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Review Commentary

Preparation of the first tricoordinate silyl cation

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ABSTRACT: The preparation of the first tricoordinate silyl cation was made possible by a sequence of discoveries over a 20 year period. The extremely high electrophilicity of the material required protection from all manner of nucleophiles. Only arenes had sufficiently low nucleophilicity to serve as solvent. Tetrakis(pentafluorophenyl) borate provided the least nucleophilic anion. All manipulations had to be carried out in an inert atmosphere, primarily as protection from moisture. Sterically bulky substituents such as mesityl were needed to protect the cation even from the optimized solvent and anion. The trimesitylsilylium ion was produced from allyltrimesitylsilane by reaction of electrophiles with the allyl double bond and extrusion of the allyl adduct. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: allyl leaving group; low-coordination anion; low-coordination solvent; ^{29}Si NMR; silylium ion; tricoordination

INTRODUCTION

The intermediates of organic chemistry have held a central position in its history for a century. The succession of roles as hypothesis, transition state, reactive intermediate and long-lived species has been a common thread in the stories of carbocations, carbanions, free radicals and carbenes alike. Considerable interest has shifted to the heteroatom analogues of these fundamental species for the last few decades, particularly those in which the central atom is close to carbon in the periodic table, such as nitrogen (nitrenium ions, nitrenes) or silicon.

The story of silicon began rather differently from those of carbon and nitrogen, because of the perceived difference in the importance of π stabilization. This phenomenon plays probably the critical role in providing long life to many of the intermediates in which carbon or nitrogen is the central atom. These latter atoms lie in the second row of the periodic table. As a result, they possess valence 2p orbitals that provide excellent overlap between adjacent π orbitals and hence strong π bonds, as for example in alkenes and the benzyl cation. In contrast, silicon lies in the third row and possesses valence 3p orbitals. The longer bonds to silicon automatically reduce overlap. Additionally, when a silicon 3p π orbital is adjacent to a filled carbon 2p π orbital, the overlap fit between 2p and 3p orbitals is poor.

The reduction of π resonance stabilization in third-row elements seemed to eliminate from silicon chemistry the important role that intermediates played in carbon chemistry. The problem initially even appeared to remove the entire concept of unsaturation from silicon chemistry, as for many decades there were no analogues of double or triple bonds. The landmark syntheses of silenes (containing the C=Si double bond with weakened 2p–3p π bonds) and of disilenes (containing the Si=Si double bond with the 3p–3p π bond) put this misconception to rest.[1] Thus unsaturation does exist in silicon chemistry and π overlap plays an important but reduced role (in comparison with carbon or nitrogen chemistry). About the same time, the silicon analogue of carbenes (silylenes) also was achieving the status of a respectable intermediate.[2]

Still lacking, however, was the silicon analogue of the carbocation, which is possibly the central intermediate in much of organic chemistry. The search for the silyl cation lasted more than half a century and involved dozens of research groups. This commentary focuses on the contributions of our own group to the solution of what came to be called the ‘silyl cation problem’ or the ‘silyl cation controversy.’ Many other groups have made very important contributions to the subject, and their work has been described in comprehensive reviews of the subject.[3–5] Our own background was in the physical organic areas of carbocation chemistry[6] and in heterocyclic conformational analysis.[7] Our prior research in these areas involved both understanding effects of heteroatoms

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and examining modes of stabilization of carbocations. Consequently, they led to consideration of silicon both as an instrument for stabilizing a carbocation[8] and as the central atom itself in the silyl cation.

The nomenclature of silyl cations has been standardized by IUPAC conventions. The term *silyl cation*, analogous to *carbocation*, refers to any positively charged species in which silicon possesses the majority of the charge. The tricoordinate species R_3Si^+ is a *silylium ion* (replacing the now discarded terms *silylenium* and *silicenium*) and is the analogue of the *carbenium* or *carbylium ion*, R_3C^+. The pentacoordinate species R_5Si^+ is a *siliconium ion* and is the analogue of the *carbonium ion* R_5C^+.

GENERATION ZERO (SUN, 1972–76)

Our first foray into silylium chemistry was an exploration of the inductive effect. In carbenium ion chemistry, stabilization of the charge on carbon is accomplished either by direct conjugation, as in the benzyl ($C_6H_5CH_2^+$), allyl ($CH_2{=}CHCH_2^+$), and methyleneoxonium ($CH_3OCH_2^+$) cations (π–π or n–π effects), or by hyperconjugation, as in alkyl cations such as the *tert*-butyl cation, $(CH_3)_3C^+$ (a σ–π effect). The aryl ring in the benzyl cation, the double bond in the allyl cation and the oxygen atom in the oxonium ion (and nitrogen in analogous ammonium or iminium ions), however, destabilize the adjacent positive charge inductively (oxygen and sp^2 carbon being more electronegative than sp^3 carbon). Thus the π–π and n–π effects must compensate for the unfavorable σ effects. Gas-phase studies of cations indicated that substituent polarizability also plays a role in stabilizing positive charge.[9] In such cases, stabilization is by means of induced charges.

Arguing that π effects were negligible in silylium cations, we thought that the effects of σ electrons and of polarizability might produce significant stabilization. We considered a variety of supporting atoms and settled on silicon as a likely candidate. Silicon is considerably more electropositive than carbon (Allred–Pauling electronegatives of 1.90 and 2.55, respectively) and, as a third-row element, silicon also is more polarizable. We therefore prepared a series of substrates with increasing numbers of silicon atoms attached to the silicon center on which positive charge would reside (**1–3**):[10]

$CH_3(C_6H_5)_2Si{-}H$ (**1**)

$[(CH_3)_3Si](CH_3)_2Si{-}H$ (**2**)

$[(CH_3)_3Si]_3Si{-}H$ (**3**)

By this argument, the cation derived from **1** should be least stabilized and that from **3** most stabilized.

Consideration of substrates **1–3** immediately brings up a second failure of analogy with carbon, in addition to the weakness of π stabilization. Carbenium ions traditionally were obtained by departure of a leaving group in the S_N1 or $E1$ reaction. Leaving groups in carbon chemistry included halides, carboxylic esters (such as benzoate) and sulfonic esters (such as tosylate or mesylate). When attached to silicon, however, these groups are bound extremely strongly, because of the high bond dissociation energies of Si—halogen and Si—O. Thus departure is unfavorable and internal return favorable, so that entirely new leaving groups had to be sought for application to silicon.

Fortunately, about the same time we were contemplating use of electropositive elements to stabilize silylium ions, J. Y. Corey reported a novel approach for their generation.[11] She employed an analogy to the Bartlett–Condon–Schneider hydride transfer, whereby a carbocation abstracts hydride from a silane:

$$Ph_3C^+ + R_3Si{-}H \longrightarrow Ph_3C{-}H + R_3Si^+ \qquad (1)$$

Whereas bonds from silicon to electronegative elements (halogen, O, N) are uniformly stronger than the analogous bonds to carbon, the Si—H bond is weaker than the C—H bond. The transformation of Eqn. (1) consequently is favored thermodynamically. Thus a series of silanes (**1–3**) was all that was required to test the importance of induction and polarizability for the stabilization of silylium ions, as hydride could provide the leaving group.

These reactions could be followed by ^1H NMR spectroscopy, from loss of the Si—H resonance, appearance of the C—H resonance in the product, or loss of the H—Si—C—H coupling for methyl-substituted cases. In solvents of relatively low nucleophilicity, such as dichloromethane, acetonitrile, and 1,4-dioxane, loss of Si—H occurred cleanly to give triphenylmethane and a single new silicon species. The anion was introduced with the trityl (triphenylmethyl) cation of Eqn. (1). Both Corey and we used perchlorate, which was one of the least nucleophilic anions then known.

In addition to NMR, the only structural test available to us at the time was conductance. The conductance of all three silyl perchlorates produced from **1–3** by Eqn. (1) proved to be uniformly low in dichloromethane (negligible in comparison with the substantial conductance of trityl perchlorate). Thus replacement of alkyl with silyl substituents failed to elicit any significant conductance in the resulting solutions. We concluded that none of the resulting species was a free or even a partially free silylium ion. We characterized them as being either covalent perchlorates ($R_3Si{-}O{-}ClO_3$) or tight ion pairs ($[R_3Si^+][^-OClO_3]$).[10]

GENERATION ONE (SCHULZ AND OTHERS, 1981–91)

The second strategy we pursued was the use of sulfur instead of silicon as the substituent on the central silicon atom. This approach was based on published calculations of Apeloig *et al.*,[12] who found that sulfur and phosphorus are particularly effective in stabilizing silyl cations in the gas phase. Sulfur not only is highly polarizable, like silicon as a substituent, but also possesses 3p lone pairs. It was thought that the stability found by the calculations arose from favorable 3p–3p overlap. Phenyl groups would have to rely on the poor 2p–3p overlap between C and Si orbitals, whereas the fit of the 3p orbitals of S and Si would be superior. In addition, sulfur has an electronegativity similar to that of carbon, so that its inductive effect, unlike that of phenyl or oxygen, should not be unfavorable. Hence sulfur has three advantages: high polarizability, electrons in 3p orbitals and low electronegativity.

Consequently, we synthesized a series of alkylthiosilanes, such as **4**:[13]

$$(\mathrm{iPrS})_3\mathrm{Si}—\mathrm{H}$$

(**4**)

These molecules, like the silylsilanes **1–3**, on treatment with trityl perchlorate according to Eqn. (1) showed clean loss of Si—H and production of a single species. In contrast to **1–3**, however, dichloromethane solutions containing the silyl perchlorate produced from **4** were highly conductive, equivalent in fact to the conductance of trityl perchlorate. Controls showed that perchloric acid conducted negligibly in dichloromethane. NMR spectra and product recovery experiments confirmed that the product was unhydrolyzed perchlorate. Cryoscopic experiments in sulfolane indicated that the product was composed of two particles, characteristic of a structure of the type $R^+ ClO_4^-$ rather the one particle covalent form, R—$OClO_3$. Subsequent experiments demonstrated that triphenylsilane and trimethylsilane produced poorly conducting perchlorates in dichloromethane. In sulfolane, however, the perchlorates formed from these substrates were highly conducting and by cryoscopy were composed of two particles, hence of the type $X^+ ClO_4^-$.[14] Direct observation of the hydrolysis product, R_3Si—O—SiR_3, indicated by NMR integration that it was not contributing significantly to the observations.

Conductance and cryoscopic molecular weights clearly indicated that the alkylthio species were ionic in all solvents and the alkyl and aryl species were ionic in sulfolane. These methods, however, do not distinguish between tricoordinate ions of the type **5** and tetracoordinate complexes of the type **6**:

$$R_3Si^+\ ClO_4^- \qquad R_3Si—M^+\ ClO_4^-$$

(**5**) (**6**)

in which M is a molecule of solvent. Cryoscopy responds only to the number of particles, which is two in both cases. Thus solvent coordination is not detected by either method.

At the time these experiments were originally carried out (early 1980s), no information was available on the expectations for ^{29}Si chemical shifts of silylium cations. As a result, we initially favored **5**. Subsequent calculations, however, indicated that tricoordinate silylium atoms should resonate at higher frequency than δ 300.[15] The observed chemical shifts for our perchlorates were typically in the range δ 30–50 and hence demanded that all the conducting perchlorates were ionic solvent complexes (**6**) rather than covalent species (R—$OClO_3$) or tricoordinate ions (**5**).

Solvent complexes with hexamethylphosphoramide, triphenylphosphine oxide, pyridine, acetonitrile and imidazoles had been reported, and some x-ray structures were available.[3] In general, the bond between silicon and solvent, Si—X, is only slightly longer than the normal covalent length, indicating a small amount of ionic character, $Si^+ X^-$ according to the Pauling valence bond model. The Pauling equation allows calculation from crystal data of the covalent bond order, which proved, for example, to be 0.71 for the acetonitrile complex of iPr_3Si–*closo*-$CB_9H_5Br_5$ (thus the bond is 29% ionic by this model).[3] The non-conducting perchlorates observed in dichloromethane likewise were predominantly covalent materials. From the solvent-free x-ray structure of Ph_3SiClO_4, the Si—O covalent bond order was calculated to be 0.68.[3] Covalencies of this order derive from lengthening of the Si—X bond (the bond from Si to solvent in the complexes, or from Si to perchlorate in the solvent-free cases) by only about 0.1 Å.

Sulfur substitution thus led to marginally different results from silyl substitution. The primary difference was the ability of solvent, even dichloromethane, to coordinate with these species and form conducting complexes. Although the complexes as a whole were ionic, silicon remained essentially tetracoordinate, as demanded by the ^{29}Si chemical shifts, with only a small amount of ionic character manifested in lengthening of the bond from silicon to solvent.

GENERATION TWO (KUHLMANN AND ZHANG, 1991–94)

The high covalency of the bond between silicon and solvent in the complexes or between silicon and anion in the solvent-free cases arose because of the strong affinity of silicon for electronegative atoms. Perchlorate had been considered a poorly nucleophilic anion, but its oxygen atoms in fact readily bond with silicon. The nucleophilicity of sulfolane is so low that it is not even protonated by concentrated sulfuric acid, but again its oxygen atoms could complex with silicon. Faced with this extraordinary ability of silicon, compared with carbon, to complex with the atoms of even weakly nucleophilic anions and solvents, we sought an environment that minimized all nucleophilic species that had to co-exist with a silylium ion.

The first breakthrough in this area was the discovery by Kuhlmann that the components of the Corey reaction [Eqn. (1)] were soluble in aromatic solvents. We had tried a variety of chlorinated solvents of low nucleophilicity, such as 1,2-dichloroethane, and found them to respond essentially as dichloromethane had. The only aliphatic solvents with lower polarity were hydrocarbons like hexane. The ionic product of Eqn. (1), however, would be entirely insoluble in these solvents, which proved impractical. Polar groups on an aromatic ring, such as the oxygen of anisole or the nitrogen of aniline, themselves are nucleophilic, so that polar aromatics could serve no better than polar aliphatics such as ethers or alcohols. Non-polar aromatics such as benzene and toluene possess considerable polarizability and high quadrupole moments and have been known to offer appreciable solubility for ions. Kuhlmann explored all these solvents in her attempts to prepare stannylium ions (tricoordinate tin), and her successes[16] with non-polar aromatics led to our applying the solvents to the silylium ion problem. Her contributions to the ultimate solution of the silylium ion problem thus are extremely important. All later studies of silylium ions, as well as of many related highly electrophilic species, have used aromatic solvents. It is clear that, to date, there rarely is a substitute for such media (dichloromethane possibly), and the silyl cation problem and many others would have remained unsolved without her contributions.

C. A. Tessier (University of Akron) later suggested to us that the solutions resulting from Eqn. (1) in fact are liquid clathrates when the solvent is non-polar and aromatic. This suggestion has not been confirmed, but it would serve to explain our observation that the Corey method [Eqn. (1)] with aromatic solvents always leads to two layers. The solvent is the same in both layers, but the ionic product in essence has oiled out, possibly as a liquid clathrate. The upper layer is a dilute benzene solution containing only the hydrocarbon byproduct of Eqn. (1) (triphenylmethane). The lower layer contains the ionic product in benzene, in a stoichiometric ratio if a liquid clathrate. Formation of two layers provides a straightforward separation of products. The reactions are carried out in a glove-box to avoid side-reaction with atmospheric water. The upper layer is syringed off and discarded, leaving the ionic species nearly uncontaminated in the aromatic solvent.

With aromatic solvents providing the best opportunity yet of avoiding solvent complexation with silylium ions, it remained to deal with the anion. There has been considerable work in the last decade on low-nucleophilic anions.[17] Workers have reached the consensus that there is no such thing as a non-nucleophilic anion, but many low-nucleophilic anions have been produced. The original members of this category included perchlorate, triflate, hexachloroantimonate and tetrafluoroborate. These all contain available halogen or oxygen atoms, which would complex readily with silicon. Schulz, in his study of alkylthio substituents,[13] in fact tried tetrafluoroborate (BF_4^-) as an alternative to perchlorate. The reaction of Eqn. (1) between the tris(alkylthio)silane and trityl tetrafluoroborate, however, produced a high yield of fluorosilane. The Si—F bond, of course, is one of the strongest in nature.

Tilley had been having considerable luck with tetraphenylborate as a low-nucleophilic anion, and in so doing had prepared trityl tetraphenylborate, Ph_3C^+ BPh_4^-.[18] We obtained the procedure from him, and Kania eventually was able to carry out the reaction of Eqn. (1) on silanes with that anion.[15] The results, however, were disappointing. Trityl tetraphenylborate proved to be unstable in our favorite solvents at the time, dichloromethane and sulfolane. We had to use the more nucleophilic acetonitrile, knowing that it would be more strongly complexing. Although stable, ionic products were formed, it appeared that eventually phenyl abstraction by silicon occurred, leading to decomposition. This anion thus did not function innocently.

It was our good fortune in 1991 to learn of the work by our colleague T. J. Marks on the investigation of low-valent zirconium species.[19] He was confronted with problems very similar to those posed by low-valent silicon species. One approach he took was abstraction of methyl from Zr—CH_3 with tris(pentafluorophenyl)borane, $(C_6F_5)_3B$. This approach had two advantages. (1) Because the electrophile is neutral [in Eqn. (1) it is positively charged], there is no byproduct [Eqn. (1) leads to triphenylmethane]. The reaction creates the zirconium cation, and the electrofuge (methyl) migrates to create a new borate anion, $CH_3B(C_6F_5)_3^-$. (2) This anion should have very low nucleophilicity and hence should not complex with silicon. The apparent drawback to tetraphenylborate was that the phenyl rings retained sufficient nucleophilicity to react with the silylium ion with abstraction of phenyl. Fluorine atoms withdraw electrons by induction, lowering the nucleophilicity of the aromatic rings. The total electronic effect of fluorine is a balance of induction and resonance. Like methoxy and amino, fluorine is electron withdrawing by induction but electron donating by resonance. Resonance delocalization, in valence bond terms $C=F^+$, lowers the nucleophilicity of the fluorine atoms. The final mix is not entirely clear, but we thought that it was feasible that inductive withdrawal by fluorine might reduce the nucleophilicity of the phenyl rings and resonance donation might reduce the nucleophilicity of the fluorine atoms. Because of the well-known strength of interactions between silicon and fluorine, we in fact did not have high hopes of the success of the Marks approach with our system. Moreover, the C—Si bond is much stronger than the C—Zr bond, so methyl abstraction should be much slower. Indeed, when Zhang reacted dimethyldiphenylsilane with tris(pentafluorophenyl)borane, no reaction occurred. The intended reaction was methyl abstraction to give $CH_3Ph_2Si^+$ $CH_3(C_6F_5)_3{}^-$.

About this same time, Chien *et al.* reported a very similar approach to the preparation of zirconium cations by means of methyl abstraction with trityl tetrakis(pentafluorophenyl)borate (we will refer to this anion henceforth as TPFPB).[20] This is the very material that could be used in the Corey reaction of Eqn. (1). Although our first attempt was to carry out methyl abstraction on dimethyldiphenylsilane by trityl to produce $CH_3Ph_2Si^+$ $TPFPB^-$, this reaction was unsuccessful. Methyl abstraction failed to occur, even at high temperatures, probably because the C—Si bond is too strong. Consequently, our ultimate recourse was the exact analogy to the Corey reaction, in which trityl is used to abstract hydride by breaking the relatively weak Si—H bond. Fluorinated borates had not been used previously for hydride abstraction, so our expectations were low. In this case, however, the reaction proceeded smoothly to give the anticipated product.[21]

Zhang then was in a position to juxtapose use of aromatic solvents, recently developed by Kuhlmann, and the TPFPB anion, just developed by Chien, for application to the silylium ion problem using the original Corey reaction [Eqn. (1)]. This combined strategy was extremely successful with a variety of silanes.[21] The ^{29}Si chemical shift obtained from the reaction of trimethylsilane with trityl TPFPB in benzene was δ 83.6, a shift ~40 ppm to higher frequency than those of our previously observed silyl species. Zhang was able to prepare the same species without solvent in the solid and to obtain a chemical shift of δ 84.8 by cross-polarization, magic angle spinning methods. The essential identity of the chemical shifts suggested that solvent was not involved. Nonetheless, the value of ca δ 84 was still considerably lower frequency than the value expected, ca δ 300, for a free trimethylsilylium ion in the gas phase.[15]

A full solvent study was carried out with triethylsilylium,[21] and the chemical shift proved to depend on the nucleophilicity of the solvent: δ 92.3 for benzene, 81.8 for toluene, 58.4 for sulfolane and 36.7 for acetonitrile. The last value is close to those observed for the perchlorates and approximates the expectation for an almost fully tetrahedral species. In the solid, triethylsilyl TPFPB exhibited a chemical shift of δ 94.3, again indicating no difference between the value in the solvent free solid and in benzene solution. The highest frequency value for alkyl substituents was obtained with triisopropylsilylium TPFPB in benzene (δ 107.5) or the solid (δ 107.6). The freedom of the anion in solution was further supported by the unvarying value of the ^{19}F chemical shifts on conversion of the trityl salt to the silylium salt, and by the ^{11}B chemical shift and narrow linewidth, characteristic of an unsymmetrical environment around boron.

The results in aromatic solvents and with the TPFPB anion clearly indicated that species had been formed with unprecedented silylium ion character.[21] The chemical shifts, however, were still insufficient to support a truly free silylium cation. There must be some sort of fourth coordination, with either solvent or anion. The solvent dependence of the ^{29}Si chemical shift for triethylsilylium TPFPB in fact is a strong indication that in solution the solvent is providing the fourth coordination. This result is not possible for the results in the solid phase, in which the silane itself served as solvent. Either excess silane can coordinate in the solid (bonding between positive silicon and the Si—H bond) or the fluorines of the anion are providing coordination when solvent no long is present, coincidentally providing the same ^{29}Si chemical shift as in benzene solution. We have not been able to distinguish between these alternatives in the solid.

Solvent mixtures produced only single ^{29}Si resonances.[22] Thus triethylsilylium TPFPB in a mixture of toluene and benzene gave one peak at the intermediate position of δ 87.1. Consequently, exchange of solvent is fast on the NMR time-scale. The complete process probably involves dissociation of solvent from the fourth coordination site on silicon to produce a short-lived silylium ion, which reacts rapidly with the alternative solvent to form the new complex, all at a rate faster than the NMR time-scale. If the exchange is dissociative (the intermediate or transition state is a silylium ion), an upper limit of 13 kcal mol^{-1} (1 kcal = 4.184 kJ) may be calculated for the barrier to solvent exchange.

The symmetry of the materials also was explored by preparation of the substrate methyldiisopropylsilane, $CH_3[(CH_3)_2CH]SiH$.[22] The isopropyl methyls of this silane were found to be diastereotopic and non-equivalent in both the ^1H and ^{13}C spectra. The silylium TPFPB formed by abstraction of hydride by trityl TPFPB offers different characteristics of the isopropyl methyls, depending on the symmetry of the silylium species. There are at least three possibilities: (1) formation of a covalent bond between silicon and either solvent or anion renders the methyls diastereotopic in a tetracoordinate species; (2) removal of hydride without further reaction leads to a tricoordinate silylium ion in which the methyls must be homotopic; or (3) rapid exchange of the fourth coordination site on the NMR time-scale as described above leads to homotopicity on average. The first possibility could be immediately rejected, as the methyls of methyldiisopropylsilylium TPFPB were observed to be homotopic. Whether they are statically homotopic as a free silylium ion or dynamically homotopic by exchange could not be answered by this approach. The value of the ^{29}Si resonances in the range δ 80–110, however, excluded a free silyl cation, which should have resonated at ca δ 300.

Consequently, we concluded that these silylium ions in aromatic solvents are not free but are loosely coordinated with the solvent.[22] Because the resonances are solvent averaged and homotopic, the barrier to removal of the

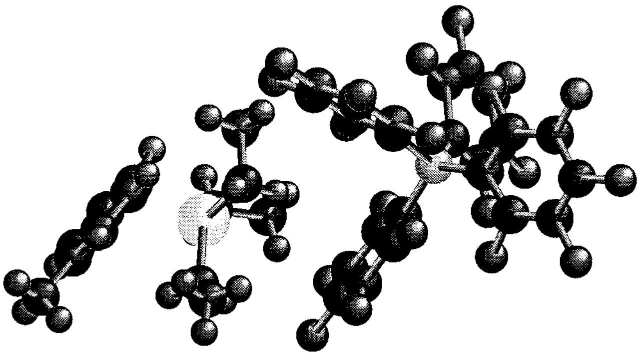
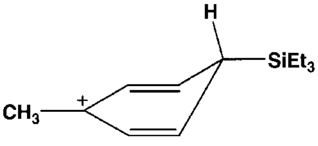


Figure 1. Juxtaposition of the TPFPB anion (right) and triethylsilylium (middle) coordinated to a molecule of toluene (left). Reprinted with permission from Lambert JB, Zhang S, Ciro SM, *Organometallics* 1994; **13**: 2435. Copyright 1994 American Chemical Society

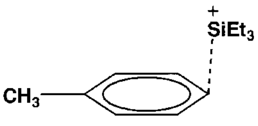
fourth coordination site has to be very small, under about 13 kcal mol^{-1}, compared with a normal bond to silicon of ~80–90 kcal mol^{-1}. It is interesting that when methyldiisopropylsilylium was produced as the perchlorate in benzene, the methyls were found to be diastereotopic (in contrast to TPFPB as anion), but in dichloromethane they were homotopic. These results suggest tighter binder in the less polar benzene than in dichloromethane. We could not isolate any TPFPB salts in dichloromethane, because of reaction with the solvent, presumably by chloride abstraction.

We were able to isolate crystals from solutions of triethylsilylium TPFPB in toluene, and the complex x-ray structure eventually was solved with the key help of J. C. Huffman at Indiana University.[23] The crystal structure is illustrated in Fig. 1. A number of conclusions were drawn from this first structure of what we called 'a silyl cation with no coordination to anion and distant coordination to solvent.' (1) The anion is completely uncoordinated. The closest approach of any of the fluorine atoms to the silicon atom is 4.04 Å, well beyond bonding distance. (2) There is a molecule of solvent serving as the fourth coordination site, consistent with the ^{29}Si chemical shifts. Toluene is loosely coordinated to silicon at the carbon *para* to the methyl group, and the C—Si distance of 2.18 Å is considerably lengthened from the normal distance of 1.85 Å. According to the Pauling equation, this distance corresponds to a bond order of 0.28. This low bond order is consistent with the rapid exchange of solvent on the NMR time-scale and the consequent low barrier to dissociation observed in solution. Bonding to the fourth group is clearly different from normal covalency. (3) The toluene ring geometry is essentially unperturbed, consistent with a weak interaction. Known σ complexes have strong alternation of bond lengths (long–short–long). (4) The silyl portion is clearly nonplanar, consistent with tetracoordination. In a tricoordinate species, the C—Si—C angles would be 120°, compared with about 114° in the structure in Fig. 1.

A lively discussion ensued as to whether the structure is best described as a σ complex (**7**) or a π complex (**8**):[24]



(7)



(8)

At no time had we suggested that it was a free silylium cation. The π complex had originally been suggested by Reed.[5] Later solid-state ^{13}C NMR studies of the toluene complex of triethyl TPFPB failed to show chemical shifts appropriate for the σ complex.[22]

There is a continuum of structures with varying σ and π character. The variability of structures between these extremes allows for a difference in opinion. The angle between the line drawn from Si to the *para* carbon and the line that bisects the internal angle at the *para* carbon varies according to the structural model (if the carbon to which methyl is attached is labeled C1 and the carbon to which silicon is coordinated is labeled C4, this is the angle between the Si—C4 and the C1—C4 vectors). This angle should be 90° in the idealized π complex and 124° in the idealized σ complex. The observed value of 104° in the crystal structure of silylium TPFPB is intermediate but closer to the π complex model. The other angles around C4 are edifying: Si—C4—C3 is 98° and Si—C4—H is 85°. Hence the silicon atom is nearly perpendicular to the aromatic ring in all dimensions, requiring bonding primarily to π rather than σ orbitals. Eventually we adopted the phrase 'solvated silylium ion' to describe the molecule whose crystal structure we had obtained.

Soon after this structure was published, Reed[5] reported the crystal structures of a series of materials 'closely approaching a silyl cation.' He used halocarboranes as the anion with low nucleophilicity. In all cases the anion and cation were coordinated through the halogen atom of the anion, so that the overall structures were electrically neutral. The silicon–halogen distance, however, was long enough for the materials to be considered as having high silyl cation character. In the crystal structures, the geometry around silicon was not planar, so trigonality clearly had not been achieved.

Discussion of the structures produced by Reed's and our groups was succeeded by the realization that triethylsilylium TPFPB in aromatic solvents is an excellent reagent for the production of a variety of previously unknown materials. It (or its trityl precursor) was a key intermediate in our preparation of the first stable, simple β-silyl carbocation,[25] of a stable silanorbornyl cation with unusual bonding properties by Steinberger *et al.*[26] and of a protonated arene [H(arene)$^{+}$] by Reed *et al.*[27]

GENERATION THREE (ZHAO AND OTHERS, 1995–PRESENT)

By the time the controversy over bonding in the trialkylsilylium ions had run its course, there was a general feeling that the silyl cation problem itself had been taken as far as possible. In 1996, Maerker *et al.* carried out high-level calculations on silyl cations, testing their ability to complex with a variety of poorly nucleophilic materials.[28] The cations complexed strongly with good Lewis bases such as water and trimethylamine, but also significantly with weaker bases such as ethene, benzene, toluene, bromomethane and fluoromethane. The calculations that silylium ions complex even with methane, argon and neon appeared to indicate that such ions could never be isolated free in any solvent. Aside from the problems of solubility, even non-polar, aliphatic hydrocarbons and rare gases cannot be considered non-complexing solvents. These authors concluded that 'Lambert's and Reed's silyl cation systems … may be about as "free" as one can hope to achieve in condensed phase.' Another calculational study of silyl cation complexes,[29] also in 1996, went further and stated 'Clearly, the free silylium cation in solution is a fiction, and the issue is not whether one can generate it, but how much silylium cation character (if any at all) can be retained in a solvent(S)-coordinated silylium cation.' Both studies show the danger of making categorical statements in science.

Reed and we had taken the attitude that we were very close to producing a free silylium cation, and only modest changes might yield a truly free species. Rather than considering that solvent and anion complexation represented an intractable problem, we viewed the last 10–30 kcal mol^{-1} of complexation energy as a modest encumbrance. Both research groups moved to employ steric effects in the hopes that large substituents on silicon would decrease or eliminate the interactions with solvent and anion. Reed found that *tert*-butyl was insufficient to remove the halocarborane anion coordination and planarize the cation,[5] and we found that hexyl was ineffective at decreasing complexation with solvent (trihexylsilylium TPFPB).[22] Both research groups found that substituents larger than *tert*-butyl rendered the Corey reaction of Eqn. (1) impossible. Apparently the trityl cation cannot approach R_3SiH closely enough to abstract hydride when R is particularly large. Hence yet another impasse had been reached. Solvents with dielectric constants below that of benzene failed for reasons of solubility, all anions except TPFPB complexed to some extent with silylium ions, all solvents that dissolved the ions also complexed with them and substituents larger than *tert*-butyl failed in the one reaction that had been useful in producing high silylium character. In unpublished experiments with L. Kania, we tried Lewis acids other than trityl, in the hope that a small electrophile might be able to penetrate the steric protection offered by large substituents. This protection on the one hand was needed to fend off complexation with solvent and anion, but on the other hand was rendering the Corey reaction impossible. We found no suitable small electrophiles. It was time to sit back and reassess the whole problem.

Carbenium ions possess sufficient thermodynamic stability to co-exist with a variety of solvents and anions, of which superacid media have been the most successful. Since silylium ions do not possess this stability, extraordinary efforts must be made to protect them. Calculations on silylium ions in the gas phase, going back to 1981,[12] had demonstrated that substituents do provide considerable stabilization, but apparently not enough to lower electrophilicity to the point that solvent and anion no longer complex with silicon.

Consequently, we began to consider a wide variety of substituents that might serve simultaneously as stabilizing groups through resonance and as protecting groups by reason of their large size. No calculations existed for aryl groups as stabilizing substituents, but with knowledge of the extent of dilution of the resonance effects of nitrogen or oxygen with silicon compared with carbon we felt that aryl groups should provide significant stabilization. Zhao also looked at many other large, resonance-stabilizing groups, but ultimate success was achieved only with aryl. The use of highly substituted aryl groups has been common in many chemical contexts, including in the protection of the double bond between carbon and silicon in silenes from reaction with electrophiles. The commonest such group is mesityl (Mes), 1,3,5-trimethylphenyl, in which the *ortho* and *para* protons of phenyl have been replaced with methyl. Many other, more sterically demanding aryl groups also have been developed. Several years earlier in unpublished work with L. Kania and K. T. Lentz, we in fact had prepared Mes_3SiH and tried without success to abstract hydride via the Corey reaction of Eqn. (1). These approaches all involved variation of the electrophile to allow it to penetrate to the hydride.

Since we could not bring the electrophile to hydride, Zhao decided to try to bring the hydride to the electrophile, in a sense. The idea requires fundamental appreciation of the difference between generating carbenium ions and silylium ions. Essentially all carbenium ions had been generated by a unimolecular process such as the S_N1 reaction, in which simple dissociation led to the cation ($R_3C—X \rightarrow R_3C^+ X^-$). Silicon had failed in this approach because of its strong affinity for the leaving group. Thus the most successful approaches to generating a silylium ion used bimolecular abstraction of hydride [Eqn. (1)]. Zhao reasoned that other groups might fulfill the role of hydride, groups that are not so small as hydride but would have sufficient dimensions to reach beyond the steric protection of whatever substituent on silicon is being used to inhibit complexation with solvent and anion.

Zhao found a plausible model in two published studies for allyl as the replacement of hydride as the leaving group. Uhlig[30] observed that allylsilanes react with triflic acid to give alkenes with removal of the allyl group. Shade and Mayr[31] found that reaction of allyltrimethylsilane with trityl tetrachloroborate leads to abstraction of allyl to give allyltriphenylmethane, chlorotrimethylsilane and presumably trichloroborane. In the first case, the proton attacks the allyl double bond to create positive charge that is β to silicon:

$$\begin{aligned}&R_3Si{-}CH_2{-}CH{=}CH_2 + H^+ \longrightarrow\\&R_3Si{-}CH_2CH^+CH_3\end{aligned}$$

Until our preparation of a simple stable β-silyl cation,[25] such species had been found uniformly to decompose with expulsion of the silyl group. In what is probably a bimolecular reaction, the silyl group reacts with adventitious nucleophiles to produce R_3SiX (X being the nucleophile) and $CH_2{=}CHCH_3$. The second case is the exact analogue of the Corey reaction, in which hydride had been replaced by allyl as the nucleofuge. There are many examples of parallels between hydride and alkyl groups such as allyl in nucleophilic chemistry (for example, both hydride and alkyllithium reagents react with carbonyl groups). For the two nucleofuges being compared, hydride is a rather hard nucleophile and allyl a rather soft one. Such a difference probably has no bearing on the desired reaction, which is given by

$$\begin{aligned}&E^+ + R_3Si{-}CH_2CH{=}CH_2 \longrightarrow\\&R_3Si{-}CH_2CH^+CH_2{-}E \longrightarrow\\&R_3Si^+ + H_2C{=}CHCH_2{-}E \qquad (2)\end{aligned}$$

Six factors operate in favor of the method now proposed to replace the Corey reaction for the formation of silylium ions, a method we have called 'the allyl leaving group approach.'[32] (1) The allyl group should extend beyond the steric compass of the mesityl methyl groups, which we had selected as the bulky substituent. (2) The β-silyl cation that is formed in the first step of Eqn. (2) is known to be unstable with respect to cleavage of the Si—C bond. (3) Moreover, in this case cleavage is encouraged by the use of bulky R groups. Whereas silicon is tetracoordinate in the β-silyl cation, it is tricoordinate in the silylium ion and hence less sterically encumbered. One reviewer referred to the process of Eqn. (2) as a ripcord reaction, whereby the allyl ripcord is pulled, releasing the silylium ion.[33] (4) Once released, the silylium ion is protected and stabilized by the mesityl groups: protected by the *ortho* methyl groups and stabilized by resonance delocalization of the positive charge from silicon to the aryl rings. (5) Use of arenes as solvent and TPFPB as anion means that the silylium ion is released into an environment with only weak, bulky nucleophiles. Bulkiness is important, as any nucleophile would have to be able to navigate around the *ortho* methyl groups in order to penetrate to the silicon atom. (6) Finally, the peculiar solubility properties of the arene solvents, possibly because they form liquid clathrates, result in the formation of two layers. The byproduct $CH_2{=}CHCH_2{-}E$ is of low polarity and should dissolve entirely in the upper layer, which is to be syringed off. The reaction should therefore yield a pure solution of the silylium ion in the remaining lower layer.

In order to implement this strategy, we needed to synthesize an allyl-substituted silane carrying three other bulky substituents. The target, allyltrimesitylsilane, was unknown. Ominously, the only known trimesitylsilanes, with one exception, carried only single atoms as the fourth group, including the hydride, fluoride, and chloride. The exception was the azido group, $—N_3$. No alkyl derivatives were known, not even methyltrimesitylsilane. Although the Wurtz coupling reaction between the allyl Grignard reaction and chlorotrimesitylsilane failed, the reaction with allyllithium worked well.[34] The product, allyltrimesitylsilane, was obtained by Zhao in good yield as x-ray-quality crystals. The crystal structure indeed showed that the double bond of the allyl group extended well beyond the *ortho* methyl groups, indicating its availability to reaction with electrophiles.[35]

In Zhao's first attempt to realize the reaction of Eqn. (2) with this material, he followed the strict analogy to the Corey reaction of Eqn. (1) and used trityl TPFPB as the electrophile.[34] Only a sluggish reaction occurred, but a resonance of low intensity appeared seductively at δ 225 after 3 days at 60 °C. Because there were no reported calculations on the ^{29}Si chemical shifts of aryl-substituted silylium ion, we had no specific expectations for the resonance frequency, except that it should be higher than the observed value of ca δ 100 for the solvated silylium ions and lower than the calculated value of ca δ 300 for free trialkylsilylium ions in the gas phase. Resonance delocalization was expected to lower the frequency by some unspecified amount. Since trityl proved to be relatively unreactive, we moved to a hotter electrophile, Zhang's solvated silylium ion, $Et_3Si(benzene)^+$. Reaction occurred instantly at room temperature but resulted in considerable decomposition. In addition to the high-frequency resonance at δ 225, several resonances were present at ca δ 50.

Having tried too cold and too hot, Zhao selected the β-silyl cation that he had just prepared[25] ($Et_3SiCH_2CPh_2^+$) as an electrophile of possibly intermediate reactivity. The reaction of Eqn. (2) in which this material served as E^+ led to a clean reaction with only a single product in the polar layer, resonating at δ 225. It should be kept in mind that the byproduct, $Et_3SiCH_2CPh_2CH_2CH{=}CH_2$, would dissolve in the upper layer, which was syringed off prior to analysis. Thus only one resonance appeared in the ^{29}Si spectrum (Fig. 2), and the ^1H and ^{13}C spectra also contained the expected resonances. The material had all the properties expected of trimesitylsilylium TPFPB and was stable at room temperature for several weeks. Reaction of the solution with tributyltin hydride produced

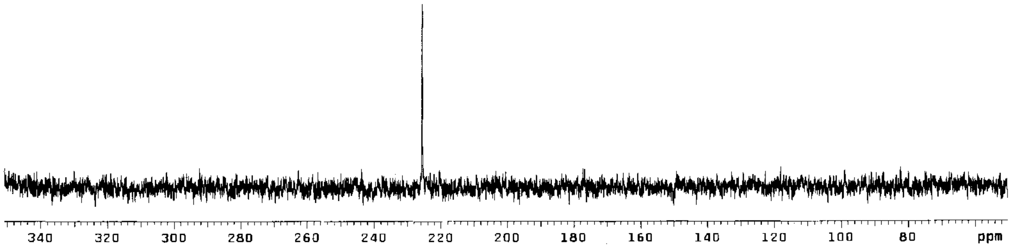


Figure 2. The 79.46 MHz ^{29}Si spectrum of trimesitylsilylium TPFPB in C_6D_6. Reprinted with permission from Lambert JB, Zhao Y, Wu H, Tse WC, Kuhlmann B. *J. Am. Chem. Soc.* 1999: **121**: 5003. Copyright 1999 American Chemical Society

trimesitylsilane as the exclusive product, in which the weaker Sn—H bond had been replaced with the stronger Si—H bond.

In the early days of stable carbocations, the electronic spectrum provided a critical measure of the extent of conjugation. The ultraviolet spectrum of trimesitylsilylium unfortunately had to be measured in benzene as solvent. Despite the large solvent absorption at 254 nm, a maximum was clearly observable at 304 nm and a shoulder at 370, tailing into the visible to provide the dark yellow color of the solution. The silylium absorptions are at shorter wavelength than those of the trityl cation at 409 and 428 nm but still indicate considerable conjugation between the empty orbital on silicon and the aryl groups. In contrast, crystals of solvated triethylsilylium TPFPB were colorless, as the ethyl groups provide no conjugative delocalization.

The production of trimesitylsilylium TPFPB came from a cascade of reactions carried out in a glove-box needed for protection from atmospheric moisture. The β-silyl cation had been prepared by the addition of the solvated triethylsilylium cation with 1,1-diphenylethene. The reaction sequence thus was $Et_3Si—H \rightarrow Et_3Si(benzene)^+ \rightarrow Et_3SiCH_2CPh_2^+ \rightarrow Mes_3Si^+$. Although alternative electrophiles surely ought to be found to be effective, to date Zhang's solvated silylium cation serves as the unique precursor to the free silylium cation. The key reaction in turn was the Zhao-developed allyl leaving group method.

To what extent could the silylium ion with δ 225 be considered to be free? To claim essential freedom meant going against the computational expectations of the time. Unfortunately, trimesitylsilylium TPFPB failed to yield crystals (in unpublished work in collaboration with Reed and Fackler, the corresponding halocarborane salt also failed). Our only tool therefore was NMR. The critical observations demonstrating complexation with solvent for the trialkylsilylium ions were the position and solvent dependence of the ^{29}Si chemical shift. Thus, for example, triethylsilylium TPFPB resonates at δ 92.3 in benzene and δ 81.8 in toluene. The low frequency and variable value of the chemical shift indicates coordination with solvent. In contrast, trimesitylsilylium TPFPB resonates at δ 225.5 in benzene, 225.7 in benzene–toluene (1:3) and 225.6 in benzene–*p*-xylene (1:1). Thus aromatic solvents appear to be non-interacting, as the resonance position is insensitive to changes in solvent nucleophilicity. Smaller, stronger nucleophiles, however, could react, as the resonance position quickly moved to lower frequencies on the addition of acetonitrile or triethylamine. Reed and Fackler succeeded in making trimesitylsilylium from a sample of allyltrimesitylsilane we supplied them, with *closo*-7,8,9,10,11,12-Cl_6-$CB_{11}H_6$ as the anion, and they measured its chemical shift in benzene to be δ 225.9. Thus the cation also is insensitive to a change in anion.

In the absence of an x-ray structure to demonstrate tricoordination, the best alternative is computation of the observed chemical shift. These calculations were carried out by T. Müller of the Humboldt Universität Berlin.[36] They provided not only a direct measure of the ^{29}Si chemical shift but also important information on the extent of conjugation between silicon and the mesityl rings. *Ab initio* calculations at the B3LYP/6–31G* level gave twist angles between the plane of the aryl ring and the plane containing silicon and the three attached *ipso* carbons of 29° for triphenylsilylium (Ph_3Si^+) and 48° for trimesitylsilylium (Mes_3Si^+). The *ortho* methyl groups thus require greater twisting within the propeller. Calculationally, Müller also examined nonequilibrium geometries, such as the D_{3h} conformation in which the aryl groups are perpendicular to the silicon plane. Conjugation is entirely absent in this arrangement. Its higher energy of 26.2 kcal mol^{-1} (at the B3LYP/6–31G*//B3LYP/6–31G* level) serves as a measure of the stabilization provided by the mesityl groups through conjugation. The value is about 60% of that calculated for the trityl (Ph_3C^+) cation. Müller's GIAO/HF-calculated ^{29}Si chemical shift for trimesitylsilylium at its equilibrium geometry was δ 230.1, very close to the observed value of δ 225.

Thus the species in solution is sufficiently free to have a ^{29}Si chemical shift essentially identical with that calculated for the gas phase. Moreover, the calculated chemical shift is insensitive to the presence of arene solvents. Whereas the calculated chemical shift for trimethylsilylium moved from δ 361.6 to 80.4 on the introduction of benzene at the fourth coordination site, the analogous values for trimesitylsilylium were δ 230.1

and 228.6. This insensitivity confirms the essential absence of interaction with solvent. These results were independently corroborated by calculations of Kraka *et al.*[37]

SUMMARY AND PROSPECTS

Several subsequent reviews have indicated general acceptance that trimesitylsilylium TPFPB is a free silylium cation.[33,38] Its preparation demonstrated that silicon can exist, even at room temperature, with tricoordination, in strict analogy with the carbenium ion, but extraordinary measures must be taken with respect to solvent, anion, leaving group, substituent and avoidance of water. Nonetheless, further progress is possible. Isolation of crystals and solution of an x-ray structure would provide detailed structural parameters. To date, trimesitylsilylium TPFPB has not been isolated in the absence of solvent.

Second, preparation of a silylium ion with alkyl substituents would be of great interest. It would have to be designed in such a way that the substituent is large enough to fend off solvent and anion, small enough to allow the preparation of the allyltrialkylsilane precursor and possessed of no C—H bond that is close enough to provide coordination to the silyl center. One of the important properties of the trimesityl structure is that no C—H bond is within bonding distance. They are all directed in such a way that they cannot approach the silicon atom without introduction of extreme angle bending strain. As a result, C—H coordination observed calculationally between methane and silyl cations (what might be called agostic interactions when intramolecular) is avoided. Any successful saturated substituent would have to be similarly constituted to prohibit C—H coordination.

The second and third free silyl cations now have been prepared, although they are based on analogy to aromatic ions (homocyclopropenylium, tropylium) rather than to trialkyl or triaryl carbenium ions.[39]

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