Group 14 Derivatives

DOI: 10.1002/anie.200601164

How Can a Carbon Atom Be Covalently Bound to Five Ligands? The Case of $Si_2(CH_3)_7^+$**

Juan Z. Dávalos, Rebeca Herrero, José-Luis M. Abboud, Otilia Mó, and Manuel Yáñez**

Dedicated to Professor José Manuel Riveros

In our Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry[1] studies on the gas-phase reactivity of Group 14 derivatives, we initially examined the behavior of tetramethylsilane, $Si(CH_3)_4$ (TMS). Using mild electron ionization (nominal energies between 10 and 12 eV) and pressures in the range 10^{-8}–10^{-5} mbar, the main ion observed is the trimethylsilyl cation, $Si(CH_3)_3^+$, formed through the fast decomposition of the radical cation $Si(CH_3)_4^{+\bullet}$. A striking feature of the spectrum is the presence at low pressures of a weak signal ($\approx 1\,\%$) at m/z 161 that fades away a few seconds after the ionization process. It corresponds to the most abundant isotopomer of the ion $Si_2(CH_3)_7^+$ ($\mathbf{I}^+$). The stoichiometry of this species suggests a somewhat unusual electronic structure, which prompted us to carry out a more detailed study.

Some important databases[2] do not report the existence of $\mathbf{I}^+$, although this ion was reported in 1974 by Klevan and Munson[3] as the product of reaction (1), which takes place under high-pressure conditions (0.3 Torr).

$$Si(CH_3)_3^+(g) + Si(CH_3)_4 \rightarrow Si_2(CH_3)_7^+ \quad (1)$$

Using high-pressure mass spectrometry, Stone and coworkers carried out a careful study of this reaction, as well as of similar processes involving Ge and Sn derivatives.[4] They also determined $\Delta_r H^\circ_m(1)$ and $\Delta_r S^\circ_m(1)$ for reaction (1) as (-22.3 ± 0.4) kcal mol^{-1} and (-35.2 ± 0.9) cal mol^{-1} K^{-1}, respectively. These values lead to a value for $\Delta_r G^\circ_m(1)$ of (-11.8 ± 0.7) kcal mol^{-1}.

Herein, we report our observations that under the lowest pressures indicated above, kinetic excitation of $Si(CH_3)_3^+$ by means of on-resonance irradiation or slightly off-resonance irradiation (SORI) under multiple-collision conditions[5] increases the yield of $\mathbf{I}^+$. In the presence of a cooling gas and without ion excitation, the abundance of this ion increases rather slowly. As expected from the value of $\Delta_r G^\circ_m(1)$, the equilibrium abundance observed under our working conditions is small.[6] Figure 1 shows a spectrum of ion $\mathbf{I}^+$.

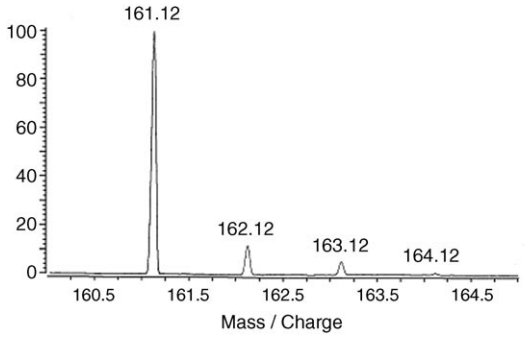


Figure 1. Mass spectrum of ion $\mathbf{I}^+$ (nominal pressure of TMS: 5×10^{-7} mbar; 100 scans).

Collision-induced decomposition (CID) experiments on $\mathbf{I}^+$ using argon as the target gas and energies at the center of mass below 2 eV show that $Si(CH_3)_3^+$ is the only ion formed. This observation also indicates a "fragile" bond between $Si(CH_3)_3^+$ and TMS, in agreement with the results reported in reference [3].

Similar experiments using perdeuterated tetramethylsilane, $Si(CD_3)_4$ (TMSD), yield the ion $Si_2(CD_3)_7^+$ ($\mathbf{I_D}^+$), and CID experiments conducted as indicated for $\mathbf{I}^+$ lead to the formation of $Si(CD_3)_3^+$ as the sole ionic product.

The study of mixtures of TMS and TMSD was generally conducted using 1:1 mixtures and nominal pressures of the individual reagents of about $1–2 \times 10^{-7}$ mbar, with argon being added up to pressures of 8×10^{-7}–1.2×10^{-6} mbar. The significant results obtained are as follows:

1. Detection at short reaction times (0.15–0.3 s after the ionization pulse) shows that the only ions present are $Si(CH_3)_3^+$ (m/z 73) and $Si(CD_3)_3^+$ (m/z 82). (See Figure SI 1 in the Supporting Information for a spectrum obtained under these conditions.)
2. Detection at reaction times of 1–2 s already reveals the formation of practically equal, substantial amounts of ions $Si(CH_3)_2CD_3^+$ and $Si(CD_3)_2CH_3^+$. Their abundances increase and approach a constant value after times of

[*] Dr. J. Z. Dávalos, R. Herrero, Prof. Dr. J.-L. M. Abboud
Instituto de Química Física Rocasolano, CSIC
C/Serrano, 119, 28006 Madrid (Spain)
Fax: (+34) 915-855-184
E-mail: jlabboud@iqfr.csic.es
Prof. Dr. O. Mó, Prof. Dr. M. Yáñez
Departamento de Química, C-9
Universidad Autónoma de Madrid
28049 Cantoblanco/Madrid (Spain)
Fax: (+34) 914-975-238
E-mail: manuel.yanez@uam.es

[**] This work was supported by the Spanish DGICYT (grant BQU2003-05827). Valuable discussions with Jorge-José Abbud are gratefully acknowledged.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

about 10–12 s.[7] Figure 2 shows the mass spectrum thus obtained which reveals the scrambling of methyl groups. As we establish below, the initial scrambling originates in reactions involving the couples $Si(CH_3)_3^+$/TMSD and $Si(CD_3)_3^+$/TMS.

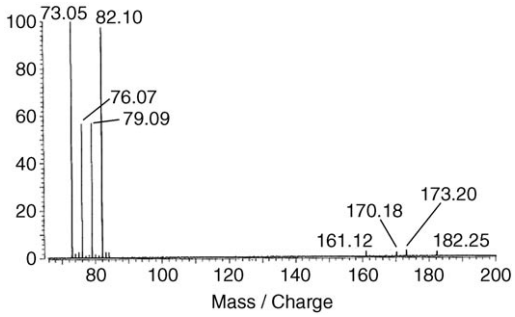


Figure 2. Mass spectrum of a 1.1:1 mixture of TMS (2.0×10^{-7} mbar) and TMSD (detection time 15 s after the ionization pulse; argon pressure: 8×10^{-7} mbar).

3. Simultaneously, ions $\mathbf{I}^+$ (m/z 161) and $\mathbf{I_D}^+$ (m/z 182) appear together with their mixed isotopomers $[(CH_3)_4Si\text{-}(CD_3)_3Si]^+$ (m/z 170) and $[(CH_3)_3Si(CD_3)_4Si]^+$ (m/z 173). These ions are presented in Figure 2, wherein their low abundance can be seen. (See Figure SI2 in the Supporting Information for a detailed spectrum of these species.)
4. After delays of 10–15 s following the selective ejection of $Si(CH_3)_3^+$ or any of its three deuterated isotopomers by a short radiofrequency burst, the deeply modified mass spectra recover and are nearly indistinguishable (in terms of the ions present and their relative intensities) from those obtained in the absence of ejection. This feature is reminiscent of chemical equilibrium. In fact, it corresponds to a steady state that involves processes such as reactions (2) and (3). The partial pressures of the neutral

$$Si(CH_3)_3^+ + TMSD \rightarrow Si(CH_3)_2(CD_3)^+ + (CD_3)_3CH_3Si \quad (2)$$

$$Si(CD_3)_3^+ + TMS \rightarrow Si(CD_3)_2(CH_3)^+ + (CH_3)_3CD_3Si \quad (3)$$

species $(CD_3)_3CH_3Si$ and $(CH_3)_3CD_3Si$ are so small that true equilibria are not established.
5. Ion $\mathbf{I}^+$ or any of its deuterated isotopomers can be isolated and allowed to react, while all other ions are ejected from the ICR cell. Without exception, after reaction times of 12–15 s, a mass spectrum similar to that presented in Figure 2 is obtained.
6. Ion $\mathbf{I}^+$ and its deuterated isotopomers are present in very low abundances at any given time. Therefore, selective ejection or excitation of any of these species for short periods of time does not significantly affect the mass spectra. However, selective ejection of any of them for periods of time of around 10–15 s brings about the complete disappearance of all ions. This observation indicates that these ions are key intermediates in the scrambling processes. The same happens if $Si(CH_3)_3^+$ or any of its deuterated isotopomers are ejected.
7. Using the same mixture, ion $Si(CD_3)_3^+$ can be isolated shortly after (ca. 0.15 s) the ionization pulse and then ion $\mathbf{I_D}^+$ can be excited by a long (6–8 s) SORI burst. This excitation leads to its decomposition according to reaction (4).

$$Si_2(CD_3)_7^+ \rightarrow Si(CD_3)_3^+(g) + TMSD \quad (4)$$

Ina mass spectrum obtained shortly (0.15–0.3 s) afterwards, one expects to find $Si(CD_3)_3^+$ as the most abundant ion. Smaller amounts of its protiated isotopomers are also expected, as a consequence of reactions such as reaction (3) and others, as discussed below, that take place during the SORI burst. Figure 3 shows a spectrum

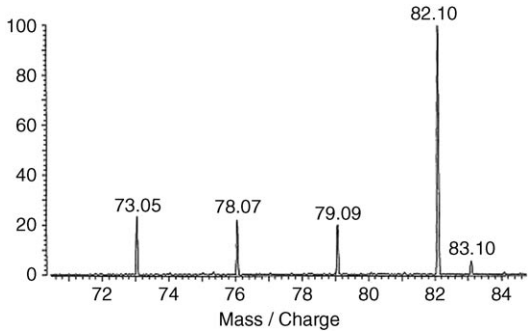


Figure 3. Mass spectrum obtained after selecting ion $Si(CD_3)_3^+$ and kinetically exciting $\mathbf{I_D}^+$ with a 7-s SORI pulse (detection time 0.2 s after the end of the pulse; argon pressure: 1.0×10^{-6} mbar; 20 transients accumulated).

obtained under these conditions that confirms these expectations. In the same vein, selection of $Si(CH_3)_3^+$ and SORI excitation of $\mathbf{I}^+$ leads to a spectrum portraying now $Si(CH_3)_3^+$, the most abundant ion, and smaller amounts of its deuterated isotopomers.
8. Let us consider now a similar experiment in which $Si(CD_3)_3^+$ is selected and ion $[(CD_3)_3Si(CH_3)_4Si]^+$ (m/z 170) is excited with SORI. On the basis of the previous results, one would expect the spectrum to show $Si(CD_3)_3^+$ as the most abundant ion and smaller amounts of its protiated isotopomers. This result would follow from the fact that $[(CD_3)_3Si(CH_3)_4Si]^+$ is expected to decompose according to reaction (5).

$$[(CD_3)_3Si(CH_3)_4Si]^+ \rightarrow Si(CD_3)_3^+ + TMS \quad (5)$$

Figure 4 portrays the spectrum obtained. It does not fulfill these expectations. It is particularly noteworthy that the abundances of ions $Si(CD_3)_3^+$ and $Si(CH_3)_3^+$ are almost the same and that the overall spectrum is quite similar to that obtained without selection and excitation (Figure 2). Reaction (5) alone is not able to explain this result.

Similar behavior is observed if $Si(CH_3)_3^+$ is isolated and ion $[(CD_3)_4Si(CH_3)_3Si]^+$ (m/z 170) is kinetically excited. The spectrum thus obtained is practically identical to that

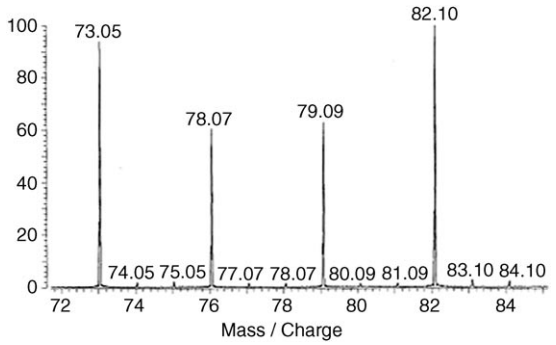


Figure 4. Mass spectrum obtained after selecting ion $Si(CD_3)_3^+$ and kinetically exciting ion $[(CD_3)_3Si(CH_3)_4Si]^+$ with a 7-s SORI pulse (detection time 0.2 s after the end of the pulse; argon pressure: 1.0×10^{-6} mbar; 20 transients accumulated).

presented in Figure 4. By analogy with the previous experiment, reaction (6) alone is not able to explain these findings.

$$[(CH_3)_3Si(CD_3)_4Si]^+ \rightarrow Si(CH_3)_3^+ + TMSD \quad (6)$$

The finding described above strongly suggests that reactions (5) and (6) compete with reactions (7) and (8), respectively.

$$[(CD_3)_3Si(CH_3)_4Si]^+ \rightarrow Si(CH_3)_3^+ + (CH_3)(CD_3)_3Si \quad (7)$$

$$[(CH_3)_3Si(CD_3)_4Si]^+ \rightarrow Si(CD_3)_3^+ + (CD_3)(CH_3)_3Si \quad (8)$$

These results shed light on the possible structure of $\mathbf{I}^+$. Several possibilities have been considered:[3,4] Recently, Riveros and co-workers examined the methide (CH_3^-) exchange between H_3Si^+ and $MeGeH_3$ and concluded that it proceeds through a methyl bridge.[8] Let us apply this model to ion $[(CD_3)_3Si(CH_3)_4Si]^+$ as an example. It can be represented as $[(CD_3)_3Si\cdots(CH_3)\cdots Si(CH_3)_3]^+$, with no hypothesis whatsoever being made about its detailed structure.

The results of the SORI experiments presented above are consistent with the fragments $(CD_3)_3Si$ and $Si(CH_3)_3$ playing essentially identical roles (except for potential isotopic effects) and allowing the decomposition of this ion according to reactions (6) and (8). In turn, this finding strongly suggests that $\mathbf{I}^+$ has a highly symmetrical (perhaps unusual) structure. Scrambling would imply the possibility for the moieties $(CD_3)_3Si\cdots(CH_3)$ or $(CH_3)\cdots Si(CH_3)_3$ to enjoy substantial freedom of rotation within the ion. Similar requirements would apply to the structure of $[(CH_3)_3Si(CD_3)_4Si]^+$.

Following our experimental study of $Si_2(CH_3)_7^+$ ($\mathbf{I}^+$) and $Si_2(C_2H_3)_7^+$ ($\mathbf{I_b}^+$) as described above, we now turn to a theoretical study of I^+ covering static and dynamic aspects in turn.

First, with regards static aspects, the geometry of $\mathbf{I}^+$ was initially optimized using the B3LYP density functional theory (DFT) method.[7–8] The geometry optimization was carried out using a very flexible basis-set expansion, namely 6-311 + G(3df,2pd). The optimized geometry of $\mathbf{I}^+$ corresponds to a C_{3h}-symmetric structure, in which a totally planar CH_3 group is symmetrically bonded to two $Si(CH_3)_3$ moieties. As illustrated in Figure 5, the two $Si(CH_3)_3$ groups adopt an eclipsed conformation, while they are staggered with respect to the central CH_3 group. This structure remained essentially unchanged at the MP2 level (Figure 5). Nevertheless, to

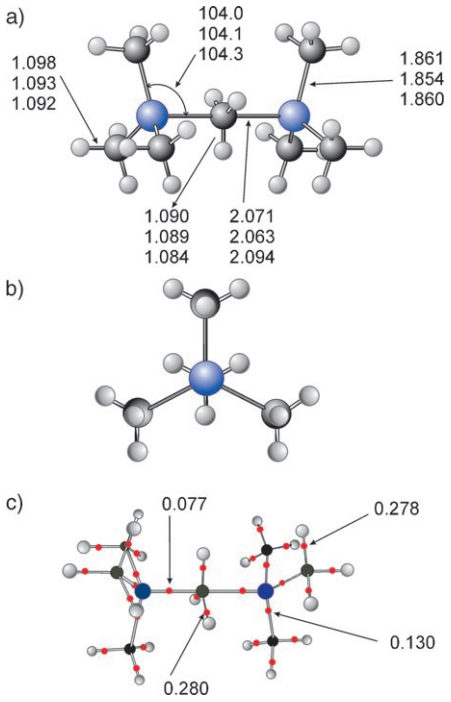


Figure 5. a) Optimized geometry for species $\mathbf{I}^+$ (Si blue, C dark gray, H pale gray). Bond lengths [Å] and bond angles [°] are indicated. The reported values are listed corresponding to the order QCISD, MP2, and B3LYP. b) View of ion $\mathbf{I}^+$ along the Si-C-Si axis. c) Molecular graph of species (red dots indicate bond critical points).

ensure that inclusion of higher-order corrections would not change this description, the B3LYP geometry was refined at the QCISD/6-311 + G(d,p) level of theory. The changes found were very small.

The most important conclusion of this theoretical study is that in $\mathbf{I}^+$, the central carbon atom is pentacoordinated. To shed some light on the bonding pattern of $\mathbf{I}^+$, we carried out a topological analysis of its electron-charge density by means of the atoms in molecules (AIM) theory.[9] For this purpose, we located the different bond critical points (bcps) and bond paths that define the corresponding molecular graph (see Figure 5), which shows the existence of a bcp between the central carbon atom and the two silicon atoms. Although the charge density at these critical points is about 60 % of that in a normal C–Si bond, the value and sign of the Laplacian of the charge density (−0.011 a.u.) undoubtedly indicates that the interaction has a clear covalent character. The obvious question to be answered is how a carbon atom can be covalently bound to five ligands. This finding can be understood if one considers that $\mathbf{I}^+$ can be viewed as a CH_3^+ cation interacting with the two $Si(CH_3)_3$ radicals. This view implies that the central carbon atom is covalently bonded to the hydrogen atoms through sp^2 hybrid orbitals, leaving an empty p orbital perpendicular to the CH_3 plane. This orbital can

interact with the appropriate singly occupied p orbitals of the two $Si(CH_3)_3$ groups, so that the three linearly independent combinations shown in Figure 6 are formed. The three-centered Ψ_1 molecular orbital bonds with the two Si atoms and should be the lowest one in energy, followed by Ψ_2 and Ψ_3 which are nonbonding and antibonding, respectively. As we have only two electrons, according to the aufbau principle, only Ψ_1 would be full, indicating that in $\mathbf{I}^+$ the central carbon atom is bonded to the two silicon atoms through a three-center, two-electron bond. This picture is ratified by an inspection of the canonical molecular orbitals of the complex which shows that Ψ_1 is the HOMO, Ψ_2 is the LUMO, and Ψ_3 is the LUMO + 3 (see Figure 6).

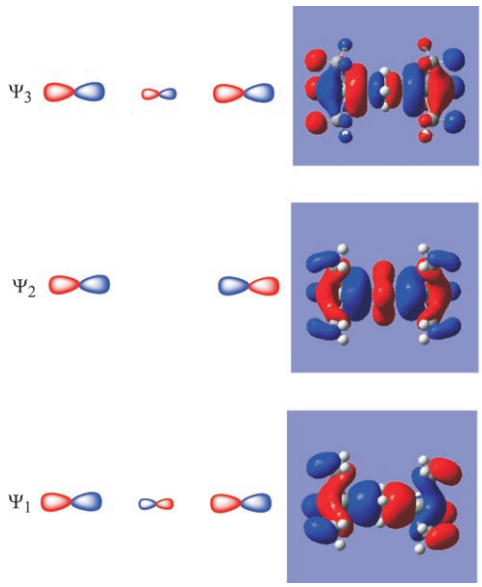


Figure 6. Schematic representation of the three-center molecular orbitals that can be formed by combination of the p orbital of the central carbon atom and the p orbitals of the terminal Si atoms in a species with C_{3h} symmetry. These combinations correspond to the canonical orbitals Ψ_1 (HOMO), Ψ_2 (LUMO), and Ψ_3 (LUMO + 3) of species $\mathbf{I}^+$.

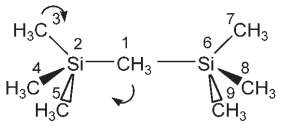
The positive charge of the $\mathbf{I}^+$ cation is spread out over the system, indicating that the central carbon atom is covalently bound to the two $Si(CH_3)_3$ moieties. In fact, the CH_3 central group bears only a net charge of +0.26, while the net charge of the two $Si(CH_3)_3$ moieties is +0.37, with most of it located at the Si atom.

The above-mentioned bonding characteristics are also consistent with the molecular-ion force field. Our calculations indicate that the C–Si stretching frequencies of the $Si(CH_3)_3$ groups appear as in-phase and out-of-phase combinations in the 600–621 cm^{-1} region, whereas the modes involving the central carbon atom appear as symmetric (inactive) and antisymmetric combinations of the two C–Si stretching displacements at 305 and 280 cm^{-1}, respectively.

A further assessment of our theoretical analysis is the evaluation of the enthalpy of the reverse of reaction (1); that is, the dissociation enthalpy of $\mathbf{I}^+$ into TMS and $Si(CH_3)_3^+$. To ensure the reliability of the theoretical estimations, the total energies of the species involved were obtained at the QCISD/6-311 + G(d,p) level.[10] The value obtained for $\Delta_r H^\circ_m(1)$ was 23.2 kcal mol^{-1}, which is in excellent agreement with the experimental value. Our estimation for $\Delta_r G^\circ_m(1)$ (9.7 kcal mol^{-1}) is slightly smaller than the experimental value and is likely due to the error in the estimation of the entropic term, based on harmonic vibrational frequencies. More detailed computational analyses of the energetics of $\mathbf{I}^+$ are presented in the Supporting Information. Also provided in the Supporting Information are comparisons between the structures found here and those pertaining to potential structural models,[13,14] as well as experimental links between the present results and recent data obtained for cognate silicon derivatives.[15]

To end our discussion of the static aspects, we note that it is well-established that $Au(PPh_3)$ often mimics H in the formation of hypercoordinated species. As such, it is well-established that the cation $Au(PPh_3)\{C(SiMe_3)_2[Au(PPh_3)]_3\}^+$ is known as its BF_4^- salt.[16]

Now, we turn to dynamic aspects in the theoretical study of $\mathbf{I}^+$. The experimentally observed methyl scrambling is not only compatible with the proposed structure for complex $\mathbf{I}^+$ but can also be taken as indirect proof that this highly symmetric arrangement is the actual structure of the system. In a $[Si(1)(CH_3)_4Si(2)(CH_3)_3]^+$ system, methyl exchange can only be achieved through two mechanisms. One possibility is a concerted double methyl transfer that simultaneously shifts one of the methyl groups initially attached to Si(1) towards Si(2), and a methyl group initially attached to Si(2) towards Si(1). If it is assumed that the structure of complex $\mathbf{I}^+$ is the one we found, with a central methyl group symmetrically bound to two $Si(CH_3)_3$ moieties, an alternative mechanism leading to methyl scrambling would involve an internal rotation of one of the $Si(CH_3)_4$ moieties with respect to the remaining $Si(CH_3)_3$ subunit (see Scheme 1).



Scheme 1. Atom-numbering scheme for cation $\mathbf{I}^+$.

Methyl-shifting processes typically involve high activation barriers,[17] which would be larger than the dissociation energy of the complex under investigation. Hence, a concerted double methyl transfer mechanism should be discarded. To investigate the feasibility of the alternative internal rotation as a suitable mechanism explaining methyl scrambling, we evaluated the corresponding energy curve by scanning the appropriate C-C-Si-C dihedral angle (3-9-6-7 in Scheme 1).

For the cation $\mathbf{I}^+$ in its equilibrium conformation, the value of the C-C-Si-C dihedral angle chosen was equal to zero and was scanned in steps of 10° up to a maximum value of 120° at which the initial equilibrium structure is recovered. Along this scan, all other geometrical parameters were fully optimized at the B3LYP/6-31G(d) level. The results obtained are plotted in Figure SI3 in the Supporting Information and reveal that the barrier associated with this internal rotation

appears as expected for a dihedral angle of 60°. To obtain a higher accuracy for the value of this barrier, the energy of the maximum was reevaluated at the B3LYP/6-311 + G(3df,2pd) level of theory. At this level, the value of the barrier is 9.7 kcal mol^{-1}, which is low enough to be easily overcome under our experimental conditions, particularly considering the energy released in reaction (1). This finding leads to the statistical methyl scrambling experimentally observed and indirectly confirms the structure of cation $\mathbf{I}^+$.

In conclusion, we have experimentally shown that $\mathbf{I}^+$ is a symmetric, fluxional ion. Theoretical calculations at a very substantial level show that the optimized geometry of the ion corresponds to a C_{3h}-symmetric structure, in which a totally planar CH_3 group is symmetrically bonded to two eclipsed $Si(CH_3)_3$ moieties. These calculations also rationalize the fluxionality of this ion.

Experimental Section

FT-ICR mass spectrometry: In this work, we made use of a modified Bruker CMS 47 FT-ICR mass spectrometer. A detailed description of the original instrument is given in reference [1d], and it has already been used in a number of studies.[12] The spectrometer was driven by an Omega data station (IonSpec, CA). The high vacuum was provided by a Varian TURBO V550 turbomolecular pump (550 L s^{-1}). Inert gases for CID studies were admitted by means of a Parker Hannifin Corp. 009-1380-900 solenoid valve. The magnetic-field strength of the superconducting magnet was 4.7 T.

Samples: TMS (Aldrich; 99.9 + %) was kept over phosphorus pentoxide (Merck). No impurities were detected. Perdeuterated tetramethylsilane (TMSD) (C/D/N Isotopes, Inc.; 99% isotopic purity) was treated likewise. The only impurity observed was $SiC_4D_{11}H$ ($\approx$1%).

Experiments are described in greater detail in the Supporting Information. Computations were carried out using the Gaussian 03 package of computer programs.[18] Coordinates of the optimized structures, together with some further statistical details, are given in the Supporting Information.

Received: March 23, 2006
Revised: October 31, 2006
Published online: December 5, 2006

Keywords: density functional calculations · ionization · isotopic labeling · mass spectrometry · thermodynamics

[1] a) A. G. Marshall, C. L. Hendrickson, *Int. J. Mass Spectrom.* **2002**, *215*, 59–75; b) J.-F. Gal, P.-C. Maria, E. W. Raczynska, *J. Mass Spectrom.* **001**, *36*, 699–716; c) "Energetics of Stable Molecules and Reactive Intermediates": J.-L. M. Abboud, J. R. Notario, *NATO Sci. Ser. Ser. C* **1999**, *535*, 281–302; d) A. G. Marshall, C. L. Hendrickson, G. S. Jackson, *Mass Spectrom. Rev.* **1998**, *17*, 1–35; e) "Fourier Transform Mass Spectrometry. Evolution, Innovation and Applications": F. H. Laukien, M. Allemann, P. Bischopfberger, P. Grossmann, P. Kellerhals, P. Kopfel, *ACS Symp. Ser.* **1987**, *359*, 5.

[2] For example, SciFinder reports "no hit" for any species, neutral or charged, of elementary composition $Si_2(CH_3)_7$.

[3] L. Klevan, B. Munson, *Int. J. Mass Spectrom. Ion Phys.* **1974**, *13*, 261–268.

[4] a) A. Wojtyniak, X. Li, J. A. Stone, *Can. J. Chem.* **1987**, *65*, 2849–2854; b) J. A. Stone, *Mass Spectrom. Rev.* **1997**, *16*, 25–49.

[5] J. Laskin, M. Byrd, J. Futrell, *Int. J. Mass Spectrom.* **2000**, *195*/196, 285–302.

[6] Ratio ($I_{\mathbf{I}^+}/I_{Me_3Si^+}$) of ionic abundances in the range 1–3% at 321 K and under a pressure of TMS of about 1×10^{-7} mbar.

[7] Assuming, for instance, that the formation of $Si(CH_3)_2CD_3^+$ originates in the bimolecular reaction between $Si(CH_3)_3^+$ and TMSD, the reaction rate constant is of the order of the collision limit.

[8] L. A. Xavier, J. R. Pliego, Jr., J. M. Riveros, *Int. J. Mass Spectrom.* **2003**, *228*, 551–562.

[9] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372–1377.

[10] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[11] R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon, Oxford, **1990**.

[12] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479–483.

[13] a) See, e.g., Z. Jin, B. J. Braams, J. M. Bowman, *J. Phys. Chem. A* **2006**, *110*, 1569–1574, and references therein. b) At the MP2/6-311 + + G(d,p) level, we find that the trigonal-bipyramidal structure of CH_5^+ corresponds to a saddle point with two imaginary frequencies.

[14] P. M. Esteves, C. J. A. Mota, A. Ramírez-Solís, R. Hernández-Lamoneda, *J. Am. Chem. Soc.* **1998**, *120*, 3213–3219.

[15] J. Z. Dávalos, T. Baer, *J. Phys. Chem. A* **2006**, *110*, 8572–8579.

[16] N. Dufour, A. Schier, H. Schmidbaur, *Organometallics* **1993**, *12*, 2408–2412.

[17] E. Quintanilla, J. Z. Dávalos, J.-L. M. Abboud, M. Alcamí, M. P. Cabildo, R. M. Claramunt, J. Elguero, O. Mó, M. Yáñez, *Chem. Eur. J.* **2005**, *11*, 1826–1832.

[18] Gaussian 03 (Revision B.05): M. J. Frisch et al., see the Supporting Information

