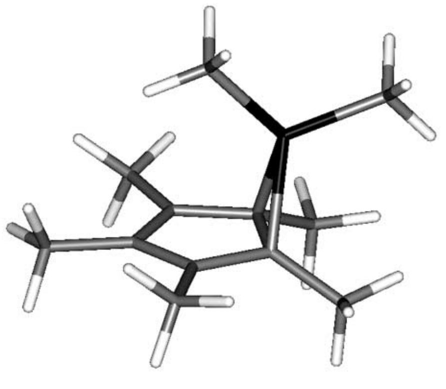
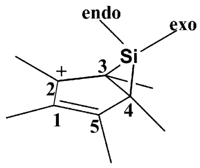


Fig. 3 The calculated global minimum for the cation, corresponding to structure B in Fig. 1.

Table 1 Calculated bond lengths (Å) and bond angles (deg)



C1–C2	1.41	C2–C1–C5	108.7
C2–C3	1.45	C1–C2–C3	110.3
C3–C4	1.52	C2–C3–C4	105.4
C4–C5	1.45	Si–C3–C4	67.0
C5–C1	1.41	CX–Si–CN[a]	114.2
C3–Si	1.97	CX–Si–C3[a]	117.6
C4–Si	1.97	CN–Si–C3[a]	122.6

[a] X represents the *exo* position and N the *endo* position.

Table 2 Atomic charges from Mulliken population analysis

Structure **B**		Structure **G**	
Si	0.75	Si	0.65
C(Si methyls)	−0.55[a]	C(Si methyls)	−0.53
H(Si methyls)	0.17	H(Si methyls)	0.15
C3, C4[b]	−0.20	C(*ortho*)	−0.08
C2, C5[c]	0.15	C(*meta*)	0.08
C1[d]	0.04	C(*para*)	0.11
C(ring methyls)	−0.35	C(ring methyls)	−0.39
H(ring methyls)	0.15	H(ring methyls)	0.16

[a] C(*exo*) is −0.55, C(*endo*) is −0.54. [b] Carbons common to both rings. [c] Allyl carbons bearing charge. [d] Nodal allyl carbon. [e] Me6 is −0.39, Me7 −0.39, Me8 −0.32, Me9 −0.32, Me10, −0.39.

The angle between the planar five-membered ring and the three-membered ring containing Si is 106°. This geometry is indicative of σ rather than π bonding between Si and the five-membered ring. In a π complex, Si should have resided above the periphery of the carbon ring, with an inter-ring angle of about 90°. The carbon five-membered ring is not C_5 symmetrical. The C–C distance for the bond common to both rings is 1.52 Å. The C–C distances are 1.45 Å adjacent to the three-membered ring and 1.41 Å for the more distant bonds (in the allyl group). The ring-methyl C–C distances cluster closely in the range 1.49–1.52 Å. The C–Si bond within the three-membered ring is 1.97 Å, and the Si–CH$_3$ distance is 1.87 Å.

Atomic charges for **B** were obtained from Mulliken population analysis (Table 2). Silicon carries the largest degree of positive charge, consonant with its high frequency chemical shift, followed by the allylic carbons (C2, C5) and the hydrogens on the methyls attached to these three atoms.

The chemical shifts for **B** were calculated without scaling factors and are reported relative to the calculated value for tetramethylsilane placed at δ 0.0 for all three nuclei. The calculated and observed values are compared in Table 3. Because the ring methyl groups exhibited only a single resonance in the ^{13}C NMR spectrum, due to rapid methyl shifts, we have averaged the calculated chemical shifts in order to make apt comparisons. Agreement is quite good between the observed shifts and those calculated for structure **B**. The value calculated for ^{29}Si is 19 ppm higher than the observed frequency of δ 107.8. The ^{13}C chemical shifts agree on average within 1.6 ppm, and the ^{1}H shifts within 0.11 ppm.

Table 3 also contains the chemical shifts calculated for the silabenzenium ion **G**. The calculated ^{29}Si chemical shift at δ −6.6 deviates from the observed position by 100 ppm. The ring methyl ^{13}C chemical shift at δ 24.3 differs from the observed position by 12 ppm, and the methyls on silicon by 2 ppm. The differences in chemical shifts between **B** and **G** arise largely because of lower positive charge on silicon and higher

Table 3 Observed chemical shifts for the cation produced in eqn. 5 and calculated chemical shifts for structure B (Fig. 1)[a]

Nucleus	δ (observed)	δ (calculated for **B**)	δ (calculated for **G**)
^{29}Si	107.8	127.1	−6.6
^{13}C (ring methyls)	11.8	13.9	24.3
^{13}C (Si methyls)	−3.3	−2.3	−5.8
^{13}C (ring)	—	135.6	184.6
^{1}H (ring methyls)	2.11	2.25	2.49
^{1}H (Si methyls)	0.62	0.70	0.66

[a] Chemical shifts are in ppm with tetramethylsilane at 0.00 for all three nuclei.

negative charge on the ring methyls for **G** (Table 2). The ^{1}H chemical shifts were not diagnostic. The calculated ^{29}Si and ^{13}C chemical shifts are in good agreement with the bicyclic form **B** and not with the higher energy benzenium form **G**.

The results of Müller *et al.*[7] on protonated decamethylsilicocene are somewhat similar to ours, in that low energy dihapto forms were found calculationally. Direct comparisons, however, are not possible, not only because the silicocene system is hypervalent but also because its two rings clearly affect the bonding of each other, whereas our system has only one ring.

Experimentally, we were not able to freeze out movement of the ring methyls, whose chemical shifts would have been a useful diagnostic, as also observed for protonated decamethylsilicocene.[6] We examined the ^{13}C spectrum as low as −70 °C (the limit permitted by the solvent dichloromethane) without observing decoalescence.

The calculated average ^{13}C chemical shift for the ring carbons of **B** is δ 135.6. This value falls in the middle of the range for the TPFPB anion, the product triphenylmethane, and excess trityl. Long-term signal averaging at 500 MHz and −70 °C failed to suggest a hint of the peak. In contrast, the ring carbons of the neutral starting material appeared quickly even at 400 MHz. The neutral, however, does not contain the competing resonances in this region from the anion, excess trityl, and the coproduct triphenylmethane. The ring carbon resonance may not have been observed not only because of the expected breadth and low intensity of quaternary carbon resonances but also because of overlap with these resonances. In contrast, the calculated position of δ 184.6 for **G** should have been clear of spectral overlap. Dynamic effects may constitute a third factor inhibiting observation of the ring carbon resonances. The calculated individual ring chemical shifts for **B** range from δ 83.0 (the carbons common with the three-membered ring) to δ 142.9 (the carbons in the allyl group bearing positive charge). If dynamic averaging is not entirely complete at the temperature of observation (−70 °C), considerable broadening is possible.

The dimethylsilyl carbon resonance observed at δ −3.3 was surprisingly weak. In the calculated, static structure, one methyl is located over the five-membered ring and the other is outside it. Dynamic exchange interconverts these *endo* and *exo* positions. The calculated individual positions are δ −8.1 and 3.6, as the methyl over the ring experiences shielding by the diamagnetically anisotropic allyl group. Spectral averaging of these carbons might contribute to the weakness of the observed peak. The ^{1}H resonances of both types of methyls (ring and silyl), however, were sharp, apparently without exchange effects. As their slow exchange chemical shift differences are expected to be smaller, the dynamic effects may not be visible in the ^{1}H spectrum at the temperature of observation. Childs and Winstein observed slow exchange between geminal dimethyl groups in **2**,[2] in accord with orbital symmetry. Either exchange is much faster in the silicon analogue, or the methyl shifts are not concerted reactions.

Conclusions

A stable cation is formed on treatment of (pentamethylcyclopentadienyl)dimethylsilane (**10a**, Cp*Me$_2$SiH) with one mole of triphenylmethylium tetrakis(pentafluorophenyl)borate (TPFPB) through abstraction of hydride in dichloromethane at −50 °C. A molar amount of triphenylmethane is the coproduct. The cation exhibits ^{1}H and ^{13}C spectra containing only a single peak for the ring methyls and a single peak for the methyls on silicon. Such an observation is consistent either with a single structure **F** (Fig. 1) with fivefold symmetry or with various structures **A–E** that undergo rapid sigmatropic shifts to interconvert the positions on the NMR time scale. The ^{29}Si chemical shift of δ 107.8 indicates considerable positive charge on silicon and a trend towards hypovalency, whereas hypervalency as in **F** should lead to a shift to low frequency. The observed value also is inconsistent with the free silylium ion **A**, which should have a much higher frequency chemical shift.

Calculations indicate that the global minimum is structure **B**, in which silicon is 1,2-bonded (dihapto) to the cyclopentadienyl ring. Structures **A** and **C–F** are not minima. The ^{1}H, ^{13}C, and ^{29}Si chemical shifts calculated for structure **B** are in good agreement with the observed values. The chemical shifts calculated for the silabenzenium ion **G** are in poor agreement with the observed values. Moreover, methyl shifts in **G** are inhibited because they would lead to unstable structures such as **H**, which contain carbon–silicon double bonding. Structure **G** also fails to explain the equivalency of the five ring methyl groups attached to carbon.

We conclude that the cation has structure **B**, in which sigmatropic shifts rapidly interconvert the five ring methyls with each other and the two methyl groups on silicon with each other. These conclusions contrast with the conclusions favored by Hogeveen, Masamune, and their co-workers for the cations shown in eqns. 1 and 3.[4,5] These authors favored the pyramidal structures of eqns. 1 and 3 over the dynamic, localized structures of eqns. 2 and 4. The cations of eqns. 1 and 3, however, are pyramidally aromatic, whereas the pyramidal structure **F** in Fig. 2 is pyramidally antiaromatic. To avoid antiaromaticity, charge is partially localized, to give the allyl structure **B**.

Experimental

Triphenylmethylium tetrakis(pentafluorophenyl)borate[15]

A solution of bromopentafluorobenzene (11.0 mL, 88.2 mmol) in hexane (250 mL) was cooled to −78 °C in a dry ice–acetone bath. Butyllithium (2.5 M in hexanes, 32.0 mL, 80 mmol) was added to the solution dropwise, and the mixture was stirred at −78 °C for 2.5 h. Boron trichloride (1.0 M in hexanes, 16.0 mL, 16.0 mmol) was added to the mixture dropwise at −78 °C, and the resulting viscous suspension was stirred and warmed to room temperature gradually overnight. The volatiles were removed from the mixture under vacuum, and the remaining solid was brought into a glovebox and ground into a fine powder. The powder was suspended in hexane (200 mL), and chlorotriphenylmethane (9.80 g, 35.2 mmol) was added. A reaction occurred immediately, and a yellow powder formed. The mixture was stirred at room temperature overnight and filtered through a glass frit. The collected powder was washed with hexane (3 × 50 mL) and dried under vacuum for 3 h. The yellow solid was taken up in dichloromethane (150 mL) and filtered to remove LiCl. The filtrate was concentrated to *ca.* 15 mL, and pentane (200 mL) was added. Phase separation occurred initially, but, as the mixture was stirred, the oily lower layer gradually solidified. The supernatant was removed by a cannula, and the remaining powder was dried under vacuum to afford triphenylmethylium tetrakis(pentafluorophenyl)borate as a brownish yellow powder: 13.50 g, 91%. It can be further purified by recrystallization from dichloromethane–hexane to yield yellow crystals.

(Pentamethylcyclopentadienyl)dimethylsilane (6a, Cp*SiMe$_2$H)[20]

A 500 mL Schlenk flask was charged with lithium pentamethylcyclopentadienide (5.0 g, 35.2 mmol) in a N$_2$ filled glovebox. Ether (200 mL) was transferred to the flask through a cannula. Chlorodimethylsilane (3.33 g, 35.2 mmol) was then added dropwise *via* a syringe to the suspension at 0 °C. The reaction mixture was stirred at room temperature for 2 h and filtered through a Celite pad to give a completely clear solution. The solvent was removed by rotary evaporation, and the orange residue was distilled under house vacuum to yield a yellow liquid: bp 111–114 °C/20 Torr, 2.90 g, 42.5%; ^{1}H NMR (toluene-d_8, 25 °C) δ −0.19 (d, 6H), 1.20 (br, 3H), 1.80 (s, 12H), 4.04 (m, 1H); ^{13}C NMR (toluene-d_8, 43.7 °C) δ −7.0, 11.2, 11.6, 14.3, 57.4, 134.5, 136.8; ^{29}Si NMR (toluene-d_8, 25 °C) δ −5.6; MS (EI) *m*/*z* 194 (M$^+$, 46), 179 (21), 134 (59), 119 (100), 105 (26), 91 (25), 73 (40), 59 (37); ^{1}H NMR (CD$_2$Cl$_2$, −50 °C) δ −0.26 (d, 6H), 1.13 (s, 3H), 1.77 (s, 12H), 3.77 (m, 1H); ^{13}C NMR (CD$_2$Cl$_2$, −50 °C) δ −7.3, 11.0, 11.4, 14.1, 52.4, 134.2, 136.8; ^{29}Si NMR (CD$_2$Cl$_2$, −50 °C,) δ −3.3. All silanes studied were unstable in the atmosphere and gave faulty elemental analyses. Molecular formulas were confirmed by high resolution mass spectrometry. HRMS: Calcd for C$_{12}$H$_{22}$Si: 194.14908. Found: 194.14975.

(Pentamethylcyclopentadienyl)diphenylsilane (6b)

According to the procedure for preparing Cp*SiMe$_2$H, Cp* SiPh$_2$H was prepared from ClSiPh$_2$H and Cp*Li as a yellow oil: bp 119.5–120.0 °C/0.4 Torr, 2.50 g, 32%; ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ 1.74 (s, 15H), 4.97 (s, 1H), 7.39–7.46 (m, 6H), 7.61 (m, 4H); ^{13}C NMR (CD$_2$Cl$_2$, 25 °C) δ 12.0 (br), 128.0, 130.1, 133.7, 136.1; ^{1}H NMR (CD$_2$Cl$_2$, −50 °C) δ 1.51 (s, 3H), 1.70 (s, 6H), 1.86 (s, 6H), 4.98 (s, 1H), 7.40–7.48 (m, 6H), 7.61 (m, 4H); ^{13}C NMR (CD$_2$Cl$_2$, −50 °C) δ 11.2, 11.9, 14.8, 54.4, 127.7, 129.7, 132.7, 135.6, 135.9, 136.4; ^{29}Si NMR (CD$_2$Cl$_2$, −50 °C) δ −8.2. HRMS: Calcd for C$_{22}$H$_{26}$Si: 318.18038. Found: 318.18131.

(Pentamethylcyclopentadienyl)methylphenylsilane (6c)

According to the procedure for preparing Cp*SiMe$_2$H, Cp*SiMePhH was prepared from ClSiMePhH and Cp*Li as a yellow oil: bp 85.0–88.0 °C/0.4 Torr, 4.90 g, 68%; ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ 7.48–7.14 (m), 5.11 (m), 4.29 (m), 1.57 (s), 0.35 (d), 0.02 (d); ^{13}C NMR (CD$_2$Cl$_2$, 25 °C) δ 137.7, 135.5, 135.1, 134.0, 130.6, 129.8, 128.6, 127.7, 11.9 (br), 0.2, −8.1; ^{1}H NMR (CD$_2$Cl$_2$, −50 °C) δ 7.49–7.14 (m), 5.11 (m), 4.29 (m), 1.83 (s), 1.58 (s), 1.18 (s), 0.35 (d), −0.02 (d); ^{13}C NMR (CD$_2$Cl$_2$, −50 °C) δ 137.3, 136.6, 136.3, 135.5, 135.4, 135.2, 134.6, 134.0, 133.8, 130.6, 129.8, 128.5, 127.6, 14.5, 14.4, 12.2, 12.1, 11.6, 11.5, −0.1, −9.1; ^{29}Si NMR (CD$_2$Cl$_2$, −25 °C) δ −6.9, −12.2; ^{29}Si NMR (CD$_2$Cl$_2$, −50 °C) δ −6.8, −11.9. HRMS: Calcd for C$_{17}$H$_{24}$Si: 256.16473. Found: 256.16468.

(Pentamethylcyclopentadienyl)methylchlorosilane (6d)

According to the procedure for preparing Cp*SiMe$_2$H, Cp*SiMeClH was synthesized from HSiMeCl$_2$ and Cp*Li as a yellow oil: bp 44–46 °C/0.4 Torr, 4.42 g, 58%; ^{1}H NMR (C$_6$D$_6$, 25 °C) δ 0.11 (d, 3H), 1.68 (s, 15H), 4.74 (m, 1H); ^{13}C NMR (C$_6$D$_6$, 25 °C) δ −3.3, 12.4; ^{29}Si NMR (C$_6$D$_6$, 25 °C) δ 13.1.

(Pentamethylcyclopentadienyl)methylsilane (6e, Cp*SiMeH$_2$)

A 250 mL, three-necked flask, equipped with a condenser, a septum, and a stopper, was charged with a magnetic stirring bar and LiAlH$_4$ (6.5 mL, 1 M in diethyl ether, 6.5 mmol). Freshly distilled diethyl ether (50 mL) was transferred to the flask *via* a cannula. The flask was cooled to 0 °C in an ice bath, and (pentamethylcyclopentadienyl)methylchlorosilane (4.0 g, 18.6 mmol) in 10 mL of diethyl ether was added slowly through a syringe. The reaction mixture was stirred at 0 °C for 10 min and then brought to reflux for 3 h. After the flask had cooled, the precipitate was removed by filtration, and the filtrate was concentrated by rotary evaporation. The residual oil was distilled under reduced pressure to afford a pale yellow liquid: bp 97–98 °C/20 Torr, 3.08 g, 92%; ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ −0.38 (t, 3H), 1.81 (s, 15H), 3.61 (q, 2H); ^{1}H NMR (CD$_2$Cl$_2$, −50 °C) δ −0.48 (t, 3H), 1.19 (s, 3H), 1.79 (s, 6H), 1.81 (s, 6H), 3.57 (q, 2H); ^{13}C NMR (CD$_2$Cl$_2$, 25 °C) δ −10.9, 11.5; ^{13}C NMR (CD$_2$Cl$_2$, −50 °C) δ −11.6, 10.9, 11.1, 14.5, 51.2, 134.5, 136.2; ^{29}Si NMR (CD$_2$Cl$_2$, 25 °C) δ −19.3. HRMS: Calcd from C$_{11}$H$_{20}$Si: 180.13343. Found: 180.13277.

Cyclopentadienyldimethylsilane (7)

Compound **7** was prepared by the method of Ciruela *et al.*[21] in 62% yield: ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ 0.08 (d, 6H), 3.50 (br, 1H), 3.80 (m, 1H), 6.66 (br, 4H); ^{13}C NMR (CD$_2$Cl$_2$, −50 °C) δ −4.5, 49.8, 130.5, 133.5; ^{29}Si NMR (CD$_2$Cl$_2$, 25 °C) δ −9.7.

Cation generation from Cp*SiMe$_2$H (6a)

In a N$_2$ filled glovebox, trityl TPFPB (240 mg, 0.26 mmol) was dissolved in dry CD$_2$Cl$_2$ (0.7 mL) in a valved 5 mm NMR tube. The solution was cooled to −78 °C with a dry ice bath, and (pentamethylcyclopentadienyl)dimethylsilane (**6a**, 50 mg, 0.26 mmol) was added. After vigorous shaking of the NMR tube, which was kept at −50 °C by frequent immersion in the cooling bath, NMR spectra were recorded: ^{1}H NMR (CD$_2$Cl$_2$, −50 °C) δ 0.62 (s, 6H), 2.11 (s, 15H); ^{13}C NMR (−50 °C, CD$_2$Cl$_2$) δ 11.8, −3.3; ^{29}Si NMR (CD$_2$Cl$_2$, −50 °C) δ 107.8.

Computational methods

Models of the isolated gas phase molecules were built with the Maestro program. The structures were subjected to unrestricted geometry optimization using the B3LYP DFT hybrid method[18,22] with the 6-31G(d,p) basis set as implanted in the Jaguar program.[23] Mulliken charges were calculated at this level. The ^{13}C, ^{1}H, and ^{29}Si chemical shielding tensors were calculated using GIAO at the DFT/B3LYP/G-31G(d,p) level as implemented in the Gaussian program.[24] This method has been demonstrated to provide accurate chemical shifts of several molecules.[25]

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