

Experimental and Theoretical Studies of Silacycloheptatrienyl Cation Formation from Phenylsilane

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Abstract: The formation of $C_6SiH_7^+$ from phenylsilane was studied using Fourier transform ion cyclotron resonance spectrometry and by *ab initio* calculations. The (parent – H or D)⁺ ions were produced by electron impact (EI) dissociation of $C_6H_5SiH_3$ and $C_6H_5SiD_3$, and their bimolecular reactivities toward phenylsilane, cycloheptatriene, benzyl chloride, benzene-*d*₆, and toluene-*d*₈ were examined. The reactive component that abstracts hydride from phenylsilane and cycloheptatriene or chloride from benzyl chloride is mostly the phenylsilyl cation $C_6H_5SiH_2^+$. The identity of the unreactive component was characterized by collision-induced dissociation and bimolecular chemical reactivity. The low-energy collision-induced dissociation of the unreactive $C_6SiH_7^+$ ion with argon yielded SiH^+ with a loss of C_6H_6 and $C_6SiH_5^+$ with a loss of H_2 as the primary fragments. Vibrationally hot $C_6SiH_7^+$ ions from EI of $C_6H_5SiH_3$ reacted with benzene-*d*₆ to form $C_6D_6\cdot SiH^+$ adducts, which after few seconds of cooling delay remained unreactive toward cycloheptatriene. *Ab initio* calculations predict the hydride affinity of $C_6H_6\cdot SiH^+$ that forms $C_6H_6 + SiH_2$ to be comparable to or lower than that of tropylium ion. The chloride affinity of $C_6H_6\cdot SiH^+$ that forms $C_6H_6 + SiHCl$ is estimated to be ~ 4 kcal mol⁻¹ lower than that of the benzyl cation. Both experiment and theory suggest the $C_6H_6\cdot SiH^+$ adduct as the unreactive $C_6SiH_7^+$ component and not the silacycloheptatrienyl cation. The mechanism of the formation of $C_6H_6\cdot SiH^+$ is presented based on the theoretical energetics of radical cations and the transition state for the [1,2] sigmatropic migration of an α -H.

Introduction

The formation of $C_7H_7^+$ isomers from the toluene radical cation has been the subject of extensive studies over the last four decades.¹ The toluene radical cation with a few electronvolts of internal energy dissociates to benzyl ($C_6H_5CH_2^+$) and tropylium ($c-C_7H_7^+$) ions with the branching ratio determined by the internal energy. On the other hand, the formation of $C_6SiH_7^+$ isomeric ions from the phenylsilane radical cation has been rarely studied.^{2–5} Early electron impact (EI) studies of deuterium-labeled phenylsilanes failed to provide evidence for or against the formation of the silacycloheptatrienyl cation $c-C_6SiH_7^+$.² Studies of ion–molecule reactions of SiD_3^+ with benzene raised a question about the possible formation of $c-C_6SiH_7^+$, but the phenylsilyl cation was considered a more viable product than $c-C_6SiH_7^+$.³ More recently, Beauchamp and co-workers studied the formation of $C_6SiH_7^+$ from EI of $C_6H_5SiH_3$.^{4,5} They observed both reactive and unreactive $C_6SiH_7^+$ ions in phenylsilane and in cycloheptatriene/phenylsilane mixtures. The reactive ion that yielded $(C_6H_5)_2SiH^+$ was assigned to the phenylsilyl cation, whereas the unreactive ion was ascribed to the $c-C_6SiH_7^+$.⁵ They proposed that the silacycloheptatrienyl cation might be more stable than the tropylium ion with H^- as a reference base. To the contrary, theoretical calculations by Nicolaides and Radom have concluded that the silacycloheptatrienyl cation lies 9 kcal mol⁻¹ above the phe-

nylsilyl cation,⁶ which raises a question about the formation of the silacycloheptatrienyl cation. Most recently, Nicolaides and Radom suggest the (η^5 -methylcyclopentadienyl)silanium cation as a more likely structure for the unreactive ion based on energetics and hydride affinity calculations.⁷ Note, however, that the preparation of dimethylsilacycloheptatriene, which is the precursor for the methylsilacycloheptatrienyl cation, has been reported by Nakadaira et al.⁸ They observed the parent, (parent – CH_3)⁺, and $Si(CH_3)_2^+$ ions in the EI mass spectrum at 11 eV.

To help resolve the current conflict on the formation of $c-C_6SiH_7^+$, bimolecular reactivities of the (parent – H or D)⁺ ions were studied using Fourier transform ion cyclotron resonance spectrometry,^{9–11} and their hydride affinities were calculated at the Hartree–Fock (HF), Møller–Plesset second-order perturbation (MP2),¹² and density-functional theory (DFT) levels.^{13,14}

In experiments, the (parent – H or D)⁺ ions were prepared by either EI or 266 nm two-photon ionization (2PI) dissociation of phenylsilane and α,α,α -*d*₃-phenylsilane. Their bimolecular reactivities toward the parent neutral, cycloheptatriene, benzyl chloride, benzene-*d*₆, and toluene-*d*₈ were studied. To help identify the structures of unreactive $C_6SiH_7^+$ ions, low-energy

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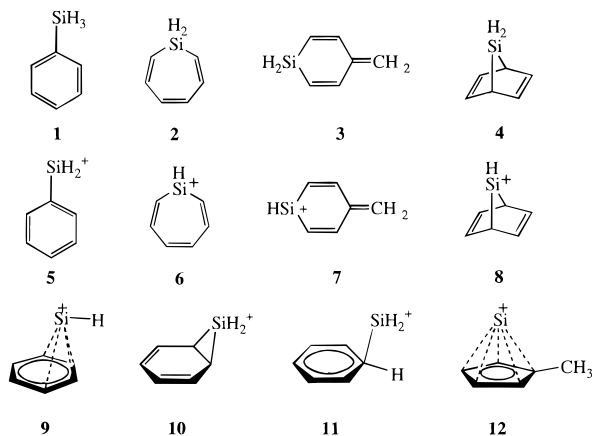
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Chart 1



collision-induced dissociation (CID)^{15,16} was examined in the presence of argon. The low-energy CID of the parent ion and the unreactive $C_6SiH_6^+$ ion were also examined. In addition, the H/D scrambling in the parent ion was observed via the $SiH_xD_{2-x}^{+}$ ($x = 0-2$) transfer reaction, and the H/D branching ratio was determined as a function of electron energy.

In theoretical calculations, the structures and energetics were determined for five different C_6SiH_8 isomers: phenylsilane (**1**), silacycloheptatriene (**2**), sila-4-methylenecyclohexa-2,5-diene (**3**), bicyclo[2.2.1]-7-silahepta-2,5-diene (**4**), and their respective (parent - H)⁺ species, phenylsilyl (**5**), silacycloheptatrienyl (**6**), sila-4-methylene-cyclohexa-2,5-dienyl (**7**), bicyclo[2.2.1]-7-silahepta-2,5-dienyl (**8**), and $C_6H_6 \cdot SiH^+$ adduct (**9**) cations. Structures are illustrated in Chart 1. Geometries and energies were calculated at HF, MP2, and DFT levels with a standard 6-311G(d,p) basis set. The relative energies of the benzyl cation to the tropylium ion and their respective hydrides (toluene and cycloheptatriene) were calculated and compared with experiments. Furthermore, the relative stabilities of the $C_6SiH_8^+$ radical cations and the transition state for the [1,2] sigmatropic α -H migration were estimated at the restricted open-shell MP2 (ROMP2) level with geometries optimized at the restricted open-shell Hartree-Fock (ROHF) level with the standard 6-311G(d,p) basis set.

Both experimental and theoretical results lead us to suggest that the unreactive $C_6SiH_7^+$ ion is most likely the $C_6H_6 \cdot SiH^+$ (**9**) adduct ion. The mechanism of the formation of **9** is proposed, and the origin of its unusual stability with respect to H^- , Cl^- , or π -donor exchange is discussed.

Experimental Section

Experimental setups were previously described in detail.¹⁷ Experiments were performed mainly with the Fourier transform ion cyclotron resonance (FT-ICR) spectrometer equipped with a 5.0 T superconducting magnet (Oxford Instrument) and a 2-in cubic trapping ICR cell in a vacuum chamber differentially pumped by three cryogenic pumps (APD-6, 690 L/s). The base pressure was typically below 9×10^{-10} Torr after 24 h bakeout. Data acquisition was accomplished with the IonSpec (Irvine, CA) Omega/486 FT-ICR data system. A typical trapping voltage was 1.5 V.

Ions were generated by either EI in the 10–25 eV range or 2PI. The 2PI was accomplished with the quadrupled output of an Nd:YAG laser (Spectra-Physics, GCR-150) at 266 nm in the pulse energy range 0.1–10.0 mJ. The laser beam entered the vacuum chamber through a

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calcium fluoride window and passed through the center of the ICR cell along the magnetic field axis. Ions of interest were isolated by double resonance techniques,¹⁸ and their reactions were monitored as a function of time delay.

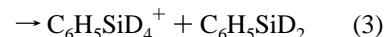
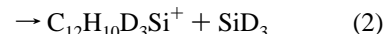
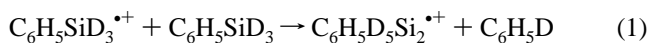
CID experiments and rate constant measurements were performed in another FT-ICR setup with a 1 T electromagnet.¹⁹ CID was carried out in the presence of argon. The collision energy was typically controlled by varying the duration of a resonant radio frequency (rf) pulse. Pressures were measured with an ionization gauge calibrated against a capacitance manometer (MKS Baratron, 390HA-00010).

All chemicals were obtained from Aldrich Chemical Inc. and used without further purifications. Phenylsilane-*d*₃ (~99% D) was made by reducing phenyltrichlorosilane with $LiAlD_4$ (>98% D).²⁰ The sample purity was checked by mass analyses. All liquid samples were used after several freeze-pump-thaw cycles. Gaseous samples were admitted to the reaction chamber through either a leak valve, or a home-built pulsed valve, both of which led to the ICR cell through electropolished 1/4-in. o.d. stainless steel tubes. Sample pressures in the ultrahigh vacuum ICR chamber were estimated from the kinetics of ion-molecule reactions with known rate constants.

Computational Details. Geometries of $C_6SiH_7^+$, C_6SiH_8 , $C_7H_7^+$, and C_7H_8 were optimized at HF, MP2, and DFT levels using Gaussian-92 and -94 programs.²¹ The DFT corresponds to a Becke's three parameter hybrid method¹³ using the correlation functional of Lee, Yang, and Parr.¹⁴ Total energies were obtained at each level. Geometries of isomeric $C_6SiH_8^{+}$ radical cations were optimized at the ROHF level. Total energies of the radical cations were calculated at the ROMP2 level. For all calculations, standard 6-311G(d,p) basis sets were used for carbon [$\zeta^d(C) = 0.626$] and hydrogen [$\zeta^p(H) = 0.75$]. For the silicon, the MacLean-Chandler (12s9p/6s5p) basis set²² was augmented with one set of d-polarization functions [$\zeta^d(Si) = 0.45$] and one set of diffuse s- and p-functions [$\zeta^{s,p}(Si) = 0.331$]. Vibrational frequencies were calculated at the HF level were scaled by 1/1.12 and zero-point energies were estimated therefrom. The transition state for the [1,2] sigmatropic α -H migration was located by following the reaction coordinate by using synchronous transit-guided quasi-Newton (STQN) method.²³

Results

A. Deuterium Scrambling in Phenylsilane-*d*₃. To clarify the structure(s) of the phenylsilane radical cation the deuterium scrambling was observed in the primary reaction products of eqs 1–3.



No H/D scrambling was observed in the products of eqs 1–3 when the parent ion was produced by 2PI. When the parent ion was generated by EI (>12 eV) H/D scrambled products were observed in eqs 1 and 2. There was, however, no difference in the branching ratios of eqs 1–3 with the two ionization methods used. The extent of H/D scrambling in the parent ion was examined as a function of electron energy from the H/D scrambling in products of reaction 1. Results are shown

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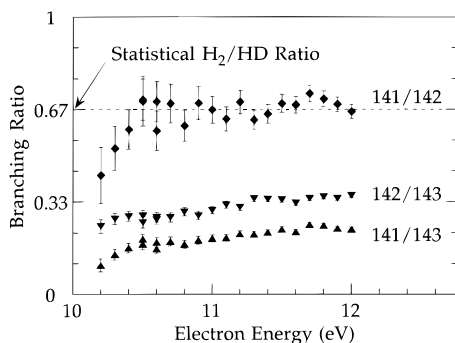


Figure 1. The H/D scrambling ratio in the product of reaction 2. $m/z = 141$: $C_6H_5SiD_3 \cdot SiH_2^{+}$, $m/z = 142$: $C_6H_5SiD_3 \cdot SiHD^{+}$, $m/z = 143$: $C_6H_5SiD_3 \cdot SiD_2^{+}$. The statistical H/D scrambling in the parent ion predicts the ratio of $SiH_2:SiHD = 2:3$.

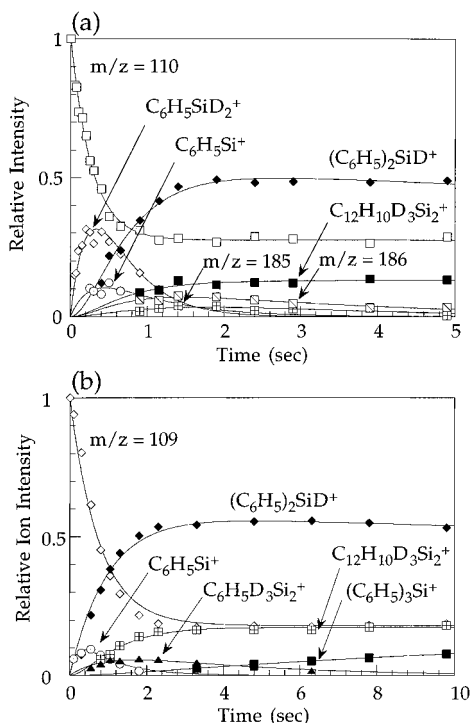


Figure 2. Temporal variations of ion abundances following the isolation of (a) (parent - H)⁺ produced by EI (15 eV) of phenylsilane-*d*₃ at a pressure of 10×10^{-8} Torr, (b) (parent - 2)⁺ produced by EI (17 eV) of phenylsilane-*d*₃ at a pressure of 7×10^{-8} Torr.

in Figure 1. Below 10 eV only unscrambled SiD_2^{+} -transfer product, $C_6H_5SiD_3 \cdot SiD_2^{+}$, was observed. As the electron energy increases, the H/D scrambled ratio [$C_6H_5SiD_3 \cdot SiH_2^{+}$]/[$C_6H_5SiD_3 \cdot SiHD^{+}$] increases to a statistical value of 2/3. The H/D scrambling in the parent ion occurs with an electron energy ~ 0.5 eV above the appearance threshold of the parent ion but definitely below that of the lowest energy pathway that forms the phenylsilyl cation by a Si-D bond cleavage.

B. Reactions of (Parent - H)⁺ Ions. (1) **Reactions with phenylsilane-*d*₃.** The $m/z = 110$ ions exhibit two distinct reactivities in phenylsilane-*d*₃. Figure 2a shows temporal variations of the isolated $m/z = 110$ generated by EI at 15 eV and their subsequent reaction products. The reactive component produced $C_6H_5SiD_2^{+}$ by deuteride-transfer in eq 4, which subsequently reacted with phenylsilane-*d*₃ to yield $(C_6H_5)_2SiD^{+}$ as indicated by eq 5. In addition, both $m/z = 185$ and 186 were produced with a loss of SiD_4 and $SiHD_3$, respectively, as indicated by eqs 6 and 7. About 28% of $m/z = 110$ remained unreactive at 15 eV EI. The relative fraction of the unreactive $m/z = 110$ in phenylsilane-*d*₃ was comparable to that of the

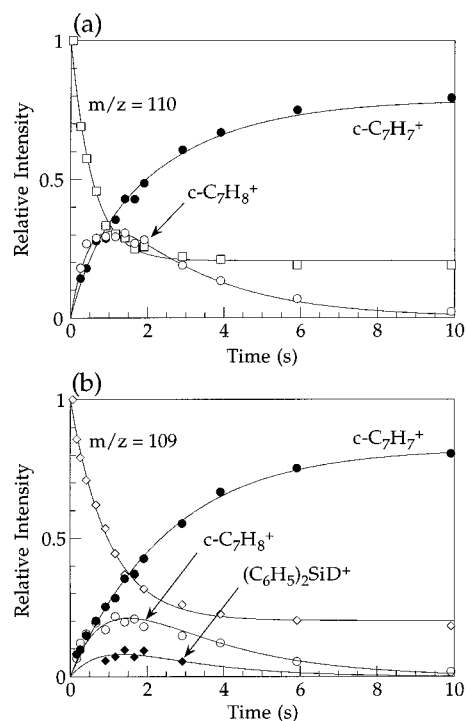
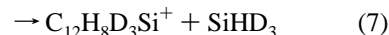
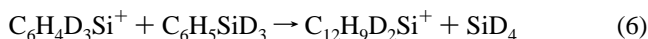
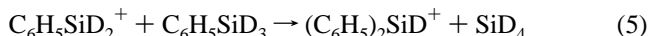


Figure 3. Temporal variations of ion abundances following the isolation of (a) (parent - H)⁺ in a 1:4 phenylsilane-*d*₃/cycloheptatriene mixture at a total pressure of 4.0×10^{-8} Torr, (b) (parent - 2)⁺ in a 1:4 phenylsilane-*d*₃/cycloheptatriene mixture at a total pressure of 4.0×10^{-8} Torr.

unreactive $C_6SiH_7^{+}$ ion in $C_6H_5SiH_3$ previously observed by Nagano et al.⁵



(2) **Reactions with Cycloheptatriene.** Figure 3a shows temporal variations of $m/z = 110$ in the presence of both cycloheptatriene and phenylsilane-*d*₃. Translationally hot $m/z = 110$ excited by near-resonance isolation pulses underwent endothermic electron-transfer reactions with cycloheptatriene. The reactive $m/z = 110$ also abstracts hydride from both phenylsilane-*d*₃ and cycloheptatriene. Both the primary and secondary products, $m/z = 109$ and 184, were completely reactive toward cycloheptatriene. There remained about 20% unreactive $m/z = 110$ at 15 eV EI.

(3) **Reactions with Benzyl Chloride.** There also were two distinct $m/z = 110$ species differentiated by reactions with benzyl chloride as shown in Figure 4. The reactive component underwent facile hydride-transfer reactions with phenylsilane-*d*₃ as well as chloride-transfer reactions with benzyl chloride. These and secondary reactions continue in a chain reaction cycle that ends with the formation of diphenylmethyl cation. These reactions are described in detail in the Supporting Information. There was about a 15% unreactive component in the presence of benzyl chloride.

C. Reactions of (Parent - H₂)⁺ and (Parent - D)⁺ Ions. (1) **Reactions with Phenylsilane-*d*₃.** Three distinct species in their reactivity with phenylsilane-*d*₃ were observed: two were reactive and one was unreactive. Figure 2b shows temporal

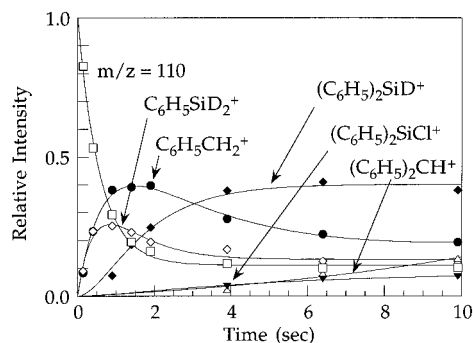
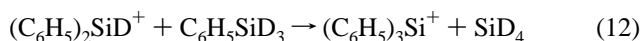
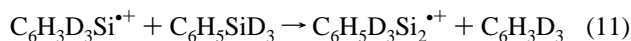
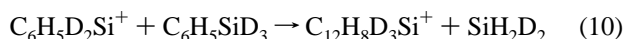
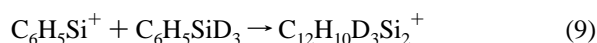
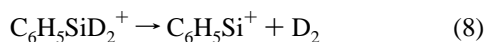


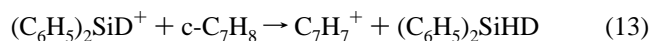
Figure 4. Temporal variations of ion abundances following the isolation of the (parent - H)⁺ in a 3:1 phenylsilane-*d*₃/benzyl chloride mixture at a total pressure of 5×10^{-8} Torr.

variations of $m/z = 109$ generated by EI at 17 eV and their subsequent reaction products. The two reactive species underwent deuteride-transfer reactions with phenylsilane-*d*₃ as evidenced in part by the appearance of the isotope signal at $m/z = 110$ due to ²⁹Si (4.67%) and ¹³C (6.6%).²⁴ The major product from (parent - D)⁺ was (C₆H₅)₂SiD⁺ by eq 5. A small fraction of the (parent - D)⁺ ions dissociated to C₆H₅Si⁺ with a loss of D₂ by eq 8. The C₆H₅Si⁺ ion subsequently formed an $m/z = 216$ adduct with phenylsilane-*d*₃ by eq 9. The H/D scrambled (parent - D)⁺ ion produces $m/z = 186$ by eq 10. The (parent - H₂)⁺ ions formed $m/z = 139$ by Si⁺ transfer to the parent neutral with a loss of benzene-*d*₃ by eq 11. (C₆H₅)₂SiD⁺ reacted slowly with phenylsilane-*d*₃ to yield (C₆H₅)₃Si⁺ via eq 12.

About 20% of $m/z = 109$ remained unreactive. The relative fraction of the unreactive $m/z = 109$ is less than that of $m/z = 110$ due to formation of the reactive (parent - H₂)⁺.



(2) Reactions with Cycloheptatriene. Figure 3b shows temporal variations of $m/z = 109$. Translationally hot $m/z = 109$ excited by near-resonance isolation pulses also underwent endothermic electron-transfer reactions with cycloheptatriene. The reactive $m/z = 109$ underwent eq 5 with phenylsilane-*d*₃ and hydride-transfer reactions with cycloheptatriene. The (C₆H₅)₂SiD⁺ ion also reacted with cycloheptatriene to produce the tropylium ion by hydride-transfer reaction 13. $M/z = 105$ from eq 8 reacted with cycloheptatriene to yield C₇H₇Si⁺ with a loss of C₆H₆ by eq 14. The C₇H₇Si⁺ ion was unreactive toward cycloheptatriene. There was about 20% unreactive $m/z = 109$ at 15 eV EI.



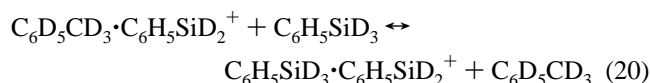
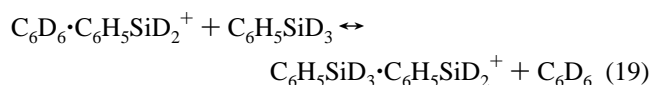
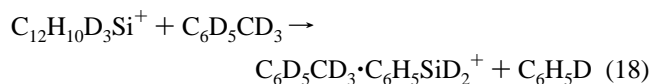
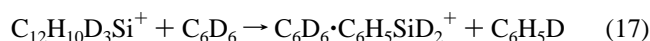
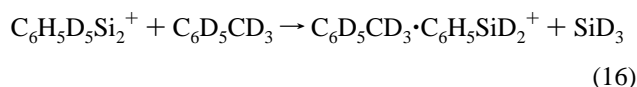
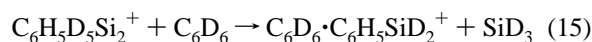
(3) Reactions with Benzyl Chloride. $M/z = 109$ from EI show two distinct species in the presence of benzyl chloride.

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The reactive species quickly enters the chain reaction by supplying C₆H₅CH₂⁺ via a chloride transfer. At longer time delays there was about a 20% unreactive component.

D. Reactions with Benzene-*d*₆ and Toluene-*d*₈. In order to identify the adduct structures of reactant and product ions in pure phenylsilane, reactions with benzene-*d*₆ and toluene-*d*₈ were examined. The low power 2PI was used to generate phenylsilane-*d*₃ radical cations in phenylsilane-*d*₃/benzene-*d*₆ and phenylsilane-*d*₃/toluene-*d*₈ mixtures. Benzene and toluene radical cations were also produced by 2PI. Benzene radical cations underwent charge-transfer reactions with phenylsilane, while toluene radical cations were unreactive toward phenylsilane; IP(phenylsilane) = 9.14 eV²⁵ is greater than IP(toluene) = 8.83 eV²⁶ but less than IP(benzene) = 9.25 eV.²⁷ The phenylsilane radical cation abstracts an electron from toluene to produce the toluene radical cation. When phenylsilane-*d*₃ radical cations were prepared by EI, a small fraction underwent the SiD₂⁺ transfer to benzene-*d*₆ as in eq 1, but no such reactions were observed when using 2PI.

New products were observed at $m/z = 193$ and 118 in benzene-*d*₆/phenylsilane-*d*₃ mixtures and at $m/z = 209$ and 134 in toluene-*d*₈/phenylsilane-*d*₃ mixtures. Reactions 15–20 were identified from isolation studies. $M/z = 143$ from eq 1 yielded $m/z = 193$ and 209 as indicated by eqs 15 and 16, respectively. $M/z = 188$ from eq 2 produced $m/z = 193$ and 209 in eqs 17 and 18, respectively. Both $m/z = 193$ and 209 underwent reversible π -donor exchange reactions with phenylsilane-*d*₃ to produce $m/z = 220$ as given in eqs 19 and 20. These results suggest adduct structures for both reactant and product ions involved in eqs 17–20.




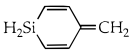
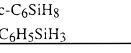
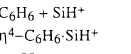

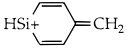
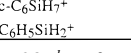
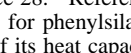
$M/z = 113$ from eq 3 transferred SiD₃⁺ to benzene-*d*₆ and toluene-*d*₈ as indicated by eqs 21 and 22, respectively. $M/z = 145$ underwent reversible SiD₃⁺ transfer equilibria between benzene-*d*₆ and phenylsilane-*d*₃ as given in eq 23. These results

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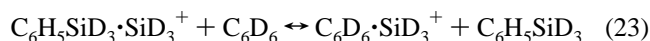
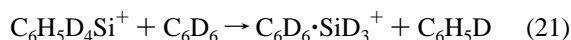
(27) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl 1).

Table 1. Relative Energies and Heats of Formation (kcal mol⁻¹) of C₇H₇⁺, C₆SiH₇⁺, and Their Hydrides within Each Structural Formula

formula	molecule	HF	MP2	DFT	expt	ΔH ^o ₁₀
C ₇ H ₇ ⁺	benzyl cation	5.1	11.1	9.0	12.0	219.6 ^a
	c-C ₇ H ₇ ⁺	0.0	0.0	0.0	0.0	207.6 ^b
C ₇ H ₈	cycloheptatriene	35.7	34.7	34.9	31.2	48.7 ^c
	toluene	0.0	0.0	0.0	0.0	17.5 ^c
C ₆ SiH ₈	C ₆ H ₆ + SiH ₂	46.1	56.9	47.3	60.2	92.4 ^d
		43.5	30.9	40.9		
		24.0	28.5	24.6		
		30.2	31.5	28.9		
		0.0	0.0	0.0	0.0	32.2 ^e
C ₆ SiH ₇ ⁺	C ₆ H ₆ + SiH ⁺	57.2	65.1	63.5	68.9	295.5 ^d
	η ⁴ -C ₆ H ₆ ·SiH ⁺	18.0	13.0	15.5		
		30.6	12.8	(38.8) ^f		
		8.3	12.3	8.9		
		13.0	11.4	8.1		
	0.0	0.0	0.0	0.0	226.6 ^{e,8}	

^a Reference 28. ^b Reference 29. ^c Reference 27. ^d Reference 27 and 30. ^e ΔH^o₁₂₉₈ for phenylsilane in ref 27 was approximated to 0 K by integration of its heat capacity using the scaled calculated vibrational frequencies. ^f Saddle point energy at C_{2v} symmetry; no DFT minimum near this configuration. ^g References 5 and 27.

also suggest adduct structures for both reactant and product ions involved in eqs 21–23.



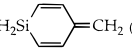
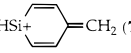


m/z = 110 and 109 were unreactive toward benzene-*d*₆ and toluene-*d*₈, unless the ions were vibrationally hot. Vibrationally hot C₆SiH₇⁺ ions produced by EI in C₆D₆/C₆H₅SiH₃ mixtures underwent SiH⁺-transfer to C₆D₆ within 100 ms of the EI pulse. These new C₆D₆·SiH⁺ ions were found to be unreactive soon after their formation.

E. Collisional Activation of Unreactive C₆SiH₇⁺ and C₆SiH₆⁺. The low energy CID of the two C₆SiH₇⁺ ion species was examined in the presence of pure phenylsilane and argon as the collision partners. The major dissociation products from the unreactive species were SiH⁺ with a loss of C₆H₆ and C₆H₅-Si⁺ with a loss of H₂. After few seconds of reaction delay from CID, both SiH⁺ and C₆H₅Si⁺ products were completely reacted away. The CID of reactive C₆SiH₇⁺ ion yielded only C₆H₅Si⁺ with a loss of H₂. The low-energy CID of unreactive C₆H₆-Si⁺ ions yielded Si⁺ with a loss of C₆H₆.

F. Energetics of C₆SiH₇⁺, C₆SiH₈, and C₆SiH₈⁺ from *ab Initio* Calculations. Total energies from the optimized geometries of C₆SiH₇⁺, C₆SiH₈, C₇H₇⁺, and C₇H₈ at three levels of theory and their scaled HF zero-point energies are included in the Supporting Information on Table S2. Relative energies corrected for the zero-point energy are listed here in Table 1. The accuracy of theoretical calculation is assessed by comparing theoretical results with the relative energies from known heats of formation listed in Table 1. Heats of formation yield a relative energy of 12.0 kcal mol⁻¹ for C₆H₅CH₂⁺ with respect

Table 2. Relative Hydride Affinities (kcal mol⁻¹) of C₇H₇⁺ and C₆SiH₇⁺

RH	→	R ⁺ + H ⁻	HF	MP2	DFT	Expt	DH ^o ₀ (R ⁺ -H ⁻)
C ₆ H ₅ CH ₃		C ₆ H ₅ CH ₂ ⁺	40.8	45.8	43.9	42.4	236.0 ^a
C ₆ H ₅ SiH ₃ (1)		C ₆ H ₅ SiH ₂ ⁺ (5)	37.0	32.0	35.4	35.0	228.6 ^b
 (4)		 (8)	24.1	13.9	-	-	-
 (3)		 (7)	21.2	15.8	19.7	-	-
c-C ₆ SiH ₈ (2)		c-C ₆ SiH ₇ ⁺ (6)	19.8	11.9	14.6	-	-
C ₆ H ₆ + SiH ₂		η ⁴ -C ₆ H ₆ ·SiH ⁺ (9)	8.9	-11.9	3.6	(-7.0) ^c	(186.6) ^c
c-C ₇ H ₈		c-C ₇ H ₇ ⁺	0.0	0.0	0.0	0.0	193.6 ^d

^a References 27 and 28. ^b Reference 5 and 27. ^c DH^o₀(R⁺-H⁻) = DH^o₀(SiH⁺-H⁻) - DH^o₀(C₆H₆ - SiH⁺); DH^o₀(SiH⁺-H⁻) = 238.7 kcal mol⁻¹ from ref 27, 30, and 31; DH^o₀(C₆H₆ - SiH⁺) = 52.1 kcal mol⁻¹ at MP2. ^d References 1, 29, and 27.

to c-C₇H₇⁺,^{28,29} whereas theory predicts 5.1 (HF), 11.1 (MP2), and 9.0 (DFT) kcal mol⁻¹. In the case of neutral C₇H₈, heats of formation provide a relative energy of 31.2 kcal mol⁻¹ for c-C₇H₈ with respect to C₆H₅CH₃,²⁷ whereas theory yields 35.7 (HF), 34.7 (MP2), and 34.9 (DFT) kcal mol⁻¹. For C₆SiH₇⁺ and C₆SiH₈ thermochemical thresholds for the formation of C₆H₆ + SiH⁺ and C₆H₆ + SiH₂ were compared. MP2 results are in better agreement with the experimental values than the other methods. Thus, further discussions of relative energies are based on MP2 predictions unless noted otherwise.

(1) **C₆SiH₈.** Four isomers considered in the present calculations include phenylsilane (1), silacycloheptatriene (2), sila-4-methylenecyclohexa-2,5-diene (3), and bicyclo[2.2.1]-7-silahepta-2,5-diene (4). Among them, phenylsilane (1) is the most stable. Structures 2, 3, and 4 lie 31.5, 28.5, and 30.9 kcal mol⁻¹ above 1, respectively. The dissociation enthalpy of 1 to C₆H₆ + SiH₂ is estimated to be 56.9 kcal mol⁻¹, whereas heats of formation yield a value of 60.2 kcal mol⁻¹.^{5,27}

(2) **C₆SiH₇⁺.** Five isomers examined herein include the phenylsilyl (5), silacycloheptatrienyl (6), sila-4-methylenecyclohexa-2,5-dienyl (7), bicyclo[2.2.1]-7-silahepta-2,5-dienyl (8), and the C₆H₆·SiH⁺ adduct (9) ions. Among them, the phenylsilyl cation (5) is the lowest in energy. The 6, 7, and 8 cations lie 11.4, 12.3, and 12.8 kcal mol⁻¹ above 5, respectively. Adduct 9 lies 13.0 kcal mol⁻¹ above 5, and the adduct binding energy is calculated to be 52.1 kcal mol⁻¹. The dissociation enthalpy of the phenylsilyl cation to C₆H₆ + SiH⁺ is estimated to be 65.1 kcal mol⁻¹, whereas heats of formation provide a value of 68.9 kcal mol⁻¹.^{27,30}


(3) **Hydride Affinities from *ab Initio* Calculations.** Table 2 summarizes hydride affinities relative to that of the tropylium ion. The accuracy of hydride affinities relative to the tropylium ion is assessed by comparing theoretical estimates with experimental values for the benzyl and phenylsilyl (5) cations. Relative experimental values are 42.4 kcal mol⁻¹ for the benzyl cation^{27,28} and 35.0 kcal mol⁻¹ for 5,⁵ whereas theory provides values of 40.8 (HF), 45.8 (MP2), and 43.9 (DFT) kcal mol⁻¹ for the benzyl cation and 37.0 (HF), 32.0 (MP2), and 35.4 (DFT) kcal mol⁻¹ for 5. It appears that DFT provides a relative hydride affinity balanced between HF and MP2. Among the five isomeric C₆SiH₇⁺ ions, 5 has the highest hydride affinity, while

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Table 3. Total (hartrees) and Relative (kcal mol⁻¹) Energies of C₆SiH₈⁺ Radical Cations

molecule	sym	ROHF	ROMP2	ZPE(i) ^a	E _{rel} ^b	
C ₆ H ₅ SiH ₃ ⁺	1 ⁺	C _s	-520.560004	-521.449167	67.0(0)	0.0
silanorcaradiene ⁺	10	C _s	-520.547775	-521.466518	68.8(1) ^c	-9.1
C ₆ H ₆ SiH ₂ ⁺	11	C _s	-520.559385	-521.457482	69.8(0)	-2.4
	4 ⁺	C _{2v}	-520.520032	-521.449411	68.1(2)	0.9
<i>o</i> -isophenylsilane ⁺		C _s	-520.544514	-521.450408	69.0(0)	1.2
<i>c</i> -C ₆ SiH ₈ ⁺	2 ⁺	C _{2v}	-520.536460	-521.425189	68.8(0)	16.8
[1,2] α-H migration transition state		C _s	-520.502657	-521.424965	65.8(0)	14.0
C ₆ H ₆ + SiH ₂ ⁺	-	-	-520.486406	-521.375183	67.1(0)	46.5

^a Calculated at UHF for doublet species (in kcal mol⁻¹) and divided by 1.12; value in parentheses is the number of imaginary frequencies.

^b Relative energies at ROMP2 including ZPE correction. ^c UHF geometry gives a twisted ring structure (C₁ symmetry) but the ROHF is at its minimum energy with C_s symmetry, therefore the UHF was constrained to C_s symmetry.

the C₆H₆•SiH⁺ adduct (**9**) has the lowest. Structure **6** is 12–20 kcal mol⁻¹ higher in hydride affinity than the tropylium ion. A value of 186.6 kcal mol⁻¹ for the hydride affinity of **9** forming C₆H₆ + SiH₂ is estimated from the hydride affinity of SiH⁺ [DH^o₀(SiH⁺–H⁻) = 238.7 kcal mol⁻¹]^{27,30,31} and the bond dissociation enthalpy of **9** [D₀(C₆H₆–SiH⁺) = 52.1 kcal mol⁻¹ obtained at the MP2 level]. This value is 7.0 kcal mol⁻¹ lower than the hydride affinity of the cycloheptatrienyl cation, DH^o₀(c-C₇H₇⁺–H⁻) = 193.6 kcal mol⁻¹.^{1,27,29} Neutral silanorcaradiene is found to be dissociative and therefore not the hydride for **9**. In addition, the chloride affinity of **9** forming C₆H₆ + SiHCl is estimated to be 148.1 kcal mol⁻¹ from the chloride affinity of SiH⁺ [DH^o₀(SiH⁺–Cl⁻) = 201 kcal mol⁻¹]^{27,32} and the calculated bond dissociation enthalpy of **9**. The chloride affinity of **9** is ~9 kcal mol⁻¹ lower than that of the benzyl cation [DH^o₀(C₆H₅CH₂⁺–Cl⁻) = 157.3 kcal mol⁻¹].^{27,28} Thus, the C₆H₆•SiH⁺ adduct may be unreactive toward both cycloheptatriene and benzyl chloride. Structure **9** has such a low hydride and chloride affinity because the cation is strongly bonded by π-donor electron-acceptor interactions, while its hydride or chloride (C₆H₆•SiH₂ or C₆H₆•SiHCl) is only weakly bound by van der Waals interactions.

(4) C₆SiH₈⁺. Isomers considered here are the phenylsilane (**1**⁺), silanorcaradiene (**10**), silacycloheptatriene (**2**⁺), the C₆H₆•SiH₂⁺ adduct (**11**), bicyclo[2,2,1]-7-silahepta-2,5-diene (**4**⁺), and 1-silylene-2,4-cyclohexadiene (*o*-isophenylsilane) radical cations. Their relative energies were calculated from the ROMP2 energies at the ROHF optimized geometries. Zero-point energies were calculated from the UHF frequencies at UHF optimized geometries. Both total energies and relative energies with respect to the phenylsilyl radical cation are listed in Table 3. The two lowest energy isomers are **10** and **11**, and they lie 9.1 and 2.4 kcal mol⁻¹ below **1**⁺, respectively. Radical cations **4**⁺ and **2**⁺ lie 0.9 and 16.8 kcal mol⁻¹ above **1**⁺, respectively. The binding energy of the C₆H₆•SiH₂⁺ radical cation to its dissociation limit of C₆H₆ + SiH₂⁺ is estimated to be 46.5 kcal mol⁻¹. The transition state for the α-H migration from silicon to the *ipso*-carbon in **1**⁺ to **11** is also calculated at the ROMP2 level with the ROHF optimized geometry. This transition state lies 14.0 kcal mol⁻¹ above **1**⁺. This calculated activation barrier is in good agreement with the experimental threshold for H/D scrambling in the C₆H₅SiD₃⁺ radical cation, whose appearance

was ~0.5 eV above the appearance threshold of the parent radical cation.

Discussion

A. Structure and Reactivity. (1) The C₆SiH₅D₃⁺ Radical Cation. It is expected that the 2PI of phenylsilane-*d*₃ yields the parent radical cation, whereas EI produce other C₆SiH₅D₃⁺ isomers by intramolecular rearrangement of vibrationally hot ions.¹⁷ The 2PI yields the same branching ratios of eqs 1–3 as EI, indicating that the phenylsilane radical cation itself can react through all the channels. Nearly identical branching ratios in the phenylsilane 2PI/EI reactions might be explained by the strong ion–dipole complex energy and the presence of an electrophilic silicon center likely mediating isomerization of the complex before dissociation to products.

When reacted with benzene, however, there are distinct differences in reactivities between the two ionization methods. The ions produced by EI underwent SiX₂⁺ (X = H, D) transfer reactions, whereas those from 2PI do not undergo any reactions with benzene. Since the electron energies of both the present and previous study⁵ were above the hydrogen scrambling threshold (~0.5 eV above the parent appearance), populations of **10** and **11** are available to transfer SiX₂⁺ to benzene.

(2) **The Reactive C₆SiH₅D₂⁺ or C₆SiH₄D₃⁺.** The reactive (parent – H or D)⁺ undergoes chloride transfer with benzyl chloride and hydride transfer with cycloheptatriene. This ion is also produced by collisional activation of *m/z* = 143, 188, and 220. It is the moiety transferred between π-donors, such as benzene-*d*₆, toluene-*d*₈, and phenylsilane-*d*₃ in eqs 17–20. This reactive species is accepted as the phenylsilyl cation (**5**).⁵ No H/D scrambling of **5** is observed with the π-donors. The low energy CID of **5** yielded C₆H₅Si⁺ with a loss of H₂ from C₆H₅SiH₂⁺ or with a loss of D₂ from C₆H₅SiD₂⁺.

(3) **The Unreactive C₆SiH₇⁺.** There were 15–30% unreactive (parent – H or D)⁺ ions in the presence of phenylsilane-*d*₃, cycloheptatriene, and benzyl chloride. Among the C₆SiH₇⁺ isomers considered here, **9** is the only ion that is predicted to have a lower hydride affinity than the tropylium ion and a lower chloride affinity than the benzyl cation. Moreover, the low energy CID of the unreactive C₆SiH₇⁺ ion in the presence of argon yielded SiH⁺ with a loss of C₆H₆ as well as C₆H₅Si⁺ with a loss of H₂ as the major fragments. Also, the formation of unreactive C₆D₆SiH⁺, by SiH⁺ transfer from “hot” C₆SiH₇⁺ ions to benzene-*d*₆, further indicates SiH⁺ as a distinct unit bonded to the benzene ring. Both theoretical and experimental results now suggest that the adduct C₆H₆•SiH⁺ is the unreactive C₆SiH₇⁺ ion.

Most recently Nicolaides and Radom⁷ suggested a nonclassical isomer as a viable candidate for the unreactive C₆SiH₇⁺, the (η⁵-methylcyclopentadienyl)silanium cation (**12**). This ion was predicted to be 24.4 kcal mol⁻¹ more stable than the phenylsilyl cation (**5**) at the G2(MP2) level of theory. This stability and its hydride affinity, calculated to be 34.9 kcal mol⁻¹ less than the tropylium ion, led them to conclude that this might be the unreactive component found experimentally. However, CID of **12** is expected to generate Si⁺ as a fragment ion, and the formation of **12** by SiH⁺ transfer to benzene is difficult to conceive. Our experimental results do not lend support to the formation of **12** as the unreactive fragment.

Calculations predict that the C₆H₆•SiH⁺ adduct (**9**) forms a 52 kcal mol⁻¹ bond with π-electrons in benzene. The coordination with benzene is evident in the geometry having one unperturbed C–C bond of 1.39 Å and five almost equivalent C–C bonds of 1.41 Å. The silicon is ~2.2 Å away from the C₆ plane with a Si–H bond almost parallel to the C₆ plane. In

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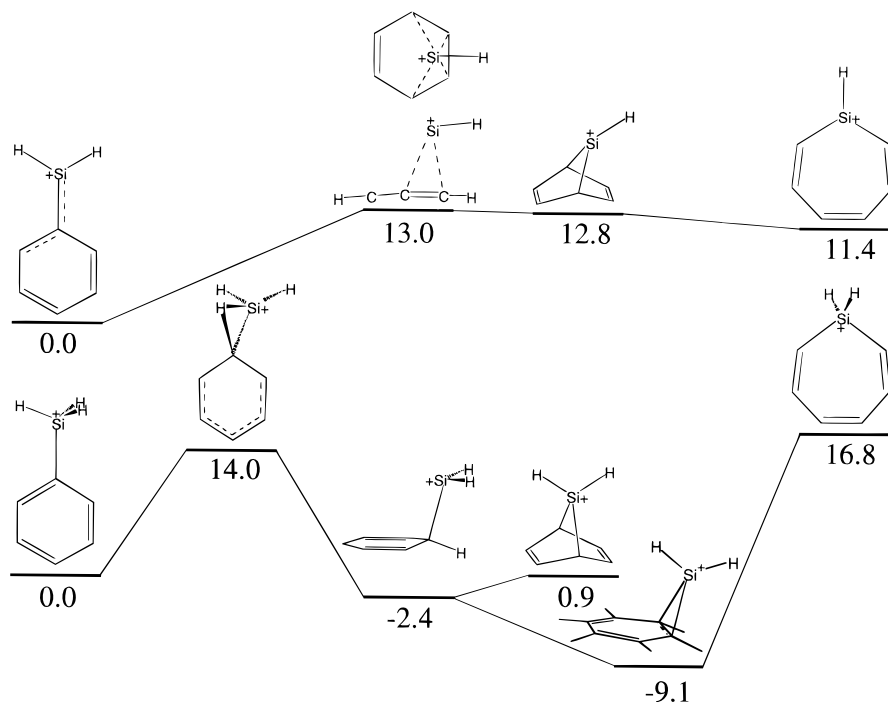


Figure 5. Energy level diagram (kcal mol⁻¹) of the C₆SiH₈⁺ and C₆SiH₇⁺ ions calculated at MP2//MP2 and ROMP2//ROHF, respectively.

contrast, **11** forms a 49 kcal mol⁻¹ dative bond with one carbon, where the ring geometry changes to two short C–C bonds of 1.37 Å, two typical C–C bonds of 1.40 Å, and two elongated C–C bonds of 1.43 Å. The Si–C bond length is 2.09 Å, which is 0.21 Å longer than the Si–C single bond of phenylsilane.

Nicolaidis and Radom⁷ calculated the η^3 -C₆H₆·SiH⁺ structure and found it to be slightly lower in energy (<1 kcal mol⁻¹) than the η^4 -complex at all levels of theory. Their DFT frequency calculations of the η^4 -coordination gave one imaginary frequency,⁷ indicating the η^4 -structure may be the transition state between two η^3 -complexes. So the unreactive C₆H₆·SiH⁺ is considered to have a thermal vibrationally averaged structure of both η^3 - and η^4 -adducts.

(4) C₆SiH_n⁺ (n = 6–8) Reactivities toward π -Donors. Typically one finds π -donor complexes thermally exchangeable,⁵ as has been observed with the other π -donor complexes: C₆H₆·Si⁺, C₆H₆·SiD₂⁺, and C₆H₆·SiD₃⁺ (eq 23). Therefore, it seems unusual for **9** not to undergo exchange reactions with benzene-*d*₆. The interaction of the empty silicon p-orbitals with benzene π -electrons orients SiH_x⁺ and aligns the nonbonding orbitals, thus affecting the reactivity for π -donor exchange. Si⁺ and SiH⁺ can utilize either one or two empty p-orbitals to accept π -electrons from benzene, giving rise to either η^3 - or η^4 -coordinations or both. Schwarz *et al.*³³ calculated the η^3 -C₆H₆·Si⁺ adduct which is structurally similar to η^3 -C₆H₆·SiH⁺. On the other hand, SiH₂⁺ and SiH₃⁺ contain only one empty p-orbital, forming a dative bond with one of the carbons in benzene. Thus, both Si⁺ and SiH⁺ favor the η^3 - or η^4 -coordination sites, while SiH₂⁺ and SiH₃⁺ favor the on-top sites forming C–Si dative bonds. This difference in donor–acceptor bonding results in two different alignments of nonbonding orbitals. With SiH₂⁺ in **11**, an unpaired electron orbital aligns along the benzene ring, whereas SiH⁺ in **9** contains a lone pair projected away from benzene. It is this orientation of the lone pair which most likely prevents the π -donor exchange of SiH⁺.

B. Mechanism of the Formation of C₆H₆·SiH⁺. In light of *ab initio* calculations and experimental results, the mechanism

of the formation of **9** is proposed. Energy levels of C₆SiH₈⁺ and C₆SiH₇⁺ isomers relevant to the proposed mechanism are shown in Figure 5. In the typical EI experiment the phenylsilane radical cation (**1**⁺) can readily isomerize to the more stable **11** by [1,2] migration of an α -H atom from the silicon to the *ipso*-carbon. This transition state is calculated to lie ~14 kcal mol⁻¹ above the phenylsilane radical cation at ROMP2. The migrating H atom at this transition state is 1.68 Å from the silicon and 1.33 Å from the *ipso*-carbon. The Si–C bond is slightly elongated from 1.81 Å to 1.85 Å, and the C–C bonds between the *ipso*- and *ortho*-carbons are extended from 1.41 to 1.44 Å. Once formed, **11** can subsequently undergo a [1,4] or [1,2] sigmatropic migration of SiH₂⁺. The [1,4] migration intermediate, **4**⁺, has a local minimum 3.3 kcal mol⁻¹ above **11**. The [1,2] migration intermediate, **10**, is actually a global minimum located 6.7 kcal mol⁻¹ below **11**. Thus, both migration processes are considered to be active following the first [1,2] α -H migration. In addition, the [1,2] H-migration from the *ipso* to the *ortho*-position may be active as well since the *o*-isophenylsilane radical cation is only 3.6 kcal mol⁻¹ above **9**. The observed statistical H/D scrambling in the SiH₂⁺- vs SiHD⁺-transfer products lends experimental support to the proposed mechanism involving [1,2] SiH₂ migrations and α -H migrations.

Ions **10** and **11** can dissociate to four different products: C₆H₆·Si⁺ with a loss of molecular hydrogen from silicon, **5** with a loss of H atom attached to the *ipso*-carbon, **9** with a loss of H atom from silicon, and SiH₂⁺ with a loss of C₆H₆. The formation of **6** from **10** requires significant bond rearrangement: both double bonds must shift position while breaking a C–C bond. Moreover, the thermochemical threshold of **6** is calculated to lie 25.9 kcal mol⁻¹ above the most stable **10**.

The formation of **9** also accounts for bimolecular reactivities observed in eqs 1 and 2: the SiH₂⁺ transfer with a loss of C₆H₆ and the proton transfer with a loss of the phenylsilyl radical. These two processes are borne out from the C₆H₆·SiH₂⁺ structure itself. The phenyl abstraction in reaction 3, with a loss of SiH₃, may be derived from the phenylsilane radical cation directly. With 2PI, ion–molecule interactions may provide the

(33) Srinivas, R.; Hrusak, J.; Sulzle, D.; Bohme, D.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 2802–2806.

internal energy to drive the [1,2] α -H migration to accommodate reactions 1 and 2, thus leading to the same observed reactivity without involving the other isomeric precursors.

Conclusion

The unreactive $C_6SiH_7^+$ ion derived from the phenylsilane radical cation is not considered to be the silacycloheptatrienyl cation (**6**) but a $C_6H_6\cdot SiH^+$ adduct ion (**9**). An important difference here between toluene and phenylsilane is the relative stability of the [1,2] α -H migrated intermediates. In the toluene system this species lies 33 kcal mol⁻¹ above the toluene radical cation,^{1,34} whereas, in the phenylsilane system, its counterpart **11** lies 2 kcal mol⁻¹ below the phenylsilane radical cation at ROMP2. The silicon substitution lowers the [1,2] α -H migration barrier and stabilizes **11** substantially. Further contrast is found where in toluene the subsequent [1,2] CH₂ migration leads to the cycloheptatriene radical cation by CH₂ insertion into the C–C bond. In phenylsilane, however, SiH₂ insertion into the C–C bond is severely hindered because of the larger silicon orbital size, even though precursor **10** is stable.

The remarkable unreactivity of **9** toward hydride or chloride is largely due to the weak van der Waals interactions in its hydride ($C_6H_6\cdot SiH_2$) or chloride ($C_6H_6\cdot SiHCl$) as compared to the strong η -coordinated donor–acceptor interactions that stabilize **9**. This is one example of how ion–molecule

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interactions in π -donor complex ions modify their reactivities toward bases. This “weakly bonded neutral” effect has to be taken into account in studies of reactivity and thermodynamics of π -donor complex ions and possibly other cluster ions.

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Supporting Information Available: EI yields vs electron energy and 2PI fragmentation vs laser power are discussed and shown (Figures S1 and S2); further phenylsilane-*d*₃ reactions are discussed and shown (Figures S3 and S4), with the rate constants that were determined (Table S1); other CID results are discussed; total HF, MP2, and DFT energies and zero point energies used to calculate the hydride affinities in Table 2 (Table S2) (12 pages). See any current masthead page for ordering and Internet access instructions.

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