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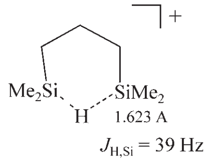
Persistent Silylium Ions Stabilized by Polyagostic Si–H···Si Interactions**

Andrey Y. Khalimon, Zi Hua Lin, R. Simionescu, Sergei F. Vyboishchikov, and Georgii I. Nikonov**

Dedicated to Professor J. Lorberth on the occasion of his 70th birthday

Silylium ions are much more reactive than corresponding carbenium ions owing to the larger size of the silicon atom and their higher electrophilicity.[1,2] In the absence of sufficient steric protection, silylium ions readily interact even with weakly nucleophilic molecules such as the perchlorate anion,[3] halocarbons,[4] alkenes,[5] alkynes,[6] arenes,[7] and even hydrocarbons and noble gases.[8,9] As a result, a genuine tricoordinate ("naked") silylium ion has been prepared only recently.[10,11] More recently, Müller et al. have reported that formation of a 3c–2e bond $(R_3Si\text{-}H\text{-}SiR_3)^+$ can stabilize a cationic silicon center (**1** and **2**) even in the absence of steric protection.[12,13] A similar $R_3B\cdots H\text{-}SiR_3$ interaction (**3**), with a stronger H–Si bond and weaker B···H bonding, was described by Wrackmeyer et al.[14] Herein we report the case of polyagostic Si-H-Si interactions in a series of silylium ions derived from polysilyl-substituted benzenes.



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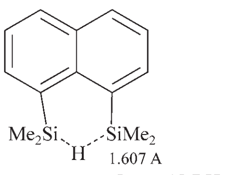

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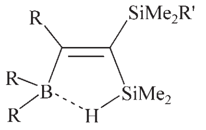

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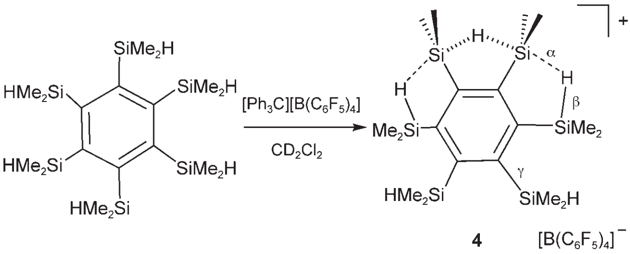
Hydride abstraction[10a] from $C_6(SiHMe_2)_6$ by $[Ph_3C][B(C_6F_5)_4]$ generates the silylium ion **4** quantitatively according to NMR spectra [Eq. (1)]. At −80 °C, the ^1H NMR spectrum of **4** in CD_2Cl_2 exhibits an effective C_{2v} structure with three broad SiH signals at $\delta = 4.64$ (γ-SiH), 4.41 (β-SiH), and 4.26 ppm (α-SiH) with relative intensities of 2:2:1 and three Me signals of equal intensity, at $\delta = 0.88$ (α-SiMe), 0.67 (β-SiMe), and 0.49 ppm (γ-SiMe).[15] The upfield shift of the α-SiH and β-SiH resonances is a characteristic signature of agostic bonding,[16] whereas the downfield shift of the α-SiMe signal reflects the electron deficiency of cationic silylium centers. The ^{29}Si NMR spectrum at −85 °C, selectively decoupled from Me groups, reveals three signals, at $\delta = 24.9$ (d, $J_{H,Si} = 46.3$ Hz), 15.3 (d, $J_{H,Si} = 118.9$ Hz), and −5.3 ppm (d, $J_{H,Si} = 170.7$ Hz)[17], assigned to the Si atoms in the α, β, and γ positions, respectively. The agostically stabilized silylium center gives rise to a downfield ^{29}Si NMR signal ($\delta = 24.9$ ppm) which is close to the value found for the H-bridged cation **2** ($\delta = 54.4$ ppm).[12b] The cation **4** is stable in CD_2Cl_2 and $CDCl_3$ solutions at least for several days.



4

(1)

The H–Si coupling constants in **4** provide important information about the bonding situation in this compound. Thus, whereas the coupling constant associated with the γ-Si atom ($J_{H,Si^{\gamma}}$) of 170.7 Hz is close to the value expected for a free $SiHMe_2$ group, the highly decreased $J_{H,Si^{\alpha}}$ value of 46.3 Hz is indicative of a H-bridged silylium ion, a structural motif similar to that one reported for **1** ($J_{H,Si} = 39$ Hz) and **2** ($J_{H,Si} = 45.7$ Hz).[12] The new prominent feature of **4** lies in the fact that the two half-charged cationic centers in the α positions induce waning agostic interactions with the hydrides bound to the β-Si atoms, resulting in a noticeable decrease of the $J_{H,Si^{\beta}}$ value compared to the $J_{H,Si^{\gamma}}$ value (118.9

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[*] Dipl.-Chem. A. Y. Khalimon, Z. H. Lin, Dipl.-Ing. R. Simionescu, Dr. G. I. Nikonov
Chemistry Department, Brock University
500 Glenridge Ave., St. Catharines, ON L2S 3A1 (Canada)
Fax: (+1) 905-6829020
E-mail: gnikonov@brocku.ca

Dr. S. F. Vyboishchikov
Institut de Química Computacional, Campus de Montilivi
Universitat de Girona, 17071 Girona, Catalonia (Spain)
Fax: (+34) 97241-8356
E-mail: vybo@stark.udg.es

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vs. 170.7 Hz). As a result of this additional $Si^{\alpha}\leftarrow H\text{-}Si^{\beta}$ bonding, each equivalent silylium center adopts a distorted TBP (trigonal-bipyramidal) geometry with the hydride atoms in the apical positions (Figure 1).

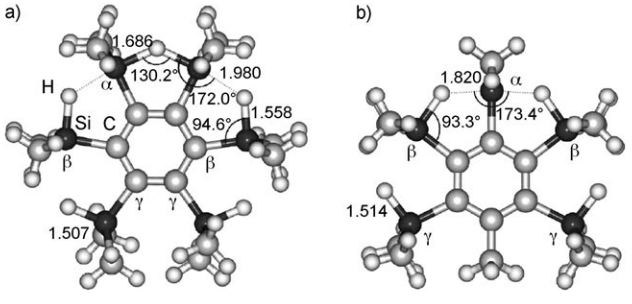


Figure 1. a) DFT-calculated structure of agostically stabilized silylium ion **4**. b) DFT-calculated structure of agostically stabilized silylium ion **5**. Interatomic separations are given in Å.

Finally, the presence of agostic H^{α} and H^{β} hydrides is clearly seen from the remarkable red shift of their Si–H bands in the IR spectrum (1725 cm^{-1} (exptl) vs. 1655 cm^{-1} (calcd) for Si–H^{α} and 1978 cm^{-1} (exptl) vs. 1898 cm^{-1} (calcd) for the symmetric stretch of two β-Si–H bonds[18]). In contrast, the γ-Si–H bonds give rise to a very broad band at about 2140 (exptl) versus 2134 and 2131 cm^{-1} (calcd), in a region typical of hydrosilanes.

The room-temperature ^1H NMR spectrum of **4** corresponds to an effective D_{6h} symmetry, giving rise to a SiH singlet at $\delta = 4.60$ ppm and a SiMe singlet at $\delta = 0.78$ ppm and indicative of fast exchange. This exchange most likely occurs through hydride transfer between the α silicon centers, assisted by the agostic bonding with the β-Si–H bond.

The suggested H-bridged silylium ion structure supported by two $Si^{\alpha}\leftarrow H\text{-}Si^{\beta}$ agostic interactions was further elucidated by DFT calculations (Figure 1 a).[19] The optimized structure of **4** exhibits C_2 symmetry. The bridging hydride forms two equivalent elongated Si–H bonds to the α-Si atoms with lengths of 1.686 Å and a Si-H-Si bond angle of 130.2°. If the Si–H bonding is neglected, the α-silylium ion is almost planar (the sum of bond angles is 358.9°). A similar geometry (1.607 Å and 134.7°) has been calculated for **2** at the MP2/6-311G** level.[12b] The agostic β-hydride forms an elongated bond to the β-Si center (1.558 Å vs. 1.4–1.5 Å in hydrosilanes), and a longer agostic bond to the α-silylium ion (1.980 Å). For comparison, the "unperturbed" γ-Si–H bond was calculated to be 1.507 Å and the $Si^{\beta}\cdots H^{\gamma}$ separation (2.504 Å) is too long for a significant interaction. Calculation of the ^{29}Si NMR parameters using the GIAO method[19] gives $\delta = 22.1$, 28.2, and -3.8 ppm for the α-, β-, and γ-Si atoms, respectively. A small $J_{Si,H}$ value of -38.2 Hz was calculated for the bridging hydride, in fair agreement with the experimental value ($|J| = 46.3$ Hz). The α-Si center is only weakly coupled with the agostic β-hydrogen atom ($J_{Si,H} = -3.5$ Hz), but the negative sign of $J_{Si,H}$ suggests direct bonding.[16] It is important to stress that this small absolute value of $J_{Si,H}$ is merely the result of the geometry of the $ArSi^{\alpha}Me_2$ group rather than reflective of the weakness of agostic interaction. In fact, the $ArSi^{\alpha}Me_2$ fragment is nearly planar, so that bonding to the hydride is primarily provided through the Si p orbital, resulting in severe reduction of the Fermi contact term.[12a,b] As noted above, the coupling constant between the β-Si and β-H atoms is decreased, (118.9 Hz (exptl) and -103.6 Hz (calcd)), which is the result of elongation of the Si–H bond and distortion of the C-Si^{β}-H bond angle to 94.6° owing to agostic bonding (compare: 101.2° for the C-Si^{γ}-H angle). Again, such a distortion leads to increased β-Si p character in the Si^{β}–H^{β} bond.

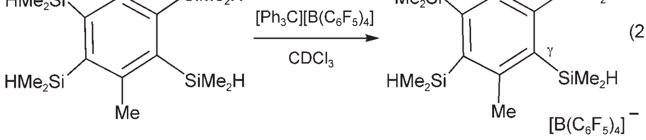
As expected, the 3c–2e Si^{α}-H^{α}-Si^{α} bond is characterized by larger Mayer bond orders (Si–H MBO = 0.445) and Wiberg bond orders (WBO = 0.426) than the $^{\alpha}Si\leftarrow HSi^{\beta}$ agostic bonding (MBO = 0.242, WBO = 0.182; Table 1).[20] The natural bond orbital (NBO)[21] occupation of the H^{β}–Si^{β} bond (1.806) is reduced in comparison with the H^{γ}–Si^{γ} single bond (1.938) owing to electron-density transfer to the cationic Si^{α} centers. Large attractive (that is, negative) values of Mayer diatomic energies[22] for the Si–H bond in **4** (right-hand column of Table 1) present strong evidence of significant Si···H interactions. Finally, bond critical points with negative energy density were found by using the AIM approach[23] both for Si^{α}-H^{α}-Si^{α} and $Si^{\alpha}\leftarrow H\text{-}Si^{\beta}$ interactions (see TableSI1 in the Supporting Information).

Table 1: Mayer bond orders, Wiberg bond orders, occupation of the H–Si natural bond orbital, and Mayer diatomic energies (MDE, in kcal mol^{-1}).

Cmpd	Bond	*d*(Si–H) [Å]	MBO	WBO	H–Si NBO occupation[a]	MDE
4	H^{α}-Si^{α}	1.686	0.445	0.426	–	−94.4
	H^{β}-Si^{α}	1.980	0.242	0.182	–	−68.4
	H^{β}-Si^{β}	1.558	0.664	0.692	1.806	−116.0
	H^{γ}-Si^{β}	2.504	0.104	0.034	–	−35.0
	H^{γ}-Si^{γ}	1.508	0.828	0.880	1.938	−126.1
5	H^{β}-Si^{α}	1.820	0.325	0.286	–	−78.2
	H^{β}-Si^{β}	1.595	0.582	0.584	1.722	−105.9
	H^{γ}-Si^{β}	2.515	0.114	0.041	–	−36.8
	H^{γ}-Si^{γ}	1.514	0.821	0.871	1.934	−122.2

[a] Missing data means that no NBO has been found.

Can we cut the "hydride current" in **4**? To do this, we introduced a "methyl insulator" in **4** by reacting the persilylated toluene derivative $MeC_6(SiHMe_2)_5$ with $[Ph_3C][B(C_6F_5)_4]$ [Eq. (2)]. Contrarily to **4**, NMR spectra of the product of this reaction, the silylium ion $[MeC_6(SiHMe_2)_4(SiMe_2)]^+$ (**5**), are temperature-independent down to −80 °C. The room-temperature ^1H NMR spectrum of **5** shows two SiH



5

(2)

signals, a septet at $\delta = 4.53$ ($^2J_{\mathrm{H,H}} = 3.6$ Hz) for the free $\mathrm{Si^{\gamma}Me_2H}$ group and an upfield-shifted singlet at $\delta = 4.28$ ppm for $\mathrm{H^{\beta}}$, indicative of agostic bonding. The methyl groups give rise to three signals at $\delta = 1.02$ (silylium ion $\mathrm{SiMe^{\alpha}{}_2}$), 0.84 (d, $^2J_{\mathrm{H,H}} = 2.1$ Hz, $\mathrm{Me^{\beta}}$), and 0.54 ppm (d, $^2J_{\mathrm{H,H}} = 3.6$ Hz, $\mathrm{Me^{\gamma}}$), with relative intensities of 1:2:2. Like **4**, the cation **5** is stable in chlorinated solvents at least for two days. The ^{29}Si NMR spectrum of **5** contains three signals. The $\mathrm{Si^{\gamma}Me_2H}$ group, which is not involved in significant agostic bonding, gives rise to a doublet of septets at $\delta = -4.5$ ppm ($^2J_{\mathrm{Si,H}} = 7.1$ Hz, $^1J_{\mathrm{Si,H}} = 166.2$ Hz). The two $\mathrm{Si^{\beta}Me_2H}$ groups, complexing the silylium ion through two Si–H agostic interactions, have a downfield-shifted (compared to the values expected for a $\mathrm{PhSiMe_2H}$ moiety) signal at $\delta = 33.5$ ppm with a *noticeably decreased direct* Si–H coupling ($^1J_{\mathrm{Si,H}} = 87.2$ Hz, $^2J_{\mathrm{Si,H}} = 6.9$ Hz). Finally, the silylium ion gives rise to a multiplet at $\delta = 34.3$ ppm, which upon selective decoupling from the Me protons resolves into a triplet with $^1J_{\mathrm{Si^{\alpha},H^{\beta}}} = 16.1$ Hz, suggesting a diagostic bonding with the β-H–Si bonds. Cooling down the sample to −80 °C does not change these spectral patterns, apart from the expected temperature-induced shifts of resonances, consistent with the absence of fluctionality in this system. The IR spectrum of **5** exhibits two red-shifted bands[16] (1747 $\mathrm{cm^{-1}}$ (exptl) vs. 1738 $\mathrm{cm^{-1}}$ (calcd) and 1810 $\mathrm{cm^{-1}}$ (exptl) vs. 1817 $\mathrm{cm^{-1}}$ (calcd)) for the agostic $\mathrm{Si^{\alpha}\text{-}H\text{-}Si^{\beta}}$ bonds and one merged band for the γ-Si–H bonds at 2107 $\mathrm{cm^{-1}}$ (2094–2098 $\mathrm{cm^{-1}}$ (calcd)). To the best of our knowledge, such a diagostic bonding is unprecedented in the chemistry of silicon cations. The closest analogy exists only with the weak B–H···Sn interactions reported by Izod et al. for a stannylene compound.[24]

The DFT-calculated structure of **5** completely supports the presence of diagostic bonding (Figure 1 b). A structure with approximate C_s symmetry was obtained as a result of optimization. The $\mathrm{Si^{\alpha}\leftarrow H^{\beta}\text{-}Si^{\beta}}$ bonds (1.818 and 1.822 Å) in **5** are longer than the $\mathrm{Si^{\alpha}\text{–}H^{\alpha}}$ bond in **4** but shorter than the $\mathrm{Si^{\alpha}\leftarrow H^{\beta}\text{-}Si^{\beta}}$ agostic interaction in **4**. The $\mathrm{H^{\beta}\text{–}Si^{\beta}}$ bond in **5** (1.594/1.596 Å) is elongated as a result of electron-density transfer to the silylium ion. The $\mathrm{Si^{\beta}}$ center exhibits the same distorted C-Si-H angle of 93.3° as the agostic $\mathrm{Si^{\beta}}$ center in **4**. The calculated $J_{\mathrm{Si,H}}$ values are in fair accord with the absolute experimental coupling constants ($|J|$ in parentheses): −14.8 Hz (16.1 Hz) for $\mathrm{H^{\beta}\text{–}Si^{\alpha}}$, −76.3 Hz (87.2 Hz) for $\mathrm{H^{\beta}\text{–}Si^{\beta}}$, and −166.2 Hz (156.2 Hz) for $\mathrm{{}^{\gamma}H\text{–}{}^{\gamma}Si}$.[25] As in **4**, the low values of $J_{\mathrm{Si^{\alpha},H^{\beta}}}$ and $J_{\mathrm{Si^{\beta},H^{\beta}}}$ are the result of a higher silicon p contribution to the Si–H bonding (NBO occupation of the "free" Si p orbital is 0.484, Table 1). The diagostic $\mathrm{Si^{\beta}\text{-}H\rightarrow Si^{\alpha}\leftarrow H\text{-}Si^{\beta}}$ interaction in **5** (MBO = 0.325) is weaker than the 3c–2e $\mathrm{Si^{\alpha}\text{-}H\text{-}Si^{\alpha}}$ bond in **4** (MBO = 0.445) but stronger than its $\mathrm{Si^{\alpha}\leftarrow H\text{-}Si^{\beta}}$ agostic bonding (MBO = 0.242). Correspondingly, the $\mathrm{H^{\beta}\text{–}Si^{\beta}}$ bond in **5** is weaker than the $\mathrm{H^{\beta}\text{–}Si^{\beta}}$ bond in **4** (MBO = 0.582 and 0.664, respectively). Finally, the AIM study of **5** revealed bond critical points for both $\mathrm{Si^{\alpha}\leftarrow H\text{-}Si^{\beta}}$ interactions.

Although a pentacoordinate silicon anion with two apical hydride atoms has been recently characterized,[26] **4** and **5** present the first examples of a compound in which two Si–H bonds serve as ligands to a hypervalent silicon center.[27] Or, if an alternative view is adopted, the structures **4** and **5** exhibit multiple agostic interactions induced by the silylium ion.

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[17] Corresponds well to the value of 171 Hz measured from the left-hand part of the γ-HSi doublet in the ^{1}H NMR spectrum. A ^{29}Si INEPT+ NMR experiment at −80°C afforded the values 116.9 Hz and 171.2 Hz for $J_{H,Si^{\beta}}$ and $J_{H,Si^{\gamma}}$, respectively (see the Supporting Information).

[18] The asymmetric stretch at 1899 cm^{-1} was calculated to be an order of magnitude weaker. The observed β-Si−H band at 1978 cm^{-1} is broad and has a shoulder at about 1909 cm^{-1} (see the Supporting Information).

[19] All geometry optimizations were carried out with the Gaussian 03 program package by applying the PBE–PBE exchange and correlation functionals. The spin–spin coupling constants were calculated within the gauge-including atomic orbitals (GIAO) method using the B3LYP hybrid functional. See the Supporting Information for more details and references.

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