

The Allyl Leaving Group Approach to Tricoordinate Silyl, Germlyl, and Stannyl Cations

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Abstract: A group 14 atom bonded to three mesityl groups (2,4,6-trimethylphenyl) and to one allyl group serves as a novel precursor to tricoordinate group 14 cations, the analogues of the carbocation. The double bond of the allyl group provides an accessible reaction site that is located beyond the ortho methyl groups. Reaction of various electrophiles with the double bond releases the allyl group and leads to formation of the group 14 cations. The mesityl groups then are of sufficient steric bulk to protect the tricoordinate metal center from attack by nucleophiles. This approach is used herein with silicon, germanium, and tin as the central atom. The ^{29}Si chemical shift (δ 225) indicates full cationic character for the silicon system. The ^{119}Sn chemical shift (δ 806) indicates less than full cationic character for the tin system. The positive charge for the germanium system has been assessed by examination of the aromatic ^{13}C chemical shifts. These results provide the highest current cationic character for silylium and stannylum ions.

Although tricoordinate carbocations (R_3C^+) have been a central feature of mechanistic organic chemistry for decades, analogous species containing other positively charged heavy atoms in place of carbon have not enjoyed a similar role. In the particular case of the group 14 congeners (Si, Ge, Sn), the search for stable, tricoordinate cations in the condensed phase has extended over more than half a century.^{1,2} The principal impediments have been high kinetic sensitivity of the species to nucleophiles and low stabilization provided by π -delocalizing substituents, compared with carbon. Inability to isolate stable group 14 cations in the condensed phase has inhibited their development as reactive intermediates in mechanistic schemes. Although thermodynamic stability of the cations increases with atoms lower in the periodic table because of their lower electronegativity, the problems facing Ge and Sn are similar to those of Si. We have recently reported a solution to the silyl cation problem,³ and we discuss herein this approach within the full context of group 14.

Nucleophilic Isolation

Our overall strategy has been to protect the cationic species from all nucleophiles. The development of this strategy, however, took more than a decade and required four separate innovations: (1) hydrocarbon solvents, (2) anions of very low nucleophilicity, (3) bulky substituents, and (4) methodology for creation of the cation. All four were necessary; the absence of any one prohibited formation of a free cation. We introduced aromatic solvents and low nucleophilicity anions in this context

in 1992 for the case of stannylum cations.⁴ Superior anions were reported in 1993.⁵ This stage of development reached its apex with the solution of the X-ray structures of several silyl cations by Reed's^{1b} and our⁶ groups. Our studies used the tetrakis(pentafluorophenyl)borate anion, $(\text{C}_6\text{F}_5)_4\text{B}^-$ (TPFPB), and resulted in species that retained solvent as a weak fourth coordination site.⁶ Reed's studies used a series of halogenated carboranes as anions and resulted in species that retained the anion as a weak fourth coordination site.^{1b} The silyl cationic character was variously estimated by these authors as about 30–50%, although other authors characterized the species as arenium and halonium ions.⁷ Theoreticians pointed out that silyl cations can complex with both saturated C–H bonds and even rare gases.⁸ This observation seemingly doomed the existence of free silyl cations in condensed phase, because any solvent or anion would necessarily possess some nucleophilicity and consequently would bind with silicon to some extent.

Steric effects provided the critical stabilizing factor in the original creation of species containing multiple bonds to silicon, such as disilenes, $>\text{Si}=\text{Si}<$,⁹ to prevent dimerization and reaction with external reagents. The idea therefore is not particularly novel that bulky substituents might protect silylium cations from reaction with nucleophiles. In fact, a decade ago we tried to remove hydride from trimesitylsilane (mesityl,

(4) Lambert, J. B.; Kuhlmann, B. *J. Chem. Soc., Chem. Commun.* **1992**, 931–932.

(5) (a) Lambert, J. B.; Zhang, S. *J. Chem. Soc., Chem. Commun.* **1993**, 383–384. (b) Xie, Z.; Liston, D. J.; Jelínek, T.; Mitro, V.; Bau, R.; Reed, C. A. *J. Chem. Soc., Chem. Commun.* **1993**, 384–386.

(6) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917–1918. Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430–2443.

(7) Olah, G. A.; Rasul, G.; Li, X.-Y.; Buchholz, H. A.; Sandford, G.; Prakash, G. K. S. *Science* **1993**, *260*, 983–984.

(8) (a) Maerker, C.; Kapp, J.; Schleyer, P. v. R. In *Organosilicon Chemistry II*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1996; pp 329–359. (b) Arshadi, M.; Johnels, D.; Edlund, U.; Ottosson, C.-H.; Cramer, D. *J. Am. Chem. Soc.* **1996**, *118*, 5120–5131.

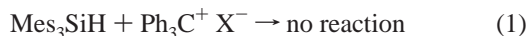
(9) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, UK, 1989; pp 1015–1142.

(1) For reviews of the Si case, see (a) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191–1201. (b) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325–332. (c) Lickiss, P. In *The Chemistry of Organic Silicon Compounds*, 2nd ed.; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: Chichester, UK, 1998; pp 557–594.

(2) In this paper, these species are, respectively, called silylium, germlylium, and stannylum ions, according to IUPAC recommendations. The terms silylenium, silicenium, and their Ge and Sn analogues have been discarded and are no longer appropriate.

(3) Lambert, J. B.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 400–401.

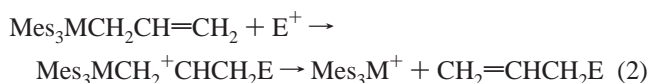
abbreviated Mes, is 2,4,6-trimethylphenyl) by reaction with trityl cation,¹⁰ the standard method at this time for trying to generate silyl cations (the Corey method).¹¹ The steric bulk surrounding the hydride, however, thwarted access of the trityl cation and led to no reaction (eq 1). We prepared trihexylsilylium TPFPB



via the Corey method and found that the hexyl chains provided little or no additional protection over methyl, as the ²⁹Si chemical shift of δ 90 in benzene confirmed complexation with an external nucleophile.⁶ Movement of the chemical shift to δ 65 in mesitylene indicated that the nucleophile was solvent. Reed and co-workers¹² succeeded in making tri(*tert*-butyl)silylium with a halocarborane anion via the Corey method, but its ²⁹Si chemical shift and X-ray structure indicated coordination with the anion through the halogen atom. Thus *tert*-butyl is insufficiently bulky to prevent access of nucleophiles. There is a further complication with alkyl side chains. As Schleyer pointed out,^{8a} the C–H bond of methane is capable of complexing with silylium cations. Both rigid and flexible alkyl groups can provide a C–H bond within binding distance to the silicon atom, so that an agostic interaction may serve as the fourth coordination. Thus, even if a large alkyl substituent could deflect solvent and anion from the silicon atom, it is possible that a C–H bond would be accessible and would provide a fourth coordination site.

Our solution to the problem of alkyl coordination was to revert to the mesityl group, all of whose C–H bonds are out of the range of coordination without requiring severe angle-bending distortion. The ortho methyl groups provide a steric shield both above and below the plane of the silylium cation, preventing access by external nucleophiles. A new method, however, was needed to generate the cation, as hydride removal (eq 1, the Corey method) is sterically prohibited.

Consequently, we used allyl as a leaving group. Although allyl is unknown as a leaving group in carbon organic chemistry, there is precedent in silicon organic chemistry.¹³ The approach is illustrated in eq 2,



in which M represents Si, Ge, or Sn and E⁺ represents an appropriate electrophile. The double bond of the allyl group is designed to provide a nucleophilic site outside the steric control of the mesityl methyl groups. Reaction of the positively charged electrophile E⁺ with the allyl double bond would result in a β -silyl, -germyl, or -stannyl cation, which normally is unstable and decomposes by expulsion of a silyl cation or its analogue.¹⁴ This step is favored by relief of steric strain, as the tetrahedral environment around Si, Ge, or Sn is reduced to a trigonal environment. The intention then is that, upon loss of allyl, the three mesityl groups snap into a cage that prevents access of external nucleophiles to the central atom and retains the tricoordinate nature of the cation.

(10) Lambert, J. B.; Lentz, K. T.; Kania, L. Unpublished results.

(11) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3237–3238.

(12) Xie, Z.; Bau, R.; Benesi, A.; Reed, C. A. *Organometallics* **1995**, *14*, 3933–3941.

(13) Shade, L.; Mayr, H. *Makromol. Chem. Rapid Commun.* **1988**, *9*, 477–482. Uhlig, W. In *Organosilicon Chemistry*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1994; pp 21–26.

(14) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677–2689.

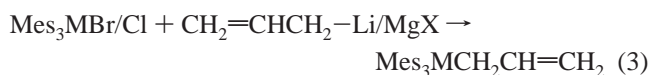
Table 1. Chemical Shifts (ppm) for Mes₃MCH₂CH=CH₂ and Mes₃M⁺ (C₆F₅)₄B[−]

M	X ^a	solvent	$\delta(^{29}\text{Si})$	$\delta(^{119}\text{Sn})$	$\delta(^{13}\text{C})$				
					ipso	ortho	meta	para	
Si	allyl	C ₆ D ₆			145.0	138.6	129.9	137.9	
		TPFPB ^b	C ₆ D ₆	225.5		150.3	144.8	130.5	–
		CH ₃ C ₆ H ₅ ^c	225.7						
		1,4-(CH ₃) ₂ C ₆ H ₄ ^d	225.6						
Ge	allyl	C ₆ D ₆				5.3	6.2	0.6	–
		TPFPB ^b	C ₆ D ₆			143.5	138.6	129.0	137.6
		CH ₃ C ₆ H ₅			148.8	141.9	130.7	139.7	
Sn	allyl	C ₆ D ₆				5.3	3.3	1.7	2.1
		TPFPB ^b	C ₆ D ₆			144.6	142.1	128.8	138.1
		CH ₃ C ₆ H ₅	806		147.1	146.3	130.4	141.9	
		1,3,5-(CH ₃) ₃ C ₆ H ₃	806						
	1,2-(Cl ₂)C ₆ H ₄	806							
	Δ^e	C ₆ D ₆			2.5	4.2	1.6	3.8	

^a X refers to the fourth group associated with Mes₃M, either allyl or the anion. ^b TPFPB is (C₆F₅)₄B[−]. ^c C₆D₆/CH₃C₆H₅ 1/3. ^d C₆D₆/1,4-(CH₃)₂C₆H₄ 1/1. ^e The difference between the ¹³C chemical shifts of the cation and of the allyl precursor in C₆D₆.

Results

The allyl derivatives were unknown, but we were able to synthesize them by reaction of the halo trimesityl derivatives with either the allyllithium reagent or the allyl Grignard reagent (eq 3).



Chlorotrimesitylsilane was prepared from trimesitylsilane. The germanium and tin halo precursors were prepared by the reaction of SnBr₄ or GeCl₄ with mesitylmagnesium bromide to produce Mes₃M–Br/Cl. The silicon and germanium derivatives were treated with allyllithium to yield allyltrimesitylsilane (**1**) and allyltrimesitylgermane (**2**), respectively, and the tin derivative was treated with allylmagnesium bromide to yield allyltrimesityltin (**3**). The structures were proved by NMR spectroscopy and X-ray crystallography.

Various electrophiles were essayed in the reaction of eq 2. We found that trityl was relatively ineffective. Our best results were obtained by use of the solvated silyl cation, Et₃Si-(C₆H₆)⁺,^{5a,6} or the free β -silyl cation, Et₃SiCH₂CPh₂⁺,¹⁵ in either case with TPFPB as the anion and arenes as the solvent. Manipulations were carried out at room temperature under nitrogen in the protected environment of a glovebox to avoid exposure to atmospheric water and oxygen. The resulting solutions were stable for weeks and exhibited only single signals in the ²⁹Si or ¹¹⁹Sn spectra. Table 1 lists the chemical shifts of the heavy atoms as a function of solvent. Figure 1 displays the ²⁹Si spectrum of Mes₃Si⁺ and the ¹¹⁹Sn spectrum of Mes₃Sn⁺.

Product recovery was explored by reaction of Mes₃Si⁺ or Mes₃Sn⁺ with Bu₃SnH. Hydride transfer occurred, and Mes₃SiH or Mes₃SnH was observed as the principal product. Ultraviolet spectra were recorded in benzene.

Discussion

The first consideration was the steric accessibility of the allyl group. Figure 2 is a stereoscopic representation of the X-ray structure of allyltrimesitylsilane (Mes₃SiCH₂CH=CH₂, **1**). The

(15) Lambert, J. B.; Zhao, Y. *J. Am. Chem. Soc.* **1996**, *33*, 7867–7868.

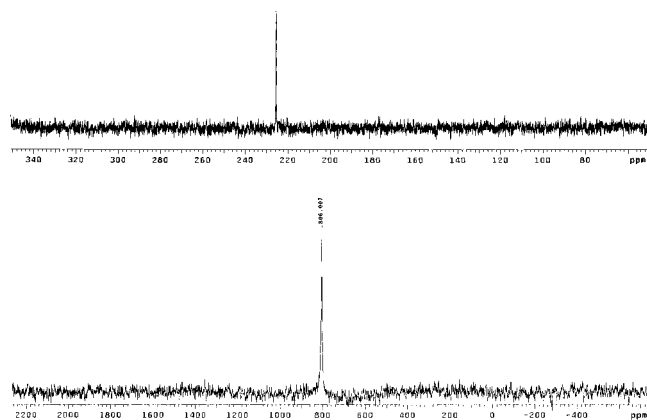


Figure 1. Upper: The 79.46 MHz ^{29}Si spectrum of trimesitylsilylium tetrakis(pentafluorophenyl)borate in C_6D_6 . Lower: The 149.15 MHz ^{119}Sn spectrum of trimesitylstannylium tetrakis(pentafluorophenyl)borate in C_6D_6 .

allyl group clearly protrudes beyond the mesityl methyl groups. Consequently and in contrast to the case of the hydride of trimesitylsilane (Mes_3SiH), the double bond of the allyl group is accessible to attack by electrophiles.

The reaction of eq 2 occurred successfully for all three central atoms, to deliver, respectively, the silylium ion (Mes_3Si^+ , **4**), the germlylium ion (Mes_3Ge^+ , **5**), and the stannylium ion (Mes_3Sn^+ , **6**), with degrees of complexation with solvent or anion that still must be assessed. The byproducts of eq 2 were $\text{CH}_2\text{CH}=\text{CH}_2\text{SiEt}_3$ or $\text{CH}_2\text{CH}=\text{CH}_2\text{CPh}_2\text{CH}_2\text{SiEt}_3$, depending on whether the solvated silyl cation or the free β -silyl carbocation served as the electrophile.

It is noteworthy that the ^{29}Si resonance for either byproduct does not appear in the upper spectrum of Figure 1. The reaction of eq 2 always produces two benzene layers (or arene layers in general). The ionic species are found in the lower layer, and the upper layer is benzene containing the nearly nonpolar byproduct. This behavior is characteristic of the formation of liquid clathrates. Such species were originally discovered with aluminate salts of a variety of cations,¹⁶ but other large anions have now been found to give this behavior, including borates.¹⁷ Liquid clathrates have been defined^{16b} as “nonstoichiometric liquid inclusion compounds [formed] upon the interaction of aromatic molecules with [salts]”. They were characterized by the formation of two solvent layers, the lower layer also containing the salt and the upper layer containing pure solvent. Our solutions look identical to the phases depicted in Figure 6.10 of ref 16b. It is likely but not proved that our materials exist as a liquid clathrate. Moreover, the precursors (the solvated silyl cation, $\text{Et}_3\text{Si}(\text{C}_6\text{H}_6)^+$, or the free β -silyl cation, $\text{Et}_3\text{SiCH}_2\text{CPh}_2^+$) also form these two layers, so they too may exist as liquid clathrates. In each case the upper layer of solvent is syringed off so that the actual reagent is the ion-containing lower layer.

Atwood has suggested that the primary condition for liquid clathrate formation is a low lattice energy. The large size of the cation, as in the present case, permits greater numbers of arene molecules in the clathrate. His suggested model is of

structured layers in the liquid.¹⁶ He found that some liquid clathrates could be enticed to crystallize at lower temperatures, as we also found for the solvated silyl cation $\text{Et}_3\text{Si}(\text{toluene})^+\text{TPFPB}^-$.⁶ The silylium, germlylium, and stannylium ions reported herein, however, have not as yet yielded crystals, possibly because of low lattice energy. Consequently, these ions have been characterized by NMR spectroscopy, as described in the next three sections.

The Silylium Ion. The chemical shift of $\text{Mes}_3\text{Si}^+\text{TPFPB}^-$ was observed at δ 225.5 in benzene. Our solvated trialkylsilyl cations^{5a,6} and Reed's similar but anion-complexed ions^{1b,5b} exhibited chemical shifts ranging up to δ 115. The solvent dependence of the chemical shift indicated that the silicon of these trialkylsilyl cations is involved in coordination with solvent, if not anion.

The sensitivity of the chemical shift of the trimesityl species to its nucleophilic surroundings and hence the coordination status of silicon can be assessed by changing the solvent and the anion. As Table 1 indicates, the chemical shift of δ 225–6 is invariant to solvent in benzene, toluene, and *p*-xylene. In contrast, the solvated trialkylsilyl cation $\text{Et}_3\text{Si}(\text{arene})^+\text{TPFPB}^-$ exhibited a solvent-dependent chemical shift: δ 92.3 in benzene, 87.1 in 3/1 benzene/toluene, and 81.8 in pure toluene.⁶ These arene solvents therefore do not penetrate the protection by the mesityl methyl groups and do not complex with the silicon (arenes are nucleophilic primarily on their π face, so their approach to silicon must be with the sterically maximal face down). We did find, however, that acetonitrile and triethylamine either were smaller or more strongly nucleophilic, as 1/3 benzene/acetonitrile led to a chemical shift of δ 37.0 and 1/1 benzene/triethylamine led to a chemical shift of δ 47.1, both consistent with tetracoordination. We supplied allyltrimesitylsilane to Reed and Fackler for reaction with electrophiles bearing carborane anions. With the *closo*-7,8,9,10,11,12- $\text{Cl}_6\text{-CB}_{11}\text{H}_6$ anion, they measured the chemical shift of Mes_3Si^+ to be δ 225.9,¹⁸ identical to the values with the TPFPB anion. Thus the chemical shift is invariant both to anion and to arene solvents, indicating the absence of or the identity of coordination in every case. The observed change in chemical shift with variation of nucleophilicities of the arenes with the trialkylsilyl cases, however, militates against identical coordination and favors absence of coordination for the solvent in the trimesityl case.

The value of δ 225 is at a considerably higher frequency than (downfield from) any previous silicon species not containing divalent silicon or attachment to a transition metal.¹⁹ For Me_3Si^+ in the gas phase, calculated values ranged from δ 351 to 418, depending on the basis set used.²⁰ Reed and co-workers made adjustments for substituents (Pr_3Si^+) and nonspecific solvation and estimated a range of δ 220–320 for the tricoordinate geometry, compared with the observed δ 115, corresponding to 36–52% silylium ion character.²¹ If compared directly with the gas-phase values, δ 115 represents 28–33% silylium character.

Alkyl groups, however, are inappropriate models for the chemical shift of silicon attached to aryl groups. At the time of our experiments, no theoretical calculations had been published for the chemical shift of triarylsilylium ions. Now, however,

(16) (a) Atwood, J. L. In *Inclusion Compounds*, Atwood, J. L., Ed.; Academic Press: London, 1984; Vol. 1, Chapter 9. (b) Atwood, J. L. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; pp 197–232.

(17) Bond, D. R.; Jackson, G. E.; João, H. C.; Hofmeyer, M. N.; Modro, T. A.; Nassimbein, L. R. *J. Chem. Soc., Chem. Commun.* **1989**, 1910–1911. Hunter, R.; Haueisan, R. H.; Irving, A. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 566–568. Dioumaev, V. K.; Harrod, J. F. *Organometallics* **1996**, 15, 3859–3867.

(18) Reed, C. A.; Fackler, N. Unpublished results.

(19) West, R.; Denk, M. *Pure Appl. Chem.* **1996**, 68, 785–788. Grumbine, S. K.; Tilley, T. D.; Arnold, F. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1994**, 116, 5495–5496. Tilley, T. D. *J. Am. Chem. Soc.* **1998**, 120, 11184–11185.

(20) Kutzelnigg, W.; Feischer, U.; Schindler, M. *NMR; Basic Principles and Progress*; Springer-Verlag: New York, 1991; Vol. 23.

(21) Xie, Z.; Manning, J.; Reed, R. W.; Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, 118, 2922–2928.

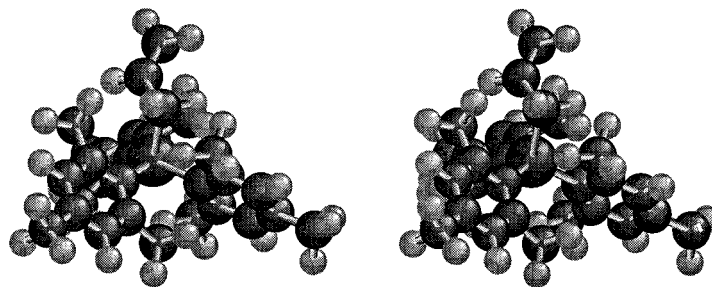


Figure 2. Stereoscopic representation of the X-ray structure of allyltrimesitylsilane.

two groups^{22,23} have published such values. The calculations vary with the choice of basis set and with the angle of twist for the arene rings. The calculated angle of twist of trimesitylsilylium was 48° , compared with 29° for triphenylsilylium (silyl) lacking the methyl groups.²² Despite this twisting distortion, there still is considerable conjugation of the phenyl rings with the empty orbital on silicon, because the calculated arene C—C bond lengths were pronouncedly unequal and in a dactylic pattern (long-short-short). The calculated chemical shift was δ 230.1, very favorably comparable to the experimental value of δ 225.5. Moreover, when benzene was introduced computationally at an appropriate geometry for complexation but at a closest approach distance, the value changed very little, to δ 228.6.²² The benzene ring could not get close enough to coordinate with silicon. In contrast, the value for trimethylsilylium changed computationally from δ 361.6 to 80.4 on addition of benzene to the system.²² These calculations confirm the conclusions that trialkylsilylium ions complex with solvent but trimesitylsilylium is an entirely free silyl cation. The calculations also confirmed that the ortho methyl C—H bonds are too far away to complex with the empty silicon 3p orbital.

Experimental evidence for conjugation of the aryl rings with silicon can be obtained by ^{13}C NMR spectroscopy and by ultraviolet spectroscopy. The NMR evidence is discussed below in the context of the germlylium cation, so that all systems can be examined together. The ultraviolet spectrum had to be taken in benzene solution, not an optimal medium. The strong 1L_b benzene peak at 254 nm provides intense end absorption. Two absorptions were observed beyond this end absorption, a maximum at 304 nm and a shoulder at 370 nm. Tailing of the latter absorption into the visible causes the dark yellow color of the solution. The triphenylmethyl cation (trityl) exhibits two peaks at 409 and 428 nm.²⁴ Thus the silylium cation absorbs at shorter wavelength than trityl. Nonetheless, its absorption close to the visible provides further support for conjugation between the mesityl rings and the silicon atom. It should be noted that the crystals of $\text{Et}_3\text{Si}(\text{toluene})^+ \text{TPFPB}^-$ were colorless.⁶

The Stannylium Ion. The strategy of an allyl leaving group also should be applicable to the case of tin. Low nucleophilic media have previously been used in attempts to prepare a free stannylium ion. In 1992 we used the trityl cation to abstract hydride from trialkylstannane (the method of eq 1) with various solvents and anions and obtained ^{119}Sn chemical shifts in the range δ 150–360.⁴ In 1994 Kira, Oyamada, and Sakurai^{25a} reported similar results with a different anion. Earlier, Birchall and Manivannan^{25b} had reported a ^{119}Sn chemical shift of δ

322 for $\text{Me}_3\text{Sn}(\text{FSO}_3)$. These values indicated considerable deshielding of the tin atom from the expectation for pure tetracoordination close to δ 0. The solvent dependence, however, is reminiscent of the case for the solvated trialkylsilylium ions. There are no calculations of tin shieldings comparable to those for silicon shieldings. Arshadi et al., however, have presented a correlation between ^{29}Si and ^{119}Sn chemical shifts, and a chemical shift of δ 360 for silicon corresponds to one of about δ 1700 for tin.²⁶ If the correlation is valid and the relationship is linear, then the observed ^{119}Sn shifts of ca. δ 350 correspond to only about 20% stannylium ion character (parallel to that for trialkylsilylium ions generated under similar conditions when compared with chemical shifts calculated for the gas phase). Arshadi et al. thus concluded and we agree that the tin cations prepared by the Japanese group and by us had low stannylium character.²⁶

To test the allyl leaving group method for tin, we first allowed allyltributylstannane to react with trityl TFPFB in benzene by analogy with eq 2. The lower layer of the presumed liquid clathrate produced a single ^{119}Sn peak at δ 262.8. Examination of the upper layer by GC/MS revealed the presence of the expected byproduct, allyltriphenylmethane. For comparison, tributyltin hydride was allowed to react with trityl TFPFB by analogy with eq 1. The resulting lower layer produced a ^{119}Sn peak at essentially the same chemical shift, δ 262.7, as for the material from the allyl leaving group method. The two methods thus produce the same stannylium cation, solvated by benzene and possessing ca. 20% stannylium character, in line with our and Sakurai's previous observations.^{4,25}

Removal of the allyl group in the case of butyl substituents in essence is superfluous, as hydride is readily extractable. The observed chemical shift indicates that, as expected, butyl is too small to prevent coordination of the stannylium cation with external nucleophiles, which appear to be solvent as judged by the solvent dependence of the chemical shift. Consequently, bulkier substituents again are needed. We prepared allyltrimesitylstannane (δ -156) and allowed it to react with trityl TFPFB. Its failure to react paralleled the situation with allyltrimesitylsilane and presumably was due to the low reactivity of trityl with a double bond. We then had recourse to the more reactive electrophiles used in the silicon case: the solvated silyl cation,^{5a,6} $\text{Et}_3\text{Si}(\text{C}_6\text{H}_6)^+$, and the free β -silyl carbocation,¹⁵ $\text{Et}_3\text{SiCH}_2\text{CPh}_2^+$. Both these electrophiles reacted successfully with allyltrimesitylstannane to give identical lower (liquid clathrate) layers that exhibited a single ^{119}Sn peak at δ 806 (lower spectrum in Figure 2). These solutions were stable at room temperature for several days.

The observed ^{119}Sn chemical shift is at a record deshielded position for species other than divalent tin and consequently indicates considerable progress toward a tricoordinate species,

(22) Müller, T.; Zhao, Y.; Lambert, J. B. *Organometallics* **1998**, *17*, 278–280.

(23) Kraka, E.; Sosa, C. P.; Gräfenstein, J.; Cremer, D. *Chem. Phys. Lett.* **1997**, *279*, 9–16.

(24) Branch, G.; Walba H. *J. Am. Chem. Soc.* **1954**, *73*, 1564–000.

(25) (a) Kira, M.; Oyamada, T.; Sakurai, H. *J. Organomet. Chem.* **1994**, *471*, C4–C5. (b) Birchall, T.; Manivannan, V. *J. Chem. Soc., Dalton Trans.* **1985**, 2671–2675.

(26) Arshadi, M.; Johnels, D.; Edlund, U. *J. Chem. Soc., Chem. Commun.* **1996**, 1279–1280.

compared with the previous extreme of about δ 360. Unfortunately, there are no calculations of ^{119}Sn chemical shifts of a free stannylum cation that can serve as a point of comparison. It is for this reason that the linear relationship of Arshadi et al.²⁶ is useful. A ^{29}Si chemical shift of δ 225 translates to a ^{119}Sn chemical shift of about δ 1100. Two conclusions may be drawn from this observation. (1) By strict linear proportionality, an observed ^{119}Sn chemical shift of δ 806 is about three-quarters of the extreme expected for a fully tricoordinate stannylum ion. (2) If the relationship is nonlinear, the possible range of stannylum character is vastly expanded, including the possibilities that we have reached the tricoordinate stannylum extreme or that we are even less than three-quarters of the way to the extreme.

As our working model, we decided to accept the linear model, meaning that our observed stannylum cation is about three-quarters of the way along the continuum from tetra- to tricoordination.^{1b} If so, then either solvent or anion must be able to have access to some degree to the tin atom. The longer C–Sn bonds, compared with C–Si bonds, or perhaps the higher electrophilicity of the tin center could bring about the residual coordination. We examined the solvent dependence of the ^{119}Sn chemical shift of trimesitylstannylum TFPFB and found it to be invariant at δ 806 for benzene, 1/2 benzene/toluene, 1/2 benzene/*p*-xylene, and 1/2 benzene/1,2-dichlorobenzene. This constancy of the chemical shift with considerable variation of the nucleophilicity of the solvent indicates that aromatic solvents are not able to coordinate with the tin cation. Two alternative conclusions remain. (1) The value of δ 806 indeed corresponds to the extreme for tricoordination. (2) A nucleophile other than solvent is able to coordinate partially with the tin cation. The only remaining possible nucleophile is the anion TFPFB, and the likely nucleophilic site would be the para or (less likely) meta fluorine atoms. Marks et al.²⁷ in fact have observed one X-ray structure in which the para and meta fluorine atoms chelate to a zirconium cation.

In light of these observations we sought to synthesize an allyltriarylstannane system with bulkier aryl groups than mesityl. We encountered considerable synthetic problems in synthesizing the precursor halostannane, Ar_3SnX . Reaction of SnBr_4 with 2,4,6-tri-*tert*-butylphenyllithium (supermesityllithium) led to introduction of only two supermesityl groups, one of which was rearranged, as the product was dibromosupermesityl(dimethyl-(3,5-di-*tert*-butylphenyl)methyl)stannane, $\text{sMesSnBr}_2\text{CMe}_2(3,5\text{-tBu}_2\text{C}_6\text{H}_3)$, in which sMes stands for supermesityl. Reaction of SnCl_4 with 2,4,6-triisopropylphenyllithium (TipLi) also led to the introduction of only two aryl groups, albeit unrearranged, to form $\text{Tip}_2\text{SnCl}_2$.

As this last procedure occurred in low yield, we had recourse to the Masamune method.²⁸ Reaction of TipMgBr with SnBr_4 led to formation of the cyclic stannoxane, $\text{di(Tip)cyclotri-stannoxane}$, $(\text{Tip}_2\text{SnO})_3$. Reaction of this material with hydrogen chloride then gave $\text{Tip}_2\text{SnCl}_2$ in good yield. It remained to introduce a third aryl group. Unfortunately, mesityllithium failed to react. Only the sterically smaller phenyllithium was successful, giving $\text{Tip}_2\text{C}_6\text{H}_5\text{SnCl}$, which successfully reacted with allyllithium to give allyldi(Tip)phenylstannane (**7**), whose structure was confirmed by X-ray crystallography.

We allowed **7** to react with $\text{Et}_3\text{Si}(\text{C}_6\text{D}_6)^+ \text{TFPFB}^-$ in order to form the stannylum cation $\text{C}_6\text{H}_5\text{Tip}_2\text{Sn}^+ \text{TFPFB}^-$. The chemical shift of the only species in the lower layer was observed at δ

697. This chemical shift is more shielded by about 100 ppm than that of the trimesitylstannylum cation, so negative progress had been achieved by attempting to bulk up the aryl substituent. Two conclusions may be drawn. (1) Two triisopropylphenyl rings and one phenyl ring are slightly less sterically constraining than three mesityl groups, allowing a nucleophile such as solvent or anion better access to the tin atom. (2) The C–H bonds of the isopropyl groups approach more closely to the tin atom than those of methyl on the mesityl groups, allowing agostic interactions in the tri(isopropyl)phenyl case that were absent in the mesityl case. Either way, we have a stannylum cation with slightly less tricoordinate (stannylum) character than that of trimesitylstannylum.

We also operated on the anion, arguing that replacement of the four para fluorine atoms of TFPFB^- might eliminate the primary nucleophilic center of the anion. We took two approaches, neither successful. On one hand, we replaced 4-F with 4- Me_3Si , in the hopes that the size of the group would prevent its access to the tin atom. Although the anion synthesis was successful, trityl tetrakis[4-(trimethylsilyl)-2,3,5,6-tetrafluorophenyl]borate proved to be intractably insoluble in aromatic solvents, so that we were not able to effect any reactions. On the other hand, we replaced 4-F with 4-H to give trityl tetrakis-(2,3,5,6-tetrafluorophenyl)borate. This material gave irreproducible results and may not have been pure.

Consequently, we are left with δ 806 as the high frequency extreme for a stannylum cation. Although, according to the assumed linear Arshadi correlation, this value corresponds to only about 75% stannylum ion character, it represents considerable progress from previous observations of ca. δ 360. It is ironic that the stannylum cation, which presumably has greater thermodynamic stability than the silylium cation because of the higher electropositivity of tin, remains a slightly more difficult goal. Thermodynamic stability of course never was the problem with silylium ions. The problem was high kinetic reactivity of the silyl center, and that problem remains or may even be heightened for the tin case, because of the higher amount of positive charge on tin and its higher polarizability. Thus the higher thermodynamic stability of tin is counterbalanced by its higher electrophilicity and by its higher accessibility because of the longer C–Sn bonds.

The ultraviolet spectrum of trimesitylstannylum TFPFB in benzene showed clear maxima at 286 and 398 nm. The latter is at slightly longer wavelength than the longest wavelength silylium absorption (370 nm) and supports on one hand high stannylum character for this species and on the other hand greater interaction of the phenyl rings when the central atom is tin rather than silicon, probably because the longer Sn–aryl bonds position the ortho methyl groups further from each other, allowing greater planarity of the aryl rings.

The Germylum Ion. The only previous study of monogermylum cations used hydride removal from R_3GeH (R alkyl) with perchlorate as the anion and solvents other than arenes.²⁹ The ionic species prepared in sulfolane most likely were solvent complexes, and the species in dichloromethane were strongly complexed with the anion. By analogy with similar silyl and stannylum species, these germylum materials may have had 10% germylum character. Sekiguchi and co-workers^{30a} have prepared a free cyclotrigermylum cation. The new, low nucleophilicity anions and solvents have not previously been examined in the monogermanium context, although Sekiguchi and co-workers^{30b}

(27) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840–842.

(28) Masamune, S.; Sita, L.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 630–631.

(29) Lambert, J. B.; Schilf, W. *Organometallics* **1988**, *7*, 1659–1660.

(30) (a) Sekiguchi, A.; Tsukamoto, M.; Ichinohe, M. *Science* **1997**, *275*, 60–61. (b) Ichinohe, M.; Fukaya, N.; Sekiguchi, A. *Chem. Lett.* **1998**, 1045–1046.

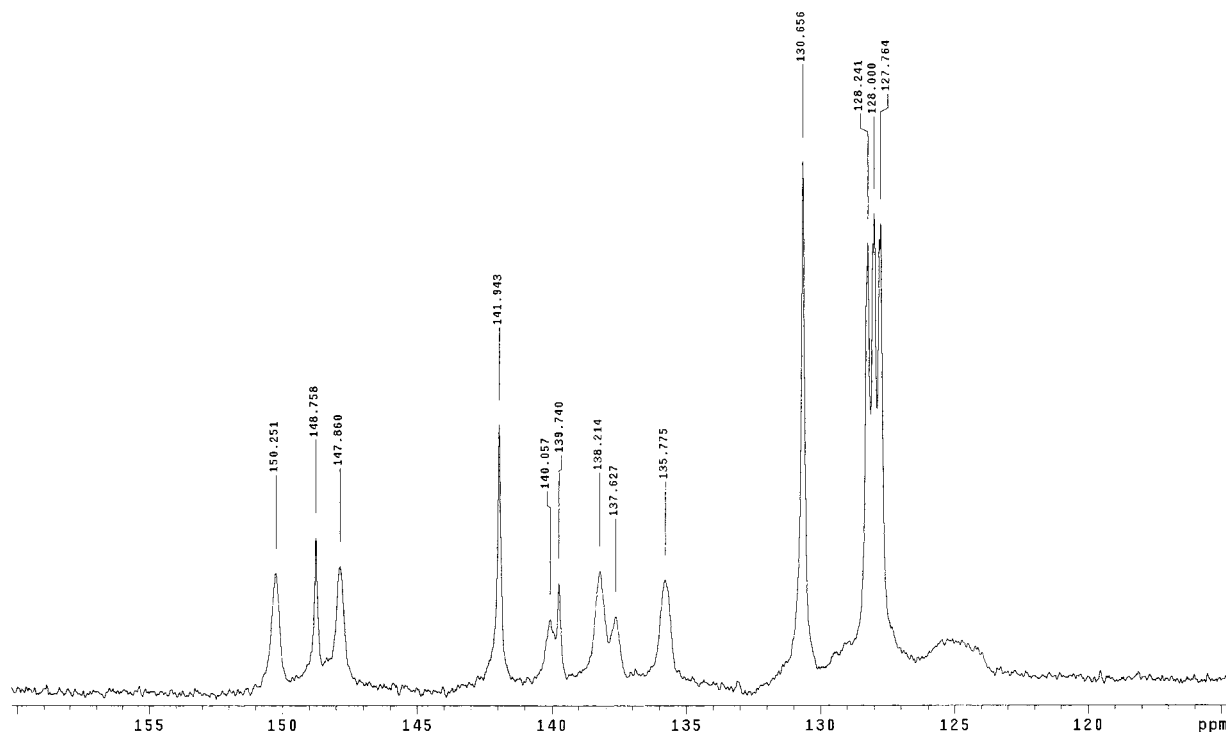


Figure 3. The 100.57 MHz ^{13}C spectrum of the aromatic region of trimesitylgermylium tetrakis(pentafluorophenyl)borate in C_6D_6 . The triplet at δ 128 is from solvent. The doublets centered at δ 149, 139, and 137 are from the carbons on the anion, each carbon split by fluorine.

have utilized them for their cyclotrimer system. For optimal results, we went directly to the mesityl system with the allyl leaving group. Treatment of allyltrimesitylgermane with $\text{Et}_3\text{Si}(\text{C}_6\text{D}_6)^+ \text{TPFPB}^-$ in benzene produced a two-layer system closely resembling those for the cases of silicon and tin.

Germanium lacks a sensitive and convenient nuclide for examination of its coordination properties (the spin of ^{73}Ge is 9/2, its natural abundance is 7.76%, and its natural sensitivity compared with ^1H is 1.09×10^{-4}).³¹ Consequently, there is no direct NMR method to assess the degree of germylium character in the species produced by the allyl leaving group method with low nucleophilic anion and solvent. When phenyl is attached to sp^2 carbon (alkene, carbonyl, carbocation, and so on), delocalization of charge through resonance generates positive charge in the phenyl ring. The extent of charge delocalization is dependent on a number of factors, such as the degree of electron deficiency at the α carbon and the angle of twist of the phenyl ring in relation to the p orbital on the α carbon. The resulting positive charge has a palpable effect on the ^{13}C shifts of the phenyl carbons, particularly the ortho and para carbons, to which positive charge is transferred by delocalization.

Thus the ^{13}C chemical shifts of the mesityl carbons can provide an alternative approach to assessing the degree of positive charge delocalization. Three factors must be taken into account: (1) the effect of the change in heteroatom (C to Si, Ge, Sn) at the α position to the aryl ring; (2) the effect of the ortho and para methyl groups; and (3) finally the desideratum, the extent of positive charge delocalization. The most straightforward comparison is between the starting material allyl derivatives and the cations. This comparison automatically takes the first two factors into consideration, as both starting material ($\text{Mes}_3\text{MCH}_2\text{CH}=\text{CH}_2$) and product (Mes_3M^+) have aryl methyl groups and the central atom M in common. The effect of the introduction of positive charge in place of allyl consequently is for the most part isolated.

Table 1 contains the aromatic chemical shifts for these six systems (three allyl, three cationic). Assignments were made according to peak intensities, expected positions, and ^{13}C – ^1H coupling relationships as revealed by gHMqBC (gradient hetero multiple quantum bond correlation) 2D spectra. Thus the meta carbons are essentially insensitive to all effects and remain constantly at about δ 129–130. Moreover this peak is the strongest in the spectrum, both because the meta carbon is the only aromatic carbon bearing a hydrogen and because there are two meta carbons per ring. Of the other three carbons, the ortho is expected to be most intense because of its 2-fold presence in each ring. The ipso carbon should appear at highest frequency, by analogy with the observations in the series $\text{C}_6\text{H}_5\text{Si}/\text{Ge}/\text{SnMe}_3$.³² The effect of methyl in our mesityl derivatives is to move the carbons 5–9 ppm to higher frequency (compared with phenyl). Such a shift, however, could put the ortho carbon in the vicinity of the ipso carbon. The gHMqBC spectra of the allyl derivatives clearly showed the relationships between each ring carbon and the methyl groups.

Figure 3 illustrates the case for the germanium cation. The aromatic region also contains the triplet for C_6D_6 at δ 128 and the aromatic carbons from the anion, $(\text{C}_6\text{F}_5)_4\text{B}^-$. We have seen these latter carbons in many spectra, and they are easily identified from their doubling through coupling to ^{19}F . In the spectrum of Figure 3, they appear as doublets centered around δ 137, 139, and 149. The meta carbon appears at its usual position (δ 130.7) and with the highest intensity. The ipso is identified at the highest frequency of the remaining carbons, the ortho by its second highest intensity, and the para by difference.

As the data in Table 1 indicate, there are shifts (from allyl starting material to product cation) to higher frequency for each of the aromatic carbons, although as expected the effect is minimal for the meta carbons (0.6–1.7 ppm). The effects at the ipso carbon are largely the result of the change in the

(31) Harris, R. K. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; p 7.

(32) Bullpitt, M.; Kitching, W.; Adcock, W.; Doddrell, D. J. *Organomet. Chem.* **1976**, *116*, 161–185.

electronegativity of the attached Si, Ge, or Sn on loss of allyl and are not of interest. The effects at the ortho and para carbons should result from the delocalization of charge on formation of the cation. These effects are in the range 2.1–6.2 (the para carbon for the Si case overlapped with anion carbons and could not be observed). Cationic character for the germyl system is comparable to those of the silyl and stannyl systems. The effects are much smaller than that for loss of hydride in the pair $\text{Ph}_3\text{CH} \rightarrow \text{Ph}_3\text{C}^+$, in which the ortho and para carbons move to higher frequency by about 15 ppm.³³ The shorter C–Ph bond length and the absence of the ortho methyl groups in trityl permit a more nearly planar system and stronger resonance interactions.

Conclusions

Treatment of allyltrimesitylsilane, -germane, and -tin with strong electrophiles, respectively, produces silylium, germlyium, and stannylum cations. Requisite conditions include arene solvents, low nucleophilicity anion [tetrakis(pentafluorophenyl)-borate], and protection from atmospheric water and oxygen. The ²⁹Si chemical shift of the silylium species (δ 225) is consistent with pure tricoordination. The ¹¹⁹Sn chemical shift of the stannylum species (δ 806) is at a record high frequency but may be short of that expected for pure coordination. Such an assessment could not be made for the germlyium ion, but analysis of the aryl ¹³C shifts on cation formation are consistent with charge development on germanium that is comparable to that on silicon and tin.

Experimental Section

Diethyl ether, benzene, and toluene were distilled from sodium/benzophenone prior to use. Pentane and hexane were refluxed with LiAlH₄ and distilled directly into the reaction vessels. Deuterated benzene was dried with Na/K alloy, vacuum-transferred to a Schlenk tube, and placed in a nitrogen-filled glovebox. Triethylsilane was dried with LiAlH₄, distilled to a Schlenk tube, and placed in the glovebox. NMR spectra were recorded on a Varian Unity Plus 400 (¹H, 400 MHz; ¹³C, 100 MHz; ²⁹Si, 79 MHz, ¹¹⁹Sn, 149 MHz), Gemini 300 (¹H, 300 MHz, ¹³C, 75 MHz), or VXR-300 (¹H, 300 MHz, ¹³C, 75 MHz) spectrometers.

Trimesitylsilane was prepared in 52% yield by the method of Gynane et al.³⁴

Chlorotrimesitylsilane was prepared in 83% yield by the method of Zigler et al.³⁵

Allyltrimesitylsilane (1) was prepared by the method of Lambert et al.³⁶ The X-ray structure has been reported.³⁶

Trimesitylsilylium Tetrakis(pentafluorophenyl)borate (TPFPB) (4). In a N₂-filled glovebox, trityl TPFPB⁶ (160 mg, 0.17 mmol) was dissolved in dry C₆D₆ (0.7 mL) in a valved 5 mm NMR tube. Addition of triethylsilane (25 mg, 0.22 mmol) produced two layers, the lower one consisting of a light brown oil. The colorless top phase was taken off with a syringe to remove the triphenylmethane byproduct. 1,1-Diphenylethene (40 mg, 0.22 mmol) was added, and the oil phase changed to deep green. Allyltrimesitylsilane (80 mg, 0.19 mmol) in C₆D₆ (0.5 mL) was added to create two layers again. The lower layer was a deep red oil. The light orange top phase was removed, and the oil was examined by NMR spectroscopy: ¹H NMR (C₆D₆) δ 1.92 (s, 9H), 2.10 (s, 18H), 6.60 (s, 6H); ¹³C NMR (C₆D₆) δ 21.5, 23.7, 130.5, 137.0 (d), 138.9 (d), 144.8, 149.1 (d), 150.3; ²⁹Si NMR (C₆D₆) δ 225.5 (¹J_{Si-C} = 70.6 Hz).

(33) Ray, G. J.; Kurland, R. J.; Colter, A. K. *Tetrahedron* **1971**, *27*, 735–752.

(34) Gynane, M. J. S.; Lappert, M. F.; Riley, P. I.; Rivière, P.; Rivière-Baudet, M. *J. Organomet. Chem.* **1980**, *202*, 5–12.

(35) Zigler, S. S.; Johnson, L. M.; West, R. J. *J. Organomet. Chem.* **1988**, *341*, 187–198.

(36) Lambert, J. B.; Stern, C. L.; Zhao, Y.; Tse, W. C.; Shawl, C. E.; Lentz, K. T.; Kania, L. J. *J. Organomet. Chem.* **1998**, *568*, 21–31.

Product Studies (Silylium Ion). (a) **1-Allyl-1,1-diphenyl-2-(triethylsilyl)ethane.** In a N₂-filled glovebox, trityl TPFPB (160 mg, 0.17 mmol) was dissolved in dry toluene (1.5 mL) in a valved 5 mm NMR tube. Addition of triethylsilane (25 mg, 0.22 mmol) produced a light brown oil at the bottom. The colorless top phase was then taken off with a syringe to remove the triphenylmethane byproduct. 1,1-Diphenylethene (40 mg, 0.22 mmol) was added, and the oil phase changed to deep green. Allyltrimesitylsilane (80 mg, 0.19 mmol) in toluene (0.7 mL) was added and a deep red oil formed. The light orange top phase was removed and analyzed by GC/MS. 1-Allyl-1,1-diphenyl-2-(triethylsilyl)ethane was found: MS (EI) *m/z* 296 (27), 295 (M⁺ – allyl, 97), 267 (81), 205 (23), 204 (100), 176 (29), 175 (45), 147 (47), 145 (24). The top layer also contained the excess of the starting materials, including CH₂=CPh₂, Mes₃SiCH₂CH=CH₂, Mes₃SiH (presumably from reaction of Mes₃Si⁺ with Et₃SiH), Et₃SiCH₂CHPh₂ (from the reaction of Et₃SiCH₂C⁺Ph₂ with Et₃SiH), and other uncharacterized materials. (b) **Trimesitylsilane.** The lower level was washed with dry toluene (3 × 2 mL) to remove all the nonpolar materials. Addition of Bu₃SnH (0.14 g, 0.48 mmol) changed the red oil on the bottom to brown. Toluene (1.5 mL) was added, and the new top layer was taken off with a syringe and analyzed by GC/MS. Many materials formed as Bu₃SnH decomposed in the GC column. The major product, however, was found to be trimesitylsilane: MS (EI) *m/z* 386 (M⁺, 1) 267 (28), 266 (99), 251 (54), 235 (38), 160 (35), 148 (16), 147 (95), 146 (100).

Tributylstannylum TPFPB Complex. (a) **By Hydride Abstraction from Bu₃SnH.** In a N₂-filled glovebox, trityl TPFPB (160 mg, 0.17 mmol) was dissolved in dry C₆D₆ (0.7 mL) in a valved 5 mm NMR tube. Addition of Bu₃SnH (60 mg, 0.21 mmol) produced a light brown oil at the bottom: ¹³C NMR (C₆D₆) δ 12.9, 24.6, 26.7, 27.3; ¹¹⁹Sn NMR (C₆D₆) δ 262.7. (b) **By the Allyl Method.** In a N₂-filled glovebox, trityl TPFPB (160 mg, 0.17 mmol) was dissolved in dry C₆D₆ (0.7 mL) in a valved 5 mm NMR tube. Addition of allyltributylstannane (63 mg, 0.19 mmol) produced a light brown oil at the bottom: ¹³C NMR (C₆D₆) δ 12.9, 24.3, 26.7, 27.4; ¹¹⁹Sn NMR (C₆D₆) δ 262.8. The colorless top layer was removed with a syringe and analyzed by GC/MS. Allyltriphenylmethane (Ph₃CCH₂CH=CH₂) was found: MS (EI) *m/z* 244 (28), 243 (M⁺ – allyl, 84), 166 (21), 165 (100), 115 (10), 91 (11), 77 (10), 51 (12), 41 (18), 39 (18).

Bromotrimesityltin.³⁷ To 100 mL of toluene containing SnBr₄ (6.0 mL, 0.046 mol) in a 500 mL flask was added dropwise an ether solution of mesitylmagnesium bromide (165.6 mL, 1.0 M). The reaction mixture was allowed to reflux for 10 h. The reaction was then quenched with H₂O and 10% aqueous HBr. Dimesityltin bromide either fell out as a dense white solid or became suspended in the organic layer. Filtration of the organic layer removed the disubstituted product. The toluene layer then was washed with H₂O (2 × 50 mL), NaHCO₃ (2 × 50 mL), and again with H₂O (2 × 50 mL). The solution was dried (MgSO₄), and the solvent was removed by rotary evaporation. Methanol was added to the resultant yellow-orange oil to aid crystal formation by solvent diffusion. The product was a white powder (8.2 g, 32%): mp 159–160 °C; ¹H NMR (CDCl₃) δ 2.23 (s, 18H), 2.25 (s, 9H), 6.78 (s, 6H); MS (EI) *m/z* 555 (M⁺ – 1, 32), 436 (100), 477 (22), 357 (13).

Allyltrimesitylstannane (3). Allylmagnesium bromide (12 mL, 0.012 mol) was added in excess to bromotrimesityltin (6.3 g, 0.011 mol) in toluene. After refluxing for 20 h, the reaction mixture was quenched with H₂O and 10% aqueous HBr. The toluene portion was washed with H₂O, NaHCO₃, and H₂O again. The solution was dried (MgSO₄), the solvent was removed by rotary evaporation, and hexane and methanol were added to force crystallization. Recrystallization from CH₃OH yielded a white powder: 2.8 g, 49.2%; mp 116–118 °C; ¹H NMR (CDCl₃) δ 2.21 (s, 18H), 2.23 (s, 9H), 2.38 (d, 2H), 4.74 (m, 2H), 5.78 (m, 1H), 6.78 (s, 6H); ¹³C NMR (CDCl₃) δ 20.9, 25.6, 26.3, 113.6, 128.8, 136.8, 138.1, 142.1, 144.6; ¹¹⁹Sn NMR (CDCl₃) δ –155.

Trimesitylstannylum Tetrakis(pentafluorophenyl)borate (TPFPB) (6). (a) **From the Solvated Triethylsilyl Cation.** In a N₂-filled glovebox, trityl TPFPB (160 mg, 0.17 mmol) was dissolved in dry C₆D₆ (0.7 mL) in a valved 5 mm NMR tube. Addition of triethylsilane (25 mg, 0.22 mmol) produced a light brown oil at the bottom. The

(37) Lapkin, I. I.; Sedel'nikova, V. A. *Zh. Obshch. Khim.* **1960**, *30*, 2771–2777 (*Engl. Trans.* 2753–2758).

colorless top phase containing the triphenylmethane byproduct was then removed with a syringe. Allyltrimesitylstannane (98.3 mg, 0.19 mmol) in C_6D_6 (0.5 mL) was added, and a deep red oil formed. The light orange top phase was removed, and the oil was examined by NMR spectroscopy: 1H NMR (C_6D_6) δ 1.95 (s, 18H), 2.01 (s, 9H), 6.63 (s, 6H); ^{13}C NMR (C_6D_6) δ 21.0, 24.1, 130.4, 137.3 (d), 138.2 (d), 141.9, 146.3, 147.1, 149.0 (d); ^{119}Sn NMR (C_6D_6) δ 806. **(b) From the Free β -Silyl Carbocation.** In a N_2 -filled glovebox, trityl TPFPPB (160 mg, 0.17 mmol) was dissolved in dry C_6D_6 (0.7 mL) in a valved 5 mm NMR tube. Addition of triethylsilane (25 mg, 0.22 mmol) produced a light brown oil at the bottom. The colorless top phase containing the triphenylmethane byproduct was then removed with a syringe. 1,1-Diphenylethene (40 mg, 0.22 mmol) was added, and the bottom oil changed to deep green. Allyltrimesitylstannane (98.3 mg, 0.19 mmol) in C_6D_6 (0.5 mL) was added, and a deep red oil formed. The light orange top phase was removed, and the oil was examined by NMR spectroscopy: 1H NMR (C_6D_6) δ 1.95 (s, 18H), 2.01 (s, 9H), 6.63 (s, 6H); ^{13}C NMR (C_6D_6) δ 21.0, 24.1, 130.4, 137.3 (d), 138.2 (d), 141.9, 146.3, 147.0, 149.0 (d); ^{119}Sn NMR (C_6D_6) δ 806.

Product Studies (Stannylum Ion). The red oil was washed with dry toluene to remove all the nonpolar materials. Addition of Bu_3SnH (0.14 g, 0.48 mmol) changed the red oil on the bottom to brown. Toluene (1.0 mL) was added. The top layer was removed with a syringe and analyzed by GC/MS. Several products formed as Bu_3SnH decomposed in the GC column. The major product, however, was found to be trimesitylstannane: MS (EI) m/z 477 (M^+ , 1), 415 (75), 359 (74), 237 (93), 207 (16), 119 (100).

Hexakis(2,4,6-triisopropylphenyl)cyclotristannoxane was prepared in 40% yield by the method of Masamune and Sita.²⁸

Chlorophenylbis(2,4,6-triisopropylphenyl)tin (7) was prepared in 81% yield by the method of Masamune and Sita.²⁸ 1H NMR ($CDCl_3$) δ 1.03 (d, 12H), 1.09 (d, 12H), 1.26 (d, 12H), 2.89 (septet, 4H), 3.11 (septet, 2H), 7.42 (m, 3H), 7.83 (m, 2H); ^{13}C NMR ($CDCl_3$) 24.00, 24.40, 25.09, 34.32, 37.68, 122.34, 128.74, 135.31, 138.95, 146.16, 150.99, 154.72. Its X-ray structure is included in the Supporting Information.

Allylphenylbis(2,4,6-triisopropylphenyl)tin (8). To a stirred solution of 0.54 g (0.00083 mol) of bis(2,4,6-triisopropylphenyl)phenyltin chloride was added slowly allylmagnesium chloride (0.54 mL, 2.0 M in diethyl ether). After addition was complete, a white precipitate formed immediately. The reaction was allowed to stir for 4 h. The reaction was quenched with H_2O , and the aqueous layer was extracted with diethyl ether. The organic layer was dried ($MgSO_4$), and the solution was concentrated to give a yellow product. Further recrystallization from ethanol gave 0.15 g (26%) of a white product: 1H NMR ($CDCl_3$) δ 0.89 (d, 12H), 0.99 (d, 12H), 1.20 (d, 12H), 2.48 (d, 2H), 2.89 (m, 6H), 4.88 (m, 2H), 6.03 (m, 1H), 6.93 (s, 4H), 7.34 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 24.2, 24.8, 25.0, 27.4, 34.6, 38.0, 112.8, 121.94, 128.9, 137.0, 137.5, 140.0, 142.5, 145.6, 150.1, 155.5; ^{119}Sn NMR ($CDCl_3$) δ -148. Its X-ray structure is provided in the Supporting Information.

Phenylbis(2,4,6-triisopropylphenyl)stannylum Tetrakis(pentafluorophenyl)borate (TPFPB). In a N_2 -filled glovebox, trityl TPFPPB (160 mg, 0.17 mmol) was dissolved in dry C_6D_6 (0.7 mL) in a valved 5 mm NMR tube. Addition of triethylsilane (25 mg, 0.22 mmol) produced a light brown oil at the bottom. The colorless top phase containing the triphenylmethane byproduct was then removed with a syringe. Allylphenylbis(2,4,6-triisopropylphenyl)stannane (122.2 mg, 0.19 mmol) in C_6D_6 (0.5 mL) was added, and a deep red oil formed. The light orange top phase was removed, and the oil was examined by NMR spectroscopy: 1H NMR (C_6D_6) δ 1.16 (d, 12H), 1.09 (d, 12H), 1.03 (d, 12H), 2.1 (m, 2H), 2.7 (m, 4H), 7.04 (s, 2H), 7.1–7.3 (m, 5H); ^{13}C

NMR (C_6D_6) δ 23.08, 23.42, 24.52, 34.80, 45.50, 46.42, 124.3, 128.0, 130.8, 135.9, 137.1 (d), 137.8, 139.4 (d), 143.6, 149.5 (d), 152.8, 154.4, 157.1; ^{119}Sn NMR (C_6D_6) δ 693.

Chlorotrimesitylgermane.³⁸ To a N_2 -protected, 250 mL, round-bottomed flask equipped with an addition funnel and a condenser and containing $GeCl_4$ (1.71 mL, 0.015 mol) was added mesitylmagnesium bromide (48 mL, 0.048 mol) dropwise. The solution was allowed to reflux overnight. The reaction solution was quenched with H_2O . The organic phase was washed with H_2O and dried ($MgSO_4$). Stripping the solvent by rotary evaporation gave a yellow-white solid. Recrystallization from ethanol yielded 2.33 g (34%) of a white solid: mp 162–164 °C; 1H NMR ($CDCl_3$) δ 2.21 (s, 18H), 2.25 (s, 9H), 6.83 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.06, 24.89, 129.83, 136.85, 139.45, 143.38.

Allyltrimesitylgermane (2). A 100 mL, round-bottomed flask fitted with a rubber septum and a N_2 inlet needle was charged with allyltrimesitylgermane (1.43 g, 3.64 mmol) and a magnetic stirring bar. Anhydrous diethyl ether (100 mL) was added to the flask via a syringe. Phenyllithium (2.43 mL, 4.37 mmol) in ether and cyclohexane was then added quickly, and a large amount of precipitate (Ph_4Sn) formed immediately. After 0.5 h, the suspension was transferred through a wide bore cannula to an enclosed glass frit under N_2 . The solution was filtered into a 250 mL flask, which had been charged with chlorotrimesitylgermane (1.0 g, 2.1 mmol) and a stirring bar. The red solution was stirred at room temperature, and the reaction was monitored by 1H NMR. After 2 days, the reaction was complete. The reaction mixture was quenched with H_2O and extracted with hexane (200 mL). The organic solution was dried ($MgSO_4$), concentrated, and recrystallized from ethanol to give a white solid (0.25 g, 49.2%): mp 160–163 °C; 1H NMR ($CDCl_3$) δ 2.12 (s, 18H), 2.26 (s, 9H), 2.48 (d, 2H), 4.88 (q, 2H), 5.65 (m, 1H), 6.84 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 20.8, 24.6, 29.2, 115.7, 129.0, 136.8, 137.6, 138.6, 143.5. Anal. Calcd for $C_{30}H_{38}Ge$: C, 76.50; H, 8.07. Found: C, 75.65; H, 8.07. Its X-ray structure is provided in the Supporting Information.

Trimesitylgermylium Tetrakis(pentafluorophenyl)borate (TPFPB) (5). In a N_2 -filled glovebox, trityl TPFPPB (160 mg, 0.17 mmol) was dissolved in dry C_6D_6 (0.7 mL) in a valved 5 mm NMR tube. Addition of triethylsilane (25 mg, 0.22 mmol) produced a light brown oil at the bottom. The colorless top phase containing the triphenylmethane byproduct was then removed with a syringe. Allyltrimesitylgermane (122.2 mg, 0.19 mmol) in C_6D_6 (0.5 mL) was added, and a deep red oil formed. The light orange top phase was removed, and the oil was examined by NMR spectroscopy: 1H NMR (C_6D_6) δ 2.11 (s, 18H), 2.24 (s, 9H), 6.82 (s, 6H); ^{13}C NMR (C_6D_6) δ 21.4, 23.2, 125, 130.7, 137.0 (d, $^1J(CF) = 245$ Hz), 138.8 (d, $^1J(CF) = 244$ Hz), 139.7, 141.9, 148.8, 149.1 (d, $^1J = 240$ Hz).

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Supporting Information Available: Experimental details and tables of results for the crystal structures of **2**, **7**, and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(38) Gynane, M. J. S.; Lappert, M. F.; Riley, P. I.; Rivière, P.; Rivière-Bandet, M. *J. Organomet. Chem.* **1980**, 202, 5–12.