

β -Silyl and β -Germyl Carbocations Stable at Room Temperature

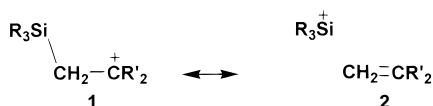
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Stable carbocations have been prepared at room temperature with benzene as solvent and tetrakis(pentafluorophenyl)borate (TPFPB) as anion by the addition of solvated triethylsilylium TPFPB or of tributylgermylium TPFPB to 1,1-diphenylethene. These carbocations are stabilized by σ conjugation with nonadjacent group 14 atoms and respectively constitute stable saturated β -silyl and β -germyl carbocations. NMR parameters, including the ^{29}Si chemical shift, the ^{13}C chemical shifts of the cationic, aryl, and methylene carbons, and the one-bond ^{13}C – ^1H coupling constant of the methylene group adjacent to the group 14 element, define the distribution of positive charge between carbon and (through σ conjugation) silicon or germanium. The extent of hyperconjugation is estimated quantitatively by comparison with models. The NMR parameters indicate that the cations are open rather than bridged.

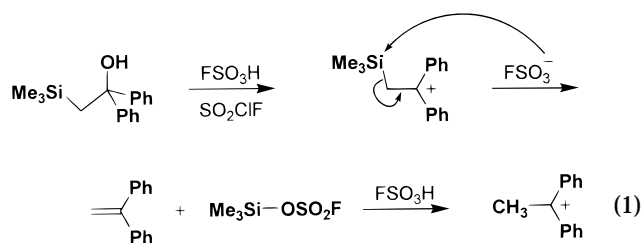
Electropositive and polarizable atoms have a remarkable ability to stabilize nonadjacent positive charge in carbocations. The best known manifestation of this phenomenon is the β effect of silicon, whereby a silicon atom two bonds from the nominal center of positive charge stabilizes the system through hyperconjugation, exemplified by structures **1** and **2**.¹ The electropositivity



and polarizability of silicon enhance its ability to delocalize positive charge through $\sigma\pi$ conjugation (often called vertical participation, although there is some nuclear movement). An alternative mechanism of stabilization, by which silicon serves as an internal nucleophile to form a three-membered ring or bridged intermediate (nonvertical participation), although theoretically viable in the primary case (**1**, $\text{R}' = \text{H}$), has not been generally supported by experiment.^{1,2} The question, however, is not entirely settled, as one recent gas-phase study still favored the bridged form.³ The β effect is best known for silicon, but analogous effects have been reported for other main group elements, including phosphorus,⁴ germanium,^{5–7} tin,^{5–7} lead,⁷ and mercury.^{7,8}

The β effects of silicon and tin have seen wide application to organic synthesis, primarily in regio- and stereo-

control of electrophilic addition reactions.^{9,10} Both the synthetic and the mechanistic investigations have been carried out on neutral starting materials. Inferences concerning the nature of the intermediate **1** were based on spectra and structure of the neutrals, kinetics of their reactions, and the nature of the products. In no case until recently was a saturated β -stabilized silicon, germanium, or tin system found to be stable in the condensed phase, even at very low temperatures. Numerous imaginative approaches to observe such long-lived cations have been reported. In 1982, Olah and co-workers¹¹ attempted to generate a β -silyl carbocation under standard superacid conditions (eq 1). Loss of the β -silyl group, however,



occurred even at $-140\text{ }^\circ\text{C}$ to give the 1,1-diphenylethyl cation and trimethylsilyl fluorosulfonate. They suggested the mechanism of eq 1, in which fluorosulfonate attacks silicon in the β -silyl cation, and the resulting diphenylethene is protonated under reaction conditions. Siehl and co-workers,¹² however, have recently overcome these difficulties by careful attention to anhydrous conditions and have observed saturated β -silyl carbocations in magic acid below $-100\text{ }^\circ\text{C}$. In 1992, Prakash et al.¹³ produced the 2-silylallyl cation **3** under

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superacid conditions at $-130\text{ }^{\circ}\text{C}$. In this cation, β -silyl



stabilization is foiled because the C–Si bond is perpendicular to the π orbitals of the allyl system, with the result that silicon carries little positive charge and is not expelled. Siehl and co-workers¹⁴ have prepared vinyl cations with various substituents (**4**) in superacid at $-100\text{ }^{\circ}\text{C}$. These systems constitute β -silyl stabilization of a vinyl cation. Lew and McClelland,¹⁵ using laser flash photolysis, reported an arenium ion σ -complexed to a silyl group (**5**) (formally a β -silyl carbocation), which decomposed with a rate constant of 10^4 – 10^5 s^{-1} , clearly short lived. We have reported the ion **6** ($\text{R} = \text{H}, \text{CH}_3$), which is



stable at room temperature, whose charge is present to a large extent on silicon, and which consequently has only partial β -silyl character.¹⁶ Thus, no efforts until the current study have succeeded in producing a stable β -silyl carbocation *under ambient conditions*. No stable β -germyl or β -stannyl carbocations have been produced under any conditions.

Although recalcitrant in condensed phase, saturated (nonvinyl) β -silyl carbocations are stable in the gas phase and have been examined extensively.^{1,17} Thus, difficulties in observing stable β -silyl cations in solution have had kinetic rather than thermodynamic causes. In the present study, we have designed conditions for the preparation and examination of a family of saturated β -stabilized carbocations that are stable under ambient conditions in solution.

Results and Discussion

Strategy. In superacid media, carbocations are produced below $-100\text{ }^{\circ}\text{C}$ by protonation of an alkene or by protonation and loss of a nucleofuge such as $-\text{OH}$. The anion may be fluorosulfonate, antimony hexafluoride, or various other species. The ease of loss of the β -silyl group in cations of type **1**, however, prevented its study under this type of condition.¹¹ Rapid decomposition may occur by attack of a nucleophile at silicon to form pentacoordinate silicon, followed by loss of tetravalent silicon, as in eq 1.¹⁸ In superacid, both oxygen and fluorine nucleophiles are present and capable of bringing about desilylation.

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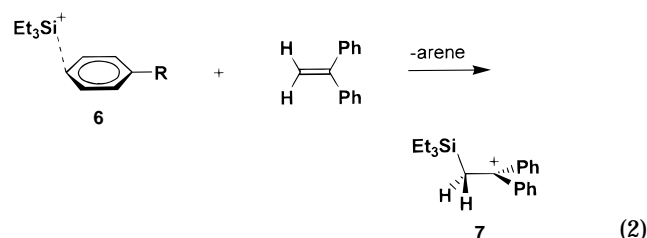
(16) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917–1918. Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430–2443.

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Our strategy to produce stable β -silyl cations was to develop conditions under which no nucleophiles capable of attack at silicon are present. The approach was suggested by the gas-phase work of the groups of Stone and Squires,¹⁷ which produced stable β -silyl cations by the addition of free silyl cations to alkenes ($\text{R}_3\text{Si}^+ + \text{C}=\text{C} \rightarrow \text{R}_3\text{SiCC}^+$). Appropriate solvent and anion would have to be chosen to ensure that they could not attack silicon. The closest approaches to a stable, free silyl cation in solution at the time were our species **6**¹⁶ and similar species reported by Reed's group.¹⁹ The silicon atom has a normal covalent bond to three alkyl groups (Me, Et, ²Pr, or others) but a much weaker bond to the fourth group. The fourth group in our systems was the arene solvent (benzene, toluene)¹⁶ and in Reed's systems a series of carborane anions.¹⁹ This view has been supported by the most recent calculations.²⁰ That the arene was exchanging between ligand and solvent faster than the NMR time scale was indicated by a single, weighted average ²⁹Si signal in a mixed benzene/toluene medium and by loss of diastereotopicity in the methyl groups of (²Pr)₂MeSi(arene)⁺.¹⁶ Our anion was tetrakis(pentafluorophenyl)borate, $(\text{C}_6\text{F}_5)_4\text{B}^-$ or TPFPB, which did not coordinate to the solvated silyl cation.¹⁶

Our current strategy is summarized in eq 2. The arene



in the solvated silyl cation **6** undergoes ligand exchange with an appropriate alkene. In our current experiments we used only benzene as the arene solvent. It is commonly recognized that benzene is less reactive than alkenes toward normal electrophiles.²¹ For example, electrophilic addition of bromine or hydrogen bromide occurs with alkenes but not with arenes because in the latter case loss of aromaticity would occur. There is a 3-fold driving force for eq 2. First, the more nucleophilic alkene ligand replaces the less nucleophilic arene ligand, presumably resulting in a stronger Lewis acid–base complex **7**. Second, delocalization of the positive charge from silicon to carbon through hyperconjugation in species **6** on the left side of the equation requires loss of aromaticity, whereas charge delocalization in species **7** on the right side has no such drawback. Third, the two phenyl groups on the carbon atom of the alkene receive part of the positive charge as the reaction proceeds to **7**. The positive charge in ion **7** thus is delocalized through hyperconjugation to silicon and by benzylic resonance to two phenyl rings. Its stability should be superior to that of diphenylmethyl cation (benzhydryl) cation but presumably less than that of triphenylmethyl cation (trityl).

The β -Silyl Carbocation. Solvated triethylsilylium TPFPB (**6**), which is straightforward to prepare and is

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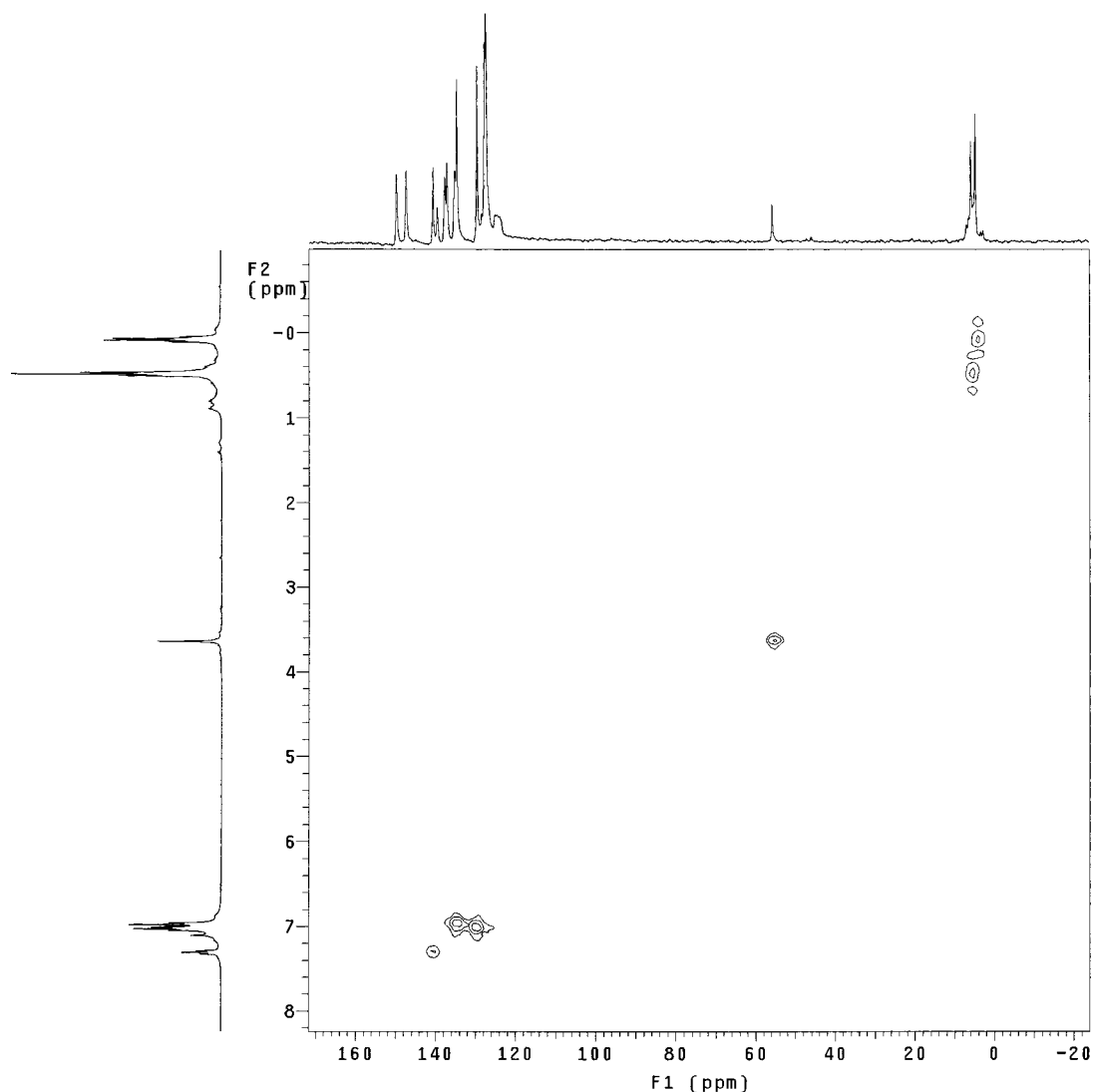


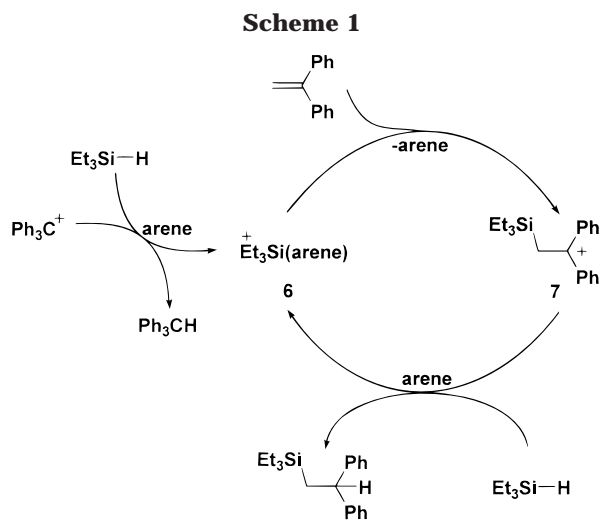
Figure 1. GHMQC $^1\text{H}/^{13}\text{C}$ correlation for 1,1-diphenyl-2-(triethylsilyl)ethylium tetrakis(pentafluorophenyl)borate (**7**).

stable,¹⁶ was allowed to react with diphenylethene in deuterated benzene. This reaction generated the stable, saturated β -silyl carbocation **7** at room temperature:²² 1,1-diphenyl-2-(triethylsilyl)ethylium TPFPB ($\text{Et}_3\text{SiCH}_2\text{C}^+-\text{Ph}_2$ TPFPB $^-$). The ^{13}C spectrum is highly diagnostic.²² The cationic carbon is found at δ 225.4, a position that indicates that the majority of positive charge resides on the carbon rather than on the silicon. In other words, the canonical form **1** ($\text{R} = \text{Et}$, $\text{R}' = \text{Ph}$) is more important than the hyperconjugative form **2**. This point is examined more fully below. The methylene carbon adjacent to silicon occurs at δ 56.2, and the aromatic region has an assembly of peaks that includes the resonances from the fluorinated carbons of the TPFPB anion, the phenyl carbons from the rings attached to the carbocation carbon in **7**, and deuterated (C_6D_6) and undeuterated (C_6H_6) benzene. Low-frequency peaks at δ 5.2 and 6.3 are from the carbons of the ethyl group. The spectrum otherwise is quite clean and stable for weeks at room temperature, in contrast to similar ions produced only below -100°C in magic acid.¹²

Comparison with a nonsilylated carbocation is provided by $\text{CH}_3\text{C}^+\text{Ph}_2$. This material was reported by Olah et al.,¹¹

and we also prepared it by the addition of fluorosulfonic acid to 1,1-diphenylethene. Its cationic carbon resonance falls at δ 229.2 for the literature¹¹ or δ 228.1 from our preparation. As this value is ominously close to that measured for the β -silyl cation **7**, we felt that further evidence was required to demonstrate the distinction. A major spectral difference is provided by the location of the saturated carbon resonance. For $\text{CH}_3\text{C}^+\text{Ph}_2$, it occurs at δ 30.5 from the literature or δ 30.7 from our measurement. These values compare with δ 56.2 for the methylene group of **7**. By way of further differentiation, we recorded the DEPT spectra of **7**.²² This experiment distinguishes carbon atoms according to the number of attached protons. The methyl subspectrum included only the methyl portion of the ethyl groups on silicon. The methylene subspectrum contained the methylene portion of the ethyl groups on silicon and the key carbon (δ 56.2) between silicon and the cationic carbon. This experiment confirms that the saturated carbon adjacent to the cationic carbon is methylene as in **7** rather than methyl as in $\text{CH}_3\text{C}^+\text{Ph}_2$. The methinyl DEPT subspectrum of **7** contained the ortho, meta, and para carbons on phenyl in the cation and a small peak from undeuterated solvent. Absent from the DEPT spectra were the fluorinated carbons from the anion, the deuterated carbons from

(22) Results on this system were communicated: Lambert, J. B.; Zhao, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7867–7868.



solvent, and the ipso carbon from the phenyl rings in **7**, as they have no attached protons.

The ^1H spectrum of **7** contains the ethyl resonances at δ 0.1–0.5, the CH_2 protons adjacent to the cationic carbon at δ 3.6, and the aromatic protons at δ 7.0–7.3. Figure 1 shows the GHMQC experiment for **7** (this variety of the H,C COSY or HETCOR experiment uses gradient pulses and inverse detection of ^{13}C through double quantum coherence). The 1D ^1H and ^{13}C spectra are illustrated, respectively, on the *F2* and *F1* axes. The H,C correlations are readily seen for the ethyl, carbocation CH_2 , and *o*-, *m*-, and *p*-phenyl groupings. The fluorinated carbons of the anion, the *ipso*-phenyl carbon, and the carbocation carbon (off scale at δ 225) appear in the 1D ^{13}C spectrum but not in the 2D spectrum because they lack attached protons. As **7** lacks vicinal relationships outside of the ethyl and phenyl groups, the H,H COSY spectrum is not structurally useful.

To confirm the overall skeleton of the species in solution, we undertook product studies by the reaction of the cation **7** with a hydride source. The expected reaction is conversion to $\text{Et}_3\text{SiCH}_2\text{CHPh}_2$, as hydride should be more reactive toward carbon than silicon, in contrast to oxygen and halogen nucleophiles. Side products were minimized by the use of a catalytic reaction scheme (Scheme 1). Triethylsilane provided the hydride and served as the ultimate source of the triethylsilyl side chain. Triethylsilane and 1 equiv of diphenylethene were allowed to react with a catalytic amount (2 mol %) of trityl TPFPB in benzene. As seen in Scheme 1, triethylsilane reacts with the catalyst to form solvated Et_3Si^+ and a small amount of triphenylmethane. Solvated Et_3Si^+ reacts with the alkene to form the β -silyl cation **7**. This material is trapped in situ by the excess triethylsilane, forming the product, $\text{Et}_3\text{SiCH}_2\text{CHPh}_2$, and a new catalytic molecule of solvated Et_3Si^+ . In this fashion, no additional triphenylmethane is formed, and the catalytic solvated silylium ion cycles through the scheme until all the alkene is consumed and a molar amount of the product is formed. The reaction was quantitative, and the product structure of $\text{Et}_3\text{SiCH}_2\text{CHPh}_2$ was proved by NMR and MS.

A long-standing question in the β -silyl problem has been whether the ion has the open structure such as **8** or a bridged structure such as **9**. Calculations by Jor-



gensen and co-workers²³ showed that the two forms ($\text{R} = \text{H}$ or Me) had similar energies in the absence of phenyl substitution. Olsson and Cremer²³ reported chemical shift calculations to distinguish open (**8**) and bridged (**9**) forms of the nonphenylated carbocation ($\text{R} = \text{H}$). A recent gas-phase study favored the bridged form.³ In the open form, the cationic carbon resonated calculationally at δ 262.8 and the methylene carbon next to silicon at δ 80.9. In the bridged form the carbons necessarily were identical and resonated calculationally at δ 139.5. The effect of ethyl substitution at silicon and of phenyl substitution on the cationic carbon must still be taken into consideration in order to compare these calculations with our experiments. The phenyl rings would draw charge off of the cationic carbon, moving its resonance to lower frequency. The expected value for the phenylated form then would be at lower frequency than the calculated value of δ 262.8 for the open form or δ 139.5 for the bridged form. Thus, the observed value of δ 225.4 is in accord only with the open form. Similar conclusions may be drawn from the resonance position of the methylene carbon attached to silicon. Although there remains no doubt that the present β -silyl carbocation is open, the presence of the two phenyl rings undoubtedly biases the preference, in comparison with the unsubstituted cases studied theoretically.^{23,24}

Some comment is warranted concerning the extent of hyperconjugation in **7**. In the hyperconjugated resonance form **2**, charge moves from carbon to silicon, the C–C bond develops double bond character, there is less charge on the cationic carbon, and in the phenylated case **7** ($\text{R}' = \text{Ph}$) there also is less charge in the phenyl rings. Several resonance positions are useful in this context. (1) The ^{13}C resonance position of the cationic carbon, δ 225.5, is at somewhat lower frequency than that in $\text{CH}_3\text{C}^+\text{Ph}_2$, δ 228–229. The absolute value and the small difference indicate that, although most of the charge is on the cationic carbon, some charge is shifted elsewhere, presumably to silicon by hyperconjugation (**2**). (2) The methylene carbon in **7** resonates at δ 56.2, compared with δ 30.7 for methyl in $\text{CH}_3\text{C}^+\text{Ph}_2$. The shift is in the opposite direction expected for silylation ($\text{CH}_3^- \rightarrow \text{Et}_3\text{SiCH}_2^-$), as in $\text{Et}_3\text{SiCH}_2\text{CHPh}_2$ ($\delta(\text{CH}_2)$ 19.3) compared with CH_3CHPh_2 ($\delta(\text{CH}_3)$ 21.8). This abnormal silylation effect is consistent with some double bond character brought about by hyperconjugation (**2**). (3) The resonance of the para carbon of a phenyl ring is the best measure of its interaction with conjugating positive charge (the meta carbon is not in conjugation and the ortho carbon also has direct β chemical shift effects). The chemical shift

(23) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496–1500. Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819–824. Olsson, L.; Cremer, D. *Chem. Phys. Lett.* **1993**, *215*, 433–443.

(24) Steinberger et al. recently reported a bridged silyl cation based on the norbornyl framework. It is not known if bridging is unique to this case or if it will prove to be common in symmetrical structures: Steinberger, H.-U.; Müller, T.; Auner, N.; Maerker, C.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 626–628; *Angew. Chem.* **1997**, *109*, 667–669.

of the para carbon in **7** is δ 141.1, compared with δ 148.1 for $\text{CH}_3\text{C}^+\text{Ph}_2$ in the literature¹¹ or δ 146.8 measured in the present study. This shift to lower frequency in the β -silyl cation indicates less positive charge on phenyl, as expected when charge is drawn off to silicon via hyperconjugation (**2**). (4) The ^{29}Si shift of **7** is δ 46.2. This value is at much lower frequency than in the solvated silyl cation **6** (92.3) for the same solvent¹⁶ or in a free alkylated silylium ion (δ 356 by calculation for Me_3Si^+),²³ so the amount of positive charge on silicon is low. Nonetheless, it is considerably higher frequency than neutral, tetrahedral silicon as in $\text{Et}_3\text{SiCH}_2\text{CHPh}_2$ (δ 6.5) and is comparable to values in trialkylsilyl perchlorates or triflates, which we estimated have about 10% silylium cation character.¹⁶ Thus some transfer of positive charge to silicon by hyperconjugation is indicated by the ^{29}Si chemical shift.

All these probes indicate that the cation is predominantly carbocationic **1** with some amount of hyperconjugative character **2**. The small extent of hyperconjugation is not unexpected, as the degree of interaction depends on the electron demand of the cation. With two phenyl rings supplying benzylic stabilization, cation **7** has little call for additional delocalization by hyperconjugation. This conclusion is supported by experiments in the gas phase¹⁷ and by the calculations of Jorgensen and co-workers.²³ In the isodesmic reaction $\text{H}_3\text{SiCH}_2\text{C}^+\text{RR}' + \text{CH}_4 = \text{HCH}_2\text{C}^+\text{RR}' + \text{H}_3\text{SiCH}_3$, the heat of reaction drops from 32.76 to 22.13 to 15.87 kcal mol⁻¹ as the system moves from primary (R,R' = H) to secondary (R = H, R' = Me) to tertiary (R,R' = Me). Thus, the β effect clearly decreases as the carbocation is stabilized. The decrease would be enhanced by phenyl substitution.

The β -Germyl and β -Stannyl Carbocations. The same strategy may be used for the generation of β -germyl and β -stannyl cations. The groups of Eaborn,²⁵ Davis, and Traylor²⁶ and our group⁵ used indirect mechanistic tools to study these intermediates. By our kinetic test,⁵ we found that the β -germyl carbocation was slightly more stable than the β -silyl carbocation, and the β -stannyl carbocation was much more stable than either. No efforts to generate stable β -germyl or β -stannyl carbocations have been reported. Given the instability of the β -silyl carbocation under superacid conditions,¹³ the germyl and stannyl analogues should have even more electrophilic germanium and tin moieties. In the current strategy, the solvated germylum or stannylum ion is added to diphenylethene. The exact analogues of the solvated silylium ion **6** have not been reported, although we prepared an earlier tin version with different anions.²⁷ In the present study, we were able to generate tributylgermylium TPFPB and tributylstannylum TPFPB solvated by benzene (**10**, $\text{Bu}_3\text{Ge}(\text{benzene})^+ \text{TPFPB}^-$, and **11**, $\text{Bu}_3\text{Sn}(\text{benzene})^+ \text{TPFPB}^-$). There is no suitable germanium nuclide for NMR analysis, but the ^{119}Sn chemical shift of the stannylum species was δ 263. This deshielded value is comparable to our previous measurements²⁷ and suggests stannylum character of about one-third by the correlations of Arshadi et al.²⁸

The addition of solvated tributylgermylium TPFPB to 1,1-diphenylethene at room temperature produced a solution with the ^{13}C spectrum given in Figure 2. The desired species was $\text{Bu}_3\text{GeCH}_2\text{C}^+\text{Ph}_2$, **12**. The cationic carbon is clearly seen at δ 213.4. The aliphatic region contains resonances from the four carbons of the butyl groups and one extraneous peak at δ 19. The only significant peaks in the aromatic region are those from the anion, the solvent, and the phenyls on the cationic carbon. The methylene region contains a single resonance at δ 66.4. The DEPT spectrum confirmed the assignments, clearly identifying the GeCH_2 resonance at δ 66.4.

The ^1H spectrum of **12** contained, in addition to the butyl resonances at δ 0.5–1.2 and the phenyl resonances at δ 7.0–7.2, the methylene singlet at δ 3.9 (somewhat higher frequency than that of the analogous methylene proton of the β -silyl cation). The GHMQC spectrum of **12** contained the expected phenyl, methylene, and butyl HC correlations.

Product studies were carried out by the catalytic procedure analogous to that used for the β -silyl system in Scheme 1. The isolated product proved to be $\text{Bu}_3\text{GeCH}_2\text{CHPh}_2$, as expected.

The increased hyperconjugation (higher proportion of the germanium analogue of canonical form **2**) expected for the β -germyl carbocation **12** over the β -silyl carbocation **7** has a number of ramifications in the NMR spectrum. The resonance of the cationic carbon occurs at δ 213.4, compared with δ 225.4 for the β -silyl carbocation, indicating less positive charge on carbon and presumably more on germanium. Similarly, the para carbon resonance moves from δ 141.1 for the silicon system to δ 138.6 for the germanium system, reflecting less positive charge delocalized onto phenyl. The resonance of the methylene group attached to silicon (δ 56.2) moves to much higher frequency (δ 66.4) in the germanium system as the result of higher double bond character of the C–C bond, as represented by the germanium analogue of canonical form **2**.

This trend was expected to continue for the tin system, but the experiment failed. When solvated tributylstannylum TPFPB (**11**) was added to diphenylethene in benzene, no changes occurred in either the ^{119}Sn resonance at δ 263 or in the ^{13}C resonances of the alkene. The solvated stannylum ion is presumably the most stable of the series because of the higher electropositivity and polarizability of tin. The ion is not sufficiently reactive to complex with the alkene. Alternatively, one may view the stannylum ion as being weakly solvated by both arene and alkene, but the much greater excess of the solvent benzene results in little time-averaged interaction with the alkene. Another view is that hyperconjugation in the tin case is so strong that there is little or no bond order between tin and carbon and a full double bond between the two carbons, i.e., full representation by the canonical form analogous to **2**.

Table 1 summarizes the NMR parameters for the H, Si, and Ge systems. The first two lines are for the methyldiphenyl carbocation, in which C–H hyperconjugation is very weak. On the next two lines are the silicon and germanium carbocations, with increasing degrees of C–Si and C–Ge hyperconjugation. The final entry is the alkene itself, which also represents the parameters for the tin case, since tributylstannylum did not appear to react with the alkene.

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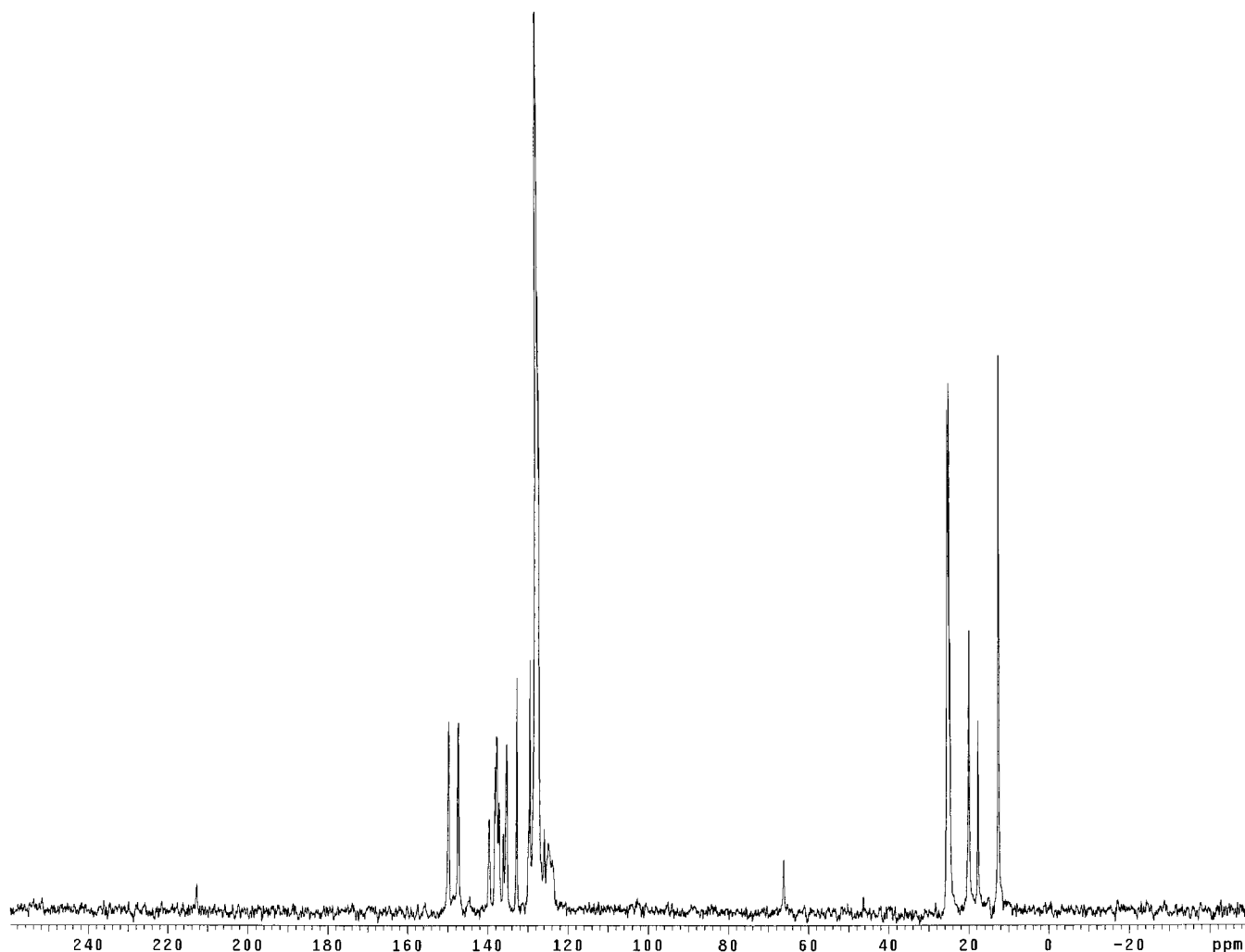


Figure 2. ^{13}C spectrum of 1,1-diphenyl-2-(tributylgermyl)ethylidium tetrakis(pentafluorophenyl)borate (**12**) in C_6D_6 at room temperature.

Table 1. ^{13}C NMR Data of Substituted 1,1-Diphenylethylidium Carbocations^a

cation	$\delta(\text{C}^+)$	$\delta(\text{CH}_2)$	$\delta(\text{C}_\beta)$	$\delta(\text{C}_\alpha)$	$\delta(\text{C}_o)$	$\delta(\text{C}_m)$	$^1J(\text{C}_\beta\text{H})$, Hz
$\text{HCH}_2\text{C}^+\text{Ph}_2$	228.1 ^b	30.7 ^b	146.8 ^b	141.4 ^b	141.0 ^b	131.3 ^b	131.4 ^b
	229.2 ^c	30.5 ^c	148.1 ^c	141.5 ^c	141.2 ^c	131.5 ^c	
$\text{Et}_3\text{SiCH}_2\text{C}^+\text{Ph}_2$ ^d	225.4	56.2	141.1	137.6	135.2	130.2	138.5
$\text{Bu}_3\text{GeCH}_2\text{C}^+\text{Ph}_2$	213.4	66.4	138.6	136.4	133.1	129.9	146.5
$\text{CH}_2=\text{CPh}_2$	150.1	114.1	127.6	141.5	128.2	128.1	158.1

^a $\text{Bu}_3\text{Sn}(\text{benzene})^+ + \text{CH}_2=\text{CPh}_2$ did not give the β -stannyl carbocation. ^b Measured as the fluorosulfonate in CD_2Cl_2 at -40°C and referenced to internal CH_2Cl_2 . ^c Data from ref 11. ^d $\delta(\text{Si})$ 46.2.

Table 1 contains an additional relevant parameter, the one-bond $^{13}\text{C}-^1\text{H}$ coupling constant for the methylene carbon attached to H, Si, or Ge (or the alkenic methylene in the unreacted alkene). In structurally parallel molecules, the one-bond $^{13}\text{C}-^1\text{H}$ coupling constant is directly proportional to the s character of the carbon orbital bonded to hydrogen.²⁹ As hyperconjugation becomes more significant and double bond character of the C-C bond increases (increased proportion of **2** over **1**), the s character of the methylene carbon orbital to hydrogen also increases. As seen in the last column of Table 1, $^1J(\text{C}_\beta-\text{H})$ increases from 131.4 Hz for the hydrogen system to 138.5 Hz for the silicon system and to 146.5

Hz for the germanium system. This trend corroborates higher sp^2 character of the β carbon orbital, as expected with increased hyperconjugation, **2**. Use of $^1J(\text{C}_\beta-\text{H})$ also serves to tie in the H system, whose data were obtained in FSO_3H and referenced to CH_2Cl_2 , with the group 14 systems, whose data were obtained in and referenced to benzene. Calibration with different standards could lead to small, systematic errors in chemical shifts but should have little effect on the coupling constants.

All the various parameters in Table 1 should reflect the same structural perturbations, as the proportions of the canonical forms **1** and **2** vary. Plots of these parameters against each other in fact are linear, as illustrated by Figure 3, in which the chemical shift of the methylene carbon attached to the metal is plotted against the chemical shift of the para carbon. The correlation coef-

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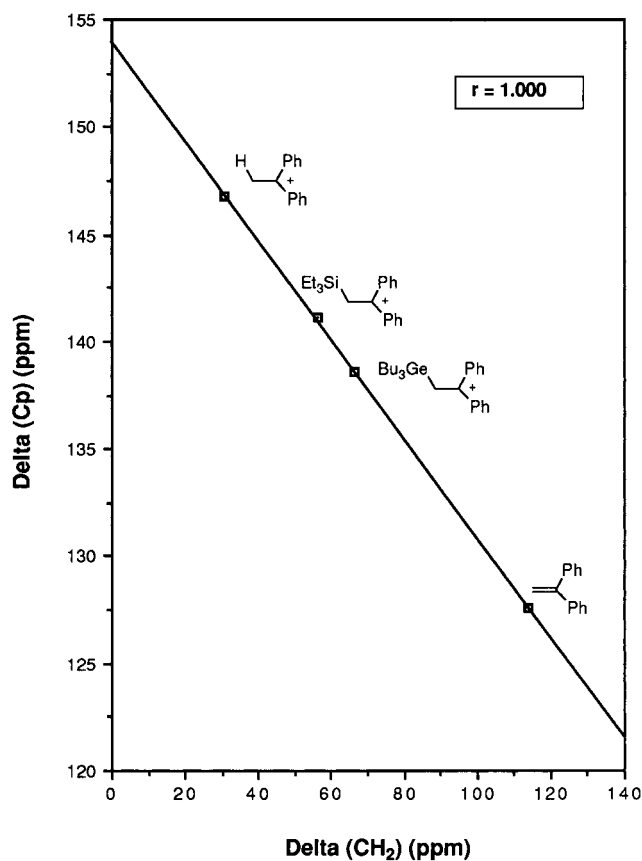


Figure 3. Linear relationship between $\delta(C_p)$ and $\delta(CH_2)$ in $MCH_2C^+Ph_2$.

ficient is 1.000. Similar plots (not shown) of the same methylene carbon chemical shift vs $^1J(C_\beta-H)$ or vs the chemical shift of the cationic carbon respectively have correlation coefficients of 0.98 and 0.95. It is particularly significant that these plots contain values not only for the hydrogen system ($HCH_2C^+Ph_2$) but also for the alkene ($CH_2=CPh_2$). High correlation coefficients for both chemical shifts and coupling constants indicate little or no referencing problem.

It is useful to compare the present NMR results of stable cations with our earlier kinetic results for the β effects of silicon,¹ germanium, and tin.⁵ Measurements at the optimal $M-C-C-X$ dihedral angle of 180° were not possible for the exceedingly fast tin system. Only in the synclinal geometry (gauche, 60°) were measurements possible for all three elements. Relative rates for the H/Si/Ge/Sn synclinal systems were found to be $1.0/3.3 \times 10^4/4.6 \times 10^5/1.3 \times 10^{11}$. Conversion of these rate ratios to free energy differences gives relative values of 0/6.2/7.7/15.2 kcal mol⁻¹. The plot of these energies for the H, Si, and Ge systems vs the chemical shift of the methylene group attached to M (Figure 4) is linear with a correlation coefficient of 0.996. Thus, the ground-state parameters for the stable ions correlate well with the transition-state data from solvolysis experiments. We omitted Sn from the plot in Figure 4 because we do not know what the chemical shift of the methylene carbon is in the β -stannyl carbocation.

Scheme 2 summarizes the structural situation for these systems. For canonical structure **1**, hyperconjugativity (extent of hyperconjugation) is zero, the $C-C^+$ bond has an order of one (single bond), and the $C-M$ bond also has an order of one (single bond). For canonical form **2**,

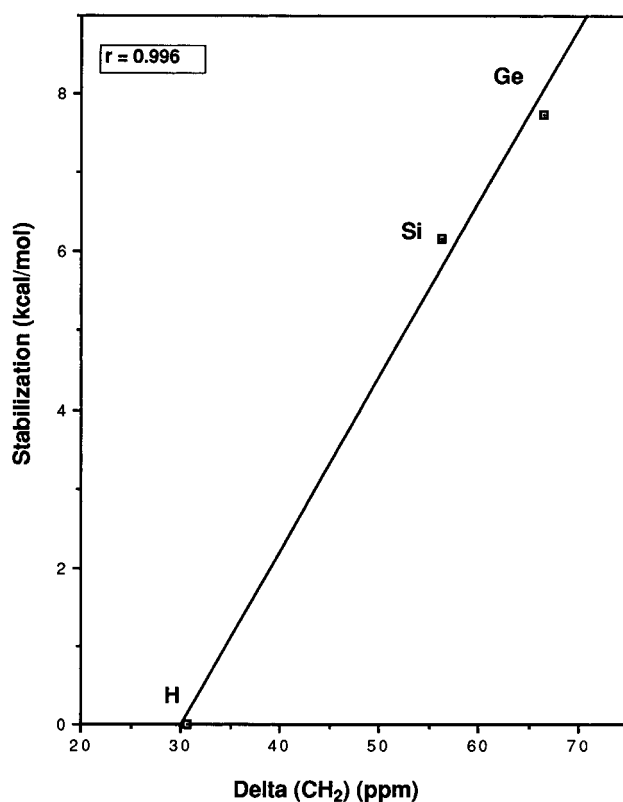


Figure 4. Linear relationship between the β -carbocation-stabilizing energy of M and $\delta(CH_2)$ in $MCH_2C^+Ph_2$.

Scheme 2

	1	M = Si	M = Ge	2
Hyperconjugativity	0.00	0.31	0.43	1.00
Bond order of $C-C^+$	1.00	1.31	1.43	2.00
Bond order of $C-M$	1.00	0.69	0.57	0.00

hyperconjugativity is unity, the $C-C^+$ bond order is 2 (double bond), and the $C-X$ bond order is 0 (no bond). The β -silyl and β -germyl systems fall somewhere between these extremes. If hyperconjugation in the carbon system $HCH_2C^+Ph_2$ is negligible compared with the other systems, we can define its hyperconjugativity as zero. The alkene diphenylethene is a model for hyperconjugativity of 1.0, as it has a full carbon-carbon double bond.

If the $C-M$ bond order for $HCH_2C^+Ph_2$ is regarded as 1.0 and that of the alkene $CH_2=CPh_2$ as zero, any of the structural parameters can be used to interpolate $C-M$ bond orders for Si and Ge. For example, under the assumption that there is a linear relationship between the $C-M$ bond order and the chemical shift of the MCH_2 carbon, the $C-Si$ bond order is calculated to be 0.69 in the β -silyl carbocation **7** (hyperconjugativity of 0.31) and the $C-Ge$ bond order to be 0.57 in the β -germyl carbocation **12** (hyperconjugativity of 0.43). Because of the linearity of the plot in Figure 4, the interpolation can be performed on the solvolysis data with the same result. Inclusion of the 15.2 kcal mol⁻¹ value for tin stabilization provides one value pertinent to the β -stannyl carbocation, from which a $C-Sn$ bond order of 0.18 is calculated for the hypothetical $Bu_3SnCH_2C^+Ph_2$ (hyperconjugativity of

0.82). Although the assumptions involved may render the bond order indistinguishable from zero, it supports the model that the hypothetical β -stannyl carbocation is almost fully hyperconjugated.

Conclusions

Addition of the solvated silyl and germly cations to 1,1-diphenylethene with benzene for solvent and with tetrakis(pentafluorophenyl)borate (TPFPB) as anion, respectively, produced the β -silyl carbocation $\text{Et}_3\text{SiCH}_2\text{C}^+\text{Ph}_2$ (**7**) and the β -germyl carbocation $\text{Bu}_3\text{GeCH}_2\text{C}^+\text{Ph}_2$ (**12**). The ^{13}C position of the cationic carbon at higher frequency than δ 200 in both cases indicates that the carbocation canonical form (**1**) predominates. These carbon resonance frequencies as well as that of the silicon confirm that some charge is delocalized onto silicon through canonical form **2**. Other chemical shifts confirm this analysis. The chemical shifts are not consistent with a bridged form analogous to **9**.

The β -silyl cation **7** serves as a contrast to the solvated silyl cation previously reported¹⁶ (**6**) (eq 2). The ^{29}Si position of δ 46.2 in **7** compares with δ 92.3 in **6**, both in benzene. Thus, there is considerably more positive charge on silicon in the latter case. The ^{13}C position of δ 225.4 for **7** contrasts with the typical aromatic values of δ 123–147 without appreciable deshielding in **6**. There is considerably less charge on carbon in the latter case. Thus, what we have been calling the solvated silyl cation $\text{Et}_3\text{Si}(\text{arene})^+$ **6** does not resemble a β -silyl cation, as now characterized by **7**.

Experimental Section

Pentane and hexane were refluxed with LiAlH_4 and distilled directly into the reaction vessels. Ether was distilled from sodium benzophenone ketyl prior to use. Bromopentafluorobenzene was commercially available from Oakwood Research Chemicals and was used as received. Deuterated benzene was dried with Na/K alloy, vacuum transferred to a Schlenk tube, and placed in a N_2 -filled glovebox. Triethylsilane (Et_3SiH) was dried with LiAlH_4 , vacuum transferred to a Schlenk tube, and placed in the glovebox. 1,1-Diphenylethene and tributyltin hydride (Bu_3SnH) were purchased from Aldrich, dried with 4 Å molecular sieves, and stored in the glovebox. Tributylgermane (Bu_3GeH) was purchased from Gelest and treated similarly as above. All other reagents were from Aldrich and were used as received.

1,1-Diphenyl-2-(triethylsilyl)ethylium Tetrakis(pentafluorophenyl)borate (7). In a N_2 -filled glovebox, trityl TFPFB¹⁶ (160 mg, 0.17 mmol) and dry deuterated benzene (0.7 mL) were placed in a valved 5-mm NMR tube. Addition of triethylsilane (25 mg, 0.22 mmol) followed by vertical shaking of the tube with the valve closed produced a light brown oil (**6**, $\text{Et}_3\text{Si}(\text{benzene})^+$ TFPFB⁻) at the bottom. The colorless top phase containing the triphenylmethane byproduct and the excess of triethylsilane was then removed with a syringe. 1,1-

Diphenylethene (40 mg, 0.22 mmol) was added, and the material changed color to deep green (the color varied from deep green to brownish red depending upon the amount of the alkene added). Deuterated benzene (0.3 mL) was added for examination by NMR: ^1H NMR (C_6D_6) δ 0.02–0.18 (q, 6H), 0.41–0.59 (t, 9H), 3.64 (s, 2H), 6.92–7.18 (m, 8H), 7.22–7.40 (t, 2H); ^{13}C NMR (C_6D_6) δ 5.2, 6.3, 56.2 ($^1J_{\text{C-H}} = 138.5$ Hz), 130.2, 135.2, 137.6, 141.1, 225.4; ^{29}Si NMR (C_6D_6) δ 46.2; UV (toluene) 310, 432 nm.

1,1-Diphenylethylium Fluorosulfonate.³⁰ 1,1-Diphenylethene (0.10 g) and CD_2Cl_2 (0.5 mL) were placed in a 5-mm NMR tube that had a screw cap. The tube was cooled to -78°C , and FSO_3H (0.3 mL) was added under N_2 protection. The solution turned brown instantaneously. The sample was then studied by NMR spectroscopy at -40°C : ^1H NMR (CD_2Cl_2) δ 3.78 (s, 3H), 7.90–8.00 (m, 4H), 8.08–8.16 (m, 4H), 8.36–9.42 (m, 2H); ^{13}C NMR (CD_2Cl_2) δ 30.7 ($J_{\text{C-H}} = 131.4$ Hz), 131.3, 141.0, 141.4, 146.8, 228.1.

1,1-Diphenyl-2-(triethylsilyl)ethane. Trityl TFPFB¹⁶ (20 mg, 0.02 mmol) was placed in a valved 5-mm NMR tube. The tube was pumped under vacuum for 1 h before it was put into a N_2 -filled glovebox. The tube was then opened and was charged with triethylsilane (0.27 g, 2.3 mmol), 1,1-diphenylethene (0.18 g, 1.0 mmol), and C_6D_6 (ca. 1 mL). After the tube was shaken for a few minutes, the reaction was complete according to ^1H NMR. The top layer was removed with a syringe and concentrated to give a colorless oil: ^1H NMR (C_6D_6) δ 0.24–0.40 (q, 6H), 0.74–0.92 (t, 9H), 1.30–1.38 (d, 2H), 3.98–4.06 (t, 1H), 6.90–7.24 (m, 10H); ^{13}C NMR (C_6D_6) δ 3.9, 7.7, 19.3, 47.5, 126.3, 127.9, 128.6, 147.6; ^{29}Si NMR (C_6D_6) δ 6.5; MS (EI) m/z 267 (M – Et, 95).

1,1-Diphenyl-2-(tributylgermyl)ethylium Tetrakis(pentafluorophenyl)borate (12). In a N_2 -filled glovebox, trityl TFPFB¹⁶ (170 mg, 0.18 mmol) and dry deuterated benzene (0.7 mL) were placed in a valved 5-mm NMR tube. Addition of tributylgermane (50 mg, 0.20 mmol) followed by vertical shaking of the tube with the valve closed produced a light brown oil (**10** ($\text{Bu}_3\text{Ge}(\text{benzene})^+$ TFPFB⁻) at the bottom. The colorless top phase containing the triphenylmethane byproduct and the excess of tributylgermane was removed with a syringe. 1,1-Diphenylethene (42 mg, 0.23 mmol) was added, and the color of the bottom oil phase changed to yellowish green. Deuterated benzene (0.3 mL) was added for examination by NMR: ^1H NMR (C_6D_6) δ 0.48–1.18 (m, 27H), 3.98 (s, 2H), 6.88–7.18 (m, 8H), 7.22–7.36 (t, 2H); ^{13}C NMR (C_6D_6) δ 13.0, 20.3, 25.5, 26.0, 66.4 ($J_{\text{C-H}} = 146.5$ Hz), 129.9, 133.1, 136.4, 138.6, 213.4; UV (toluene) 300, 372 (sh), 436 nm.

1,1-Diphenyl-2-(tributylgermyl)ethane. In a N_2 -filled glovebox, trityl TFPFB¹⁶ (20 mg, 0.02 mmol), tributylgermane (0.22 g, 0.90 mmol), 1,1-diphenylethene (0.17 g, 0.94 mmol), and deuterated benzene (~0.7 mL) were placed in a valved 5-mm NMR tube. After the tube was shaken for a few minutes, the reaction was complete according to ^1H NMR. The top layer was removed with a syringe and concentrated to give a colorless oil: ^1H NMR (C_6D_6) δ 0.52–0.62 (q, 6H), 0.82–0.92 (t, 9H), 1.14–1.32 (m, 12H), 1.50–1.56 (d, 2H), 4.02–4.06 (t, 1H), 6.92–7.26 (m, 10H); ^{13}C NMR (C_6D_6) δ 13.1, 14.1, 20.8, 27.1, 27.8, 48.6, 126.3, 127.9, 128.6, 147.5; MS (EI) m/z 371 (28), 370 (30), 369 (M – Bu, 100).

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