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Modern Approaches to Silylium Cations in Condensed Phase

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Contents

I. Introduction

Many silicon analogues to carbon-based functionalities were considered to be unlikely structural entities until recently. Numerous examples of π-bonded silicon, however, now have been prepared and X-ray structures obtained, including Si=C, Si=N, and Si=Si.[1] A prominent exception to these advances has been tricoordinate, positively charged silicon, R_3Si^+, the analogue of the carbenium ion. The central importance of the carbenium ion in organic chemistry seemed to demand a similar role for its silicon analogue that nature resisted. To overcome this reticence on the part of nature, chemists have sought to produce such materials, both as reactive intermediates and as stable species. As other bastions of silicon intermediates fell, the tricoordinate cation became a focus of attention that probably exceeded its inherent value.

For the purposes of this review, *free silylium ions* (formerly *silylenium* or *silicenium ions*) are positively charged, planar, three-coordinate species. In addition, cations may have varying degrees of silylium ion character when the silicon is four coordinate with partial covalent bonding to the fourth coordination site and possesses the preponderance of the positive charge. In contrast, *siliconium ions* are positively charged species in which silicon has higher than four coordination. Some authors prefer to restrict the term silylium ion to the fully tricoordinate form. A continuum of charged structures, however, is well precedented in carbanion chemistry, in which carbon–metal bonds can have varied degrees of covalent character.[2] The term *silyl cation* or *silicocation* may apply to either silylium or siliconium ion, within context.

The field of silylium ions was reviewed by Corriu and Henner in 1974,[3] and the subject of the present review is the progress of the field of low-coordination, positively charged silicon since that review. Several less comprehensive reviews or commentaries have appeared since the review of Corriu and Henner.[4–7] The fields of organosilicon radical cations[8] and high-coordination, positively charged silicon[9] have been reviewed recently and lie outside the present subject. This review further focuses on results in condensed phase. Silylium ions have been studied widely in the gas phase, and this field has been reviewed.[10] There have been numerous theoretical studies on silylium ions, and these will be mentioned when they have direct bearing on results in condensed phase.

II. Approaches to Forming Stable Ions

A. From Hydrides

The intermolecular reaction between carbenium ions and the carbon–hydrogen bond of hydrocarbons was first studied mechanistically in the classic paper by Bartlett, Condon, and Schneider.[11] They found that electrophilic reagents such as aluminum bromide catalyze the interchange of hydride and halide between substrates, as in eq 1.

$$(CH_3)_3CCl + C_2H_5(CH_3)_2CH \xrightarrow{AlBr_3} (CH_3)_3CH + C_2H_5(CH_3)_2CBr \quad (1)$$

They interpreted their results in terms of an intermolecular hydride shift (eq 2), by

$$(CH_3)_3C^+ + H{-}C(CH_3)_2C_2H_5 \rightarrow (CH_3)_3C{-}H + {}^+C(CH_3)_2C_2H_5 \quad (2)$$

analogy with already known intramolecular 1,2-hydride shifts. The authors did not address whether the carbocations are short- or long-lived intermediates.

This reaction appears to be well adapted for the production of silylium ions, because it trades the weaker Si–H bond for the stronger C–H bond. Although silicon generally has stronger bonds than carbon to electronegative elements such as oxygen, nitrogen, and halogens, which provide the common leaving groups in carbocation chemistry, the reverse is true for the bond to hydrogen.[12] The saturated carbon–hydrogen bond dissociation energy generally exceeds the silicon–hydrogen energy by ca. 10 kcal mol^{-1} (MH_4, 105 and 91.6 kcal mol^{-1}; Me_3MH, 96.4 and 90.3 kcal mol^{-1}).[12] With the common carbocation triphenylmethyl or trityl, the reaction takes the form of eq 3.

$$Ph_3C^+ + R_3Si{-}H \rightarrow Ph_3C{-}H + R_3Si^+ \quad (3)$$

The reaction has the considerable advantage that the only byproduct is the inert hydrocarbon triphenylmethane.

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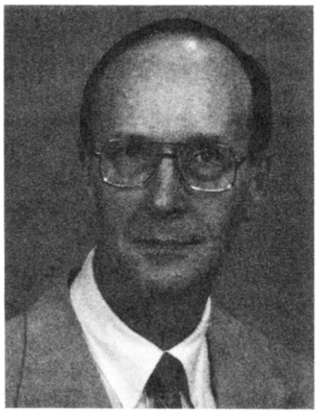

Joseph B. Lambert, after receiving his bachelor's degree from Yale University and his doctor's degree from the California Institute of Technology, has spent his entire career at Northwestern University, where he is Clare Hamilton Hall Professor of Chemistry. In addition to organosilicon chemistry, he has been involved in research in other main group chemistry, nuclear magnetic resonance spectroscopy, conformational analysis, organic reaction mechanisms, and archaeological chemistry. He has been a Sloan and a Guggenheim Fellow. His awards include the National Fresenius Award of Phi Lambda Upsilon, the Fryxell Award of the Society for American Archaeology, and the National Catalyst Award of the Chemical Manufacturers Association. He is the editor-in-chief of the *Journal of Physical Organic Chemistry*, past president of the Society for Archaeological Sciences, and past chairman of the Department of Chemistry at Northwestern University.

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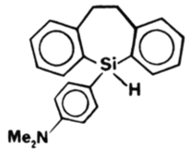
Shizhong (Mark) Zhang is currently a Research Associate and Adjunct Lecturer at Northwestern University. He received his Ph.D. at the University of North Texas in 1990 with Robert T. Conlin, M.S. at Dalian Institute of Chemical Physics in 1985, and B.S. at Helongjiang University in 1982. His research interests are in the field of reactive organosilicon intermediates, more recently in the effects of silicon on carbon radicals and carbanions.

Within a decade of the paper by Bartlett, Condon, and Schneider,[11] Eaborn used a similar method for the production of silylium perchlorates in the reaction of silanes with silver perchlorate, in which metallic silver and molecular hydrogen are byproducts.[13] Whitmore, Sommer, and co-workers studied the reaction that was the strict analogue of the Bartlett–Condon–Schneider reaction, between silane and halocarbons (eq 4).[14–16] Silanes substituted with four

$$(CH_3)_3Si{-}H + Ph_3C{-}Cl \xrightarrow{AlCl_3} (CH_3)_3Si{-}Cl + Ph_3C{-}H \quad (4)$$

different groups racemized when the solvent was the poorly nucleophilic dichloromethane. Free silylium cations were not invoked, as racemization "could easily arise from partial breakage of the Si−H bond, and rotation of the R_3Si moiety followed by return of the hydride". Corey and West[17] also studied the reaction in dichloromethane and suggested as the mechanism a four-centered interchange of hydride and chloride between carbon and silicon. Carey and co-workers[18,19] examined the reaction in detail for the first time with carbocations as the electrophile, formed from carbinols in acid. In the solvents used (acetic acid or dichloromethane containing 2 equiv of trifluoroacetic acid), the products were silanols.



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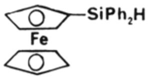

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Optimized conditions for forming long-lived silylium ions were finally brought together by Corey, when she studied the reactions of silanes **1** and **2** with trityl perchlorate in dichloromethane.[20,21] For the first time, stabilizing substituents, low-coordinating solvent, and low nucleophilicity anion were examined in the same study. At temperatures below −40 °C, highly colored solutions were formed by eq 3, and reaction of these solutions with sodium borodeuteride regenerated the original substrate, with hydride replaced by deuteride. Barton and co-workers[22] showed that the color could come from radical cations associated with the dimethylamino and ferrocenyl groups. Barton, Mislow, and their co-workers[22,23] showed that covalent silylium perchlorates react with borohydrides to form silanes. Thus none of the Corey observations required long-lived silylium ions. Lambert and Sun in unpublished work in collaboration with Corey found that the dichloromethane solutions of **1** after reaction with trityl perchlorate were essentially nonconducting. Lambert and Sun[24] also studied the reactions of triphenylsilane, methyldiphenylsilane, pentaphenyldisilane, pentamethyldisilane, and tris(trimethylsi-

Table 1. Conductance Properties of Trityl Perchlorate and of Silyl Perchlorates, Triflates, and Azides

system	molar conductance[a] (Λ), Ω cm² equiv⁻¹		ref
	CH_2Cl_2	sulfolane	
$HClO_4$ (70% aq)	0.1[b]	120[b]	27
Ph_3CClO_4	420	130	30
$(iPrS)_3SiClO_4$	320[b]	42[b]	27
Ph_3SiClO_4	0.46	105	30
$PhMe_2SiClO_4$	0.46	150	30
Me_3SiClO_4	0.38	104	30
$(Me_2N)Me_2SiClO_4$	15	120	31
$(Me_2N)_2MeSiClO_4$	25	130	31
$(Me_2N)_3SiClO_4$	33	40	31
Me_3SiOTf	0.57	57	30
Me_3SiN_3	0	0.70	30

[a] At 0.01 M. [b] Recalculated by B. Kuhlmann from ref 27 on the same basis as the remaining data.

Table 2. Cryoscopic Molecular Weights in Sulfolane

system	MW, theoretical	MW, found	error, %	v[a]	ref
$(iPrS)_3SiClO_4$	353.0	377	+6.8	2	27
Ph_3SiClO_4	358.5	380	+6.0	2	27
$PhMe_2SiClO_4$	234.6	242	+3.2	2	30
Me_3SiClO_4	173.0	170	−1.7	2	30
$(Me_2N)Me_2SiClO_4$	201.6	218	+8.1	2	31
$(Me_2N)_2MeSiClO_4$	230.6	238	+3.2	2	31
$(Me_2N)_3SiClO_4$	259.5	283	+9.1	2	31
Ph_3SiOTf	408.5	407	−0.4	1	27
Me_3SiOTf	222.3	220	−1.0	1	30
Ph_3SiN_3	301.4	299	−0.8	1	27
Me_3SiN_3	115.2	114	−1.0	1	30
Ph_3CClO_4[b]	342.8	367	+7.1	2	27
Ph_3CH	244.3	232	−5.0	1	27

[a] Number of particles. [b] Determined in the presence of an equimolar amount of triphenylmethane, as was the case with all silyl perchlorates.

lyl)silane with trityl perchlorate in dichloromethane and found all the solutions to be essentially nonconducting. They concluded that the reaction "leads to the formation of a covalent or tight ion pair" species in dichloromethane. Although silylium ions could have been formed as reactive intermediates, just as in the case of halides, long-lived intermediates could at best be tight ion pairs for these substrates with perchlorate as anion and dichloromethane as solvent.

In 1983, Lambert and Schulz[25] used the same approach as Corey with the substrate $(RS)_3SiH$ (R = Me, Et, iPr). The sulfur substituent was chosen for its ability to stabilize charge through polarization, since the efforts of Corey and many others to stabilize charge on silicon through 2p−3p conjugation had not met with success. In contrast to the cases studied by Corey[20,21] and by Lambert and Sun,[24] the sulfur system was highly conducting even in dichloromethane.[25] Control studies eliminated hydrolysis as the source of conductance (addition of water to bring about hydrolysis and characterization of the resulting conductance). Finally, cryoscopic studies in sulfolane, a highly ionizing and poorly nucleophilic solvent, found the molecular species to be made up of two particles, with a molecular weight within 7% of theoretical for the silylium perchlorate. Although the authors eliminated a number of alternative representations to the silylium ion $(RS)_3Si^+$, complexation with solvent was not eliminated, only said in the case of dichloromethane to be "unlikely".

In a series of papers,[26−31] Lambert and co-workers examined several other substrates. The conductance and cryoscopic results are summarized in Tables 1 and 2. In dichloromethane, the results ranged from extremely low conductance for the hydrolysis product perchloric acid and for a silylium azide, to low conductance for a silylium triflate and for methyl- and phenylsilylium perchlorates, to intermediate conductance for aminosilylium perchlorates, finally to high conductance for the (alkylthio)silylium perchlorates and trityl perchlorate.

The cryoscopic results on these substrates are summarized in Table 2. All the silylium perchlorates exist as two particles in dilute sulfolane with their expected molecular weight, not those of hydrolyzed materials such as silanols or of one-particle covalent perchlorates. The errors ranged from 1.7 to 9.1%. In contrast, silylium triflates and azides were found to exist as one particle in dilute sulfolane.

These cryoscopic results clearly indicated unhydrolyzed, free ions in sulfolane and ruled out covalency. In no case, however, was a ^{29}Si resonance obtained that indicated silylium character. Extreme low shielding expected by analogy with carbenium ions was not observed. Olah and co-workers[32] applied the IGLO method of Kutzelnigg and Schindler to calculate the ^{29}Si shifts of free silylium ions and obtained a value of δ 355.7 for Me_3Si^+. The triphenylsilylium and trimethylsilylium perchlorate resonated respectively around δ 3 and δ 47, both indicative of very close association between silicon and a fourth coordination ligand and hence little planar, tricoordinate character. No reliable ^{29}Si results were obtained with the thioalkylsilylium ions because of poor long-term stability.

Olah and co-workers[32−34] suggested that the solutions studied by Lambert and co-workers were hydrolyzed. As both Olah and Lambert demonstrated, hydrolysis is a legitimate concern. None of the results of Tables 1 and 2, however, could be explained by hydrolysis. Lambert et al.[30] measured the amount of water in their solutions directly by integration of the relative sizes of the proton resonances of the silylium perchlorate and the hydrolysis product. In dichloromethane, water was present at the level of 0.0004 M and in sulfolane at 0.0024 M, in both cases more than 1 order of magnitude lower than substrate concentrations respectively in the conductance and cryoscopic experiments. Hydrolysis therefore proved to be a red herring in trying to understand the apparent contradiction between the clear proof of ions by conductance and cryoscopy and the clear proof of tetracoordination by ^{29}Si NMR.

Lickiss[6] pointed out, however, that one of Lambert's experiments very likely was affected by hydrolysis. Plots of the ^{35}Cl shifts and line widths were obtained by increasing dilution of single samples.[29] The procedure involved taking the ^{35}Cl spectrum, removing a portion of the sample, and replacing it with additional solvent. In this way the substrate was exposed to the aqueous impurity several times over. By Lickiss' calculations, this procedure led to complete hydrolysis at the lowest concentrations. In contrast, the cryoscopic and conductance experiments of Tables 1 and 2 were based on undiluted samples prepared initially with dry solvents and yielded unhydrolyzed products.

Much later than these experiments, an entirely different approach further supported the case that these materials did not exist as fully covalent perchlorates in dichloromethane. Lambert and Zhang[35] prepared the substrate methyldiisopropylsilane (Me(iPr)$_2$SiH), in which the isopropyl methyl groups are diastereotopic in both the ^{1}H and ^{13}C spectra, because the adjacent silicon atom has three different groups attached. They converted the silane to the silylium perchlorate by the usual Corey procedure in several solvents. A fully covalent perchlorate would retain the diastereotopicity of the isopropyl methyls, but conversion to a planar, tricoordinate species or to a tetracoordinate species capable of dissociating to the planar form would render the methyls equivalent. They found that in dichloromethane the methyls were equivalent, but in a new solvent, benzene, they remained diastereotopic. Apparently the association between silylium and a fourth ligand is strong enough in benzene to keep the methyls nonequivalent, but in dichloromethane the interaction is sufficiently weak (for the conditions, no more than about 13 kcal mol^{-1}) to allow their interconversion. These results do not demonstrate tricoordination in CH_2Cl_2, but they do corroborate the conductance results that the fourth coordination is weak enough to dissociate to an ionic form or forms in which the methyls may interconvert.

Lambert and co-workers[26-31] carried out a number of tests in order to determine whether solvent was an integral part of the ions formed. A solvent complex of the form R_3Si-S^+ is both ionic and tetracoordinate and hence can explain both conductance and NMR results. Cryoscopic experiments only count particles and cannot distinguish between $R_3Si^+\ ClO_4^-$ and $R_3Si-S^+\ ClO_4^-$. Either structure can explain the free ions found in sulfolane by cryoscopy and conductance and the more associated forms found in dichloromethane varying from fully covalent for Me_3SiN_3 to highly conducting ions for the alkylthiosilylium perchlorates (Table 1). Moreover, solvent complexes should have shielded chemical shifts resembling tetracoordinate species such as covalent perchlorates. The relevant solvent complexes would have the forms

$R_3Si-\overset{+}{Cl}CH_2Cl$

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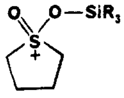

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respectively for dichloromethane and sulfolane (for dichloromethane both chlorines alternatively can ligate to silicon in a four-membered ring).

The primary test used by Lambert and co-workers to determine whether complexation was important in their solutions was a standard conductance procedure.[27,30] A dichloromethane solution of 1.0 equiv of silane containing 0.5 equiv of a suspected complexing agent was titrated from 0.0 to 1.0 equiv of trityl perchlorate. In the absence of complexation, the conductance would remain low for such substrates as trimethylsilane, triphenylsilane, and dimethylphenylsilane over the entire range of trityl concentrations in dichloromethane. If a complex forms, however, the initial species is R_3Si-S^+, which would be highly conducting. Thus the conductance would increase from 0.0 to 0.5 equiv, at which point the complexing agent is used up. From 0.5 to 1.0 equiv the conductance would then level off since the silylium perchlorate being formed has little conductance. For these silanes, the strong nucleophiles *N*-methylpyrrole and pyridine, present in the dichloromethane solution, exhibited behavior indicative of complex formation, but the weaker nucleophiles sulfolane and acetonitrile showed low conductance over the full concentration range.

On the basis of these experiments, the authors concluded that *N*-methylpyrrole and pyridine form complexes but sulfolane and acetonitrile do not. The latter conclusion, however, assumed that sulfolane and acetonitrile could displace perchlorate in dichloromethane. Although in pure sulfolane and acetonitrile, perchlorate clearly has ionized, the more poorly solvating environment of dichloromethane may not permit acetonitrile or sulfolane to displace perchlorate and bring about the expected results for the complexation test. Thus the conductance tests carried out by Lambert and co-workers could not definitively eliminate complex formation for sulfolane and acetonitrile, and their conclusions that such complexes did not form were unjustified. The ions formed in pure sulfolane most likely had structures such as **4**. For the more highly conducting alkylthio substrates, the test for complexation was not applicable, so that **3** was never ruled out. Moreover, the solvent complexes as the conducting entities in dichloromethane and sulfolane rather than tricoordinate silylium ions are consistent with Eaborn's observation[5] that $(Me_3Si)_3CSiMe_2OClO_3$ reacts slowly in methanol and therefore does not ionize to a silylium intermediate.

Numerous complexes of this sort had been prepared in solution by earlier workers. Chojnowski and co-workers[36a] prepared complexes of trimethylsilylium with hexamethylphosphortriamide and triphenylphosphine oxide, both strong nucleophiles. Bassindale and Stout[36b] prepared complexes of trimethylsilylium with pyridine and 3-methyl- and 3-(trimethylsilyl)imidazole, again strong nucleophiles. Olah et al.[36c] suggested nitrile complexes. The X-ray structure of the pyridine complex of trimethylsilylium was reported by Hensen et al.[37] Chojnowski and Stańczyk[7] reviewed solution data on tetracoordinate silyl cations.

The role of solvent complexation was considerably clarified as investigators moved toward less nucleophilic anions and solvents. Lambert and Kuhlmann discovered that stannylium ions could be examined in aromatic solvents such as benzene or toluene.[38] Lambert and Zhang then utilized these aromatic solvents to examine silylium ions. They adapted tetrakis(pentafluorophenyl)borate (TPFPB$^-$, $(C_6F_5)_4B^-$) for use with silylium ions,[39] and Reed and co-workers adapted the carborane *closo*-$CB_9H_5Br_5^-$ for the same purposes.[40] Sakurai,[41] Boudjouk,[42] and their co-workers at the same time were examining tetrakis-

[3,5-bis(trifluoromethyl)phenyl]borate ($(3,5\text{-}(CF_3)_2C_6H_3)_4B^-$). All of these investigators treated silanes with the appropriate trityl salt in their attempts to produce silylium ions (eq 3). Sakurai and co-workers[41] did not obtain stable solutions in dichloromethane, but isolated mixtures of chloro- and fluorosilanes. When ethers were present, however, they obtained stable oxonium ions of the form $Me_3Si-O^+Et_2$ with broadened lines from apparent ether exchange and deshielded ^{29}Si resonance positions (δ 66.9 compared with δ 46 for the triflate or perchlorate). They interpreted these results as involving "significant development of positive charge on silicon". Similarly, Bahr and Boudjouk[42] isolated only the fluorosilane in dichloromethane but obtained nitrilium salts of the type $R_3Si-N^+{\equiv}CR'$ for a variety of silanes and nitriles. They presented evidence that the nitrile ligand exchanges by a dissociative mechanism, i.e., through a free silylium ion. Exchange on the NMR time scale clearly implied a weakened bonding interaction between silicon and nitrogen.

The results of Lambert,[39] Reed,[40] and their co-workers provided evidence for a continuum of structures and established the current experimental standards for the accessible ionic extreme. Lambert and Zhang[39] reported that the ^{29}Si position for triethylsilylium–TPFPB respectively in acetonitrile, sulfolane, toluene, and benzene was δ 36.7, 58.4, 81.8, and 92.3, and in the solid state without solvent was δ 94.3. The results in sulfolane were noteworthy, as the intermediate ^{29}Si value clearly indicates weak complexation, the first unequivocal evidence that the earlier conductance and cryoscopic experiments of Lambert et al. referred to silylium ions complexed to solvent to some extent (**4**). Even more deshielded was triisopropylsilylium–TPFPB at about δ 108 in both benzene and the solid and tris(trimethylsilyl)silylium–TPFPB at δ 111 in benzene. Because of the normal strong shielding effect of the trimethylsilyl group, the latter value actually represents a shift of 228.5 ppm from that of the hydride, compared with shifts of up to 101 ppm for the alkyl-substituted silylium ions. The authors stated that "these values indicate reduced coordination to anion or solvent." Free silylium ions were not claimed because further shifts of up to another 250 ppm might be expected on the basis of the IGLO calculations.[32]

Reed et al.[40] also documented the complexation continuum, with ^{29}Si resonances ranging from δ 33.8 for triisopropylsilylium (with the anion *closo*-$CB_9H_5Br_5^-$) in acetonitrile to δ 97.9 in toluene. They reported the X-ray structure of the acetonitrile complex of triisopropylsilylium and a solvent-free structure as well. The acetonitrile complex resembled the previously reported pyridine complex.[37] The solvent-free structure was weakly coordinated to the anion through a bromine atom, with the Si–Br bond distance about 0.2 Å longer than the covalent value, resembling the perchlorate structure of Prakash et al.[33] Reed and co-workers[40] concluded that the solvent-free ion pair had "about one third silylium character". Reed and co-workers[43] also obtained the crystal structure of a protonated silanol (*tert*-butyl)$_3$Si–O$^+$H$_2$, in which the Si–O bond is considerably lengthened. They concluded that it possesses predominate silyl cation rather than covalent oxonium ion character. Both Lambert and Reed noted that the ^{11}B line width and chemical shift for the TPFPB$^-$ solutions indicated a relatively free borate anion, which can reorient through dissociation and recombination in order to reduce the interaction between the quadrupole and the electric field around the nucleus, in contrast to the case of the perchlorates, for which broadened ^{35}Cl resonances were observed.[27]

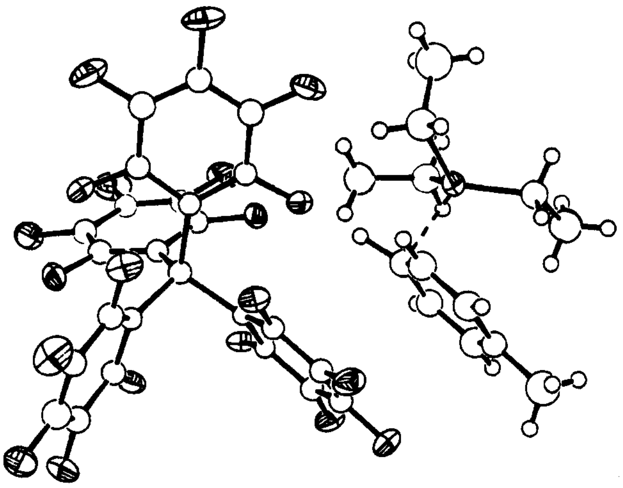


Figure 1. Molecular structure of triethylsilylium·toluene tetrakis(pentafluorophenyl)borate. Silylium cation, upper right; TPFPB anion, left; toluene, lower right. (Reprinted with changes from ref 44. Copyright 1993 American Association for the Advancement of Science.)

In 1993, Lambert and Zhang obtained crystals of triethylsilylium–TPFPB from hexane/toluene and with Stern and Huffman solved its X-ray structure.[44] The structure contained several molecules of the solvent toluene, one of which occupied a fourth coordination site around silicon (Figure 1). The distance from silicon to the nearest atom of toluene, the para carbon, at 2.18 Å, was much longer than the longest previously known tetracoordinate C–Si bond distance, 2.03 Å in an extremely crowded molecule[45] (the normal C–Si bond length has a mean of 1.85 Å). The anion is clearly free, its closest approach being a Si–F distance of 4.02 Å. Lambert et al. referred to the structure as having "no coordination to anion and distant coordination to solvent",[44] rather than as a free silylium ion. The geometry around silicon is nonplanar, the Si atom being about 0.45 Å out of the plane of the methylene carbons. Later Schleyer et al., Olsson and Cremer, and Olah et al.[46] characterized the interaction between Si and toluene in the Lambert/Zhang structure as σ bonding (an arenium ion) and Reed[47a] as π bonding. Reed pointed out that the geometry of Si with respect to the toluene ring is much closer to that expected for π rather than σ bonding, and Lambert and Ciro[35] concluded from the solid-state ^{13}C chemical shifts that very little positive charge is present in the toluene ring. Lambert et al. concluded that the structure is best termed a silyl cation "with weak η^1 π coordination to toluene" [35] (Figure 1). Cacace et al.[48] carried out ion cyclotron resonance studies in the gas phase in order to distinguish the σ and π models. They found that reaction of triethylamine with the complex between triethylsilylium (Et_3Si^+) and C_6D_6 resulted in the transfer of both D^+ and Et_3-

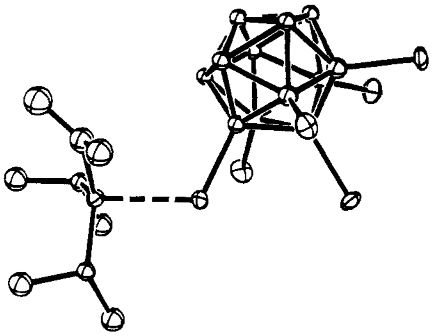


Figure 2. Molecular structure of triisopropylsilylium *closo*-$CB_{11}H_6Br_6^-$. (Adapted from ref 47.)

Si^+. Although the transfer of Et_3Si^+ can be interpreted in terms of either σ or π model, the transfer of D^+ is best explained by the σ model. The authors, however, point out that an equilibrium between σ and π structures also is in accord with their results. The difficulty in providing an unequivocal distinction may result not only from possible gas/solid structural differences but also from the fact that the Lambert/Zhang geometry is indeed intermediate between the σ and π extremes in terms of the Si–C(1)–C(4) angle.[47a]

Lambert and co-workers[35] carried out several experiments to assess the approximate energy of the interaction between Si and toluene on the NMR time scale. They found that a mixture of benzene and toluene gave a chemical shift, δ 87.1, intermediate between the values for the separate solvents. Since only a single peak was observed, they concluded that "binding and dissociation between solvent and silylium are fast on the NMR time scale". In addition, they found that the protons and carbons of the isopropyl methyl groups in methyldiisopropylsilylium/TPFPB were homotopic in benzene, acetonitrile, and even pyridine, again indicating rapid dissociation on the NMR time scale. They set an upper limit of about 13 kcal mol^{-1} to the dissociation of the complex into free silylium ion and solvent. In the gas phase, the association energy of Me_3Si^+ with benzene was found to be 23.9 kcal mol^{-1} and that between Me_3Si^+ and toluene 28.4 kcal mol^{-1},[49] compared with about 90 kcal mol^{-1} for the bond dissociation energy for a maximally covalent Si–C bond. Thus the discussion of σ vs π models distracts from the fact that bonding between silicon and carbon in the Lambert/Zhang structure is much weaker than in maximally covalent cases.

With a new carborane anion, *closo*-$CB_{11}H_6Br_6^-$, Reed et al.[47a] obtained the X-ray structure of triisopropylsilylium with a geometry most closely approaching the planar ideal (Figure 2). The C–Si–C angle averaged 117°, compared with the ideal 120° and the 114° of the structure of Lambert et al.[35,44] In this case the silicon was weakly coordinated to a bromine atom of the anion, with a Si–Br distance of 2.48 Å, about 0.2 Å longer than normal, so that in classical carbenium ion terminology it resembles an intimate ion pair. The ^{29}Si chemical shift in the solid state was δ 109.8 and in toluene δ 105. Reed and co-workers described the molecule as "an ionic-like species that lies along a continuum that ranges from four-coordinate covalent to trigonal-planar ionic".[47a]

Reed and co-workers later obtained crystal structures for the triethyl, tri-*tert*-butyl, and di-*tert*-butylmethyl systems with the same carborane anion.[47b] Although the *tert*-butyl systems would seem to be the most sterically crowded, the original triisopropylsilylium system proved to have the longest C–Br distance, the largest mean C–Si–C angles, and the smallest deviation of Si from the plane of its attached atoms. The system remains the geometrically closest material to a trigonal silylium ion.

Table 3 summarizes the structural parameters for silylium-like species. Pauling[50] pointed out the applicability of his equation to assessing bond orders in these systems. The Pauling bond order n is obtained from the expression $0.60 \log n = D(1) - D(n)$, in which $D(1)$ is the bond distance when the covalent bond order is unity, and $D(n)$ is the observed distance when the bond order is n. The results of these calculations are included in Table 3. In general, the systems with the carborane and TPFPB anions have low covalencies and those with halide or perchlorate have high covalencies. Probably only this qualitative conclusion is appropriate for this empirical approach. High level ab initio calculations by Schleyer and co-workers[46,51] found a Wiberg bond index of 0.44 for SiH_3^+ complexed with benzene (about half the 0.82 for neutral $MeSiH_3$); the comparable value for a complex of Et_3Si^+ with toluene should be lower, and hence not very different from the Pauling 0.28. Similar calculations on the complex of Me_3Si^+ with toluene found a charge of +0.71 on Si and +0.29 on toluene. In comparison, free Me_3C^+ carries a charge of +0.65 on the central carbon. Although considerable positive charge is present on Si in the Lambert/Zhang structure, free Me_3Si^+ has a calculated charge of about +2.2 on Si, with negative charges on the substituents to balance out the greater-than-unity positive charge on Si. The more electropositive Si can sustain a much higher amount of positive charge in Me_3Si^+ than can C in Me_3C^+. The calculated value of +0.71 on Si in the toluene complex (full charge +2.2),[46,51] the ^{29}Si chemical shifts of circa δ 100 (full shift δ 350),[44,47] and the gas-phase association energy of 23–28 kcal mol^{-1} between Me_3Si^+ and arene (full bond 90 kcal mol^{-1}) agree with Reed's conclusion[47] that both the Lambert[44] and Reed[47] systems (Figures 1 and 2) probably are about a third of the way from full covalent bonding to a free silylium cation.

B. From Halides and Related Materials

Numerous groups have attempted to generate silylium ions by traditional carbenium ion approaches involving the removal of electron-withdrawing groups such as halides or esters. Ionizing solvents are used, and usually a Lewis acid is added to promote ionization. This was the procedure, for example, by which Wannagat and Liehr[52] originally prepared silylium perchlorates, through the treatment of chlorosilanes with silver perchlorate. The isolated perchlorates were distillable liquids with properties resembling covalent materials, albeit with a weakened bond and tendencies toward explosiveness. In 1980, Cowley et al.[53] reacted tris(dimethylamino)silylium chloride and fluoride with a variety of Lewis acids, such as aluminum hexachloride, phosphorus pentafluoride,

Table 3. Structural Parameters for Silylium-like Systems

subst	solvent	anion	Si–L distance, Å obs	cov[a]	Pauling bond order[b]	C–Si–C,[c] deg	out-of-plane,[d] Å	ref
		Solvent-Separated Ion Pairs ($R_3Si{\cdot}solvent{\cdot}anion$)						
Et$_3$	toluene	$TPFPB^-$ [e]	2.18	1.85	0.28	114	0.462	35,44
Me$_3$	pyridine	I^-, Br^-	1.86	1.73	0.61	113.5	0.485	37
iPr$_3$	acetonitrile	*closo*-$CB_9H_5Br_5^-$	1.82	1.73	0.71	115.5	0.410	40
tBu$_3$	water	*closo*-$CB_{11}H_6Br_6^-$	1.78	1.64	0.58	116.0		43
		Intimate Ion Pairs ($R_3Si{\cdot}anion$)						
iPr$_3$		*closo*-$CB_{11}H_6Br_6^-$	2.479	2.24	0.40	117.0	0.300	47a,b
tBu$_2$Me		*closo*-$CB_{11}H_6Br_6^-$	2.466	2.24	0.42	115.3	0.408	47b
tBu$_3$		*closo*-$CB_{11}H_6Br_6^-$	2.465	2.24	0.42	116.2	0.371	47b
iPr$_3$		*closo*-$CB_9H_5Br_5^-$	2.44	2.24	0.46	115.8	0.392	38
Et$_3$[f]		*closo*-$CB_{11}H_6Br_6^-$	2.444	2.24	0.46	115.0	0.419	47b
Et$_3$′[f]		*closo*-$CB_{11}H_6Br_6^-$	2.430	2.24	0.48	116.3	0.348	47b
Ph$_3$		ClO_4^-	1.74	1.64	0.68	113.5	0.479	33

[a] Normal C–L covalent bond length. [b] Calculated from the Pauling equation. [c] Mean value. [d] Distance of Si from plane of attached carbons. [e] Tetrakis(pentafluorophenyl)borate. [f] The structure contained two independent molecules.

and arsenic pentafluoride. Cowley and others had demonstrated that nitrogen effectively stabilizes the isoelectronic phosphenium ion. By X-ray they found that aluminum coordinated with the lone pair of nitrogen rather than serving to abstract chloride. They suggested that the same reaction occurred in dichloromethane. The Lewis acids containing fluorine gave mixtures.

In 1982, Olah and Field[54] similarly treated bromotrimethylsilane with 3 equiv of aluminum tribromide. In this case the Lewis acid complexed with the halogen, weakening the Si–Br bond. In carbon disulfide the complex had a ^{29}Si chemical shift of δ 54.2 and in dibromomethane of δ 62.7, the deshielded position indicating some positive charge on silicon. When Olah et al.[55] treated trimethylsilylium triflate with boron trichloride or tribromide, the resulting chemical shifts respectively were δ 72.4 and 61.5. Triethylsilylium triflate when treated with boron trichloride produced a chemical shift of δ 76.7. The ^{11}B chemical shift of δ −2.62 suggested a shielded, tetracoordinate species. They concluded that the silyl products were "strongly polarized donor–acceptor complexes". Olah et al.[33] treated trialkylfluorosilanes with antimony pentafluoride in SO_2ClF at −78 °C and obtained at least two species, whose concentrations depended on the amount of Lewis acid. The most deshielded species were obtained with excess antimony pentafluoride, the ^{29}Si resonances from trimethyl, triethyl, and triisopropyl occurring respectively at δ 102, 95, and 93. These represented the most deshielded species until the carborane and TPFPB anions were developed by Reed[40] and Lambert.[39]

Eaborn and co-workers have carried out extensive studies on the substrates $(Me_3Si)_3CSiR_2I$, for which the reactivity pattern is greatly influenced by the bulk of the $(Me_3Si)_3C$ group. Reactions with silver or mercury salts gave rearranged products, which they interpret as evidence for a cationic intermediate. The authors suggested that the intermediate contains a methyl group bridged between two silicon centers, the charge being largely divided between those centers.[56] Solvolysis of $(Me_3Si)_2(PhMe_2Si)CSiMe_2I$ in trifluoroethanol also appears to involve a cationic intermediate, whose bridge in this case is provided by phenyl, on which much of the charge resides.[57] Other groups such as methoxyl can provide even more effective bridging.[57]

Hwu et al.[58] treated trimethylchlorosilane, trimethyliodosilane, methyldiphenylchlorosilane, and dimethyldichlorosilane with silver salts of a variety of anions such as BF_4^-, SiF_6^{2-}, and $PtCl_6^{2-}$ in acetonitrile at −50 °C and obtained mixtures of fluorosilanes. They concluded that "the formation of transient Si^+ ions or Si^+ X^- ion pairs is likely", although the nucleophilicity of the acetonitrile solvent would militate against long-lived free ions.

Because of the nucleophilicity of halogens, or their silaphilicity in particular, even when complexed with the Lewis acid, it is unlikely that this family of approaches can lead to free silylium ions. Hydride abstraction has the advantage that a covalent C–H bond forms and the byproduct is a hydrocarbon, so that the focus can remain on the solvent and the anion.

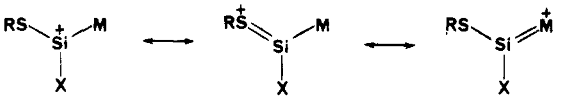
C. By Other Methods

Russian workers at the Institute of Silicate Chemistry in St. Petersburg have developed a novel method to generate silylium ions by nuclear chemistry. Nefedov, Kochina, and their co-workers[10,59–61] adapted a known procedure for generating carbenium ions to the analogous silicon case, taking advantage of the nuclear decay of tritium to helium with the expulsion of a β particle and an antineutrino. The helium atom bears a positive charge, which is transferred to trivalent silicon on loss of helium (eq 5). Silylium

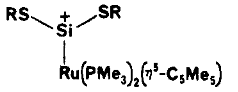
$$R_2SiT_2 \xrightarrow[-\bar{\nu}]{-\beta} R_2SiT{-}^3He^+ \rightarrow R_2SiT^+ + {}^3He \qquad (5)$$

ions can be produced in this fashion in the gas, liquid, or solid phases, independent of temperature, pressure, and solvent (nuclear reactions are not sensitive to these conditions). The silylium ions are trapped by reaction with nucleophiles such as methanol or hexamethylsiloxane. Because only small amounts of nuclear decay occur (10^{-9}–10^{-10} g ions in about 10 days), products are detected by gas radiochromatographic methods at the 10^{-8} mg level, for which the second tritium atom is required. As a result, only the secondary systems Me_2SiT^+ (in the gas phase[59]) and Et_2SiT^+ (in solution[60]) have been examined. Tertiary systems could be examined if the residual tritium atom were placed on a substituent. Although the proposed silylium ions may be sufficiently short-lived to qualify as reactive intermediates rather than long-lived species, the technique could feasibly be used for more stable cases.

Tilley and co-workers[62-64] have produced a series of molecules that are formally trivalent silylium ions, in which one or more of the ligands is a transition metal and the remaining ligands are alkylthio. The several resonance structures (eq 6) include the silylium ion, forms π bonded to sulfur, and forms π bonded to the transition metal. The first such molecule[62] (**5**, shown in the silylium ion form, which is probably not the dominant resonance contributor) carries two sulfur substituents and a ruthenium substituent. It was prepared by replacement of triflate with tetraphenylborate. Its X-ray structure was not obtained, but in dichloromethane below −60 °C the ^{29}Si chemical shift for R = p-tolyl was δ 259.4 and for R = Et δ 264.4. These remarkably deshielded positions, much more so than any other molecules prepared up to that time, suggest trigonality around silicon. This supposition was confirmed by X-ray crystallographic solution of the structure of the platinum complex **6** (Cy = cyclohexyl).[63] The ^{29}Si resonance of this material occurred at the extremely deshielded position of δ 308.7 (the triflate resonates at δ 89.7). The sum of the angles around silicon was 359.9°, essentially trigonal. Both the Si–S and Si–Pt distances were short, but the authors concluded that double bonding is primarily between silicon and sulfur. A neutral analogue with bonding to osmium and ruthenium also was obtained.[64] Although the silicon was trigonal in the crystal, the ^{29}Si chemical shift at δ 19.4 was not deshielded.



(6)



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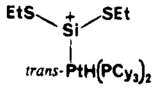
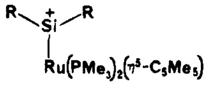


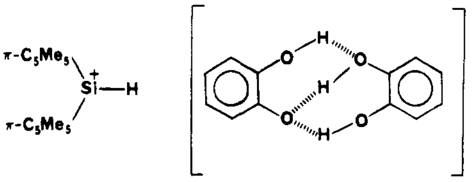
6

In 1994, Tilley and co-workers succeeded in obtaining complexes of this type without sulfur ligands.[65] Compounds of formula **7** with two phenyl or two methyl groups as R, with ruthenium as the metal, and with TPFPB⁻ as the anion were obtained by treatment of the triflate with $LiB(C_6F_5)_4OEt_2$ at −30 °C. In dichloromethane the materials were not stable at room temperature but at low temperatures gave ^{29}Si resonances at the highly deshielded positions δ 299 (phenyl) and 311 (methyl), the latter being the current deshielded record for low coordination silicon. The crystal structure of the methyl compound had a trigonal, planar silicon with 359° as the sum of the bond angles around silicon. The record short Si–Ru length of 2.238 Å indicated strong double-bond character. The inorganic chemist generally views these species as transition metal complexes of divalent silicon (silylenes) rather than as silylium ions, just as the analogous carbon molecules are considered to be complexes of carbenes. Viewed as a whole, such molecules of course are neither silylenes nor carbenes. Whether they qualify as silylium ions depends on how one interprets π delocalization in eq 6 (is $Me_2C(OMe)^+$ a carbenium or an oxonium ion?; what about $(p\text{-MeO-}C_6H_4)_3C^{+}$?).



7

Jutzi and Bunte[66] treated decamethylsilicocene with catechol and obtained the novel structure **8**, in which silicon is bonded to hydrogen and to two π-pentamethylcyclopentadienyl ligands (cp*). The structure was inferred from the various NMR spectra. The ^{29}Si shift occurred at δ −12.1 and represented a deshielding of 386 ppm compared with the silicocene. The one bond $^{29}Si-^{1}H$ coupling constant of 302 Hz is consistent with bonding to three ligands, as $cp^*_2SiH_2$ with four ligands had a one bond coupling of only 194 Hz. The increase in coupling is related to the increase in s character on going from sp^3 to sp^2, as has been observed in numerous other cases but originally for $^{13}C-^{1}H$ couplings. An unstable solution of the same cation was obtained with the $(F_3CSO_3)_2H$ anion, for which the ^{29}Si shift was δ 51.6 and the $^{29}Si-^{1}H$ coupling was 338 Hz. Although silicon is bonded to only three ligands in **8**, the coordination is actually high, since each π-cyclopentadienyl ligand contributes six electrons to bonding with silicon.



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III. Reactive Intermediates

Because early work[3] did not uncover a large body of evidence in favor of a silicon analogue of the S_N1 reaction and because the existence of long-lived silylium ions has been controversial, workers have been very wary about proposing such ions even as reactive intermediates. For example, acid-catalyzed polymerization of cyclic siloxanes has been shown to occur by a mechanism illustrated in eq 7 for the cyclic

$$D_3 + A \rightarrow A{-}D_2{-}OMe_2Si^* \xrightarrow{D_3} A{-}D_5OMe_2Si^* \rightarrow\rightarrow \quad (7)$$

trisiloxane D_3 (D represents an $-OSiMe_2-$ unit).[67-71] The active propagating center is evasively represented by $-OMe_2Si^*$, in which the asterisk may indicate either a silylium ion or a silyl radical. The most likely intermediate, however, is an oxonium ion formed by complexation of positive silicon with ether

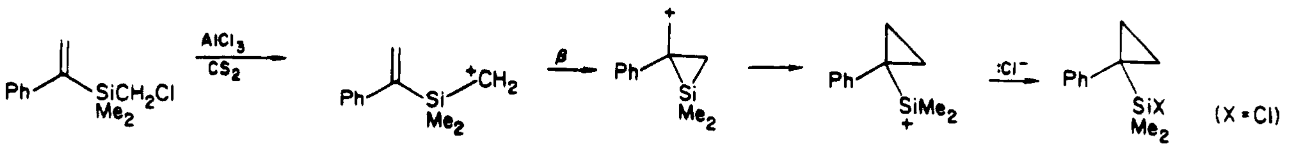

Figure 3. The mechanism for the rearrangement of (chloromethyl)vinylsilanes to cyclopropylchlorosilanes. (Adapted from ref 76.)

oxygens from other siloxanes. Chojnowski and Kurjata presented kinetic evidence for oxonium ions in 1994.[72]

The most extensive studies have been expended on the hydride transfer reaction related to eq 3, which has been used as the predominant means to try to form long-lived silylium ions. Early mechanistic studies[5,16-19] have already been reviewed.[3] The studies of Carey et al.[18-19] were carried out in nucleophilic solvents (acetic acid or dichloromethane containing trifluoroacetic acid). By varying electron demand in aryl rings, they found a Hammett ϱ value of -1.84 for Ar_3SiH and -1.1 for $ArMe_2SiH$, with a better correlation with σ than with σ^*. They also found k_H/k_D to be 1.51–1.89. They suggested a four-membered transition state with Si–H bond breaking preceding Si–O bond making in order to have positive charge well developed on silicon, as required by the negative ϱ values. The transition state resembled that proposed by Corey and West.[17] Sommer and Bauman[16] depicted a more linear transition state ($Ph_3C^{\delta+}{-}H^{\delta-}{-}SiR_3^{\delta+}$).

The first thorough mechanistic study in a low nucleophilic medium (dichloromethane) was carried out by Chojnowski et al.[73,74] with trityl as the hydride transfer agent and antimony hexafluoride and other halogen-containing anions. The larger ϱ value in this solvent (-3.5) suggested much more development of positive charge on silicon than in the solvents used by Carey. The independence of the rate on the nature of the anion suggested that the rate-determining step did not involve the atoms of the anion. They first suggested that hydride transfer in the rate-determining step led to "formation of a positively-charged silicon intermediate", followed by reaction with anion eventually to give the halosilane product. In further studies they also concluded that "a transient silicocation must appear in the system", although most likely solvated.[73] They interpret the low values of k_H/k_D (1.41–1.49) as indicating a very unsymmetrical position of hydride in a concerted transfer or a secondary kinetic isotope effect in a single electron transfer (SET) mechanism. From studies on four-membered rings they favored the SET mechanism, which would involve initial movement of one electron to form a cation radical on silicon ($Ph_3C^{\delta\bullet}{-}H^{\delta\bullet}{-}SiR_3^{\delta\bullet+}$).

Mayr and co-workers[75] examined the hydride transfer from silanes to diarylmethyltitanium pentachlorides in dichloromethane. They found a ϱ of -2.46. They excluded the SET mechanism by demonstrating that the kinetic isotope effect was primary rather than secondary because of the relative values for Ph_2SiHD and Ph_2SiD_2. The argument is somewhat softened by the necessity of having to use secondary systems for comparison with the tertiary systems of Chojnowski. The preponderance of evidence, however, favors "a polar mechanism with rate-determining formation of silicenium ions".[75]

Barton and co-workers[76] examined the reaction of a variety of (chloromethyl)vinylsilanes with aluminum chloride in carbon disulfide. They interpreted the formation of cyclopropylchlorosilanes by the pathway depicted in Figure 3. Partial or complete removal of chloride by the Lewis acid results in an unstable primary carbenium ion that undergoes an allylcarbinyl–cyclopropylcarbinyl-like rearrangement to form a silacyclopropylcarbinyl cation. Some products come from this intermediate, which also can undergo a cyclopropylcarbinyl–cyclopropylcarbinyl-like rearrangement to form a cyclopropylsilylium ion. The major products then come from this intermediate. Although the authors depict only classical carbenium and silylium ions, they point out that the intermediates could be bridged, delocalized structures such as those discussed in the context of all-carbon cyclopropylcarbinyl chemistry.

According to ab initio calculations, an α-silylcarbenium ion is less stable than the isomeric silylium ion in the gas phase. Apeloig and Stanger[77] tested this prediction in adamantyl systems and concluded that silylium ions indeed were present as intermediates. They found in aqueous mixtures that 2-(trimethylsilyl)adamantyl systems gave both the unrearranged 2-(trimethylsilyl)adamantyl product from the α-silylcarbenium ion and the rearranged dimethyl(2-methyladamant-2-yl)silyl product from the silylium ion. The unrearranged/rearranged ratio favored the unrearranged material (91/9) in 80% acetone but increasingly favored the rearranged material as the solvent nucleophilicity was decreased and ionizing power increased: 64/36 in 93% trifluoroethanol, 32/68 in 98% trifluoroethanol, and $<1/>99$ in hexafluoroisopropyl alcohol. They concluded that the data "strongly support the formation of a silicenium ion (either as a free ion or as an ion pair)", but they pointed out that methyl-bridged species were not ruled out). Kevill[78] refined the mechanism in terms of solvent-separated ion pairs in order to allow for proper relative reactivities of water and hexafluoroisopropyl alcohol.

None of these studies can address structural details about the proposed intermediate silylium ions. In particular, it is impossible to determine whether they are planar sp^2 silylium ions or silylium ions with a loosely coordinated fourth ligand (solvent or anion), like those observed by X-ray crystallography.[44,47] Any degree of ion pairing probably requires moving away from planar systems. Thus the comment by Kevill[78] requires that the ions suggested by Apeloig and Stanger[77] are of the nonplanar type with a loose fourth coordination site. Intermediates in the siloxane polymerization reaction[67-71] and in the rearrangements of (chloromethyl)vinylsilanes[76] fall more in the hypothetical category and have not been structurally defined in any detail. Even in the case of hydride transfer from silanes to carbenium ions, there is no evidence that the intermediate silylium ions are free.[75] Nuclear decay of silanes carrying tritium[59-61] can in principle form free sp^2 silylium ions, but this approach is still embryonic.

IV. Summary

Considerable progress has been made in the study of silylium ions in condensed phase over the last 20 years, since the review by Corriu and Henner.[3] The hydride abstraction reaction,[20,21] although not ideal, has become the method of choice for the attempted generation of such species in condensed phase. The introduction of aromatic solvents[38] has provided a medium that made possible the generation of the most deshielded partial silylium ions to date. Although fluorocarbons, chlorofluorocarbons, or saturated hydrocarbons may be less nucleophilic, low solubility has prevented their use for the study of silylium ions. Solid-state NMR[39] also has provided a new perspective on these species, since solvent is entirely absent. These studies also introduced anions of lower nucleophilicity than perchlorate, and the broadest success has been achieved with tetrakis(pentafluorophenyl)borate[39] and bromocarboranes.[40]

By combining these advances, Lambert,[44] Reed,[47] and their co-workers have obtained X-ray crystal structures of materials with considerable silylium ion character. Continued refinement of borate and carborane anions may produce silylium ions even closer to the planar arrangement. The use of metal ligands and borate anions has produced the first examples of tricoordinate, positively charged silicon with highly deshielded ^{29}Si chemical shifts.[62-65] This work by Tilley et al. set new standards in the field that metal-free systems have not attained. Thus the last 20 years have witnessed the preparation of partial silylium ions in solution and the solid with decreased covalency of the fourth coordination site, including complexes of acetonitrile,[40-42] ethers,[41] water,[43] sulfolane,[24-31] aromatics,[35,44] and dichloromethane,[24-31] as well as solvent-free bromocarboranes[38,47a,b] and finally metal-bound, tricoordinate systems.[62-65]

Recent calculations of Schleyer and co-workers[51] indicated that there are interactions even between SiR_3^+ and argon or methane, enough to provide significant nuclear shielding. They in fact conclude that "Lambert's and Reed's silyl cation systems...may be about as free as one can hope to achieve in condensed phase". This pessimistic prognostication does not take into consideration possible improvements in substituents. Steric fences may be built about the central silicon that can prohibit interactions with solvent or anion, but at the same time they may prohibit the abstraction of hydride and they may produce bridged species instead of trigonal silicon. The challenge remains.

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References

(1) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; Part 2, pp 1015–1142.
(2) Lambert, C.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1974**, *33*, 1129–1140.
(3) Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1–28.
(4) Lambert, J. B.; Schulz, W. J., Jr. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; Part 2, pp 1007–1014.
(5) Eaborn, C. *J. Organomet. Chem.* **1991**, *405*, 173–177.
(6) Lickiss, P. D. *J. Chem. Soc., Dalton Trans.* **1992**, 1333–1338.
(7) Chojnowski, J.; Stańczyk, W. *Adv. Organomet. Chem.* **1990**, *30*, 243–307. Chojnowski, J.; Stańczyk, W. *Main Group Chem. News* **1994**, *2*, 6–15.
(8) Bock, H.; Kaim, W. *Acc. Chem. Res.* **1982**, *15*, 9–17.
(9) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371–1448.
(10) Nefedov, V. D.; Kochina, T. A.; Sinotova, E. N. *Russ. Chem. Rev.* **1986**, *55*, 426–438. Schwarz, H. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; Part 1, pp 445–510.
(11) Bartlett, P. D.; Condon, F. E.; Schneider, A. *J. Am. Chem. Soc.* **1944**, *66*, 1531–1539. Deno, N. C.; Peterson, H. J.; Gaines, G. S. *Chem. Rev.* **1960**, *60*, 7–14.
(12) Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; Part 1, pp 371–391. Brinkman, E. A.; Salomon, K.; Tumas, W.; Brauman, J. I. *J. Am. Chem. Soc.* **1995**, *117*, 4905–4910.
(13) Eaborn, C. *J. Chem. Soc.* **1955**, 2517–2519.
(14) Whitmore, F. C.; Pietrusza, E. W.; Sommer, L. H. *J. Am. Chem. Soc.* **1947**, *69*, 2108–2110.
(15) Sommer, L. H.; Bauman, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 7045–7051.
(16) Sommer, L. H.; Bauman, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 7076–7078.
(17) Corey, J. Y.; West, R. *J. Am. Chem. Soc.* **1963**, *85*, 2430–2433.
(18) Carey, F. A.; Tremper, H. S. *J. Am. Chem. Soc.* **1968**, *90*, 2578–2583.
(19) Carey, F. A.; Hsu, C.-L. W. *J. Organomet. Chem.* **1969**, *19*, 29–41.
(20) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3237–3238.
(21) Corey, J. Y.; Gast, D.; Mislow, K. *J. Organomet. Chem.* **1975**, *101*, C7–C8.
(22) Barton, T. J.; Hovland, A. K.; Tully, C. R. *J. Am. Chem. Soc.* **1976**, *98*, 5695–5696.
(23) Bickart, P.; Llort, F. M.; Mislow, K. *J. Organomet. Chem.* **1976**, *116*, C1–C2.
(24) Lambert, J. B.; Sun, H.-n. *J. Am. Chem. Soc.* **1976**, *98*, 5611–5616.
(25) Lambert, J. B.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 1671–1672.
(26) Lambert, J. B.; McConnell, J. A.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 2482–2484.
(27) Lambert, J. B.; Schulz, W. J., Jr.; McConnell, J. A.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 2201–2210.
(28) Lambert, J. B.; McConnell, J. A.; Schilf, W.; Schulz, W. J., Jr. *J. Chem. Soc., Chem. Commun.* **1988**, 455–456.
(29) Lambert, J. B.; Schilf, W. *J. Am. Chem. Soc.* **1988**, *110*, 6364–6367.
(30) Lambert, J. B.; Kania, L.; Schilf, W.; McConnell, J. A. *Organometallics* **1991**, *10*, 2578–2584.
(31) Lambert, J. B.; Kania, L.; Kuhlmann, B.; McConnell, J. A. Unpublished results.
(32) Olah, G. A.; Rasul, G.; Heiliger, L.; Bausch, J.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1992**, *114*, 7737–7742.
(33) Prakash, G. K. P.; Keyaniyan, S.; Aniszfeld, R.; Heiliger, L.; Olah, G. A.; Stevens, R. C.; Choi, H.-K.; Bau, R. *J. Am. Chem. Soc.* **1987**, *109*, 5123–5126.
(34) Olah, G. A.; Heiliger, L.; Li, X.-Y.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1990**, *112*, 5991–5995.
(35) Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430–2443.
(36) (a) Chojnowski, J.; Cypryk, M.; Michalski, J. *J. Organomet. Chem.* **1978**, *161*, C31–C35. (b) Bassindale, A. R.; Stout, T. *J. Chem. Soc., Perkin Trans. 2* **1986**, 221–225. (c) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1249–1251.

(37) Hensen, K.; Zengerly, T.; Pickel, P.; Klebe, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 725–726; *Angew. Chem.* **1983**, *95*, 739–740.
(38) Lambert, J. B.; Kuhlmann, B. *J. Chem. Soc., Chem. Commun.* **1992**, 931–932.
(39) Lambert, J. B.; Zhang, S. *J. Chem. Soc., Chem. Commun.* **1993**, 383–384.
(40) Xie, Z.; Lison, D. J.; Jelínek, T.; Mitro, V.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1993**, 384–386.
(41) Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *114*, 6697–6700.
(42) Bahr, S. R.; Boudjouk, P. *J. Am. Chem. Soc.* **1993**, *115*, 4514–4519.
(43) Xie, Z.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2519–2520.
(44) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917–1918.
(45) Schäfer, A.; Weidenbruch, M.; Pohl, S. *J. Organomet. Chem.* **1985**, *282*, 305–313.
(46) (a) Schleyer, P. v. R.; Buzek, P.; Müller, T.; Apeloig, Y.; Siehl, H.-U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1471–1473; *Angew. Chem.* **1993**, *105*, 1558–1560. (b) Olsson, L.; Cremer, D. *Chem. Phys. Lett.* **1993**, *215*, 433–443. (c) Olah, G. A.; Rasul, G.; Li, X.-y.; Buchholz, H. A.; Sandford, G.; Prakash, G. K. S. *Science* **1994**, *263*, 983–984.
(47) (a) Reed, C. A.; Xie, Z.; Bau, F.; Benesi, A. *Science* **1993**, *262*, 402–404. (b) Xie, Z.; Bau, R.; Benesi, A.; Reed, C. A. Private communication and unpublished results presented at the XXVII Organosilicon Symposium, Troy, NY, March, 1994.
(48) Cacace, F.; Attinà, M.; Fornarini, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 654–655.
(49) Wojtyniak, A. C. M.; Stone, J. A. *Int. J. Mass Spectrom. Ion Processes* **1986**, *74*, 59–79. Stone, J. M.; Stone, J. A. *Int. J. Mass Spectrom. Ion Processes* **1991**, *109*, 247–264.
(50) Pauling, L. *Science* **1994**, *263*, 983.
(51) Maerker, C.; Kapp, J.; Schleyer, P. v. R. Private communication and unpublished results, presented at the 12th IUPAC Conference on Physical Organic Chemistry, Padua, Italy, September, 1994.
(52) Wannagat, U.; Liehr, W. *Angew. Chem.* **1957**, *69*, 783–784.
(53) Cowley, A. H.; Cushner, M. C.; Riley, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 624–628.
(54) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485–1487.
(55) Olah, G. A.; Laali, K.; Farooq, O. *Organometallics* **1984**, *3*, 1337–1340.
(56) Eaborn, C. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, 1985; pp 123–130. Azarian, D. B.; Eaborn, C.; Lickiss, P. D. *J. Organomet. Chem.* **1987**, *328*, 255–282.
(57) Eaborn, C.; Jones, K. L.; Lickiss, P. D. *J. Chem. Soc., Perkin Trans. 2* **1992**, 489–495. Eaborn, C.; Romanelli, N. M. *J. Organomet. Chem.* **1993**, *431*, 45–52.
(58) Wang, N.; Hwu, J. R.; White, E. H. *J. Org. Chem.* **1991**, *56*, 471–475.
(59) Nefedov, V. D.; Kharitonov, N. P.; Sinotova, E. N.; Kochina, T. A.; Balakin, I. M. *J. Gen. Chem. USSR* **1980**, *50*, 2020–2022.
(60) Kochina, T. A.; Nefedov, V. D.; Sinotova, E. N. The IV All-Union Symposium on Structure and Reactivity of Organosilicon Compounds, Abstracts; Irkutsk, 1989, p 107.
(61) Kochina, T. A. Private communication.
(62) Straus, D. A.; Grumbine, S. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 7801–7802.
(63) Grumbine, S. D.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 7884–7885.
(64) Grumbine, S. D.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 358–360.
(65) Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, *116*, 5495–5496.
(66) Jutzi, P.; Bunte, E.-A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1605–1607; *Angew. Chem.* **1992**, *104*, 1636–1637.
(67) Chojnowski, J.; Mazurek, M.; Ścibiorek, M.; Wilczek, L. *Makromol. Chem.* **1974**, *175*, 3299–3303.
(68) Souverain, D.; Leborgne, A.; Sauvet, F.; Sigwalt, P. *Eur. Polym. J.* **1979**, *16*, 861–865.
(69) Wilczek, L.; Rubinsztajn, S.; Chojnowski, J. *Makromol. Chem.* **1986**, *187*, 39–51.
(70) Lambert, J. B.; Kania, L.; Schulz, W. J., Jr. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 1697–1700.
(71) Kendrick, T. C.; Parbhoo, B. M.; White, J. W. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Busso, S., Sigwalt, P., Eds.; Pergamon: Oxford, 1989; Vol. 4, pp 459–523.
(72) Chojnowski, J.; Kurjata, J. *Macromolecules* **1994**, *27*, 2302.
(73) Chojnowski, J.; Wilczek, L.; Fortuniak, W. *J. Organomet. Chem.* **1977**, *135*, 13–22.
(74) Chojnowski, J.; Fortuniak, W.; Stańczyk, W. *J. Am. Chem. Soc.* **1987**, *109*, 7776–7781.
(75) Mayr, H.; Basso, N.; Hagen, G. *J. Am. Chem. Soc.* **1992**, *114*, 3060–3066.
(76) Robinson, L. R.; Burns, G. T.; Barton, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3935–3941.
(77) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1987**, *109*, 272–273.
(78) Kevill, D. N. *J. Chem. Res.* **1987**, 272–273.

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