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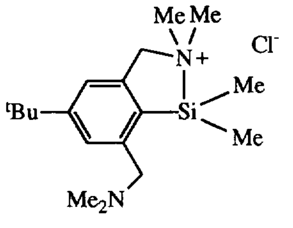
More Information About the Existence of Siliconium Ions

Moni Chauhan, Claude Chuit, Robert J.P. Corriu*, and Catherine Reyé

Université de Montpellier II, Sciences et Techniques du Languedoc, Laboratoire d'Hétérochimie et des Aminoacides, associé au CNRS, Place Eugène Bataillon, Case courrier 007 - F-34000 Montpellier (France)

Abstract : We confirm that compounds **2** bearing a Si-H bond are siliconium ions. In contrast we show that the non-functional cationic compounds **4-7** exist as silylammonium ions or siliconium ions depending on the counteranion and on the solvent.

Recently, Willcott et al[1] showed from ^1H NMR data in CD_3OD that compound **1** with a non-functional silicon atom is a *silylammonium* ion, in which dynamic coordination-decoordination of the two NMe_2 groups occur at room temperature. At low temperature, this process is slowed down and the two NMe_2 units become magnetically non-equivalent, each of them appearing as a singlet.



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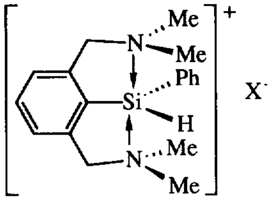
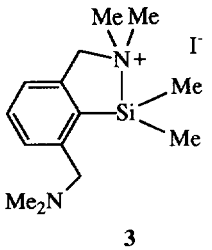


2
(X = Cl, Br, I, BF_4, CF_3SO_3)

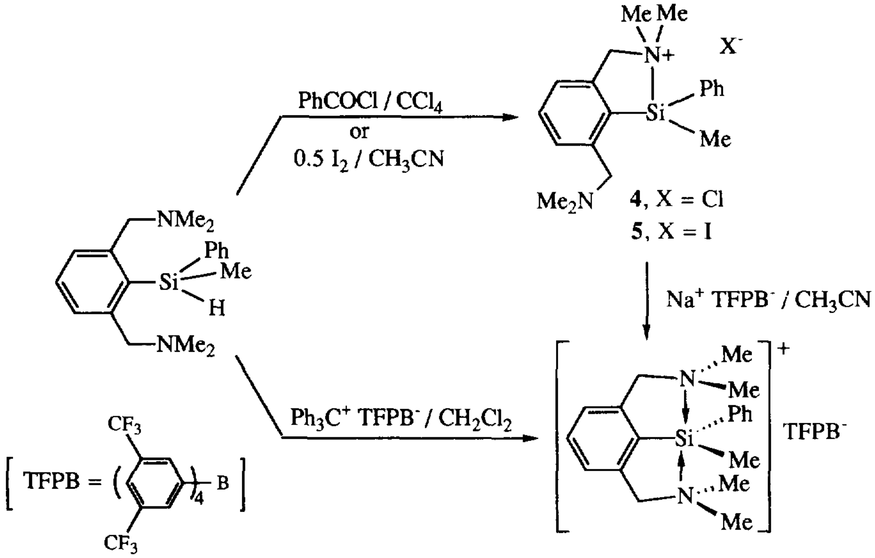


3

From this study, these authors concluded that all compounds of this generic type would have the same structure, refuting the possible existence of the *siliconium* ions **2** we have described previously[2]. However, our results are unambiguous; the ^1H NMR spectra of compounds **2** in CD_2Cl_2 exhibit at all temperatures two singlets for the NMe_2 protons and an AB system for the benzylic protons.

These data are in agreement with a structure of siliconium ion, but not with that of a silylammonium ion. Furthermore, since this publication the X-ray structures of two siliconium ions (with rather short Si-N lengths of 2.0 - 2.1 Å) bearing one Si-H bond, have been reported, one by us[3] and the other by Belzner et al[4]. It is worth noting that the ^1J(Si-H) coupling constants of these compounds are in the same range as those observed for compounds **2**.

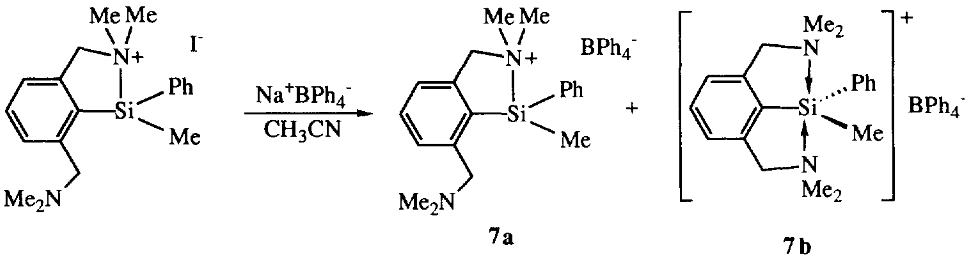
In the case of non-functional compounds, we actually found that the ^1H NMR spectrum of **3** in CD_3OD at room temperature exhibits a broad signal at 2.5 ppm for the NMe_2 groups and a broad signal for the benzylic protons at 4 ppm. As the temperature is decreased these signals are split into two singlets. This behaviour is consistent with the existence of a tetracoordinate silylammonium structure.



Scheme 1

To obtain more information about the mode of coordination in these non-functional derivatives, we studied compounds **4** - **7** (Scheme 1 and eq 1) in which the silicon atom is surrounded by different substituents. If these compounds exist as silylammonium ions, we should observe one signal for the NMe_2 groups at room temperature because of the dynamic coordination - decoordination of the two NMe_2 groups. Conversely, if they exist as siliconium ions we should observe diastereotopic methyl groups owing to the chirality around the silicon atom.

The ^{1}H NMR spectra of compounds **4**, **6**, and **7** are reported in Figure 1 and the chemical shifts of the NMe_2 groups of **4** - **7** are indicated in Table 1. From these data, it is clear that two kinds of structures exist as a function of the counteranion. The spectra of compounds **4** and **5** which display one signal in the range of 2.25 - 2.31 ppm assigned to the NMe_2 protons are consistent with the silylammonium ion, while that of compound **6** which exhibits two signals for the NMe_2 protons at 1.88 and 2.46 ppm is consistent with the siliconium ion. Interestingly, with BPh_4^- as counteranion, we observed both siliconium and silylammonium ions. Furthermore, in CD_3CN at room temperature, the siliconium ion is slowly transformed into the silylammonium ion. Based on the ^{1}H NMR data, we can attribute the ^{29}Si NMR signals at -7.0, -8.0 ppm to the silylammonium ion and that at -15.0 ppm to the siliconium ion.



(1)

Table 1. Relevant NMR data for compounds **4** - **7**

Compound	Anion	^{29}Si	^{1}H (NMe_2)
4	Cl	-7.0^{a}	2.31^{b}
5	I	-8.0^{a}	2.25^{b}
6	TFPB	-15.0^{a}	1.88 - 2.46^{a}
7	BPh_4	-8.5 and -14.5^{b}	1.90 and 1.82 - 2.43^{a}

^{a} in CD_2Cl_2, ^{b} in CD_3CN

The solvent plays an important role in the existence of these cations. Thus the siliconium ion **6** in CD_3CN solution is immediately transformed into the silylammonium cation by adding a drop of water or methanol into the solution.

In conclusion, the stability of the siliconium ions depends strongly on the environment around the silicon atom . Compounds such as **2** with one Si-H bond exist only as siliconium ions while compounds **4** - **7** exist as siliconium or silylammonium ions depending on the counteranion and on the solvent. In particular , methanol strongly stabilises the silylammonium ions most probably by solvation of the nitrogen center.

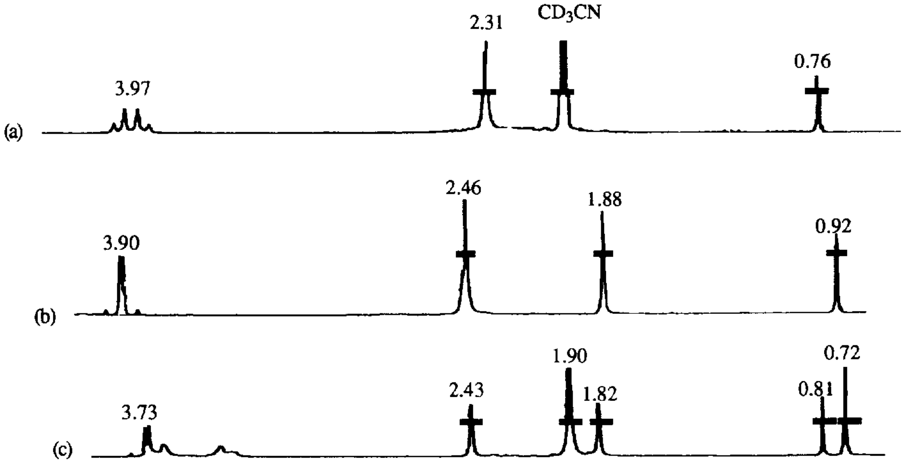


Figure 1. ^{1}H NMR spectra of compounds **4** in CD_3CN (a), **6** in CD_2Cl_2 (b), **7** in CD_2Cl_2 (c) at room temperature.

Finally we acknowledge the importance of the work of Willcott et al[1] which has revealed to us the complexity of the problem described in this paper. Full details of the present studies will be published shortly.

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