Properties of R_3SiX Compounds and R_3Si^+ Ions: Do Silylium Ions Exist in Solution?

Lars Olsson, Carl-Henrik Ottosson, and Dieter Cremer*

Contribution from the Department of Theoretical Chemistry, University of Göteborg, Kemigården 3, S-412 96 Göteborg, Sweden

Received November 18, 1993. Revised Manuscript Received April 27, 1995®

Abstract: More than 40 Si compounds comprising R_3SiX (R = H or CH_3; X = H, CH_3, CN, OH, Cl, $OClO_3$), $R_3SiX(S)$ (S = NH_3, H_2O, HCl), and $R_3Si(S)_n^+$ (S = NH_3, HCN, CH_3CN, H_2O, $(CH_3)_2O$, HCl, CH_3Cl for $n = 1$; HCN, NH_3, H_2O for $n = 2$; H_2O for $n = 3, 4, 5$) have been investigated at the Hartree–Fock level with both the 6-31G(d) and the 6-311G(d,p) basis sets. IGLO/[7s6p2d/5s4p1d/3s1p] NMR chemical shift calculations have been carried out at optimized HF/6-31G(d) and HF/6-311G(d,p) geometries. Solvent effects on calculated chemical shifts have been determined with the PISA continuum model. In addition, the nature of SiX or SiS interactions has been investigated on the basis of calculated electron density and energy density distributions. R_3Si^+ ions (R = Me, Et) possess in the gas phase δ ^{29}Si values at 400 ppm, in noncoordinating solvents between 370 and 400 ppm, and in very weakly coordinating solvents between 200 and 370 ppm. In weak or normal nucleophilic solvents, silylium cations react with one or more solvent molecules to form tetra- or pentacoordinated covalently bonded Si compounds with complexation energies that can be as high as 100 kcal/mol and δ ^{29}Si values between −50 and 190 ppm ($SiR_3(S)^+$) or −30 and 210 ppm ($SiR_3(S)_2^+$). Any silylium cation character is lost in these compounds. There are chances of generating silylium cations in solution, but silyl perchlorates are not good starting compounds for this purpose. Calculations indicate that carbocations differ from silylium ions in so far as their positive charge is largely delocalized due to hyperconjugative and inductive effects, and therefore, they interact much weaker with solvent molecules than silylium cations.

1. Introduction

Trivalent silicon cations (silylium ions)[1] are known to be more stable in the gas phase than their carbon analogues, which is due to the fact that silicon is more electropositive than carbon.[2] Accordingly, silylium cations are easily observable by mass spectrometry or ion cyclotron resonance spectroscopy of triorganosilyl compounds.[3,4] However, their existence in solvent phases is difficult to prove and, therefore, is still a matter of dispute.[5] Early attempts to synthesize silylium ions in solution with methods successful in the preparation of carbocations were not successful.[6,7] The lack of stability was attributed to several factors concerning the interaction with the experimental environment:

(1) Because of its empty 3d orbitals, Si prefers to extend its coordination sphere and to adopt hybridization states like sp^3d or sp^3d^2 rather than reduce hybridization to sp^2 as carbon does in carbocations.[6]

(2) Typical π-donor groups involving a first row atom such as N, O, etc., stabilize silylium cations only moderately via charge donation into the empty $3p\pi$ orbital of Si. This is partly due to the large energy gap between the $2p\pi$ orbitals of first row atoms and the $3p\pi$ orbital of Si,[2a] and partly due to the poor $\pi-\pi$ overlap between first row atoms and Si.

(3) Silicon has a high affinity to oxygen, fluorine, and chlorine, making the traditional methods for preparing carbocations unsuitable because they involve solvents or reagents which will react with the developing silylium ion.[6]

During the last few years, Lambert and co-workers reported a number of experiments, which gave indication that free silylium ions R_3Si^+ (**1**) may exist in solution.[7–11] The alleged silylium ions were prepared by hydrid abstraction from an alkylsilane with triphenylcarbenium perchlorate.[12]

$$R_3SiH + R'_3C^+ClO_4^- \rightarrow R_3Si^+ClO_4^- + R'_3CH \quad (1)$$

The experiments involved compounds such as Me_3SiClO_4,[9–11] Ph_3SiClO_4,[8,9] $PhMe_2SiClO_4$,[11] $MePh_2SiClO_4$,[11] $(MeS)_3SiClO_4$,[10] $(EtS)_3SiClO_4$,[10] and $(i\text{-}PrS)_3SiClO_4$[7,10] in solvents ranging from sulfolane, dichloromethane, 1,2-dichloroethane to acetonitrile. The evidence for the existence of free **1** came from conductance measurements and $^{35}Cl/^{37}Cl$ NMR spectroscopy. According to conductance measurements, R_3Si^+ with R = Me and Ph exist

® Abstract published in *Advance ACS Abstracts,* June 15, 1995.

(1) We use the term silylium cation for R_3Si^+ rather than silicenium ion, silylenium ion, or silyl cation, thus following recent IUPAC recommendations. See: *Nomenclature of Inorganic Chemistry*; Leigh, G. J., Ed.; Blackwell: Oxford, U.K., 1990; p 106.

(2) (a) Apeloig, Y.; Schleyer, P. v. R. *Tetrahedron Lett.* **1977**, 4647. (b) Apeloig, Y.; Godleski, S. A.; Heacock, D. J. *Tetrahedron Lett.* **1981**, *22*, 3297. (c) Truong, T.; Gordon, M. S.; Boudjouk, P. *Organometallics* **1984**, *3*, 484. (d) Shin, S. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 900.

(3) (a) Weber, W. P.; Felix, R. A.; Willare, A. K. *Tetrahedron Lett.* **1970**, 907. (b) Litzow, M. R.; Spaulding, T. R. *Mass Spectrometry of Inorganic and Organometallic Compounds*; Physical Inorganic Chemistry Monograph 2; Lappert, M. F., Ed.; American Elsevier: New York, 1973; Chapter 7 and references cited therein.

(4) (a) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 5781 (b) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 2085.

(5) For a recent review of the work on silylium cations, see: Lickiss, P. D. *J. Chem. Soc., Dalton Trans.* **1992**, 1333 and references cited therein.

(6) (a) Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1. (b) O'Brien, D. H.; Hairston, T. J. *Organomet. Chem. Rev. A* **1971**, *7*, 95.

(7) Lambert, J. B.; Schulz, W. J. J. *J. Am. Chem. Soc.* **1983**, *105*, 1671.

(8) Lambert, J. B.; McConnell, J. A.; Schulz, W. J. J. *J. Am. Chem. Soc.* **1986**, *108*, 2482.

(9) Lambert, J. B.; Schilif, W. *J. Am. Chem. Soc.* **1988**, *110*, 6364.

(10) Lambert, J. B.; Schulz, W. J. J.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201.

(11) Lambert, J. B.; Kania, L.; Schilf, W.; McConnell, J. A. *Organometallics* **1991**, *10*, 2578.

(12) Cowley, A. H.; Cushner, M. C.; Riley, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 624.

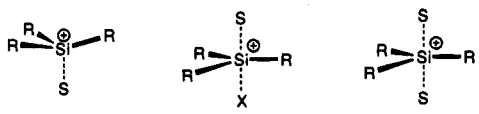
0002-7863/95/1517-7460$09.00/0 © 1995 American Chemical Society

as free ions in dilute solutions of sulfolane (below 0.05 m) and as covalent R_3SiClO_4 or $R_3Si^+ClO_4^-$ ion pairs in equilibrium with the free ionic form, in concentrated sulfolane solutions, and in weakly ionizing solvents such as dichloromethane or 1,2-dichloroethane. $^{35}Cl/^{37}Cl$ NMR measurements support these results by giving a measure for the amount of free ionic perchlorate.[9]

Lambert's results have been questioned by Olah and co-workers,[13-15] who have focused their attention to known difficulties in making solvents free of water down to the low concentrations needed. These authors criticize the methods used to dry solvents, and they argue that residual water impurities in the solvents would cause hydrolization of R_3SiClO_4 to form free perchlorate ions, which would explain the $^{35}Cl/^{37}Cl$ NMR observations. Strong evidence against the alleged observation of free **1** also comes from ^{29}Si NMR measurements on trimethylsilyl perchlorate in sulfolane, which reveal no dependence of δ ^{29}Si on the concentration of the perchlorate.[13,15] The observed ^{29}Si shift of 47 ppm corresponds to that of nondissociated trimethylsilyl perchlorate in solution. Unfortunately, no observations of ^{29}Si shift values for concentrations below 0.1 m have been possible.

Criticism as to the alleged existence of free **1** in solution has also come from other authors.[16] Lambert has rejected this criticism by pointing out that water was present in the solvents used at a molarity 1 order of magnitude below that of the observed silylium cations.[11] Furthermore, he and his co-workers have improved experiments and have published new evidence for free or nearly free **1** in solution.[17,18] Additional evidence supporting Lambert's interpretation of experimental results comes from other authors.[19] Although these results do not offer a final conclusion as to the existence or nonexistence of **1** in condensed phases, they clearly reveal differences between **1** and carbocations. The latter possess similar stabilities for gas and solution phases.[20] ^{13}C NMR chemical shifts for carbocations calculated with ab initio methods for the gas phase agree remarkably well with those obtained experimentally for carbocations in solution phases.[21] It seems that counterions and solvents such as SO_2F_2 and SO_2FCl used in connection with FSO_3H, SbF_5, etc.,[22] do not change the properties of carbocations very much, and therefore, medium effects can often be neglected when discussing the properties of carbocations in solution.

For the properties of **1**, one cannot expect a similar independence of the medium. Silicon can easily extend its coordination sphere by forming hypervalent compounds with five or six ligands, and this tendency is often used in synthetic chemistry.[23] Several ab initio investigations have confirmed that the formation of penta- or even hexacoordinated Si compounds is energetically favorable.[24-29] Therefore, solvents and/or counterions with any nucleophilic character will interact with **1** in solution. One can expect a broad spectrum of interactions ranging from weak association between ions and solvent molecules (S) to strong bonding in $R_3SiX(S)_n$ and $R_3Si(S)_n^+X(S)_m^-$ coordination complexes. The four- and five-coordinated adducts **2**, **3**, and **4** with tetragonal or trigonal bipyramidal geometries can be formed. Even a weakly associated S molecule will transfer more negative charge to Si, thus leading to changes in its electronic structure, geometry, and magnetic properties. For example, charge transfer will shield the Si nucleus and, as a consequence, δ ^{29}Si NMR chemical shifts untypical of a silylium cation will result. Therefore, it is not so much the question whether **1** exists in solution, which has to be answered, but the chemically more demanding question whether **2**, **3**, or **4** still represents to some extent a silylium cation. It is not difficult to predict that totally free **1** does not exist in solution (which is also true in the case of carbocations) and that the degree of association between solvent molecules S (anion X^-) and cations will be much higher for silylium cations than for carbocations. But it is very difficult to exactly describe and classify possible types of ion−ion and ion−solvent interactions.

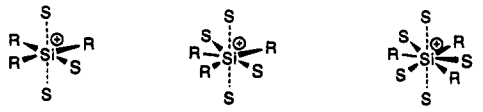


2 **3** **4**

In view of the many controversial experimental observations that have been reported, an investigation of the whole spectrum of possible R_3Si^+−S interactions in solvents S and a clear description of silylium cations in solution is urgently needed. Such a description is best given by ab initio calculations, which with the techniques available today can provide rather accurate data even in those cases where experimental investigations are limited by technical difficulties.

In this paper, we will investigate the different types of association between Si cations and solvent molecules. In particular, we will concentrate on the tetragonal and trigonal bipyramidal adducts **2** and **4**. Apart from this, we will investigate the effects of additional solvent molecules coordinating with the Si cation leading to $SiR_3(S)_n^+$ as in **5** ($n = 3$), **6** ($n = 4$), and **7** ($n = 5$). Typical solvents which have been used in

(13) Olah, G. A.; Heiliger, L.; Li, X. Y.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1990**, *112*, 5991.
(14) Prakash, G. K. S.; Keyaniyan, S.; Aniszfeld, R.; Heiliger, L.; Olah, G. A.; Stevens, R. C.; Choi, H, K.; Bau, R. *J. Am. Chem. Soc.* **1987**, *109*, 5123.
(15) Olah, G. A.; Rasul, G.; Heiliger, L.; Bausch, J.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1992**, *114*, 7737.
(16) Eaborn, C. *J. Organomet. Chem.* **1991**, *405*, 173.
(17) Lambert, J. B.; Zhang, S. *J. Chem. Soc., Chem. Commun.* **1993**, 383.
(18) (a) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917. (b) Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430.
(19) (a) Xie, Z.; Liston, D. J.; Jelinek, T.; Mitro, V.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1993**, 384. (b) Reed, C. A.; Xie, Z. *Science* **1993**, *263*, 986.
(20) *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1968−76; Vols. 1−5.
(21) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020.
(22) Olah, G. A.; Prakash, G. K.; Sommer, J. *Superacids*; Wiley-Interscience: New York, 1985.
(23) For a recent review on hypervalent Si compounds, see: Chult, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.
(24) (a) Marsden, C. J. *Inorg. Chem.* **1983**, *22*, 3177. (b) Chehayber, J. M.; Nagy, S. T.; Lin, C. S. *Can. J. Chem.* **1984**, *62*, 27. (c) Greenberg, A.; Plant, C.; Venanzi, C. A. *J. Mol. Struct. (THEOCHEM)* **1991**, *234*, 291.
(25) (a) Gordon, M. S.; Davis, L. P.; Burggraf, L. W. *Chem. Phys. Lett.* **1989**, *163*, 371. (b) Gordon, M. S.; Carroll, M. T.; Jensen, J. H.; Davis, L. P.; Burggraf, L. W.; Guidry, R. M. *Organometallics* **1991**, *10*, 2657.
(26) Sheldon, J. C.; Hayes, R. N.; Bowie, J. H. *J. Am. Soc.* **1984**, *106*, 7711.
(27) (a) Davis, L. P.; Burggraf, L. W.; Gordon, M. S.; Baldridge, K. K. *J. Am. Chem. Soc.* **1985**, *107*, 4415. (b) Gordon, M. S.; Davis, L. P.; Burggraf, L. W.; Damrauer, R. *J. Am. Chem. Soc.* **1986**, *108*, 7889. (c) Davis, L. P.; Burggraf, L. W.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 3056. (d) Damrauer, R.; Burggraf, L. W.; Davis, L. P.; Gordon, M. S. *J. Am. Chem. Soc.* **1988**, *110*, 6601. (e) Carroll, M. T.; Gordon, M. S.; Windus, T. L. *Inorg. Chem.* **1992**, *31*, 825.
(28) Gordon, M. S.; Carroll, M. T.; Davis, L. P.; Burggraf, L. W. *J. Phys. Chem.* **1990**, *94*, 8125.
(29) (a) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 1686. (b) Deiters, J. A.; Holmes, R. R.; Holmes, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 7672. (c) Deiters, J. A.; Holmes, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 7197.

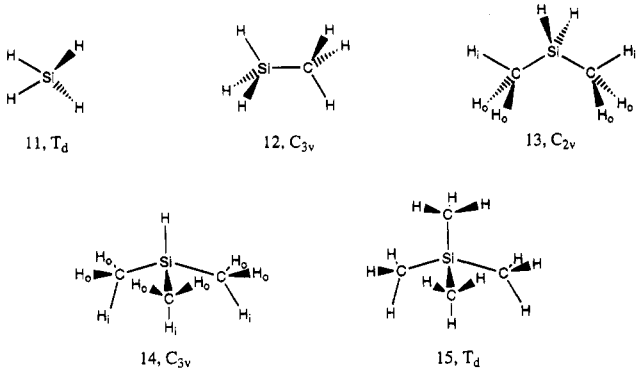


5 6 7

studies on **1**[7-19,30] are summarized in Table 1. They can be classified according to their ionizing strength (dielectricity constant ϵ) and their donicity.[31] Since the calculation of interaction complexes between **1** and sulfolane, HMPA, DMPU, etc., is not feasible, we have used simple model compounds to describe interaction complexes **2**–**7**. In some cases, model solvents contain the same functional group as the actual solvent (e.g., –CN, ROR, –Cl), but in other cases, we have contented ourselves with simple model solvents (H_2O, NH_3) that will provide just a lower limit to the true interactions between **1** and solvents such as HMPA, sulfolane, or pyridine.

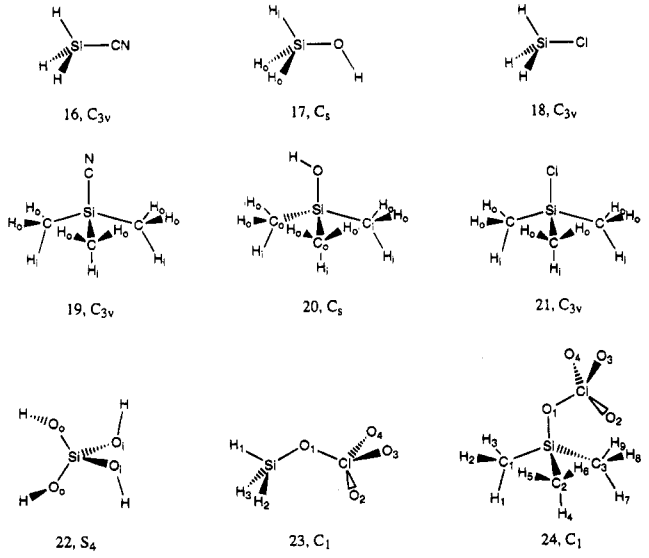
The compounds investigated in this work can be divided into the following six groups (subscripts i and o denote in-plane and out-of-plane atoms with regard to a given reference plane, and a and e denote axial and equatorial positions).

Group I, silane and the four methylsilanes:



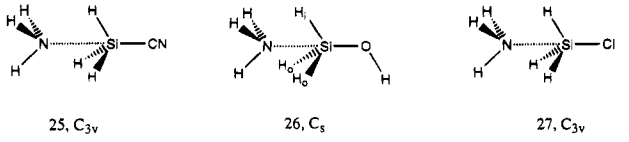
11, T_d 12, C_{3v} 13, C_{2v} 14, C_{3v} 15, T_d

Group II, covalently bonded R_3SiX (**8**) compounds:

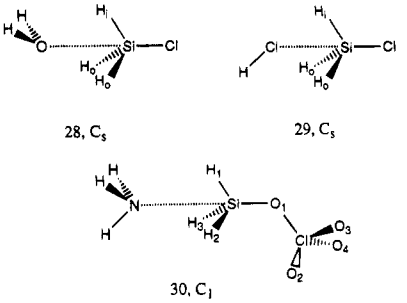


16, C_{3v} 17, C_s 18, C_{3v} 19, C_{3v} 20, C_s 21, C_{3v} 22, S_4 23, C_1 24, C_1

Group III, solvent complexes $R_3SiX(S)$ of group II:

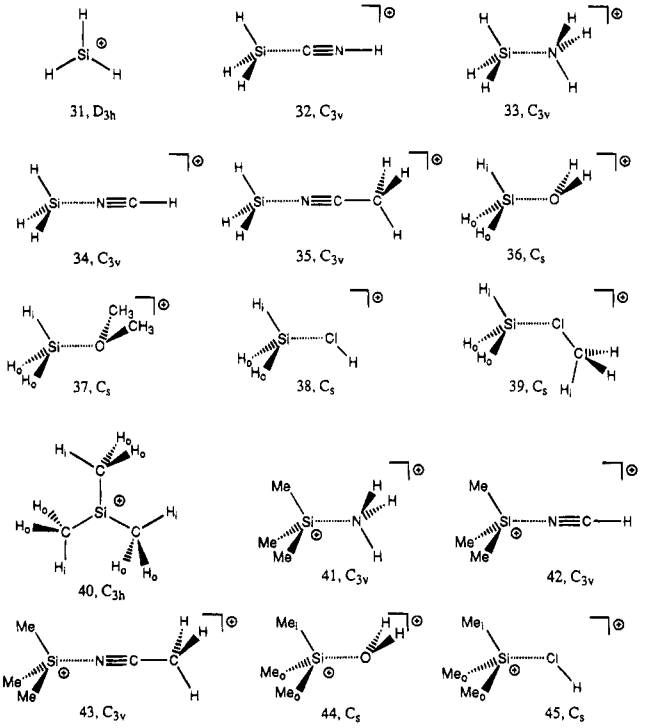


25, C_{3v} 26, C_s 27, C_{3v}



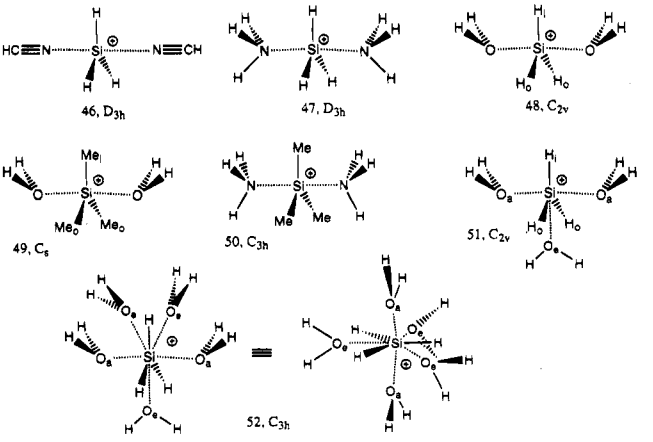
28, C_s 29, C_s 30, C_1

Group IV, silylium cation–solvent complexes of type **2**:



31, D_{3h} 32, C_{3v} 33, C_{3v} 34, C_{3v} 35, C_{3v} 36, C_s 37, C_s 38, C_s 39, C_s 40, C_{3h} 41, C_{3v} 42, C_{3v} 43, C_{3v} 44, C_s 45, C_s

Group V, silylium cation–solvent complexes of types **4**, **5**, **6**, and **7**:



46, D_{3h} 47, D_{3h} 48, C_{2v} 49, C_s 50, C_{3h} 51, C_{2v} 52, C_{3h}

(30) Edlund, U. Personal communication.

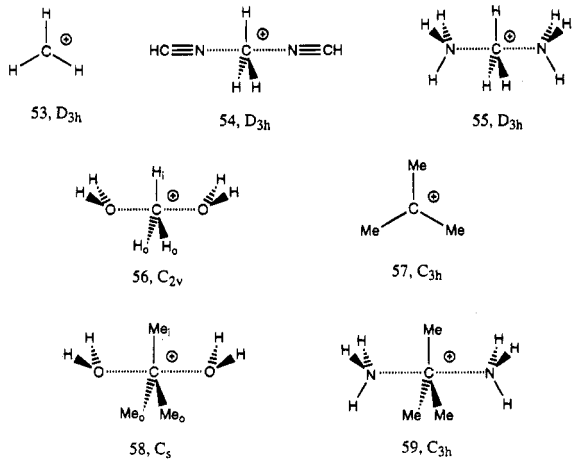
(31) (a) Riddick, J. A.; Bunger, W. B. *Organic Solvents*, 3rd ed.; Techniques of Chemistry, Vol. 2; Weissberger, A., Ed.; Wiley: New York, 1970. (b) Gutmann, V. *Coord. Chem. Rev.* **1976**, *18*, 225.

Table 1. Solvents Used in Experimental Studies of Silylium Cations[a]

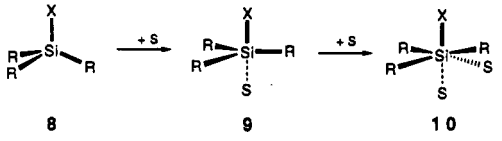
solvent	active site	ϵ value	dipole moment	donicity	model solvent[b]
THF	>O	7.6	1.6	20.0	$(CH_3)_2O$
CH_2Cl_2	−Cl	9.1	1.6	small	HCl, CH_3Cl
pyridine	>N	12.3	2.2	33.1	(NH_3)
sulfolane	$>SO_2$	43.3	4.8	≤29.8	(H_2O)
$(Me_2N)_3PO$ (HMPA)	PO	30	5.5	38.8	(H_2O)
DMPU[c]	>C=O	36.1	4.2	≥26.6	(H_2O)
CH_3CN	−CN	37.5	3.9	14.1	HCN, CH_3CN
$(CH_3)_2SO$ (DMSO)	>SO	46.7	3.9	29.8	(H_2O)
C_6H_6	π-ring	2.3	0	0.1	
H_2O	>O	78.5	1.9	18.0	H_2O

[a] Dielectricity constants from ref 31a; dipole moments in debye from ref 52; donicities from ref 31b. [b] Model solvents are chosen to possess the same functional group. However, in several cases (indicated by parentheses), the model solvent just possesses the same donor atom in a different electronic environment. [c] *N,N*-Dimethylpropylurea.

Group VI, carbocation−solvent complexes $CR_3(S)_2^+$:



Investigation of group I and group II compounds provides needed reference data and, in addition, reveals how well theory can reproduce geometries, stabilities, and NMR chemical shift data of **1** in solution. Covalently bonded Si compounds **8** will also associate with S molecules in solution as indicated by reaction 2. Interaction complexes **9** and **10** may be formed, which will be appropriate reference structures for complexes **4** and **5**.



(2)

In the following, we will discuss the properties of Si compounds belonging to groups I−V and carbocation complexes of group VI. In our discussion, we will concentrate on questions 1−7.

(1) Is ab initio theory able to describe silylium cations in solution?

(2) What are the properties of silylium cations in the gas phase and in noncoordinating solvents?

(3) What happens if silylium cations are generated from covalent R_3SiX compounds in a nucleophilic solvent? Are silyl perchlorates good starting compounds for this process?

(4) How do the properties of silylium cations in nucleophilic solvents differ from those of silylium cation in the gas phase? Can one still speak of silylium cations in the former case?

(5) Is it possible to study the solvation process with experimental means?

(6) Is there any chance to obtain (free or) nearly free silylium cations in solution?

(7) Is there a difference in the solvation of silylium cations compared to that of carbocations?

By answering these questions with the help of ab initio theory, we intend to make a contribution to the pending problem of the existence of silylium cations in solution.

2. Computational Methods

The geometries of compounds **11−51** (above) have been fully optimized using Hartree−Fock (HF) and, in some selected cases, second-order Møller−Plesset perturbation theory (MP2) in connection with the 6-31G(d) and 6-311G(d,p) basis sets, which are of DZ+P and TZ+P quality in the valence shell.[32] In those cases where several conformations exist, the most stable one has been found by repeatedly varying conformational parameters and checking each time second derivatives at the HF/3-21G level of theory.

NMR chemical shift calculations have been carried out with the IGLO (individual gauge for localized orbitals) method of Kutzelnigg and Schindler[33,34] in a version[35] designed for routine calculations with the programs COLOGNE[36] and GAUSSIAN 92.[37] The (11s7p2d/9s5p1d/5s1p) [7s6p2d/5s4p1d/3s1p] basis set recommended by Kutzelnigg and Schindler[34] (called by these authors basis II) for ^{29}Si and ^{13}C NMR chemical shift calculations has been employed, which is a TZ+P basis similar to 6-311G(d,p) but with less primitive GTFs and a smaller degree of contraction. Basis II has been especially designed for NMR chemical shift calculations. In some cases IGLO calculations had to be performed with the 6-31G(d) basis set because of computational limitations. IGLO ^{29}Si shifts for **1** have also been checked with the GIAO-MP2 method of Gauss that contains correlation corrections and, therefore, leads to very reliable results.[38]

We have simulated the influence of the medium by the PISA solvent model[39] where the wave function of the solute is recalculated in a solvent cage under the influence of a polarizable continuum that is characterized by the dielectricity constant ϵ of the solvent. IGLO NMR chemical shifts are then obtained for a solvent-dependent SCF wave function. Such an approach may be denoted as PISA-IGLO/basis-B//HF/basis-A if it is carried out at HF/basis-A geometries.[40]

The nature of cation−solvent interactions has been investigated with the help of the calculated electron density distribution $\varrho(r)$, its associated Laplace concentration $-\nabla^2\varrho(r)$, and the energy density distribution $H(r)$ in the way described by Cremer and Kraka.[41] These authors have given two conditions for the existence of a covalent bond between two atoms A and B:

(1) Atoms A and B have to be connected by a path of maximum electron density (MED). The existence of such a MED path implies a

(32) (a) 6-31G(d): Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) 6-311G(d,p): Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(33) (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919.

(34) Kutzelnigg, W.; Schindler, M.; Fleischer, U. *NMR, Basic Principles and Progress*; Springer: Berlin, 1989; Vol. 23.

(35) Reichel, F. Ph.D. Dissertation, University of Köln, 1991.

(36) Gauss, J.; Kraka, E.; Reichel, F.; Cremer, D. *COLOGNE93*; University of Göteborg: Göteborg, Sweden, 1993.

(37) Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian 92*; Gaussian Inc.: Pittsburgh, PA, 1992.

(38) (a) Gauss, J. Chem. Phys. Lett. **1992**, *191*, 614. (b) Gauss, J. *J. Chem. Phys.* **1993**, *99*, 3629. (c) Gauss, J.; Stanton, J. To be published.

(39) (a) Miertus, S.; Scrocco, E.; Tomasi, *J. Chem. Phys.* **1981**, *55*, 117. (b) Bonaccorsi, R.; Cimiraglia, R.; Tomasi, J. *J. Comput. Chem.* **1983**, *4*, 567. (c) Bonaccorsi, R.; Pala, P.; Tomasi, J. *J. Am. Chem. Soc.* **1984**, *106*, 1945. (d) Pascual-Ahuir, J. L.; Silla, E.; Tomasi, J.; Bonaccorsi, R. *J. Comput. Chem.* **1987**, *8*, 778.

(40) Reichel, F.; Cremer, D. To be published.

(41) (a) Cremer, D.; Kraka, E. *Croat. Chem. Acta* **1984**, *57*, 1259. (b) Cremer, D.; Kraka, E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 62.

(3, −1) saddle point r_b of the electron density distribution $\varrho(r)$ as well as a zero-flux surface between A and B (necessary condition). (2) The local energy density $H(r_b)$ has to be stabilizing, i.e. it must be smaller than zero (sufficient condition).

These two criteria have helped to distinguish covalent bonding from noncovalent, ionic, or electrostatic interactions in many cases and to characterize covalent bonding in molecules with both classical and nonclassical structures.[42,43] The bond analysis is based on the virial partitioning method of Bader and co-workers,[44] which has been derived from first principles and is particularly suited to be applied in connection with ab initio calculations.

Calculations have been performed on a CRAY YMP-464 using the ab initio program packages COLOGNE,[36] GAUSSIAN92,[37] and ACES.[45]

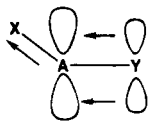
3. Results and Discussion

For molecules **11**−**59**, which can adopt several conformations, the most stable conformations and their symmetries are given above. Calculated energies of **11**−**59** are summarized in the supporting information deposited with this paper. HF/6-31G(d) and in some cases HF/6-311G(d,p) geometries together with the available experimental data are listed in Table 2. In Tables 3 and 4, the calculated interaction energies for group III, IV, V, and VI compounds and methyl stabilization energies are listed. IGLO chemical shifts are given in Table 5 for neutral Si compounds and in Table 6 for compounds with potential silylium and carbocation character. Tables 7 and 8 contain calculated charges, dipole moments, and the relevant data of the bond density analysis. Finally, in Table 9, properties of weakly associating $SiR_3(S)^+$ complexes can be found.

Methylsilanes (Group I). When replacing stepwise the H atoms of SiH_4 (**11**) by methyl groups, compounds **12**, **13**, **14**, and **15** are formed. Calculated geometries suggest that both the SiC (1.89 Å, Table 2) and the SiH bond lengths (1.48 Å) increase negligibly by 0.002 and 0.001 Å, respectively, with each methyl group, which is in line with experimental observations.[46] Methyl groups slightly destabilize silane, which is reflected by the calculated SiC−SiC interaction energies (−0.1 to −0.7 kcal/mol, Table 4) obtained from the isodesmic reaction 3:

$$(CH_3)_nSiH_{4-n} + (n-1)SiH_4 \rightarrow nCH_3SiH_3 \qquad (3)$$

Obviously, methyl or alkyl silanes take an intermediate position between alkanes, which benefit from stabilizing CC−CC interaction energies (2−12 kcal/mol[47,48]), and stannanes, which are clearly destabilized by alkyl groups (−1 to −5 kcal/mol[49]). Stabilizing interactions result from complementing σ-withdrawing, π-donating interactions between two substituents X and Y and a central atom A.[47]



A = C, Si, Sn

X, Y = CH_3, NH_2, OH, F

Since C is more electronegative than Si, a methyl (alkyl) group (X) can withdraw electronic charge from Si (A) thus making it prone to accept electrons from another methyl group (Y) via its pπ- (or pseudo π-) orbitals. This, however, requires that pπ- (or pseudo-π-) orbitals efficiently overlap, which is the case when A, X, and Y are all first row elements. Accordingly, stabilizing AX−AY bond−bond interactions are found. In the series 2pπ(C)−2pπ(C), 2pπ(C)−3pπ(Si), and 2pπ(C)−5pπ(Sn), overlap is more and more reduced, thus decreasing π-donation to the central atom A. As a consequence, the σ-withdrawal ability of the substituents prevails, leading to increasingly negative charges at X and Y, which in turn cause Coulomb repulsion between substituents and, accordingly, destabilizing bond−bond interactions.

With a weak first row π-donor such as methyl, bond−bond interactions are negligible, but with stronger σ-acceptor, π-donor substituents such as F, OH, or NH_2, 2pπ(Y)−3pπ(Si) overlap is still large enough to lead to considerable bond−bond interaction energies. For example, $Si(OH)_4$ (**22**) possesses stabilizing interaction energies of 28.5 kcal/mol (HF/6-31G(d)) and 26.0 kcal/mol (HF/basis II), respectively.

Experimentally observed SiC bond lengths are 0.02 Å shorter while SiH bond lengths are slightly longer than the corresponding HF/6-31G(d) values. At the HF/6-311G(d,p) level, agreement between experimental and computed bond lengths is slightly but not substantially improved (Table 2). Since relative energies, charge distributions, and other molecular properties also do not change significantly when going from 6-31G(d) to 6-311G(d,p), we conclude that there is no need to perform geometry optimizations with the more expensive TZ+P basis set.

This is also reflected by the IGLO NMR chemical shifts, which for ^{29}Si and ^{13}C coincide within 1 ppm when calculated with HF/6-31G(d) and HF/6-311G(d,p) geometries (Tables 5 and 6). Both IGLO/basis II//HF/6-31G(d) and IGLO/basis II//HF/6-311G(d,p) values are in excellent agreement with measured ^{29}Si and ^{13}C chemical shifts[50] (Table 5). This observation has also been made by other authors,[34,15] and therefore, we exclusively refer to IGLO/basis II//HF/6-31G(d) NMR chemical shifts in the following discussion.

(42) (a) Kraka, E.; Cremer, D. In *Theoretical Models of the Chemical Bond, Part 2: The Concept of the Chemical Bond*; Maksic, Z. B., Ed.; Springer: Berlin, 1990, p 453. (b) Cremer, D. In *Modelling of structure and properties of molecules*; Maksic, Z. B., Ed.; Ellis Horwood: Chichester, England, 1988; p 125. (c) Cremer, D.; Kraka, E. In *Molecular Structure and Energetics, Structure and Reactivity*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1988; Vol. 7, p 65. (d) Cremer, D. *Tetrahedron* **1988**, *44*, 7427.

(43) (a) Cremer, D.; Gauss, J.; Schleyer, P. v. R.; Budzelaar, P. H. M. *Angew. Chem., Int. Edt. Engl.* **1984**, *23*, 370. (b) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800, 3811. (c) Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467. (d) Cremer, D.; Bock, C. W. *J. Am. Chem. Soc.* **1986**, *108*, 3375. (e) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D.; Sawaryn, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 5732. (f) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1986**, *108*, 5808. (g) Budzelaar, P. H. M.; Cremer, D.; Wallasch, M.; Würthwein, E.-U.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 6290. (h) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D.; Collins, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5917. (i) Cremer, D.; Gauss, J.; Kraka, E. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 531. (j) Frenking, G.; Koch, W.; Reichel, F.; Cremer, D. *J. Am. Chem. Soc.* **1990**, *112*, 4240.

(44) (a) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* **1981**, *44*, 893. (b) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem*, **1981**, *14*, 63.

(45) Stanton, J. F.; Gauss, J.; Watts, J. D.; Lauderdale, W. J.; Bartlett, R. J. *ACES II*, Quantum Theory Project, University of Florida, 1992.

(46) (a) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 621. (b) Hengge, E.; Keller-Rudek, H.; Koschel, D.; Krüerke, U.; Merlet, P. *Silicon, Gmelin Handbook of Inorganic Chemistry*; Springer: Berlin, 1982; Suppl. Vol. B1.

(47) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 289.

(48) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.

(49) Cremer, D.; Olsson, L.; Reichel, F.; Kraka, E. *Isr. J. Chem.* **1993**, *33*, 369.

(50) (a) Williams, E. A.; Caryioli, J. D. *Annu. Rep. NMR Spectrosc.* **1979**, *9*, 221. (b) Löwer, R.; Vongehr, M.; Marsmann, H. C. *Chem.-Ztg.* **1975**, *99*, 33. (c) Harris, R. K.; Kimber, B. J. *J. Magn. Reson.* **1975**, *17*, 174. (d) Niemann, U.; Marsmann, H. C. *Z. Naturforsch.* **1975**, *30b*, 202. (e) Marsmann, H. C.; Horn, H.-G. *Z. Naturforsch.* **1972**, *27b*, 1448. (f) Löwer, R.; Vongehr, M.; Marsmann, H. C. *Chem. Ztg.* **1972**, *96*, 456.

(51) Bergmann, D.; Hinze, J. T. *Struct. Bonding* **1987**, *66*, 145.

Table 2. Calculated Geometries of Molecules **11**–**59**[a]

molecule	sym	parameters
11, SiH_4	*Td*	SiH 1.475, *1.477*
12, SiH_3CH_3	C_{3v}	SiC 1.888, *1.882* (1.867); SiH 1.478, *1.480* (1.485); CSiH 111.1, *110.5* (110.7); SiCH 111.6, *110.9* (111.2)
13, $CH_3SiH_2CH_3$	C_{2v}	SiC 1.890, *1.884* (1.867); SiH 1.481, *1.483* (1.483); CSiC 111.4, *111.3* (111.0); HSiH 107.5, *107.6* (107.8); $SiCH_i$ 111.3, *111.1*; $SiCH_o$ 111.2, *111.1*; H_oCH_o 107.7, *107.9* (108.0)
14, $(CH_3)_3SiH$	C_{3v}	SiC 1.891, *1.886* (1.868); SiH 1.484, *1.487* (1.489); CSiC 110.4, *110.4* (110.2); CSiH 108.5, *108.6*; $SiCH_i$ 111.4, *111.2*; $SiCH_o$ 111.4, *111.2* (108.0); H_oCH_o 107.5, *107.7*
15, $(CH_3)_4Si$	T_d	SiC 1.894, *1.888*; SiCH 111.5, *111.3*
16, SiH_3CN	C_{3v}	SiC 1.866; SiH 1.467; CN 1.138; CSiH 107.5
17, SiH_3OH	C_s	SiO 1.647, *1.639*; SiH_i 1.469 *1.471*; SiH_o 1.477 *1.479*; OH 0.946, *0.939*; $OSiH_i$ 106.9, *106.9*; $OSiH_o$ 111.4, *111.4*; H_oSiH_o 107.6, *107.7*; SiOH 119.0, *121.6*
18, SiH_3Cl	C_{3v}	SiCl 2.068, *2.070* (2.048); SiH 1.468, *1.468* (1.50); ClSiH 108.3, *107.9*
19, $(CH_3)_3SiCN$	C_{3v}	SiC_N 1.886; SiC_M 1.880; CN 1.139; CSiC 106.7; $SiCH_i$ 110.6; $SiCH_o$ 111.5; H_oCH_o 107.7
20, $(CH_3)_3SiOH$	C_s	SiO 1.661; SiC_i 1.877; SiC_o 1.887; OH 0.946; $OSiC_i$ 105.5; $OSiC_o$ 110.2; C_0SiC_0 109.2; SiOH 118.6; SiC_iH_i 111.6; SiC_iH_o 111.0; $H_oC_iH_o$ 107.5; $SiC_oH_{i'}$ 111.2; SiC_oH_o 111.9; $SiC_oH_{o'}$ 111.2; $H_oC_oH_{o'}$ 107.5; $H_oC_oH_{i'}$ 107.1; $H_{o'}C_oH_{i'}$ 107.6
21, $(CH_3)_3SiCl$	C_{3v}	SiCl 2.095, *2.099*; SiC 1.879, *1.872*; ClSiCC 107.3, *107.2*; $SiCH_i$ 110.6, *110.3*; $SiCH_o$ 111.4, *111.3*; H_oCH_o 107.8, *108.0*
22, $Si(OH)_4$	S_4	SiO 1.629; OH 0.947; O_iSiO_i 106.4; O_oSiO_i 115.8; SiOH 117.0; HO_iSiO_i 84.8
23, SiH_3OClO_3	C_1	SiO 1.737, *1.727*; O_1Cl 1.571, *1.562*; ClO_2 1.425, *1.417*; ClO_3 1.415, *1.406*; ClO_4 1.411, *1.402*; SiH_1 1.462, *1.463*; SiH_2 1.461, *1.464*; SiH_3 1.461, *1.463*; SiOCl 124.0, *127.6*; $OClO_2$ 104.5, *104.5*; $OClO_3$ 105.4, *105.4*; $OClO_4$ 104.4, *104.6*; $OSiH_1$ 100.9, *101.3*; $OSiH_2$ 108.2, *107.8*; $OSiH_3$ 108.6, *108.2*; $SiOClO_2$ 25.2, *22.0*; $SiOClO_3$ −94.3, *−97.5*; $SiOClO_4$ 145.2, *141.9*; $ClOSiH_1$ 168.1, *169.7*; $ClOSiH_2$ 49.4, *50.7*; $ClOSiH_3$ −73.5, *−71.4*
24, $(CH_3)_3SiOClO_3$	C_1	SiO 1.770; O_1Cl 1.557; ClO_2 1.426; ClO_3 1.419; ClO_4 1.413; SiC_1 1.870; SiC_2 1.870; SiC_3 1.869; SiOCl 127.3; $OClO_2$ 105.7; $OClO_3$ 105.8; $OClO_4$ 104.4; $OSiC_1$ 99.7; $OSiC_2$ 108.4; $OSiC_3$ 107.1; SiC_1H_1 110.7; SiC_1H_2 111.2; SiC_1H_3 111.3; SiC_2H_4 109.5; SiC_2H_5 111.6; SiC_2H_6 112.1; SiC_3H_7 110.3; SiC_3H_8 111.6; SiC_3H_9 111.1; $ClOSiC_1$ 161.4; $ClOSiC_2$ 42.5; $ClOSiCC_3$ −80.6; $SiOClO_2$ 36.3; $SiOClO_3$ −83.4; $SiOClO_4$ 156.4; $OSiC_1H_1$ 178.0; $OSiC_1H_2$ −62.1; $OSiC_1H_3$ 58.2; $OSiC_2H_4$ 173.6; $OSiC_2H_5$ 54.3; $OSiC_2H_6$ −67.0; $OSiC_3H_7$ −174.1; $OSiC_3H_8$ 65.9; $OSiC_3H_9$ −54.8;
25, $H_3N{\cdot}SiH_3CN$	C_{3v}	SiN 2.819; SiC 1.891; SiH 1.464; CN 1.139; CSiH 103.7; NH 1.003; SiNH 111.6
26, $H_3N{\cdot}SiH_3OH$	C_s	SiN 3.031; SiO 1.661; SiH_1 1.466; SiH_o 1.476; OH 0.946; NSiO 176.7; $OSiH_i$ 104.3; $OSiH_o$ 109.0; H_oSiH_o 109.7; SiOH 118.0; NH 1.026; SiNH 111.0
27, $H_3N{\cdot}SiH_3Cl$	C_{3v}	SiN 2.780; SiCl 2.104; SiH 1.464; ClSiH 104.2; NH 1.003; SiNH 111.5
28, $H_2O{\cdot}SiH_3Cl$	C_s	SiO 2.912; SiCl 2.088; SiH_i 1.466; SiH_o 1.464; OH 0.948; OSiCl 178.6; $ClSiH_i$ 105.9; $ClSiH_o$ 106.1; H_oSiH_o 113.1; SiO(HH) 145.4; HOH 106.1
29, $HCl{\cdot}SiH_3Cl$	C_s	$SiCl_H$ 4.049; SiCl 2.071; SiH_i 1.468; SiH_o 1.467; ClH 1.267; ClSiCl 176.9; $ClSiH_i$ 107.9; SiH_o 108.0; H_oSiH_o 111.0; SiClH 105.3
30, $H_3N{\cdot}SiH_3OClO_3$	C_1	SiN 2.317; SiO 1.822; O_1Cl 1.544; ClO_2 1.429; ClO_3 1.422; ClO_4 1.417; SiH_1 1.460; SiH_2 1.458; SiH_3 1.458; NH 1.005; OSiN 176.0; SiOCl 124.0; $OClO_2$ 105.8; $OClO_3$ 106.3; $OClO_4$ 105.2; $OSiH_1$ 92.5; $OSiH_2$ 99.2; $OSiH_3$ 99.2; $SiOClO_2$ 35.0; $SiOClO_3$ −84.6; $SiOClO_4$ 155.1; $ClOSiH_1$ 163.9; $ClOSiH_2$ 44.1; $ClOSiH_3$ −77.3; SiNH 110.7; H_1SiNH 180.0
31, SiH_3^+	D_{3h}	SiH 1.454, *1.457*
32, SiH_3CNH^+	C_{3v}	SiC 1.984, *1.982*; SiH 1.457, *1.460*; CN 1.128, *1.124*; NH 0.999, *0.999*; CSiH 101.1, *101.1*
33, $SiH_3NH_3^+$	C_{3v}	SiN 1.917, *1.904*; SiH 1.457, *1.460*; NH 1.012, *1.010*; NSiH 102.2, *102.4*; SiNH 112.2, *112.1*
34, SiH_3NCH^+	C_{3v}	SiN 1.888, *1.885*; SiH 1.455, *1.458*; NC 1.125, *1.121*; NSiH 101.4, *101.3*
35, $SiH_3NCCH_3^+$	C_{3v}	SiN 1.856; SiH 1.456; NC 1.131; CC 1.465; NSiH 102.5
36, $SiH_3OH_2^+$	C_s	SiO 1.859, *1.846*; SiH_i 1.454, *1.457*; SiH_o 1.454, *1.457*; OH 0.960, *0.953*; $OSiH_i$ *103.2*, 103.2; $OSiH_o$ 99.5, *99.7*; H_oSiH_o 117.5, *117.3*; SiO(HH) 171.5, *176.9*; HOH 110.9, *111.0*
37, $SiH_3O(CH_3)_2^+$	C_s	SiO 1.796; SiH_i 1.459; SiH_o 1.456; OC 1.466; $OSiH_i$ 104.8; $OSiH_o$ 102.2; H_oSiH_o 115.8; SiOC 121.6; COC 114.2
38, SiH_3ClH^+	C_s	SiCcl 2.339, *2.340*; SiH_i 1.453, *1.456*; SiH_o 1.454, *1.456*; ClH 1.278, *1.284*; $ClSiH_i$ 95.4, *95.9*; $ClSiH_o$ 99.9, *99.6*; H_oSiH_o 117.3, *117.4*; SiClH 104.8, *103.1*

Table 2 (Continued)

molecule	sym	parameters
39, $SiH_3ClCH_3^+$	C_s	SiCl 2.248; SiH_i 1.454; SiH_o 1.456; ClC 1.859; $ClSiH_i$ 98.3; $ClSiH_o$ 101.6; H_oSiH_o 115.7; SiClC 108.7; $ClCCH_i$ 103.2; $ClCH_o$ 106.4; H_oCH_o 114.1
40, $(CH_3)_3Si^+$	C_{3h}	SiC 1.847, *1.838*; $SiCH_i$ 112.6, *112.6*; $SiCH_o$ 110.1, *109.7*; H_oCH_o 106.4, *106.5*
41, $(CH_3)_3SiNH_3^+$	C_{3v}	SiN 1.957; SiC 1.865; NSiC 102.5; $SiCH_i$ 109.6; $SiCH_o$ 112.4; H_oCH_o 108.4; SiNH 112.2
42, $(CH_3)_3SiNCH^+$	C_{3v}	SiN 1.940; SiC 1.862; NC 1.125; NSiC 101.2; $SiCH_i$ 109.4; $SiCH_o$ 112.1; H_oCH_o 108.5
43, $(CH_3)_3SiNCCH_3^+$	C_{3v}	SiN 1.902; SiC 1.864; NC 1.131; CC 1.466; NSiC 102.2; $SiCH_i$ 109.6; $SiCH_o$ 112.0; H_oCH_o 108.4; CCH 108.9
44, $(CH_3)_3SiOH_2^+$	C_s	SiO 1.910; SiCC 1.860; OH 0.958; $OSiC_i$ 103.1; $OSiC_o$ 99.4; SiO(HH) 165.1; HOH 110.3; $SiCH_i$ 109.5; $SiCH_o$ 112.3; H_oCH_o 108.4;
45, $(CH_3)_3SiClH^+$	C_s	SiCl 2.545; SiC_i 1.855; SiC_o 1.855; ClH 1.274; $ClSiC_i$ 94.3; $ClSiH_o$ 99.2; C_oSiC_o 118.0; SiClH 106.5; SiC_iH_i 108.4; SiC_iH_o 112.3; $H_oC_iH_o$ 109.1
46, $SiH_3(NCH)_2^+$	D_{3h}	SiN 2.096, *2.109*; SiH 1.451, *1.453*; NC 1.127, *1.122*; CH 1.066, *1.064*
47, $SiH_3(NH_3)_2^+$	D_{3h}	SiN 2.073, *2.066*; SiH 1.460, *1.463*; NH 1.008, *1.007*; SiNH 112.1, *112.0*
48, $SiH_3(OH_2)_2^+$	C_{2v}	SiO 2.027; SiH_i 1.454; SiH_o 1.455; OH 0.947; SiO(HH) 175.8; H_oSiH_o 121.3; HOH 109.7
49, $(CH_3)_3Si(OH_2)_2^+$	C_s	SiC_i 1.868; SiC_o 1.864; SiO 2.176; OH 0.946; $SiCH_i$ 112.3; C_oSiC_o 119.4; HOH 108.6
50, $(CH_3)_3Si(NH_3)_2^+$	C_{3v}	SiC 1.887; SiN 2.149; NH 1.007; SiCH 112.7; SiNH 112.3; CSiNH 68.2
51, $SiH_3(OH_2)_3^+$	C_{2v}	SiO_a 2.026; SiO_e 3.172; SiO_a(HH) 174.9; SiH_i 1.457; SiH_o 1.451; HO_a 0.946; HO_e 0.943; H_oSiH_o 126.6; HO_aH 109.9; HO_eH 105.3
52, $SiH_3(OH_2)_5^+$	C_{3h}	SiO_a 2.044; $SiO_{e'}$ 3.387; $SiO_{e''}$ 3.593; SiH_i 1.453; SiH_o 1.449; SiO_a(HH) 165.6; SiO_e(HH) 178.3; H_oSiH_o 123.0; O_aH 0.946; $O_{e'}H$ 0.942; $O_{e''}H$ 0.942; HO_aH 110.0; $HO_{e'}H$ 105.3; $HO_{e''}H$ 104.8
53, CH_3^+	D_{3h}	CH 1.078
54, $CH_3(NCH)_2^+$	C_{3v}	CN 2.107; CH 1.067; NC 1.128; CH 1.064
55, $CH_3(NH_3)_2^+$	C_{3v}	CCN 2.075; CH 1.065; NH 1.006; CNH 112.0
56, $CH_3(OH_2)_2^+$	C_{2v}	CO 2.041; CH_i 1.065; CH_o 1.064; H_oCH_i 120.6; OCH_i 91.1; OH 0.952; HOH 107.7
57, $(CH_3)_3C^+$	C_{3h}	CC 1.473; CH 1.084; CCHi 113.7; CCH_o 108.2
58, $(CH_3)_3C(OH_2)_2^+$	C_s	CO_1 2.715; CO_2 2.872; CC_i 1.471; CC_o 1.481; O_1H 0.950; O_2H 0.950; O_2CC_i 91.3, *91.1*; CO_1(HH) 71.2; CO_2(HH) 179.4; C_oCC_i 120.9; HO_1H 105.2; HO_2H 105.1
59, $(CH_3)_3C(NH_3)_2^+$	C_{3v}	CC 1.478; CN 2.928; CH 1.082; NH 1.005; CNH 113.1; CCNH 76.3

[a] Distances in Å, angles in deg. For the notation of the atoms see structure in text. CH bond lengths are not given. In complexes $R_3SiX(AH_n)$ (**25**−**30**) not all AH parameters are given. Numbers in italics correspond to HF/6-311G(d,p) geometries, numbers in parantheses to experimental geometries taken from ref 46.

As described above, methyl groups lead to charge withdrawal from Si, which is also reflected by the charges listed in Table 7. The IGLO ^{29}Si chemical shifts show a clear dependence on the partial charge at Si, as is shown in Figure 1. For example, three methyl groups deshield the Si nucleus so strongly that a downfield shift of 82 ppm results for δ ^{29}Si (Table 5). This has to be kept in mind when computational results for H_3SiX are compared with experimental data obtained for alkyl-substituted systems R_3SiX.

Covalently Bonded R_3SiX Compounds (Group II). Molecules **16**−**24** similarly to molecules **11**−**15** have been investigated to obtain suitable reference data of covalently bonded Si compounds. For R = CH_3, geometries and NMR chemical shifts of R_3SiX are known in some cases and, accordingly, these data provide an additional possibility of analyzing the reliability of HF/6-31G(d) geometries and IGLO/basis II//HF/6-31G(d) shift values. Apart from this, we have selected molecules that with regard to the electronic nature of the substituent X are close to X = $OClO_3$ since experimental attempts to generate silylium cations have concentrated on $R_3SiOClO_3$ compounds such as **24**.

Calculated geometries indicate that typical HF/6-31G(d) SiC, SiO, and SiCl bond lengths are 1.88, 1.65, and 2.08 Å, respectively, which are 0.01−0.02 Å longer than experimentally observed bond lengths (Table 2). Both calculated and observed bond lengths[46] reveal that replacement of all H atoms of SiH_3X by methyl groups increases SiX bond lengths by about 0.02 Å. This is parallel to a stabilization measured by the isodesmic reaction 4 by 4−5 kcal/mol (see Table 4) and reflects the

$$(CH_3)_3SiX + SiH_4 \rightarrow (CH_3)_3SiH + SiH_3X \qquad (4)$$

increase in σ-acceptor−π-donor interactions between X and the methyl groups. There are not enough data to establish clear trends. However, both stronger π-donors (X = CN) and π-donors with better overlap (Cl) seem to increase stabilization. The strongest effect (9 kcal/mol, Table 4) is calculated for perchlorate **24**, which is a consequence of the fact that the $OClO_3$ group atom in **23** and **24** is much more electron withdrawing than a normal OH group as in **17** or **20**.

It has to be noted that our HF/6-31G(d) geometry of the perchlorate **24** differs from that published by Olah and co-workers.[15] It seems that differences result from the fact that these authors assumed C_s symmetry for **24**, while a full geometry optimization without any symmetry constraints leads to a C_1 form of lower energy and different geometry. The same is true for SiH_3OClO_3 (**23**), which may be best characterized by 25° and 12° rotations of ClO_3 and SiH_3 groups out of the C_s-symmetrical form (Table 2). The corresponding angles for **24** are 36 and 19°, respectively (Table 2). Parallel to these deviations from C_s symmetry is a shortening of the three ClO bonds, which probably results from anomeric delocalization of O electron lone pairs and hyperconjugative effects of the Me groups. This is in line with the fact that both SiO and O_1Cl bonds of **24** are longer for the C_1 form than the C_s form calculated by Olah and co-workers.[15]

Table 3. Calculated Complexation Energies and Proton Affinities[a]

molecule	sym	6-31G(d)	TZ+P[b]	6-311G(d,p)
A. Complexation Energies				
25, $H_3N{\cdot}SiH_3CN$	C_{3v}	6.1	4.8	
26, $H_3N{\cdot}SiH_3OH$	C_s	3.2	2.3	
27, $H_3N{\cdot}SiH_3Cl$	C_{3v}	5.9	3.9	
28, $H_2O{\cdot}SiH_3Cl$	C_s	4.2	3.0	
29, $HCl{\cdot}SiH_3Cl$	C_s	0.6	0.9	
30, $H_3N{\cdot}SiH_3OClO_3$	C_1	12.3	8.9	
32, SiH_3CNH^+	C_{3v}	62.9	61.4	59.8
33, $SiH_3NH_3^+$	C_{3v}	77.8	76.6	76.0
34, SiH_3NCH^+	C_{3v}	59.6	59.9	58.0
35, $SiH_3NCCH_3^+$	C_{3v}	72.0	72.3	
36, $SiH_3OH_2^+$	C_s	57.7	56.4	56.9
37, $SiH_3O(CH_3)_2^+$	C_s	70.0	70.2	
38, SiH_3ClH^+	C_s	22.6	26.0	21.6
39, $SiH_3ClCH_3^+$	C_s	36.5	40.6	
41, $(CH_3)_3SiNH_3^+$	C_{3v}	56.6	54.4	
42, $(CH_3)_3SiNCH^+$	C_{3v}	40.1	40.1	
43, $(CH_3)_3SiNCCH_3^+$	C_{3v}	50.5	50.6	
44, $(CH_3)_3SiOH_2^+$	C_s	40.6	38.8	38.7
45, $(CH_3)_3SiClH^+$	C_s	9.3	12.2	
46, $SiH_3(NCH)_2^+$	D_{3h}	79.9	80.0	77.5
47, $SiH_3(NH_3)_2^+$	D_{3h}	109.1	105.0	104.7
48, $SiH_3(OH_2)_2^+$	C_{2v}	83.3	79.9	81.9
49, $(CH_3)_3Si(OH_2)_2^+$	C_s	52.5	47.7	49.7
50, $(CH_3)_3Si(NH_3)_2^+$	C_{3h}	72.0	65.7	
51, $SiH_3(OH_2)_3^+$	C_{2v}	91.7	87.7	90.4
52, $SiH_3(OH_2)_5^+$	C_{2v}	102.7	97.8	101.8
54, $CH_3(NCH)_2^+$	D_{3h}	63.6	61.9	
55, $CH_3(NH_3)_2^+$	D_{3h}	86.0	78.6	
56, $CH_3(OH_2)_2^+$	C_{2v}	64.0	58.9	
58, $(CH_3)_3C(OH_2)_2^+$	C_s	25.7	23.2	
59, $(CH_3)_3C(NH_3)_2^+$	C_{3h}	27.2	23.6	
60, $(CH_3)_2O{\cdot}SiH_3Cl$	C_s	3.8	2.9	
B. Proton Affinities				
16, SiH_3CN	C_{3v}	194.5	195.2	
53, SiH_3NH_2	C_s	221.7	220.7	
17, SiH_3OH	C_s	189.0	189.6	
18, SiH_3Cl	C_{3v}	151.6	158.1	
20, $(CH_3)_3SiOH$	C_s	203.2	204.0	
21, $(CH_3)_3SiCl$	C_{3v}	168.7	175.2	

[a] All values in kcal/mol. [b] [7s6p2d/5s4p1d/3s1p].

Table 4. Calculated Methyl Stabilization Energies[a]

molecule	sym	6-31G(d)	TZ+P[b]
19, $(CH_3)_3SiCN$	C_{3v}	4.8	4.7
20, $(CH_3)_3SiOH$	C_s	4.7	3.9
21, $(CH_3)_3SiCl$	C_{3v}	5.6	5.1
24, $(CH_3)_3SiOClO_3$	C_1	9.0	8.3
40, $(CH_3)_3Si^+$	C_{3h}	36.0	36.0
41, $(CH_3)_3SiNH_3^+$	C_{3v}	14.7	13.8
42, $(CH_3)_3SiNCH^+$	C_{3v}	16.5	16.2
43, $(CH_3)_3SiNCCH_3^+$	C_{3v}	14.4	14.2
44, $(CH_3)_3SiOH_2^+$	C_s	18.9	18.3
45, $(CH_3)_3SiClH^+$	C_s	22.7	22.7
49, $(CH_3)_3Si(OH_2)_2^+$	C_s	5.3	3.7
50, $(CH_3)_3Si(NH_3)_2^+$	C_{3h}	1.1	3.3
57, $(CH_3)_3C^+$	C_s	67.7	67.5
58, $(CH_3)_3C(OH_2)_2^+$	C_s	29.5	31.8
59, $(CH_3)_3C(NH_3)_2^+$	C_{3h}	9.0	12.5

[a] Stabilization energies are given by the energy of the formal reaction 4; all energies in kcal/mol. [b] Basis II: [7s6p2d/5s4p1d/3s1p].

Since $OClO_3$ is a very strong electron-withdrawing group with an estimated group electronegativity larger than 5 (χ(OH) = 3.58, χ(Cl) = 2.94, χ(CN) = 3.78[51]), Si bears a relatively large positive charge in both **23** and **24** (Table 7). The SiO bond is lengthened to 1.74 (**23**) and 1.77 Å (**24**, Table 2), which is 0.1 Å longer than a normal SiO bond in compounds such as **17** or **20**. Dissociation, in particular when assisted by a polar medium, should be facilitated. We calculate with IGLO/basis II a δ ^{29}Si of 44 ppm for **24** which agrees with the corresponding values found for **24** in various solutions (27−47 ppm).[15,30] Olah and co-workers[15] get from IGLO/[7s6p2d/5s4p1d/3s] calculations (basis II without polarization functions for H) δ ^{29}Si = 40.2 ppm, indicating that the difference in geometries leads to a 4 ppm shift difference. Since IGLO/PISA calculations reduce the δ ^{29}Si value for perchlorates **23** and **24** only slightly, ^{29}Si shift values of **24** for weakly nucleophilic solvents should be at 40−50 ppm, but change to higher field in the case of coordination with more nucleophilic solvent molecules (see below).

IGLO ^{29}Si NMR chemical shifts for SiH_3X are between −87 (X = CN) and −28 ppm (X = $OClO_3$) and between −10 and 70 ppm for the corresponding $Si(CH_3)_3X$ compounds, in reasonable agreement with experiment (Table 5). Three methyl groups lead to downfield shifts of 60−90 ppm, which on the average is somewhat smaller than the corresponding value for SiH_4 (82 ppm, Table 5). Calculated δ ^{29}Si values show some dependence on the charge at Si and, thereby, the electronic nature of X although there is no simple relationship between δ ^{29}Si and the (group) electronegativity of X.

Complexes between R_3SiX and Solvent Molecules (Group III). In view of the relatively large positive charge at Si in covalently bonded molecules (see Table 7), it is possible that in solution these molecules are able to coordinate one or more solvent molecules S at Si provided the latter are strong enough nucleophiles. There is ample experimental evidence on the existence of penta- or hexacoordinated Si complexes in solution,[23] which is supported by ab initio and semiempirical investigations.[24−29] We have calculated complexes **25**−**30**, in which HCl, H_2O, and NH_3 are used for modeling solvent molecules with increasing donicity, to investigate energetic, electronic, and magnetic consequences of complex formation.

Calculated complexation energies for **25**, **27**, and **30** are larger than 3 kcal/mol (Table 3), which suggests that they are kept together by forces much stronger than those typical of van der Waals complexes. Analysis of our ab initio results reveals that, beside electrostatic interactions, complexes are also stabilized by charge transfer from solvent molecule S to SiH_3X. This is nicely reflected by calculated charge transfer values derived from Mulliken charges (Table 7). They indicate that the donor ability of the model solvents reduces from NH_3 to H_2O and HCl and that the acceptor ability of Si strongly depends on the electronic nature of X. Both increased electronegativity of X (e.g., X = $OClO_3$) and π-acceptor ability of X (X = CN) or improved overlap with the Si orbitals (X = Cl) can enhance charge transfer and thereby the complex stability.

Gordon and co-workers[25] investigated neutral pentacoordinated Si molecules of the type $XSiY_3{-}NH_3$ by ab initio theory and found that the "solvent" NH_3 prefers an axial position. N, Si, and the axial ligand X are linked by a four-electron three-center bond. For X = Cl, three-center bonding is more effective than for X = F while strongly electronegative equatorial substituents increase the complex stability by increasing the positive partial charge at Si and thereby its acceptor ability.

These observations are in line with our results. Charge transfer occurs from an electron lone pair orbital of the S molecule to the σ^*(SiX) orbital, which implies a proper alignment of these orbitals. This is best accomplished when the S molecule pushes its lone pair into the open SiH_3 umbrella of SiH_3X, thus adopting an axial position in the complex $XSiH_3{-}S$ (see geometries above and Table 2). The S−Si distances of complexes $XSiH_3{-}S$ are 0.5 up to 1.2 Å shorter than typical van der Waals distances between S and Si (Si−N

Table 5. IGLO/[7s6p2d/5s4p1d/3s1p] NMR Chemical Shifts for Compounds **11**–**30**[a]

molecule	sym	^{29}Si, ^{37}Cl, ^{17}O, ^{13}C, ^{1}H NMR chemical shifts				
11, SiH_4	T_d	Si	H			
		−99.1, −99.4	3.6, 3.6			
		−91.9, −93.1				
12, SiH_3CH_3	C_{3v}	Si	C	H(Si)	H(C)	
		−66.5, −66.4	−9.1, −9.1	3.8, 3.9	0.1, 0.2	
		−65.2				
13, $CH_3SiH_2CH_3$	C_{2v}	Si	C	H(Si)	H(C)	
		−38.8, −38.4	−5.2, −5.1	4.1, 4.1	0.1*, 0.1*	
		−41.5, −37.3				
14, $(CH_3)_3SiH$	C_{3v}	Si	C	H(Si)	H(C)	
		−16.6, −16.0	−2.2, −2.1	4.3, 4.3	0.1*, 0.1*	
		−16.3, −15.5	*−2.6*	*3.9*	*0.1*	
15, $(CH_3)_4Si$	T_d	Si	C	H(C)		
		0	0	0		
16, SiH_3CN	C_{3v}	Si	C	H(Si)		
		−86.7	126.0	4.2		
17, SiH_3OH	C_s	Si	O	H(Si)	H(O)	
		−42.5	−36.4	4.7*	1.0	
18, SiH_3Cl	C_{3v}	Si	Cl	H(Si)		
		−39.3	−102.8	4.7		
		−36.1				
19, $(CH_3)_3SiCN$	C_{3v}	Si	C(N)	C(CH_3)	H(C)	
		−10.4	132.0	−1.0	0.3*	
		−12.3, −12.2				
20, $(CH_3)_3SiOH$	C_s	Si	O	C	H(O)	H(C)
		13.0	−11.2	−0.6–1.8	1.1	0.1*
		1.0				
21, $(CH_3)_3SiCl$	C_{3v}	Si	C	Cl	H(C)	
		30.6	3.2	−37.4	0.3*	
		30.2, 29.9				
22, $Si(OH)_4$	S_4	Si	O	H(O)		
		−66.6	−15.7	2.2		
		−73.3				
23, SiH_3OClO_3	C_1	Si	O(Si)	O(Cl)	Cl	H(Si)
		−27.7	253.3	257.1–263.8	933.8	4.8*
24, $(CH_3)_3SiOClO_3$	C_1	Si	O(Si)	O(Cl)	Cl	C
		43.6	270.5	253.7–265.9	934.5	−0.8*
		47				
25, $SiH_3CN(NH_3)$	C_{3v}	Si	C	H(Si)	H(N)	
		−99.9	131.6	4.1	0.5	
26, $SiH_3OH(NH_3)$	C_s	Si	O	H(Si)	H(O)	H(N)
		−48.0	−21.0	4.4*	0.6	0.2*
27, $SiH_3Cl(NH_3)$	C_{3v}	Si	Cl	H(Si)	H(N)	
		−58.5	−54.3	4.5	0.4	
28, $SiH_3Cl(OH_2)$	C_s	Si	Cl	H(Si)	H(O)	
		−43.7	−79.6	4.6*	1.4	
29, $SiH_3Cl(HCl)$	C_s	Si	Cl	H(Si)	H(Cl)	Cl(HCl)
		−38.9	−99.2	4.7*	0.7	1.7
30, $SiH_3OClO_3(NH_3)$	C_1	Si	O(Si)	O(Cl)	Cl	H(Si)
		−93.8	277.0	253.4*	936.7	4.1*

[a] Shift values relative to TMS (δ ^{29}Si, δ ^{13}C, δ ^{1}H), liquid water (δ ^{17}O), or aqueous Cl^- (δ ^{37}Cl) in ppm. The first entry refers to the HF/6-31G(d) geometry, the second (if present) to the HF/6-311G(d,p) geometry. Values in italics denote experimental NMR shifts taken from ref 50. Asterisks indicate that the average of the calculated shifts is taken because of internal rotation of the molecule. Atoms in parentheses are given to specify the position of the nucleus in question.

= 3.54; Si–O = 3.40; Si–Cl = 3.81 Å[52]), which again indicates the existence of overlap interactions beside electrostatic interactions. The charge transfer from S to Si leads to lengthening of the SiX bond and to a reduction of the XSiH angles, which means that pyramidalization of the SiH_3 group is reduced to approach the trigonal bipyramidal geometry of a pentacoordinated Si atom.

Complex **29** with an interaction energy of less than 1 kcal/mol is the only real van der Waals complex because of the relatively low donor ability of HCl, the small charge transfer into σ^*(SiCl), and the moderate electrostatic interactions between HCl and SiH_3Cl. On the other hand, **30** is the strongest complex (9–12 kcal/mol, Table 3) because both charge transfer and electrostatic interactions are relatively large. They lead to a rather short Si–N distance (2.32 Å) close to that found for silatranes (2.2–2.3 Å)[24,25] and a large degree of planarization at the Si atom. The SiO bond (1.82 Å) becomes 0.1 Å longer than in gaseous **23**, while the geometry of the ClO_3 group is largely unaffected by complexation with S (NH_3, Table 2).

In line with previous investigations,[24–29] we find that Si has a large tendency to coordinate with solvent molecules S of sufficiently large donicity and to approach a pentacoordinated state with trigonal bipyramidal geometry. Because of the size of the Si atom, steric repulsion in such a geometry is not as problematic as it would be in a pentacoordinated carbon atom.[25,27] IGLO ^{29}Si chemical shifts reveal that the degree of coordination is reflected by upfield shifts of 13, 19, and 66 ppm

(52) *Handbook of Chemistry and Physics*, 64th and 72nd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1983 and 1991.

Table 6. IGLO/[7s6p2d/5s4p1d/3s1p] NMR Chemical Shifts for Cations **31–59**[a]

molecule	sym	^{29}Si, ^{37}Cl, ^{17}O, ^{13}C, ^{1}H NMR chemical shifts				
31, SiH_3^+	D_{3h}	Si	H			
		270.2	7.5			
32, $SiH_3(CNH)^+$	C_{3v}	Si	C	H(Si)	H(N)	
		−60.1	130.7	4.9	7.4	
33, $SiH_3(NH_3)^+$	C_{3v}	Si	H(Si)	H(N)		
		−28.7	5.0	3.8		
34, $SiH_3(NCH)^+$	C_{3v}	Si	C	H(Si)	H(C)	
		−26.2	123.3	5.2	6.5	
35, $SiH_3(NCCH_3)^+$	C_{3v}	Si	C(N)	$C(CH_3)$	H(Si)	H(C)
		−35.3	140.3	5.6	3.0	5.1
36, $SiH_3(OH_2)^+$	C_s	Si	O	H(Si)	H(O)	
		13.4	−43.1	5.4	6.2	
37, $SiH_3(O(CH_3)_2)^+$	C_s	Si	O	C	H(Si)	$H(CH_3)$
		6.0	−77.0	68.8	5.0	4.3
38, $SiH_3(ClH)^+$	C_s	Si	Cl	H(Si)	H(Cl)	
		26.7	28.1	5.7	4.5	
39, $SiH_3(ClCH_3)$	C_s	Si	C	Cl	H(Si)	H(C)
		3.6	57.9	−18.9	5.4	4.6
40, $(CH_3)_3Si^+$	C_{3h}	Si	C	H		
		355.9	9.0	1.8*		
41, $(CH_3)_3Si(NH_3)^+$	C_{3v}	Si	C	$H(CH_3)$	$H(NH_3)$	
		52.8	−1.3	0.9	3.5	
42, $(CH_3)_3Si(NCH)^+$	C_{3v}	Si	C(Si)	C(N)	$H(CH_3)$	H(N)
		67.0	−1.0	121.2	0.8	6.3
43, $(CH_3)_3Si(NCCH_3)^+$	C_{3v}	Si	C(Si)	C(N)	C(C)	$H(CH_3)$
		52.2	−0.9	136.4	5.0	0.8
44, $(CH_3)_3Si(OH_2)^+$	C_s	Si	C(Si)	O	$H(CH_3)$	H(O)
		99.0	−1.0	−22.1	0.9	5.6
45, $(CH_3)_3Si(ClH)^+$	C_s	Si	C	Cl	$H(CH_3)$	H(Cl)
		183.5	2.3–4.0	53.5	1.3*	3.5
46, $SiH_3(NCH)_2^+$	D_{3h}	Si	C(N)	H(Si)	H(C)	
		−102.8	116.4	4.5	5.4	
47, $SiH_3(NH_33)_2^+$	D_{3h}	Si	H(Si)	H(N)		
		−127.7	4.4	2.4		
48, $SiH_3(OH_2)_2^+$	C_{2v}	Si	O	H(Si)	H(O)	
		−69.3	24.6	4.7*	4.3	
49, $(CH_3)_3Si(OH_2)_2^+$	C_s	Si	C(Si)	O	$H(CH_3)$	H(O)
		58.2	2.2*	−15.7	0.8	3.5
50, $(CH_3)_3Si(NH_3)_2^+$	C_{3h}	Si	C(Me)	$H(CH_3)$	H(N)	
		−43.6	2.3	0.5*	2.0	
51, $SiH_3(OH_2)_3^+$	C_{2v}	Si	O	H(Si)	H(O)	
		−64.3	24.0–36.8	4.5	1.6–4.1	
52, $SiH_3(OH_2)_5^+$	C_{2v}	Si	O	H(Si)	H(O)	
		−51.5	23.4–38.8	4.7*	1.3–3.8	
53, CH_3^+	D_{3h}	C^+	H			
		370.5	15.3			
54, $CH_3(NCH)_2^+$	D_{3h}	C^+	C(N)	$H(C^+)$	H(C)	
		42.4	79.4	8.0	4.9	
55, $CH_3(NH_3)_2^+$	D_{3h}	C^+	$H(C^+)$	H(N)		
		96.5	6.1	1.5		
56, $CH_3(OH_2)_2^+$	C_{2v}	C^+	O	$H(C^+)$	H(O)	
		168.1	−49.9	8.7	3.0*	
57, $(CH_3)_3C^+$	C_{3h}	C^+	C(Me)	$H(CH_3)$		
		371.7	46.4	4.1*		
58, $(CH_3)_3C(OH_2)_2^+$	C_s	C^+	$C(C^+)$	O	$H(CH_3)$	H(O)
		359.2	153.4*	−33.6	3.5*	1.9*
59, $(CH_3)_3C(NH_3)_2^+$	C_{3h}	C^+	$C(C^+)$	$H(CH_3)$	H(O)	
		354.2	43.9	3.3*	0.3	

[a] Shift values relative to TMS (δ ^{29}Si, δ ^{13}C, δ ^{1}H), liquid water (δ ^{17}O), or aqueous Cl^- (δ ^{37}Cl) in ppm. The first entry refers to the HF/6-31G(d) geometry, the second (if present) to the HF/6-311G(d,p) geometry. Values in italics denote experimental NMR shifts taken from ref 50. Asterisks indicate that the average of the calculated shifts is taken because of internal rotation of the molecule. Atoms in parentheses are given to specify the position of the nucleus in question.

(Table 5) relative to the uncomplexed parent compounds **16**, **18**, and **23**. It is appealing to bring these shift changes into relation to the charge transfer from S to Si. However, the charge transfer is not parallel to trends in calculated Si atomic charges, which increase rather than decrease upon complexation by S (see Table 7), indicating that the negative charge is passed on from Si to X. Instead, our calculations suggest that the upfield shifts of δ ^{29}Si are more a consequence of changes in the geometry at the Si atom: planarization of SiR_3 is accompanied by upfield, pyramidalization of SiR_3 by downfield shifts. This is illustrated in Figure 2, where both energy and δ ^{29}Si shift values of SiH_3Cl are plotted for various degrees of pyramidalization.

Investigation of complexes **25–30** reveals that in solvents with strong donicity considerable upfield shifts of δ ^{29}Si occur, which can be as large as 100 ppm and more. There are two reasons to expect such large changes. First, the model solvent NH_3 certainly possesses a much lower donicity than, e.g.

Table 7. Calculated Mulliken Charges and Dipole Moments[a]

molecule	sym	TZ+P Mulliken charges		charge transfer	dipole moment	
		Si	SiH_n		6-31G(d)	TZ+P
11, SiH_4	T_d	0.692	0.000		0	0
12, SiH_3CH_3	C_{3v}	0.747	0.203		0.7	0.6
13, $CH_3SiH_2CH_3$	C_{2v}	0.791	0.422		0.7	0.6
14, $(CH_3)_3SiH$	C_{3v}	0.819	0.634		0.5	0.5
15, $(CH_3)_4Si$	T_d	0.825	0.825		0	0
16, SiH_3CN	C_{3v}	0.804	0.421		3.7	3.7
17, SiH_3OH	C_s	0.994	0.405		1.5	1.5
18, SiH_3Cl	C_{3v}	0.907	0.430		2.1	1.6
19, $(CH_3)_3SiCN$	C_{3v}	0.901	0.901		4.4	4.5
20, $(CH_3)_3SiOH$	C_s	1.102	1.102		1.5	1.4
21, $(CH_3)_3SiCl$	C_{3v}	1.014	1.014		2.8	2.2
22, $Si(OH)_4$	S_4	1.616	1.616		0	0
23, SiH_3OClO_3	C_1	0.951	0.554		4.4	4.2
24, $(CH_3)_3SiOClO_3$	C_1	1.032	1.032		5.4	5.2
25, $H_3N{\cdot}SiH_3CN$	C_{3v}	0.868	0.422	0.044	7.3	7.1
26, $H_3N{\cdot}SiH_3OH$	C_s	1.040	0.404	0.025	3.3	3.1
27, $H_3N{\cdot}SiH_3Cl$	C_{3v}	0.976	0.450	0.041	5.9	5.2
28, $H_2O{\cdot}SiH_3Cl$	C_s	0.950	0.443	0.023	5.2	4.6
29, $HCl{\cdot}SiH_3Cl$	C_s	0.911	0.426	0.010	3.0	2.5
30, $H_3N{\cdot}SiH_3OClO_3$	C_1	1.020	0.531	0.114	10.4	10.0
31, SiH_3^+	D_{3h}	0.967	1.000		0	0
32, $SiH_3(CNH)^+$	C_{3v}	0.806	0.666	0.334	2.7	2.6
33, $SiH_3(NH_3)^+$	C_{3v}	0.841	0.632	0.368	3.3	3.2
34, $SiH_3(NCH)^+$	C_{3v}	0.866	0.687	0.313	3.7	3.7
35, $SiH_3(NCCH_3)^+$	C_{3v}	0.855	0.635	0.365	2.5	2.5
36, $SiH_3(OH_2)^+$	C_s	0.948	0.749	0.251	2.8	2.7
37, $SiH_3(O(CH_3)_2)^+$	C_s	0.910	0.662	0.338	1.1	1.1
38, $SiH_3(ClH)^+$	C_s	0.864	0.763	0.237	2.1	1.7
39, $SiH_3(ClCH_3)^+$	C_s	0.858	0.700	0.300	2.0	1.9
40, $(CH_3)_3Si^+$	C_{3h}	0.947	0.947		0	0
41, $(CH_3)_3Si(NH_3)^+$	C_{3v}	0.883	0.883	0.317	4.6	4.5
42, $(CH_3)_3Si(NCH)^+$	C_{3v}	0.932	0.932	0.216	5.5	5.4
43, $(CH_3)_3Si(NCCH_3)^+$	C_{3v}	0.928	0.928	0.273	5.1	5.1
44, $(CH_3)_3Si(OH_2)^+$	C_s	0.954	0.954	0.201	4.0	3.9
45, $(CH_3)_3Si(ClH)^+$	C_s	0.812	0.812	0.171	1.6	1.3
46, $SiH_3(NCH)_2^+$	D_{3h}	1.035	0.738	0.262	0	0
47, $SiH_3(NH_3)_2^+$	D_{3h}	0.956	0.543	0.457	0	0
48, $SiH_3(OH_2)_2^+$	C_{2v}	1.055	0.699	0.300	0.3	0.3
49, $(CH_3)_3Si(OH_2)_2^+$	C_s	1.067	1.067	0.203	0.7	0.7
50, $(CH_3)_3Si(NH_3)_2^+$	C_{3h}	0.981	0.981	0.336	0	0
51, $SiH_3(OH_2)_3^+$	C_{2v}	1.088	0.692	0.308	0.3	0.2
52, $SiH_3(OH_2)_5^+$	C_{2v}	1.068	0.700	0.302	0.7	0.7
53, CH_3^+	D_{3h}	0.414	1.000		0	0
55, $CH_3(NCH)_2^+$	D_{3h}	0.379	0.827	0.257	0	0
56, $CH_3(NH_3)_2^+$	D_{3h}	0.257	0.620	0.354	0	0
57, $CH_3(OH_2)_2^+$	C_{2v}	0.368	0.778	0.210	1.1	1.0
54, $(CH_3)_3C^+$	C_{3h}	0.225	0.225		0	0
58, $(CH_3)_3C(OH_2)_2^+$	C_s	0.311	0.311	0.052	0.1	0.1
59, $(CH_3)_3C(NH_3)_2^+$	C_{3h}	0.341	0.341	0.056	0	0
60, $(CH_3)_2O{\cdot}SiH_3Cl$	C_s	0.955	0.448	0.017	4.7	4.2

[a] Charges in electrons and dipole moments in debye. In cases of ions, dipole moments are given with regard to the standard orientation used in ref 37. The TZ+P basis corresponds to basis II: [7s6p2d/5s4p1d/3s1p].

pyridine, DMPU, or HMPA (Table 1), which should lead to a much larger charge transfer, larger complexation energies, and stronger geometrical changes. Secondly, there is both calculational and experimental evidence that HF/6-31G(d) underestimates the degree of R_3SiX-S interactions. With MP2/6-311G(d,p), the S−Si interaction distance is reduced by 0.2−0.3 Å while the complexation energy is increased by 10%. A recent X-ray structure investigation of the coordination complex between SiH_3Cl and dimethyl ether (**52**)[53] suggests a Si−O interaction distance of just 2.27 Å compared to a HF/6-31G(d) value of 2.93 Å (Table 2). It is well-known that the description of van der Waals complexes requires a TZ+2P basis set and at least MP4 calculations, but such calculations are outside the scope of the present investigation. Nevertheless, our calculations clearly show that *large solvent shifts of δ ^{29}Si can even be found for covalently bonded SiR_3X compounds* (see Table 5). In the case of **30**, the density analysis (Table 8) reveals a weak (polar) covalent bond between Si and $S = NH_3$ that would further develop if the interaction distance would become shorter. This has to be kept in mind when using solvent-dependent changes of δ ^{29}Si values to detect silylium cations.

Silylium Cations. Cations **31** and **40** both possess a planar equilibrium geometry at the Si atom. Methyl substitution leads to stabilization of the cation by 36 kcal/mol (Table 4). This is considerably larger than the methyl stabilization calculated for SiH_3X (4−9 kcal/mol, X = CN, OH, Cl, $OClO_3$, Table 4) but only half as large as the corresponding value for CH_3^+ (65 kcal/mol, HF/6-31G(d);[54] 85 kcal/mol, experimental estimate[55]). Again, the magnitude of these effects has to do with the overlap between 2pπ(C) and 3pπ(Si) orbitals, which is considerably

(53) Blake, A. J.; Cradock, S.; Ebsworth, E. A. V.; Franklin, K. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 76.

Table 8. Bond Analysis[a]

molecule	sym	atoms involved (A, B)	distance A−B	type of crit pt	$\varrho(r_b)$	$H(r_b)$	
12, SiH_3CH_3	C_{3v}	Si, C	1.888	(3, −1)	0.79	−0.43	covalent
16, SiH_3CN	C_{3v}	Si, C	1.866	(3, −1)	0.71	−0.31	covalent
17, SiH_3OH	C_s	Si, O	1.647	(3, −1)	0.85	−0.10	covalent
18, SiH_3Cl	C_{3v}	Si, Cl	2.068	(3, −1)	0.63	−0.31	covalent
19, $(CH_3)_3SiCN$	C_{3v}	Si, C_N	1.886	(3, −1)	0.68	−0.29	covalent
		Si, C_{Me}	1.880	(3, −1)	0.82	−0.46	covalent
20, $(CH_3)_3SiOH$	C_s	Si, O	1.661	(3, −1)	0.82	−0.10	covalent
		Si, C_i	1.877	(3, −1)	0.82	−0.45	covalent
		Si, C_o	1.887	(3, −1)[b]	0.80	−0.44	covalent
21, $(CH_3)_3SiCl$	C_{3v}	Si, Cl	2.095	(3, −1)	0.59	−0.29	covalent
		Si, C	1.879	(3, −1)	0.82	−0.46	covalent
23, SiH_3OClO_3	C_1	Si, O	1.737	(3, −1)	0.64	−0.05	(covalent)
24, $(CH_3)_3SiOClO_3$	C_1	Si, O	1.770	(3, −1)[b]	0.58	−0.05	(covalent)
		Si, C_1	1.870	(3, −1)[b]	0.84	−0.49	covalent
		Si, C_2	1.870	(3, −1)[b]	0.84	−0.49	covalent
		Si, C_3	1.870	(3, −1)[b]	0.84	−0.49	covalent
25, $H_3N{\cdot}SiH_3CN$	C_{3v}	Si, N	2.819	(3, −1)	0.11	−0.01	no bond
26, $H_3N{\cdot}SiH_3OH$	C_s	Si, N	3.031	(3, −1)	0.08	0.00	no bond
27, $H_3N{\cdot}SiH_3Cl$	C_{3v}	Si, N	2.780	(3, −1)	0.12	−0.01	no bond
28, $H_2O{\cdot}SiH_3Cl$	C_s	Si, O	2.912	(3, −1)	0.08	0.00	no bond
29, $HCl{\cdot}SiH_3Cl$	C_s	Si, Cl	4.049	(3, −1)[b]	0.02	0.00	no bond
30, $H_3N{\cdot}SiH_3OClO_3$	C_1	Si, O	1.822	(3, −1)	0.51	−0.04	(covalent)
		Si, N	2.317	(3, −1)[b]	0.23	−0.05	(covalent)
32, SiH_3CNH^+	C_{3v}	Si, C	1.984	(3, −1)	0.51	−0.16	covalent
33, $SiH_3NH_3^+$	C_{3v}	Si, N	1.917	(3, −1)	0.53	−0.13	covalent
34, SiH_3NCH^+	C_{3v}	Si, N	1.888	(3, −1)	0.49	−0.06	(covalent)
35, SiH_3NCCH_3	C_{3v}	Si, N	1.856	(3, −1)	0.53	−0.07	(covalent)
36, $SiH_3OH_2^+$	C_s	Si, O	1.859	(3, −1)	0.44	−0.01	(covalent)
37, $SiH_3O(CH_3)_2^+$	C_s	Si, O	1.796	(3, −1)	0.56	−0.03	(covalent)
38, SiH_3ClH^+	C_s	Si, Cl	2.339	(3, −1)	0.33	−0.13	covalent
39, $SiH_3ClCH_3^+$	C_s	Si, Cl	2.248	(3, −1)[b]	0.41	−0.17	covalent
41, $(CH_3)_3SiNH_3^+$	C_{3v}	Si, N	1.957	(3, −1)	0.49	−0.12	covalent
42, $(CH_3)_3SiNCH^+$	C_{3v}	Si, N	1.940	(3, −1)	0.43	−0.06	(covalent)
43, $(CH_3)_3SiNCCH_3^+$	C_{3v}	Si, N	1.902	(3, −1)	0.47	−0.07	(covalent)
44, $(CH_3)_3SiOH_2^+$	C_s	Si, O	1.910	(3, −1)	0.39	−0.02	(covalent)
45, $(CH_3)_3SiClH^+$	C_s	Si, Cl	2.545	(3, −1)[b]	0.21	−0.06	(covalent)
46, $SiH_3(NCH)_2^+$	D_{3h}	Si, N	2.096	(3, −1)	0.30	−0.05	(covalent)
47, $SiH_3(NH_3)_2^+$	D_{3h}	Si, N	2.073	(3, −1)	0.37	−0.09	(covalent)
48, $SiH_3(OH_2)_2^+$	C_{2v}	Si, O	2.027	(3, −1)	0.30	−0.03	(covalent)
49, $(CH_3)_3Si(OH_2)_2^+$	C_s	Si, O	2.176	(3, −1)[b]	0.22	−0.04	(covalent)
50, $(CH_3)_3Si(NH_3)_2^+$	C_{3v}	Si, N	2.149	(3, −1)	0.33	−0.08	(covalent)
51, $SiH_3(OH_2)_3^+$	C_{2v}	Si, O_a	2.026	(3, −1)	0.30	−0.03	(covalent)
		Si, O_e	3.172	(3, −1)	0.06	0.00	no bond
52, $SiH_3(OH_2)_5^+$	C_{2v}	Si, O_a	2.044	(3, −1)	0.29	−0.03	(covalent)
		Si, $O_{e'}$	3.387	(3, −1)	0.04	0.00	no bond
54, $CH_3(NCH)_2^+$	D_{3h}	C, N	2.041	(3, −1)	0.30	−0.02	(covalent)
55, $CH_3(NH_3)_2^+$	D_{3h}	C, N	2.075	(3, −1)	0.39	−0.07	(covalent)
56, $CH_3(OH_2)_2^+$	C_s	C, O	2.107	(3, −1)	0.29	−0.01	(covalent)
58, $(CH_3)_3C(OH_2)_2^+$	C_s	C, O	2.715	(3, −1)	0.11	0.00	no bond
		C, O	2.872	(3, −1)	0.07	0.01	no bond
59, $(CH_3)_3C(NH_3)_2^+$	C_{3h}	C, N	2.928	(3, −1)	0.07	0.01	no bond
60, $(CH_3)_2O{\cdot}SiH_3Cl$	C_s	Si, O	2.934	(3, −1)	0.07	0.00	no bond

[a] Distance in Å, $\varrho(r_b)$ in electron Å^{-3}, $H(r_b)$ in hartree Å^{-3}. Each critical point r_b is characterized by (rank, signature). The character of the bond is given according to the criteria of Cremer and Kraka.[41] If the bond is strongly polar (partially ionic) but still covalent, the bond character is given in parentheses. [b] Several other critical points are located in the vicinity of the (3, −1) point, thus indicating an insufficient description of the electron density distribution by the basis set used.

smaller than the $2p\pi-2p\pi$ overlap between first row atoms and, therefore, leads to a reduction of hyperconjugative stabilization of Si by methyl groups as compared to the corresponding stabilization of a C atom. However, a large positive charge at the Si atom as in a silylium cation implies that the $3p\pi$(Si) orbital is contracted and, therefore, better matches the size of a $2p\pi$(C) orbital. This effect and a slight decrease of the SiC bond length (1.85 Å compared to 1.89 Å for **14**, Table 2) enlarges $3p\pi-2p\pi$ overlap and hyperconjugative stabilization, thus leading to the relatively large methyl effect obtained for **40**.

For **31** and **40**, we calculate δ ^{29}Si shifts of 270 and 356 ppm in line with similar values found by Kutzelnigg and co-workers[34] and by Olah and co-workers.[15] When calculations are performed at the GIAO-MP2/basis II level of theory we get for **31** δ ^{29}Si = 310.8 ppm, which indicates a correlation correction of 40 ppm. Recently, Gauss and Stanton[38c] have shown that GIAO-MP2 might slightly exaggerate correlation effects in the case of simple carbocations. Therefore, we can estimate that the true δ ^{29}Si shift of **31** in the gas phase. is ca. 300 ppm and the corresponding value for **40** is 385 ppm. For $Si(CH_2CH_3)_3^+$, another downfield shift of 32 ppm (δ ^{29}Si = 377 ppm, IGLO/[7s6p2d/5s4p1d/3s]) is obtained, which suggests that typical δ ^{29}Si values for alkylsilylium cations in the gas phase are at 400 ± 20 ppm. In a noncoordinating solvent with

(54) (a) Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819. (b) Wiberg, K. B.; Murcko, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 8029.
(55) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067.

Table 9. Interactions between SiH_3^+ (**31**) and Solvent Molecule S at Fixed van der Waals Distance[a,b]

solvent (S)	distance Si−S	dissn energy	δ ^{29}Si	$\Delta\delta$ ^{29}Si	charge transfer from S	charge at Si
NH_3	3.02	33.0	171.5	−98.7	131	881
HCN	3.02	24.8	209.9	−60.3	63	922
H_2O	2.88	26.0	209.1	−61.1	63	930
HNC	3.33	21.8	215.2	−55.0	93	886
HCl	3.29	10.4	211.0	−59.2	70	891

[a] Distances in Å, energies in kcal/mol, δ ^{29}Si values in ppm relative to TMS, charges in millielectrons. Dissociation energies and charge values from HF/6-31G(d) calculations; chemical shifts from IGLO/[7s6p2d/5s4p1d/3s1p] calculations. [b] van der Waals distances have been calculated from known van der Waals radii (N, 1.54; O, 1.40; C, 1.85; Cl, 1.81 Å) and the one estimated for Si^+ (1.48 Å, see text). The dissociation energy is defined by the formal reaction: $SiH_3(S)^+ \rightarrow SiH_3^+ + S$. Its negative value is the complexation energy. $\Delta\delta$ ^{29}Si gives the difference between the gas phase shift for SiH_3^+ (δ ^{29}Si = 270.2 ppm) and that for the $SiH_3(S)^+$ van der Waals complex. If reflects shielding of the Si nucleus by charge transfer from S.

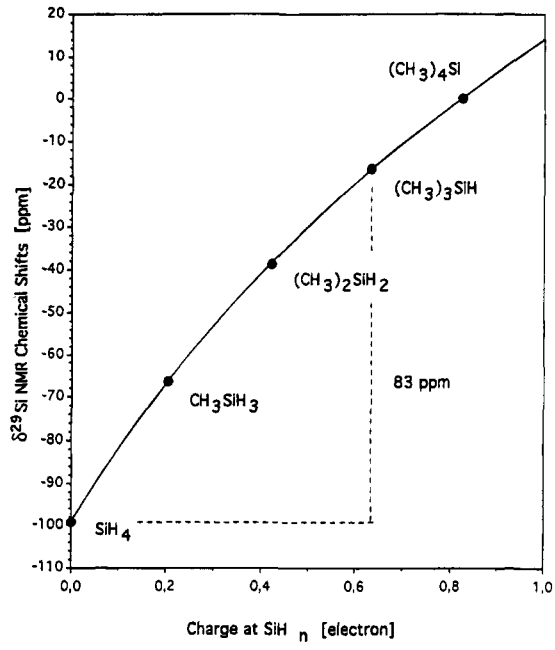


Figure 1. Dependence of IGLO δ ^{29}Si values on the charge at the Si atom (Mulliken values calculated with the 6-31G(d) basis).

large dielectricity constant (ϵ = 80), shift values of **31** and **40** are reduced by 10 and 18 ppm according to PISA-IGLO calculations.

Recently, it has been suggested that silylium cations can also adopt pyramidal geometries at the Si atom in order to reduce steric or environmental forces.[18] A change from planar to pyramidal geometry has been considered as leading to large upfield shifts of δ ^{29}Si values. Since such effects are important for the understanding of experimentally observed δ ^{29}Si values of potential silylium cations in solution, we have recalculated **31** and **40** with pyramidalization angles τ reaching from 0° to 19.5°, where the latter value corresponds to a tetrahedral arrangement of bonds at the Si atom. Figures 3 and 4 show the calculated changes in energy and δ ^{29}Si shifts in dependence on the pyramidalization angle τ. They reveal that, for τ = 19.5°, both **31** and **40** are destabilized in the gas phase by 24 and 21 kcal/mol, respectively, where even a relatively small distortion of the bond angles at Si already leads to a considerable energy increase. If these calculations are repeated for a noncoordinating solvent with a dielectricity constant ϵ = 80 (dashed curves in Figures 3 and 4), then a somewhat smaller energy increase (22.3 and 20.2 kcal/mol for τ = 19.5°) will be obtained, indicating

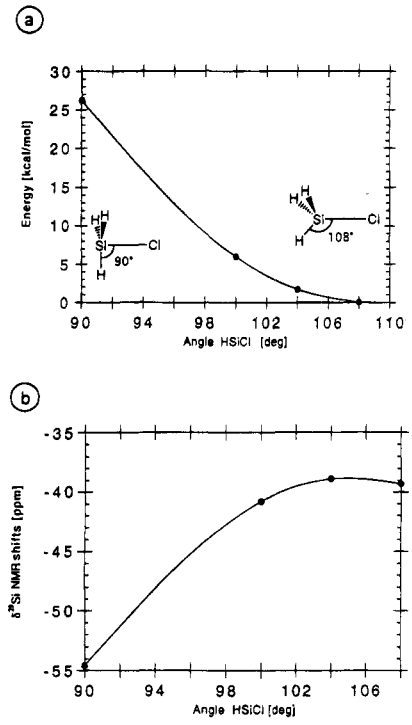


Figure 2. Changes of (a) energy and (b) δ ^{29}Si shift of SiH_3Cl in dependence of a planarization of the SiH_3 group (HF/6-31G(d) and IGLO/[7s6p2d/5s4p1d/3s1p] (basis II) calculations).

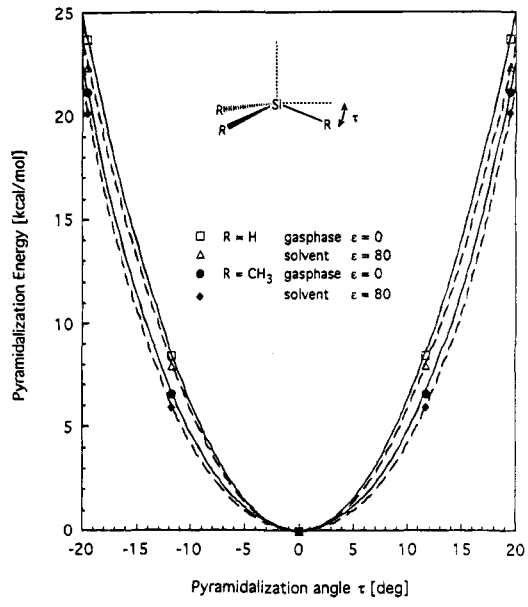


Figure 3. Dependence of the energy of SiR_3^+ (R = H, CH_3) on the pyramidalization angle τ, which is 0° for the equilibrium geometry and 19.5° for a tetrahedral arrangement of SiR bonds. Solid lines denote HF/[7s6p2d/5s4p1d/3s1p] (basis II) calculations, dashed lines PISA/HF/[7s6p2d/5s4p1d/3s1p] calculations.

that it will be difficult to distort silylium cations from planarity, even if environmental effects are present.

With pyramidalization at the Si atom in **1**, a downfield shift of as much as 90 (**31**) and 40 (**40**) ppm (Figure 4) is obtained, indicating strong deshielding rather than shielding of the Si nucleus. IGLO-PISA/basis II calculations lead to similar shift changes in noncoordinating solvents (78 and 33 ppm, see Figure 4). Deshielding of the Si nucleus in planar silylium cations is the result of paramagnetic currents in the plane of the σ-bonds.[34] They depend on the availability and energy of the empty pπ-orbital since they are caused by $\sigma-\pi$ excitations. Upon

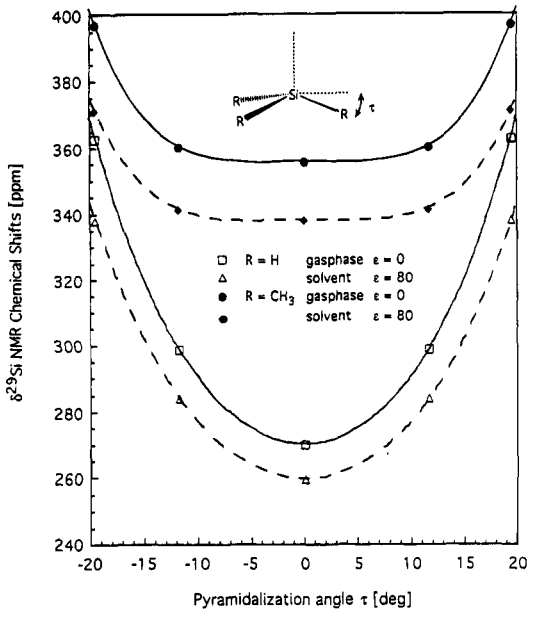


Figure 4. Dependence of the δ ^{29}Si shift of SiR_3^+ (R = H, CH_3) on the pyramidalization angle τ. Solid lines denote IGLO/[7s6p2d/5s4p1d/3s1p] (basis II) calculations, dashed lines PISA-IGLO/[7s6p2d/5s4p1d/3s1p] calculations.

pyramidalization of the silylium cation, the pπ-orbital mixes with σ-orbitals and obtains partial s character. Its energy is lowered, $\sigma-\pi$ excitations are facilitated, and paramagnetic ring currents are enhanced. As a consequence, there is an increased deshielding and a downfield shift of the Si nucleus with increasing pyramidalization. We conclude that neither geometrical changes nor general environmental effects (noncoordinating solvents) lead to upfield shifts of δ ^{29}Si contrary to what has been predicted by experimentalists.[18]

Olah and co-workers[15] have considered the possibility that incomplete dissociation may lead to experimental δ ^{29}Si values that are averages of that of the parent covalent compound R_3-SiX and the corresponding cation **1**. For a solution of **24** in sulfolane, it was claimed that between 20% and 35% free **40** are present depending on the concentration of **24**.[11] Considering that sulfolane possesses a dielectricity constant $\epsilon = 43.3$, we get δ ^{29}Si values of 265 and 346 ppm for cations **31** and **40** under the assumption that sulfolane molecules do not coordinate with silylium cations. Since the experimental δ ^{29}Si for **24** is 47 ppm,[15] incomplete dissociation of **24** would imply δ ^{29}Si shifts of 107 (20%) to 152 ppm (35%), similar to those predicted by Olah and co-workers.[15] These shift values are still 50−100 ppm downfield from experimentally observed δ ^{29}Si values of alleged **40** generated from solutions of perchlorate **24**. *Neither distortion of the silylium ion geometry, substitutent effects (e.g., replacing Me by Et, see above), nor the use of stronger dissociating solvents can explain this difference.* The only possible influence not considered so far is a direct interaction between cation and solvent molecules, which may lead to tetra-, penta-, or hexacoordinated Si. Silicon is known to have a strong tendency for coordination of nucleophilic molecules, and therefore, we will investigate in the next section how cation−solvent interactions might lead to changes in the properties of silylium cations, in particular their δ ^{29}Si shift values.

Interaction between Silylium Cations and Solvent Molecules (Group IV Compounds). Cations **32**−**39** can be considered as complexes between **31** and a solvent molecule, while cations **41**−**45** represent similar complexes between **40** and a solvent molecule. HF/6-31G(d) equilibrium geometries of these complexes (Table 2) reveal that because of the interaction with S the geometry at Si is pyramidal rather than planar. This is also the case for those ionic complexes that have been investigated so far by X-ray structure determinations. For example, Hensen and co-workers[56] have found a Si−N distance of 1.858 Å and a pyramidalization angle $\tau = 13.5°$ for a complex between **40** and pyridine. A somewhat shorter Si−N distance of 1.82 Å and an averaged pyramidalization angle of 12° has been observed by Reed and co-workers for the crystal structure of $[Pr^i_3Si(MeCN)]^+[Br_5CB_9H_5]^-$.[19] The calculated Si−N distances for $SiH_3(NCCH_3)^+$ (**35**) and $SiMe_3(NCCH_3)^+$ (**43**) are 1.86 and 1.90 Å (Table 2), somewhat longer than the experimental value, as are the corresponding values for SiH_3-$(NCH)^+$ (**34**) and $SiMe_3(NCH)^+$ (**42**) (1.89 and 1.94 Å, Table 2). These deviations seem to indicate that a HF/6-31G(d) description of complexes $SiR_3(S)^+$ is as satisfactory as in the case of compounds R_3SiX but that there is already a tendency of underestimating interaction distances Si−S as found for complexes $SiR_3X(S)$ (see above).

For all complexes considered, the calculated complexation (dissociation) energies measured by (reverse) reaction 5 are at

$$R_3Si^+ + S \rightarrow R_3Si(S)^+ \qquad (5)$$

least 10 times larger than those obtained for complexes **25**−**30** (Table 3) and, by this, come close to typical SiX dissociation energies (SiC, 78; SiN, 80; SiO, 88; SiCl, 86 kcal/mol[57]). The strongest interaction is calculated for $SiH_3(NH_3)^+$ (**33**, 78 kcal/mol, Table 3) while the weakest is obtained for $SiH_3(ClH)^+$ (**38**, 23 kcal/mol), which is in line with the higher electron donor ability of NH_3 as compared to that of HCl. There are some results from mass spectrometry[58] that allow a direct comparison of experimental and theoretical results. For example, the binding energy of $SiMe_3^+$ and H_2O (cation **44**) in the gas phase has been measured, and values between 30 and 45 kcal/mol have been obtained, which bracket our values of 41 (HF/6-31G-(d), Table 3) and 39 kcal/mol (HF/basis II), respectively. The uncertainty of experimental values results from uncertainties in the proton affinity of trimethylsilanol (experimental values between 166 and 197 kcal/mol,[58] HF/6-31G(d), 203 kcal/mol, Table 3) and in the heat of formation of **41** ($\Delta H_f°$ values between 147 and 155 kcal/mol).[58] Other experimental complexation energies in the gas phase could only be given relative to the water value (ion **44**), but they are in line with observations made in this work. For example, methyl substitution of the solvent molecule increases complexation energies by somewhat more than 10 kcal/mol (compare **34** and **35**, **36** and **37**, **38** and **39**, Table 3). This is confirmed by experimental values (e.g., OH_2 and $O(CH_3)_2$: ions **36** and **37**, increase of 12 kcal/mol, HF/6-31G(d), Table 3; OH_2 and $O(C_2H_5)_2$: ions **44** and $SiMe_3$-$(O(C_2H_5)_2)^+$, increase of 14 kcal/mol, experimental value). In this connection, it is interesting to note that compared to the complexation energies of $Li(S)^+$, $Na(S)^+$, etc. (S = H_2O, NH_3, CH_3CN),[59] the values obtained for the corresponding $SiR_3(S)^+$ ions are more than twice as large. This suggests that interactions between silylium cations and solvent molecules differ from the predominantly electrostatic interactions between alkali ions and solvent molecules (see below).

When going from ion **31** to ion **40**, complexation with solvent molecules S is less strong as is reflected by dissociation energies

(56) Hensen, K.; Zengerly, T.; Pickel, P.; Klebe, G. *Angew. Chem.* **1983**, *95*, 739.
(57) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nutall, R. L. *J. Phys. Chem. Ref. Data, Suppl. 2* **1982**, 11.
(58) Wojtyniak, A. C. M.; Stone, J. A. *Int. J. Mass Spectrom. Ion Processes* **1986**, *74*, 59.
(59) See, e. g.: Marcus, Y. *Ion Solvation*; Wiley: Chichester, U.K., 1985.

that are 13−21 kcal/mol smaller than for the corresponding SiH_3-$(S)^+$ ions (Table 3). This has to do with the fact that both methyl groups and S compete with each other to donate electrons to the positively charged Si atom. Si becomes less charged (see atomic charges in Table 7) and, therefore, its $3p\pi$ orbital is less contracted, and hyperconjugative stabilization between Si and the Me groups is reduced.

The relatively large complexation energies are parallel to the short SiS interaction distances (SiC, 1.98; SiN, 1.88−1.92; SiO, 1.86; SiCl, 2.34 Å, Table 2), strong pyramidalization at Si (Table 2), and charge transfer from S to Si as reflected by the calculated atomic charges for Si (Table 7). As a consequence, IGLO δ ^{29}Si chemical shifts for **32−39** and **41−45** differ considerably from those calculated for free silylium cations in the gas phase or in a noncoordinating solvent. On the average, they are 300 ppm at higher field in a region between −60 and 100 ppm (Table 6), where for R = Me, δ ^{29}Si is 85−110 ppm more positive (δ ^{29}Si = 60−100 ppm) than for R = H (δ ^{29}Si = −60 to 30 ppm). There is a considerable overlap with shift values of covalently bonded compounds R_3SiX interacting with solvent molecules S. A very weak nucleophilic solvent such as HCl (modelling CH_2Cl_2) would lead to δ ^{29}Si = 183 ppm (Table 6), suggesting a solvent-dependent shift range of at least 130 ppm (compare δ ^{29}Si for **41** and for **45**, Table 6).

The calculated δ ^{29}Si values seem to confirm NMR measurements that silylium cations in solutions have totally different shifts than in the gas phase.[9−15,30] For example, ion **40** in CH_3-CN with a measured ^{29}Si shift value in the range 28.4−38.5 ppm[60] is close to that of perchlorate **24** (Tables 5 and 6) and a δ ^{29}Si value of 67 ppm for $SiMe_3^+$ in CH_2Cl_2/OEt_2 should be consistent with formation of Me_3SiOEt_2.[60] However, by an appropriate variation of the solvent (from weakly to strongly nucleophilic), a complexed silylium cation should be distinguishable from a covalent compound R_3SiX.

The question is whether cations **32−39** and **41−45** still represent silylium ions or whether the silylium ion character has been lost in these compounds. Analysis of the electron density distribution $\varrho(r)$ in the region between Si and S reveals that contrary to interaction complexes **25−29**, there are actually covalent bonds connecting Si and S (C, N, O, Cl, Table 8). Dissociation energies, SiS distances, partial charges at Si, and bond density analysis all consistently describe complexes R_3-$Si(S)^+$ as covalently bonded molecules with a strongly polar SiS bond. They possess a tetra- rather than a tricoordinated Si atom and, therefore, have totally lost their silylium cation character. According to their properties, they may be better addressed as protonated or CH_3^+-substituted R_3SiX compounds where X and S are related by protonation or CH_3^+ addition. Such an interpretation is in line with the known properties of protonated alcohols: their CO bonds are considerably elongated, CO dissociation energies are reduced, C atoms become more positively charged, and ^{13}C shifts are downfield shifted because of deshielding of C.[61]

We conclude that silylium cations cannot exist in nucleophilic solvents. They immediately add a solvent molecule in a strongly exothermic process and form a tetracoordinated Si compound. This is in line with X-ray structure investigations for $SiMe_3$-$(Pyridine)^+$ [56] and $[Pr^i_3Si(MeCN)]^+[Br_5CB_9H_5]^-$.[19]

Although such a conclusion seems to be in line with experimental findings, a caveat is appropriate. In solution, silylium cations will interact with several solvent molecules, which will also interact among each other. The question is whether the formation of 1:1 adducts between the cation and a solvent molecule S is energetically more favorable than the formation of 1:2, 1:3, etc., adducts or of solvated ions that are surrounded by one, two, or more solvation shells. Description of the latter situation requires molecular dynamics calculations, which are beyond the scope of this investigation. Instead, we will try to describe the first solvation shell of a silylium cation by successively adding solvent molecules to the cation.

4. Toward a More Realistic Description of Solvated Silylium Cations (Group V Compounds)

Complexes with Pentacoordinated Silicon. Molecules **46−50** represent systems in which two solvent molecules are added to silylium cations **31** (**46−48**) and **40** (**49**, **50**). HCN (for CH_3-CN), NH_3 (for pyridine), or H_2O (for THF or dialkyl ether) have been used as appropriate model solvents (see Table 1). The two solvent molecules are kept at the same distance from the Si atom to describe the situation in solution. Actually, these configurations do not always correspond to an energy minimum since configurations that have one solvent molecule in closer contact with the silylium cation can sometimes possess lower energies. But, we have refrained from investigating the latter because the former fit better into a stepwise build up of the first solvation shell around a silylium cation.

In all systems investigated, the SiR_3 group adopts a planar geometry, thus leading to a trigonal bipyramidal structure with pentacoordinated Si. Complexation energies increase by about 20−30 kcal/mol to 80 (**46**), 109 (**47**), and 83 kcal/mol (**48**, Table 3). For the trimethyl-substituted cations **49** and **50**, increases are just 12 kcal/mol (complexation energy 52 kcal/mol) and 15 kcal/mol (72 kcal/mol), which again reflects the unfavorable competition between solvent molecules and methyl groups to transfer charge to Si. The interaction distances Si−S are 0.1−0.2 Å larger than the corresponding values for the 1:1 adducts, but calculated distances are still in the range of very long SiS bonds. This is confirmed by the bond density analysis (Table 8), according to which Si is connected to the solvent molecules by weak covalent SiN or SiO bonds. Therefore, coordination complexes **46−50** all contain a hypervalent Si atom connected by five covalent bonds to H (CH_3) and the two S molecules. In silyl cations **46−50**, the planar arrangement of the three SiR bonds leads to a more shielded Si nucleus than in the corresponding $R_3Si(S)^+$ ions (compare with Figure 2b). In the case of R = H, large upfield shifts of 77−99 ppm are calculated for δ ^{29}Si while for **49** and **50** (R = CH_3) the upfield shifts are 41 and 96 ppm (Table 6). Despite the trigonal planar geometry at the Si atom, there is no doubt that 1:2 coordination complexes have even further moved away from silylium cation character than the 1:1 coordination compounds.

Solvated Silicon Complexes. If additional solvent molecules are added, property changes are reverted to some extent as can be seen from the 1:3 and 1:5 water adducts **51** and **52**. The third, fourth, and fifth water molecule are located in equatorial positions between the SiH (SiR) bonds of the trigonal bipyramidal 1:2 adducts. Complexation energies (Table 3) reveal that addition of the third water molecule increases the complexation energy just by 8 kcal/mol and that for additional water molecules the increase becomes even smaller. This is also shown in Figure 5, where HF/6-31G(d) complexation energies for the model solvent water are plotted against the number of water molecules added. Obviously with just a few more water molecules the complexation energy converges toward a limit value of about 100 kcal/mol, which suggests that the first solvation shell is filled up with about 6−8 molecules.

(60) (a) Kira, M.; Hino, T.; Sakurai, H. *Chem. Lett.* **1993**, 153. (b) Kira, M.; Hino, I.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6697.

(61) (a) Radom, L.; Nobes, R. H. *Chem. Phys.* **1983**, *74*, 163. (b) Raghavachari, K.; Chandrasekhar, J.; Burnier, R. C. *J. Am. Chem. Soc.* **1984**, *106*, 3124.

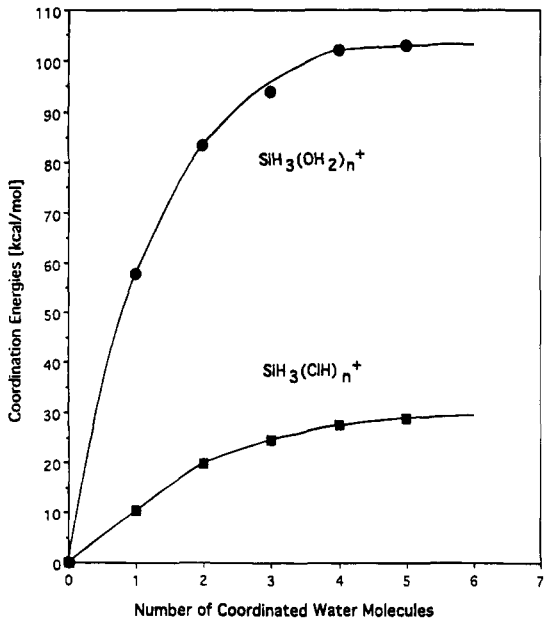


Figure 5. Increase of complexation energies of $SiH_3(H_2O)_n^+$ and $SiH_3(HCl)_n^+$ in dependence on n. For $SiH_3(HCl)_n^+$, the Si−Cl distance is kept at a van der Waals value of 3.24 Å while all other parameters have been optimized (HF/6-31G(d) calculations).

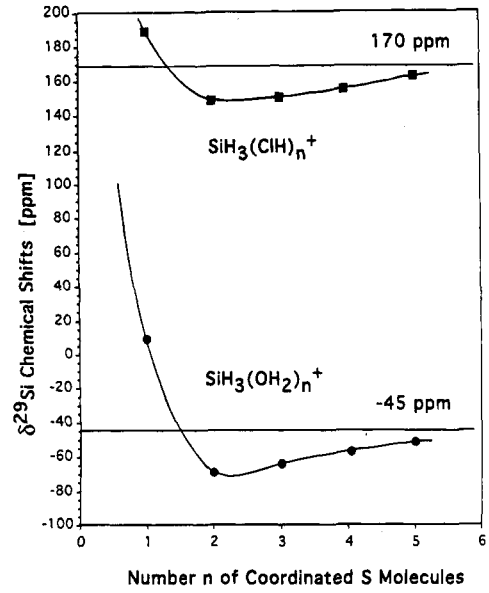


Figure 6. Dependence of the δ ^{29}Si shift of $SiH_3(H_2O)_n^+$ and $SiH_3(HCl)_n^+$ on n. For $SiH_3(HCl)_n^+$, the Si−Cl distance is kept at a van der Waals value of 3.29 Å while all other parameters have been optimized (IGLO/[7s6p2d/5s4p1d/3s1p]//HF/6-31G(d) calculations).

The equatorially positioned H_2O molecules have a long interaction distance of more than 3 Å to the Si atom while the axially positioned H_2O molecules largely keep their relatively short distance of 2.03 Å. Analysis of the electron density distribution confirms that just the axially but not the equatorially positioned water molecules are covalently bonded to Si (Table 8). This suggests that only the 1:1 and 1:2 adducts with water are chemically distinct species, which can be isolated and investigated while additional water molecules do not enlarge the coordination sphere of Si but lead to solvation of the 1:2 adduct.

Addition of water molecules reverts trends in δ ^{29}Si chemical shifts. The third and additional water molecules lead to downfield rather than upfield shifts. Similar to the complexation energy, δ ^{29}Si values of $SiH_3(H_2O)_n^+$ seem to converge to a limit value (about −45 ppm, Table 6, Figure 6). We expect similar trends for other complexes of the type $R_3Si(S)_n^+$ and, therefore, conclude that typical shift values of coordination complexes between silylium cations and solvent molecules in solution will be bracketed by those of the 1:1 and the 1:2 adducts. They can be expected in the region between −150 and 100 ppm, in which also the δ ^{29}Si values of most other covalently bonded organic silyl compounds can be found.[50]

Solvation by Weakly Nucleophilic Solvents. From our investigation, we can conclude that nucleophilic solvents will form coordination complexes with silylium cations in solution and, as a consequence, the later will lose their silylium cation character. NMR spectroscopy is an excellent instrument to detect these coordination complexes and to distinguish them from free or nearly free silylium cations. While such a distinction will be relatively easy for δ ^{29}Si values below 150 ppm (covalently bonded R_3SiX or $R_3Si(S)_n^+$ compounds) and above 250 ppm (free silylium cations), there exists a problem of interpreting δ ^{29}Si values in the range between 150 and 250 ppm, which may indicate interaction complexes between weakly nucleophilic solvents and silylium ions. An example is **45**, which has a δ ^{29}Si value of 184 ppm (Table 6) indicative of a weak interaction between **40** and HCl. Of course, HCl is only a model solvent for CH_2Cl_2 (Table 1) often used in the search for silylium cations. From the ab initio results for **38** and **39**, one can see that a methyl group actually leads to an increase of the nucleophilic character of the chlorine compound, a larger charge transfer to the silylium cation, additional shielding of the Si nucleus, and an increase of covalent SiCl bonding. In CH_2Cl_2, the second Cl atom will reduce the methyl effect and, therefore, HCl is probably a reasonable model for the solvent CH_2Cl_2.

According to our calculations, **45** contains a weak covalent bond between Si and Cl and, therefore, can no longer be considered as a free silylium cation. But since it possesses a clearly distinct δ ^{29}Si value, it is reasonable to separate ions such as **45** from normally bonded coordination compounds and to speak of weakly bonded coordination complexes. Obviously, such complexes can lead to δ ^{29}Si values up to about 200 ppm.

Interactions in the Solvent Cage. It is obvious from these results that any closer contact between solvent and **1** drastically changes the electronic nature of the latter and, therefore, reduces its silylium cation character. Of course, solvation implies not only interactions between solute and solvent molecules but also interactions between the solvent molecules. The latter interactions may hinder a closer contact of one or two solvent molecules with a solute molecule and, therefore, a cage of solvent molecules develops around the solute molecule. Typical interaction distances between solute and solvent molecules in the cage are given by the sum of the van der Waals radii of directly interacting atoms. Since a van der Waals radius of a cation is not defined, we have estimated such a radius for Si^+ to be 1.48 Å by using the difference between the covalent radii for Si (1.17 Å) and Si^+ (0.65 Å) as a correction for the van der Waals radius of Si (2.0 Å).[47] With this estimate, we have predicted the influence of a solvent cage on the properties of a silylium cation in two ways.

(a) We have placed various solvent molecules at the Si^+−S van der Waals distance and have calculated the properties of the corresponding interaction complex. The results of these calculations are shown in Table 9.

(b) For several $H_3Si(S)^+$ complexes, we have increased the interaction distances stepwise to 4 Å, i.e. values considerably larger than the estimated van der Waals distance. For each distinct interaction distance, we have reoptimized the geometry,

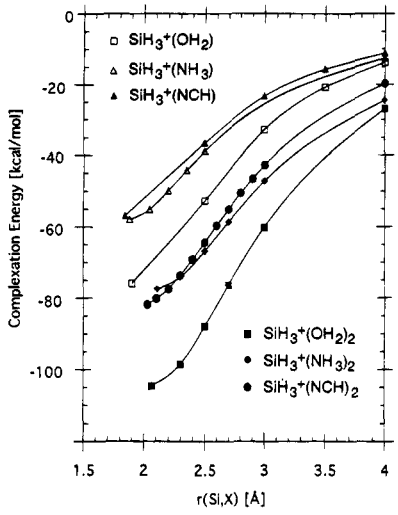


Figure 7. Dependence of complexation energies of $SiH_3(S)_n^+$ for n = 1 (S = HCN, NH_3, H_2O, HCl) and n = 2 (S = HCN, NH_3, H_2O) on the interaction distance Si,S (HF/6-311G(d,p) calculations).

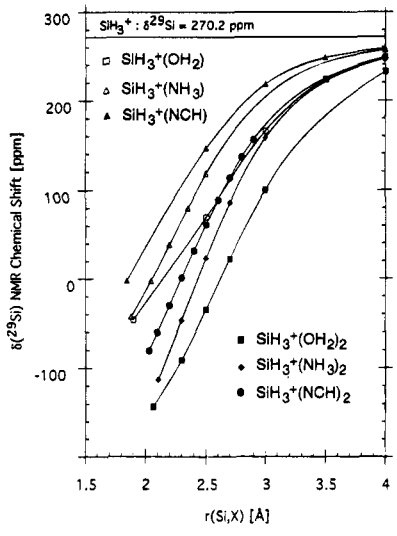


Figure 8. Dependence of δ ^{29}Si shifts of $SiH_3(S)_n^+$ for n = 1 (S = HCN, NH_3, H_2O, HCl) and n = 2 (S = HCN, NH_3, H_2O) on the interaction distance Si−S (IGLO/[7s6p2d/5s4p1d/3s1p]//HF/6-311G-(d,p) calculations).

calculated the complexation energy, and determined δ ^{29}Si shifts. Energies and shifts thus obtained are shown in Figures 7 and 8 in dependence on the interaction distance.

For both 1:1 and 1:2 complexes, changes of energetic and magnetic properties are very similar in a region between 2 and 3.5 Å (Figures 7 and 8). In this region, there is an almost linear dependence of complexation energies, δ ^{29}Si chemical shifts, and charge transfer values (not shown) on the interaction distance Si−S, where the curves are just shifted along the ordinate axis according to their starting value at equilibrium distance. As discussed above, complexation energies and δ ^{29}Si shifts increase with charge transfer, where the charge transfer depends on the overlap between Si and S orbitals, which in turn depends on the distance Si−S.

It is interesting to note that at given van der Waals distances (Table 9) complexation energies are still between 10 (HCl) and 30 kcal/mol (NH_3) for the 1:1 complexes and between 40 and 60 kcal/mol for the 1:2 complexes, indicating in both cases considerable interactions. In line with this is the fact that δ ^{29}Si values are shifted by 50−100 ppm to higher field, thus leading for SiH_3^+ to δ ^{29}Si = 210 ppm in the case of a weakly nucleophilic solvent molecule such as HCl and 170 ppm for a strongly nucleophilic solvent molecule such as NH_3. There is still some charge transfer from S to Si (as suggested by the complexation energies), but there are no longer covalent bonds between Si and S. Even at interaction distances of 4 Å (Figures 7 and 8), the influence of nucleophilic solvent molecules such as H_2O, NH_3, or HCN leads to considerable interaction energies of 11−27 kcal/mol while δ ^{29}Si values can be found between 230−260 ppm.

If further HCl molecules are added to the van der Waals complex between **31** and HCl, the complexation energy will increase from 10 to about 30 kcal/mol (see Figure 5) and δ ^{29}Si will drop to 170 ppm (Figure 6). Similar results can be expected for the interaction between **31** and CH_2Cl_2. Since the Si atom is no longer covalently bonded to the solvent molecules, $H_3Si(HCl)_5^+$ or $(CH_3)_3Si(HCl)_5^+$ with SiCl distances kept at van der Waals values are reasonable models for silylium cations such as **31** or **40** in weakly interacting solvents. We can predict that **31** and **40** should possess under these circumstances δ ^{29}Si values of about 170 ± 10 and 255 ± 10 ppm. However, the generation of **31** or **40** in such a medium will be difficult if one starts from a perchlorate. According to PISA-SCF calculations, ionization of **23** (and probably also of **24**) is exothermic (−67 kcal/mol, PISA/6-31G(d)) in sulfolane (ϵ = 43.3) and in solvents with larger dielectricity constant, but it is still endothermic for ϵ < 10. If just electrostatic effects dominate the interactions between solvent and perchlorate, the latter will show little tendency to dissociate to silylium cations in a solvent such as CH_2Cl_2 because solvation energies are smaller than the energy required for heterolytic dissociation of the perchlorate.

5. Do Silylium Cations Exist in Solution?

Ab initio calculations clearly reveal the strong coordination ability of silylium cations. If they are generated in solution, they will immediately react with nucleophilic solvent molecules to form very stable covalently bonded tetra- or pentacoordinated Si compounds that have completely lost their silylium cation character. Therefore, any search for silylium cations in condensed phases has to solve two major problems, namely (1) to find a weakly coordinating anion that because of charge delocalization and/or steric shielding of the negative charge does not recombine with the silylium cation and (2) to find a weakly nucleophilic solvent with a very low coordination tendency that can still be used as a reaction medium.

The first problem seems to be solved by exprimentalists who have suggested the use of either the tetrakis(pentafluorophenyl)-borate anion, $(C_6F_5)_4B^-$ ($TPFPB^-$),[17,18] or the carborane anion *closo*-6,7,8,9,10-$Br_5CB_9H_5^-$.[19]

However, an acceptable solution for the second problem is much more difficult. Among the solvents normally used for NMR measurements of Si compounds are, with the exception of water, mostly those shown in Table 1. Our calculations show that, apart from CH_2Cl_2, all of these solvents will form covalently bonded coordination complexes with potential silylium cations. For example, if the search for **40** is started with the perchlorate **24**, then it is very likely that complexes between **24** and solvent molecules are formed that are characterized by upfield shifts of δ ^{29}Si of as much as 60 ppm. In such a complex, ionization is facilitated by charge transfer from the solvent to the perchlorate molecule. If the silylium cation is formed by ionization of the perchlorate, it will be formed as a coordination complex rather than a free silylium cation. Our investigation indicates that *perchlorates such as **24** are not good starting compounds for the generation of silylium cations.*

A weak nucleophilic solvent such as CH_2Cl_2 (but definitely not sulfolane, see Table 1) would probably lead to less stable

Table 10. Estimated Ranges of δ ^{29}Si Values (ppm) for Silylium Cations in the Gas Phase and in Solution Phases[a]

R_3Si^+	gas phase	noncoordinating solvent ($0 < \epsilon \leq 80$)	weakly interacting solvents ($0 < D \leq 1$)	weakly coordinating solvents ($1 < D \leq 10$)	strongly coordinating solvents ($10 < D$)
R = H	300[b]	290−300	120−290	10−110	−130 to 10
R = CH_3	385[b]	370−385	200−370	90−190	−50 to 90
R = C_2H_5	410[b]	390−410	220−390	110−210	−30 to 110
Si−S interaction		solvation[c]	van der Waals[d]	weakly bonding	stronger bonding
ion character		free silylium ions	partial loss of silylium ion character	total loss of silylium ion character	

[a] Solvent S characterized by dielectricity constant ϵ and donicity D (see ref 31b). [b] Including estimated correlation corrections of 30 ppm (see text). [c] Solvation without any charge transfer from S to R_3Si^+. [d] van der Waals interactions imply here already some charge transfer.

coordination complexes, which may conserve some of the silylium ion character of **40**. Better, however, would be aromatic compounds or alkanes as solvents in the presence of a weakly coordinating anion. Lambert and co-workers have suggested to use benzene or toluene as solvent for the generation of silylium cations.[17,18] Although we have not included such solvents into our study, it is very likely that these solvents will lead to weakly solvated silylium ions in the sense described above *provided direct coordination is sterically hindered.*[62]

In view of our ab initio results, it seems to be impossible to generate silylium cations in solution that possess the same properties as silylium cations in the gas phase. However, there is a good chance to generate solvated silylium cations with complexation energies of about 10−20 kcal/mol and a small amount of charge transfer to the Si atom. The detection of these ions will be best done by NMR spectroscopy where the results of this work can be used to classify the ion in question (see Table 10).

There is certainly no chance to generate **31** in solution because it is too reactive. But if it would exist in solution it should possess δ ^{29}Si between 120 and 290 ppm for weakly interacting solvents and between 290 and 300 for noncoordinating solvents (Table 10). Under the same conditions, cation **40** should have δ ^{29}Si values between 200−370 and 370−385 ppm, respectively, while the values for Et_3Si^+ should be between 220−390 and 390−410 ppm, respectively (Table 10). Cation **45** (δ ^{29}Si = 183 ppm, Table 6) falls into the region of weakly coordinated silylium cations which have some weak polar bonding between Si and S.

Both the regions of weak coordination with the solvent and weak van der Waals type interactions with the solvent are chemically interesting because they show how solvent−solute interactions gradually develop. In view of the recent experiments by Lambert and co-workers, we see possibilities of advancing in these regions.[62] This will require a new strategy in the use of solvents, which very much depends on experimental inventiveness. We predict a number of steps that will push forward measured δ ^{29}Si values in the direction of first 200 ppm and later 300 ppm. Each of these experimental steps should be accompanied by ab initio calculations to guarantee correct interpretation of experimental data. The work on silylium cations in solution opens a new area of fruitful interactions between experimental and theoretical chemists where, in particular, ab initio NMR chemical shift calculations will show their exceptional value. Joint enterprises of this nature have become possible because of the enormous progress in NMR chemical shift calculations during the last 10 years, which has added a "third dimension to quantum chemistry".[49]

6. Why Do Nearly Free Carbocations Exist in Solution?

As mentioned above carbocations possess similar properties in gas and solution phases. This is particularly true for measured ^{13}C chemical shifts if one disregards small carbocations such as CH_3^+ (**53**), $C_2H_5^+$, etc. The latter react with solvents to form covalently bonded molecules. For example, ion **53** is such a strong electron acceptor that it forms with S = HCN, NH_3, or H_2O the strongly bound 1:2 complexes **54**, **55**, and **56** that possess complexation energies between 60 and 80 kcal/mol (Table 3). One has to note however that the complexation energies of **54**, **55**, and **56** are 20 kcal/mol smaller than those of the corresponding SiH_3^+ complexes **46**, **47**, and **48**. This decrease in complexation energies is relevant for answering the question posed in the section title.

The carbocations observed in solution normally possess more than one alkyl or aryl substituent at the cationic center. A typical example is $(CH_3)_3C^+$ (**57**). For complexes $(CH_3)_3C^+(S)_2$, bond lengths between C^+ and S (2.715 and 2.928 Å, Table 2) are 0.54 Å (**58**) and 0.78 Å (**59**) longer than the corresponding Si−S distances in **49** and **50** despite the smaller covalent radius of C^+. The increase in the interaction distance between cation and S is accompanied by a reduction in complexation energies (23 kcal/mol for **58**, 24 kcal/mol for **59**, Table 3) by 25 and 42 kcal/mol in comparison to those of **49** and **50**.

There are three factors that are responsible for the difference in stabilities of $(CH_3)_3C^+(S)_2$ and $(CH_3)_3Si^+(S)_2$.

(a) Hyperconjugative Effects. These are much stronger for carbocations than for silylium cations because of the shorter bonds between methyl groups and cation center (CC compared to SiC bonds) and the better overlap between pseudo-π(Me)- and 2pπ(C^+)-orbitals (compared to that between pseudo-π(Me)- and 3pπ(Si^+)-orbitals).[63] A measurement of the increase in hyperconjugative effects is given by the methyl stabilization energies of Me_3C^+ (**57**) and Me_3Si^+ (**40**), which are 67 and 36 kcal/mol (Table 4). Hyperconjugative effects lead to a transfer of negative charge to the C^+ atom and reduce its electrophilic character. For comparison, the partial charge at C^+ in **57** is 0.225 e while that at Si^+ in **40** is 0.947 e. The corresponding partial charges for CH_3^+ (**53**) and SiH_3^+ (**31**) are 0.414 and 0.967 e, respectively (Table 7).

(b) Inductive Effects. The difference in electronegativities between Si and C leads to electron withdrawal from the Si atom in **40**, and accordingly, it also adds to the relatively large positive charge at Si. In **57**, C^+ withdraws electron density from the methyl groups both via the π- and the σ-orbitals, thus reducing its positive charge.

Both hyperconjugative and inductive effects lead to an "internal solvation" of C^+ by the methyl groups, and in this way, external solvation by S is only weak (complexation energies < 25 kcal/mol).

(c) Steric Effects. These hinder external solvation of the carbocations such as **57** by sterically demanding solvents. Silylium cations such as **40** are less sensitive to steric effects because of the larger size of Si.

(62) Olsson, L.; Cremer, D. *Chem. Phys. Lett.* **1993**, *215*, 433.

(63) Basso, N.; Görs, S.; Popowski, E.; Mayr, H. *J. Am. Chem. Soc.* **1993**, *115*, 6025.

Internal solvation of carbocations is responsible for the similarity of properties both in the gas and solution phases. For the carbocations **53** and **57**, calculated ^{13}C NMR chemical shifts are 371 and 372 ppm (Table 6), respectively, and the experimentally measured value of the latter ion is 335 ppm.[22] For $H_3C(S)_2^+$ complexes, calculated δ ^{13}C values (96 (**55**) and 168 ppm (**56**), Table 6) indicate strong cation, solvent interactions, whereas in **58** and **59**, the $\delta^{13}C$ values of 359 and 354 ppm are close to that of **57**. The complex **58** could serve as a model for carbocation–solvent complexes formed in SO_2, SO_2ClF, and SO_2F_2, which are normally used in the synthesis of carbocations. The difference of 24 ppm between measured and calculated ^{13}C NMR chemical shifts can be reduced by performing the IGLO calculation at the MP2/6-31G(d) geometry of **58**, which leads to a δ ^{13}C value of 346 ppm. Additional decreases in the shift value are obtained by considering the actual dielectricity of the solvent used, reoptimizing the geometry under solvent conditions, and using SO_2 rather than H_2O as a solvent. Hence, our calculations come close to the experimental value for **57** in SO_2 (335 ppm).[22]

In summary, calculations indicate that the difference between carbocations and silylium cations results from "internal solvation" of the former, which make carbocations less sensitive to solvation or other environmental effects than silylium cations. The stronger the internal solvation of the carbocation center by hyperconjugative and inductive effects is, the more likely are nearly free carbocations in solution.

6. Conclusions

The following conclusions can be drawn from this work.

(1) HF/DZ+P calculations are sufficient to describe energy, geometry, and charge distribution of Si compounds, while IGLO/TZ+P calculations lead to rather accurate δ ^{29}Si NMR chemical shifts. However, more accurate basis sets and methods are needed to get reliable descriptions of solvent–solute complexes for neutral Si compounds. Also, an accurate determination of δ ^{29}Si for silylium cations requires correlation corrections at least at the GIAO-MP2 level theory.

(2) SiR_3X and SiR_3^+ compounds are differently stabilized by alkyl groups. While hyperconjugative stabilization by alkyl groups is moderate for SiR_3X molecules (<10 kcal/mol) because of insufficient $2p\pi(C)-3p\pi(Si)$ overlap, alkyl stabilization in SiR_3^+ ions is much larger (R = Me, 36 kcal/mol) because of increased $2p\pi(C)-3p\pi(Si)$ overlap caused by $3p\pi(Si)$ orbital contraction in the cation. As a consequence, SiR_3^+ is less electrophilic than SiH_3^+.

(3) Values of δ ^{29}Si NMR chemical shifts strongly depend on the charge at the Si atom. Within a class of compounds SiR_3X, δ ^{29}Si can be described as a function of Si atomic charges (see Figure 1).

(4) Neutral SiR_3X compounds can form coordination complexes with nucleophilic solvent molecules. The Si atom is pentacoordinated in these complexes, which are characterized by significant planarization at the Si atom. δ ^{29}Si NMR chemical shifts of complexes $SiR_3X(S)$ are at higher field and, accordingly, make it possible to distinguish $SiR_3X(S)$ from uncomplexed SiR_3X compounds in solution by NMR spectroscopy.

(5) There is a considerable transfer of charge from the solvent molecule S to the SiR_3X molecule. The negative charge does not stay at the Si atom but is passed on to the group X, which gets enough negative charge to dissociate as an anion X^-. It seems that formation of $SiR_3X(S)$ is a prerequisite for dissociation of SiR_3X in nucleophilic solvents. In this medium, free silylium cations are never formed because dissociation leads to $SiR_3(S)^+$ cations, which have no silylium cation character.

(6) Dissociation of silyl perchlorates in noncoordinating solvents requires a dielectricity constant $\epsilon > 10$ to make the dissociation process exothermic. However, for $\epsilon < 10$, dissociation is possible when the solvent is nucleophilic and can associate with the perchlorate in the way described above. Solvents such as sulfolane or acetonitrile previously used in silylium cation studies will definitely lead to dissociation of the perchlorate, yielding stable complexes of the type $SiR_3(S)_n^+$ rather than SiR_3^+ cations.

(7) Silylium cations posses a planar geometry. Pyramidalization leads to a considerable energy increase and a downfield shift of δ ^{29}Si as shown in Figures 3 and 4. It is unlikely that steric or environmental effects distort silylium cations from their planar geometry.

(8) Silylium cations R_3Si^+ with R = Me, Et, etc., possess in the gas phase δ ^{29}Si NMR chemical shifts at 400 ± 20 ppm, which are slightly reduced (10–20 ppm) in noncoordinating solvents. In weakly interacting solvents (e.g., alkanes), δ ^{29}Si values are reduced to 200–390 ppm because of charge transfer to the electrophilic Si atom and partial loss of silylium cation character. Silylium cation character is totally lost in nucleophilic solvents, which form coordination complexes with silylium cations. Bonding between Si and S is covalent. The δ ^{29}Si NMR chemical shifts for the coordination complexes are typically between −50 and 200 ppm (see, Table 10).

(9) It should be possible to generate nearly free silylium cations in weakly interacting solvents provided weakly coordinating anions such as the tetrakis(pentafluorophenyl)borate anion, $(C_6F_5)_4B^-$ ($TPFPB^-$),[17,18] can be used as counterions. Silyl perchlorates are not good starting compounds for this purpose.

(10) Carbocations differ from silylium cations in so far as they are internally "solvated" at the cationic center by charge transfer from alkyl (aryl) groups due to hyperconjugative and inductive effects. Therefore, external solvation by nucleophilic solvents leads only to weak cation–solvent interactions and does not change the cation properties so much as in the case of silylium cations. The relatively small changes of carbocation properties in solution phases as compared to those in the gas phase can be used as a measure for the degree of solvent complexation.

After this paper had been submitted, various papers appeared in the literature that discussed Lambert's claim[17,18] of nearly free silylium cations in solution. Schleyer and co-workers[64] published an ab initio investigation on the silylium cations, which comes to the same conclusions as the investigation by Olsson and Cremer,[62] namely that silylium cations in aromatic solvents react with solvent molecules to form Wheland σ-complexes. After these two papers had appeared, Pauling[65] and Olah[66] also criticized Lambert's claim of nearly free silyl cation with just a distant coordination to a solvent molecule. These critical comments were followed by replys by Lambert[67] and Reed.[68] A summary on the pros and cons of the existence of nearly free silyl cations proposed by Lambert and Reed was given by Strauss.[69]

(64) Schleyer, P. v. R.; Buzek, P.; Müller, T.; Apeloig, Y.; Siehl, H.-U. *Angew. Chem.* **1993**, *105*, 1558.
(65) Pauling, L. *Science* **1994**, *263*, 983.
(66) Olah, G. A.; Rasul, G.; Li, X.; Buchholz, H. A.; Sandford, G.; Prakash, G. K. S. *Science* **1994**, *263*, 983.
(67) Lambert, J. B.; Zhang, S. *Science* **1994**, *263*, 984.
(68) Reed, C. A.; Xie, Z. *Science* **1994**, *263*, 986.
(69) Strauss, S. H. *Chemtracts: Inorg. Chem.* **1993**, *5*, 119.

Acknowledgment. This work was supported by the Swedish Natural Science Research Council (NFR). All calculations were done on the CRAY YMP/464 of the Nationellt Superdatorcentrum (NSC), Linköping, Sweden. The authors thank the NSC for a generous allotment of computer time. Technical assistance in some of the calculations by Dr. Elfi Kraka is acknowledged. We thank Dr. Jürgen Gauss for providing a copy of his GIAO-MP2 program.

Supporting Information Available: Calculated energies of **11−68** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA933805Y