## **ORGANOMETALLICS**

# Solution and Gas-Phase Investigations of Trimethylsilylpropyl-Substituted Pyridinium Ions. Manifestation of the Silicon $\delta$ Effect

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Supporting Information

**ABSTRACT:** Computational studies on the *N*-methyl-2-trimethyl-M-propylpyridinium ions **15a** (M = Si), **15b** (M = Ge), **15c** (M = Sn), and **15d** (M = Pb) and *N*-methyl-4-trimethyl-Mpropylpyridinium ions **16a** (M = Si), **16b** (M = Ge), **16c** (M = Sn), and **16d** (M = Pb) provide evidence for a significant through-bond (double hyperconjugative) interaction between the M-CH<sub>2</sub> bond and the low-lying  $\pi^*$  orbital of the pyridinium ion. The strength of this interaction increases in the order Si < Ge < Sn < Pb, in line with the  $\sigma$ -donor abilities of the C-M bond. The through-bond interaction for M = Si has been



studied in solution using  $^{13}$ C and  $^{29}$ Si NMR studies; however, the effect is small. The collision-induced dissociation fragmentation reactions of **15a** and **16a** are strongly influenced by the through-bond interaction, with the major fragmentation pathway proceeding via extrusion of ethylene to yield the trimethylsilylmethyl-substituted pyridinium ions **1a** and **2a**.

#### ■ INTRODUCTION

The silicon  $\beta$  effect describes the well-known stabilizing effect that silicon substituents have on positive charge at the  $\beta$ position.<sup>1</sup> The origin of this stabilization is due to strong hyperconjugation between the high-lying polarizable C-Si bond and the carbocation p orbital and has been demonstrated in a number of model systems. These range from trialkylsilylmethylbenzene derivatives with low electron demand<sup>2</sup> through to cations with substantially higher electron demand, including the silyl-substituted tropylium ion<sup>3</sup> and a range of vinyl cations.<sup>4</sup> The trialkylsilylmethyl-substituted pyridinium cations 1 and 2 provide a convenient system for investigating C-Si hyperconjugation in cationic systems with relatively low electron demand, and these studies have been extended to related organogermanium systems.<sup>5</sup> These crystalline cations are relatively easy to handle and are readily prepared by methylation of the corresponding neutral substituted-pyridine precursors 3 and 4.

In the solution phase C–Si  $\pi$  hyperconjugation reveals itself in the <sup>29</sup>Si NMR spectrum, with a downfield <sup>29</sup>Si chemical shift and a decrease in the <sup>29</sup>Si–<sup>13</sup>C one-bond coupling constant upon methylation of the precursor pyridine derivatives **3** and **4**.<sup>5</sup> Both effects are larger in magnitude for the 2-substituted derivatives **1**, in qualitative agreement with calculations. In the solid state X-ray analysis reveals that C–Si hyperconjugation in **1** and **2** manifests itself in lengthening of the CH<sub>2</sub>–Si bond distance and shortening of the CH<sub>2</sub>–C(Ar) bond distance, relative to those in **3** and **4**, reflecting contributions of the double-bond– no-bond resonance forms **1**′ and **2**′ to the ground-state structures of these ions.



The  $\delta$  effect of silicon, which is substantially smaller in magnitude than the  $\beta$  effect, describes the stabilizing effect of silicon substituents at the  $\delta$  position and arises from a throughbond ( $\sigma_{\rm CSi} - \sigma_{\rm CC} - p$ ) interaction between the C–Si bond and a carbenium p orbital, which can be represented by the resonance forms shown in Figure 1. This type of interaction is also referred to as double hyperconjugation.<sup>6</sup>

The  $\delta$  effects of silicon, germanium, and tin are demonstrated by the unimolecular solvolyses of 4-MMe<sub>3</sub>-substituted (M = Si, Ge, Sn) bicyclo[2.2.2]oct-1-yl mesylates 5–7, which occur at

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rates that are 49, 71, and 2841 times faster than that of the parent system,  $^{7}$  8.



The dependence of the  $\delta$  effect on stereochemistry is provided by the solvolysis of the *E* and *Z* isomers of 5-(trimethylsilyl)- and 5-(trimethylstannyl)-2-adamantyl brosylate. Rate accelerations were observed for the *E* isomers 9 and 10 (with Me<sub>3</sub>Sn > Me<sub>3</sub>Si) (for which the stereoelectronic requirements of the throughbond interaction are fulfilled), in comparison with the *Z* isomers 11 and 12 (for which concerted through-bond participation in the developing carbonium ion is not possible).<sup>8</sup> A similar result was obtained from solvolysis of *cis*- and *trans*-4-trimethylstannylcyclohexyl tosylates 13 and 14.<sup>9</sup>

Thus, interest lay in determining the properties of 2-trimethylmetalpropyl- and 4-trimethylmetalpropyl-substituted pyridinium ions, 15a-d and 16a-d, in particular to determine the magnitude of the stabilization provided to these ions by the silicon substituent and to find whether the structural effects arising from double hyperconjugation between the C–Si bond and the electron-deficient pyridinium ion  $\pi$  system would be observable in the solution-phase and solid-state structures.



#### COMPUTATIONAL STUDIES

To gain some initial insight into the structures and properties of these ions, we carried out ab initio calculations on the model systems **15** (M = Si) and **16** (M = Si) and the heavier group IV congeners where M = Ge, Sn, Pb for comparison. In addition, the neutral pyridine precursors **17** and **18** (M= Si, Ge, Sn, Pb), for which the through-bond interaction should be less pronounced, were also calculated. Calculations were performed at the B3LYP/GEN (where C, H, and N were calculated at 6-311g(dp)<sup>10</sup> and Si, Ge, Sn, and Pb were calculated at SDD) level of theory.<sup>11</sup>

#### RESULTS AND DISCUSSION

The optimized geometries of 15 and 16 and the precursors 17 and 18 (for M = Si) are shown in Figure 2.<sup>19</sup> The preferred

**Figure 1.** Double hyperconjugation in  $\delta$ -silyl carbenium ions.

conformation adopted by these ions allows for double hyperconjugation between the C–M bond and the low-lying  $\pi^*$  orbital of the pyridinium ions. Thus, the C2–C3 bond is essentially orthogonal to the plane of the aromatic ring and can therefore overlap effectively with the  $\pi^*$  orbital of the aromatic ring, while the antiperiplanar arrangement about the C2–C1 bond allows for the C1–M  $\sigma$  bonding orbital to overlap with the C2–C3  $\sigma^*$ orbital. The alternative conformation in which the C2–C3 bond lies in the plane of the pyridinium cation ring was found to be 4-5 kJ mol<sup>-1</sup> higher in energy in all cases.

The structural effects of double hyperconjugation which are manifested upon conversion of the neutral pyridine precursors 17 and 18 into their corresponding pyridinium ions 15 and 16 are apparent upon inspection of the calculated bond distances, which are presented in Table 1 for the 2-substituted derivatives 15 and 17 and in Table 2 for the 4-substituted derivatives 16 and 18. It is most revealing to consider the changes that occur to these selected bond distances upon conversion of the neutral pyridine precursors to the pyridinium ions; these are presented in Table 3. Thus, upon conversion of the neutral pyridines 17 and 18 (M = Si, Ge, Sn, Pb) into the pyridinium ions 15 and 16 an increase in the M-C1 distance, a decrease in the C1-C2 distance, an increase in the C2-C3 distance, and a decrease in the C3-Ar bond distance are observed. Although the individual bond length changes are small, the qualitative trends are consistent with increased contribution of the resonance forms 15', 15" and 16', 16'' to the ground-state structures of these ions (Figure 3). The magnitude of these structural effects increases from M = Sidown to M = Pb, consistent with the increasing  $\sigma$ -donor abilities of the C–M bond with Si < Ge < Sn < Pb.<sup>2c</sup>

**NBO Analysis.** NBO analysis of the interacting orbitals<sup>12</sup> ( $\sigma$ (M–  $C_1$ ),  $\sigma(C_2-C_3)$ ,  $\pi^*$ ) provides some insight into the nature and magnitude of the donor-acceptor interactions which characterize the through-bond interaction between the C–M bond and the pyridinium  $\pi^*$  orbital for M = Si, Ge, Sn, Pb. The interaction energies between the  $\sigma_{M-C1}$  donor orbital and the  $\sigma^*_{C2-C3}$  acceptor orbital in addition to the interaction energy between the  $\sigma_{C2-C3}$  donor orbital and the  $\pi^*$  acceptor orbital of the pyridinium cation are presented in Tables 4 and 5 for the 2- and 4-substituted pyridinium ions 15 and 16, respectively. These orbital interactions are slightly stronger in the 2-substituted pyridinium cations 15 than in the 4-substituted derivatives 16, in support of our conclusions from previous studies on  $\beta$ silyl-substituted pyridinium cations 1a and 2a that the pyridinium cation exerts stronger electron demand at the 2-position than at the 4position. The donor-acceptor interactions in 15 and 16 (M = Si, Ge) are significantly weaker in magnitude to those calculated for the 4-silyland 4-germyl-substituted cyclohexyl cation 19, consistent with the much higher electron demand of the secondary carbenium ion p orbital in **19**.<sup>13</sup>



The strength of both the  $\sigma_{M-C1} - \sigma^*_{C1-C2}$  and  $\sigma_{C2-C3} - \pi^*$  orbital interactions increases from M = Si to Ge to Sn but then appears to level off, with interactions for M = Pb decreasing slightly.

M Si Ge Sn

Pb

2.284



**Figure 2.** Calculated structures of **15** (M = Si) and **16** (M = Si) at the B3LYP/GEN level, where the basis set used was 6-311g(d,p) for C, H, and N and SDD ECP for Si, Ge, Sn, and Pb.

Table 1. Selected Bond Distances for the Neutral Species 17 and Methylated 2-Trimethylmetal-Substituted Pyridinium Ions 15, Where the Basis Set Used Was 6-311g(d,p) for C, H, and N and SDD ECP for Si, Ge, Sn, and Pb

$$\overbrace{C_3}^{(+)} C_2 C_1^{(H(CH_3)_3)}$$

(17;	M =	= Si,	Ge,	Sn,	Pb)

		17					15		
М	M–C1 (Å)	C3–Ar (Å)	C1–C2 (Å)	C2-C3 (Å)	М	M–C1 (Å)	C3–Ar (Å)	C1–C2 (Å)	C2-C3 (Å)
Si	1.925	1.510	1.536	1.542	Si	1.942	1.500	1.532	1.557
Ge	2.005	1.510	1.533	1.543	Ge	2.026	1.499	1.529	1.559
Sn	2.196	1.510	1.534	1.544	Sn	2.222	1.498	1.528	1.562
Pb	2.281	1.510	1.530	1.545	Pb	2.310	1.500	1.525	1.565

Table 2. Selected Bond Distances for the Neutral Species 18 and Methylated 4-Trimethylmetal-Substituted Pyridinium Ions 16, Where the Basis Set Used Was 6-311g(d,p) for C, H, and N and SDD ECP for Si, Ge, Sn, and Pb

$C_3 C_2 C_1 M(CH_3)_3$			$C_{3}^{C_{2}}C_{1}^{(CH_{3})_{3}}$					
		(18; M = Si, Ge, Sn,	Pb)		(16; M = Si, G	e, Sn, Pb)		
	18					16		
M–C1 (Å)	C3–Ar (Å)	C1-C2 (Å)	C2-C3 (Å)	М	M–C1 (Å)	C3–Ar (Å)	C1–C2 (Å)	C2-C3 (
1.927	1.509	1.535	1.544	Si	1.940	1.497	1.532	1.557
2.006	1.509	1.533	1.545	Ge	2.023	1.496	1.529	1.560
2.199	1.509	1.534	1.546	Sn	2.219	1.495	1.528	1.566

Pb

2.307

1.548

The overall stabilization afforded to the 2- and 4-substituted pyridinium cations **15** and **16** by the presence of the group 4 metal substituent was assessed by calculating the enthalpy change in the isodesmic equations (eqs 1 and 2 in Table 6). The stabilization is small and may be close to the significance level for the level of theory used in these calculations; however, the errors associated with this level of theory would substantially cancel in these equations. In all cases the degree of stabilization provided by the metal substituent is greater at the 2-position than at the 4-position, consistent with greater electron demand at the 2-position. The degree of stabilization increases down the group

1.509

1.530

Pb > Sn > Ge > Si, consistent with the increasing ability of the C-M bond to donate electron density by hyperconjugation.

1.494

**Synthesis.** Preparation of 2- and 4-trimethylsilylpropyl pyridines **15** and **16** for the experimental studies was achieved according to the method outline in Scheme 1. Thus, bromopyridines **20** and **21** were treated with propargyltrimethylsilane under Sonogashira conditions,<sup>14</sup> followed by hydrogenation of the intermediate pyridine derivatives **22** and **23** to give 2- and 4-trimethylsilylpropyl pyridines **17** and **18** in 41% and 13% yields, respectively. Conversion of the neutral pyridines **17** and **18** into the corresponding pyridinium ions **15** and **16** was

1.524

1.566

achieved by treatment with methyl iodide, methyl tosylate, or methyl triflate.

Conversion of the neutral pyridines 17 and 18 into pyridinium ions 15 and 16 results in a small and, in the case of 16, barely significant decrease in the <sup>29</sup>Si-<sup>13</sup>C one-bond coupling constant for the Si-CH<sub>2</sub> bond (Table 7). In contrast, the one-bond <sup>29</sup>Si-<sup>13</sup>C coupling constants for the Si–CH<sub>3</sub> bonds, which are not involved in this interaction, remain essentially unchanged, while the <sup>29</sup>Si chemical shifts undergo only a slight, but measurable, downfield shift. These spectroscopic effects, which are consistent with small contributions of the resonance forms 15', 15" and 16', 16'' (Figure 3) to the ground-state structures, are substantially smaller than those observed for the silylmethylpyrininium ions 1a-c and 2a-c, where conversion from the neutral pyridine precursors results in a decrease in the <sup>29</sup>Si-1<sup>3</sup>C one-bond coupling constant by ca. 7-9 Hz, while the <sup>29</sup>Si chemical shifts move downfield by 7–12 ppm. This is consistent with the  $\beta$ effect of silicon being substantially stronger than the  $\delta$  effect.<sup>5</sup>

With the view to investigating whether the through-bond interaction between the trimethylsilyl substituent and the electron-deficient pyridinium ion would lead to observable effects

Table 3. Changes to Selected Bond Distances That Occur upon Conversion of the Neutral Precursors 17 and 18 into the Pyridinium Ions 15 and 16

-C3
05
.015 .017 .019
.020
-C3
.013
.015
.020 .018

on the structures of these ions in the solid state, several attempts were made to obtain crystals of the *N*-methylpyridinium ions **15** and **16**. However, with a variety of counterions and solvents these all resulted in oily liquids. Low-quality crystals could however be obtained for the protonated salt of the pyridine precursor **17a** as its picrate salt. The structure of **17aH**<sup>+</sup> within the picrate salt is presented in Figure 4.

Although the quality of the structural determination for 17aH precludes any useful comments being made regarding the bond distances in the structure, it does however establish that the molecule exists in the solid state in a conformation which allows for the through-bond interaction to occur and is in qualitative agreement with the lowest energy computed structure for the corresponding pyridinium ion 15 (Figure 2).

**Gas-Phase Studies.** To determine the impact that throughconjugation between the trimethylsilyl substituent and the pyridinium cation might have on the fragmentation behavior, **15** and **16** were subjected to electrospray ionization mass spectrometry followed by low energy collision-induced dissociation (CID). The substituted precursors **17** and **18** were methylated with either CH<sub>3</sub>I or CD<sub>3</sub>I immediately prior to ESI/MS. The *N*-CH<sub>3</sub> pyridinium ions **15** and **16** both gave rise to the precursor ions at m/z 208; subsequent isolation and CID of these pyridinium ions gave rise to product ions at m/z 180, 108, and 73 (Figures 5A and 6A). Similarly the *N*-CD<sub>3</sub> pyridinium ions **15d** and **16d** gave precursor ions at m/z 211, which upon CID gave rise to product ions m/z 183, 111, and 73 (Figures 5B and 6B).

## Table 4. NBO Interaction Energies for the $2-Me_3M(CH_2)_3$ -Substituted Pyridinium Ions $15^a$

		M(CH <sub>3</sub> ) <sub>3</sub> 1
М	$\sigma_{\mathrm{M-C1}} - \sigma^*_{\mathrm{C1-C2}}  (\mathrm{kJ} \; \mathrm{mol}^{-1})$	$\sigma_{\rm C2-C3}{-}\pi^*(\rm kJ\;mol^{-1})$
Si	16.4 (13.8)	27.7 (16.9)
Ge	19.4 (16.3)	28.1 (16.9)
Sn	23.7 (19.7)	28.5 (16.9)
Pb	22.3 (20.5)	28.2 (16.9)
	C 1 1 11	· · · ·

<sup>*a*</sup> Energies for the neutral pyridine precursor 17 are given in parentheses.



Figure 3. Resonance forms representing the through-bond interactions in the pyridinium ions 15 and 16.

Μ

When the product ions at m/z 180 (Figures 5A and 6A) (or m/z 183 (Figures 5B and 6B)) derived from CID of **15** and **16** (or **15d** and **16d**) were isolated and then subjected to further CID, the spectra shown in parts A and B of Figure 7 were recorded. These spectra are essentially identical with those previously reported for the CID of 2- and 4-trimethylsilylmethyl pyridinium ions **1a** and **2a** (and their corresponding *N*-CD<sub>3</sub>

## Table 5. NBO Interaction Energies for the 4-Me<sub>3</sub>M(CH<sub>2</sub>)<sub>3</sub>-Substituted Pyridinium Ions $16^{a}$



Si	16.0 (13.8)	24.9 (18.3)
Ge	18.9 (16.3)	25.2 (18.2)
Sn	23.1 (19.9)	25.6 (18.4)
Pb	21.9 (20.8)	25.4 (18.4)
<sup>a</sup> Energies for	the neutral pyridine precurs	or <b>18</b> are given in parentheses

derivatives).<sup>15</sup> Thus, we propose that the ions m/z 180 derived from 15 and 16 correspond to ions 1a and 2a by formal loss of ethylene from the parent ion. The fragmentations that result upon CID of these ions (m/z 180) are summarized in Schemes 2 and 3 respectively.

Thus, CID of m/z 180 derived from 15 gave rise to ions at m/z 108 and 106, which have previously been assigned to the structures 24 and 25, in addition to ions m/z 73 and 91, which correspond to the Me<sub>3</sub>Si<sup>+</sup> ion and its H<sub>2</sub>O adduct, respectively (Scheme 2). These ions arise from competing proton transfer (path a), hydride transfer (path b) between the enamine 26 and Me<sub>3</sub>Si<sup>+</sup> and dissociation (path c) from the ion—molecule complex

Table 7.  ${}^{29}$ Si $-{}^{13}$ CH<sub>2</sub> and  ${}^{29}$ Si $-{}^{13}$ CH<sub>3</sub> Coupling Constants (±0.5 Hz) and  ${}^{29}$ Si NMR Data (±0.01 ppm) for Pyridinium Ions 15 and 16 and Their Neutral Precursors 17 and 18

compd	$^{1}J(^{29}\text{Si}-^{13}\text{CH}_{2})$	$^{1}J(^{29}\text{Si}-^{13}\text{CH}_{3})$	$\delta(^{29}\text{Si})$
17 (M = Si)	51.6	50.2	1.25
<b>18</b> (M = Si)	51.2	50.6	1.36
15 (M = Si)	49.7	50.9	1.55
16 (M = Si)	50.3	50.8	1.42

Table 6. Isodesmic Equations for  $Me_3M(CH_2)_3$ -Substituted (M = Si, Ge, Sn, Pb) Pyridinium Cations



	$\Delta E \; (\mathrm{kJ \; mol}^{-1})$		
М	eq 1	eq 2	
Si	-5.8	-5.4	
Ge	-6.5	-6.4	
Sn	-7.8	-7.7	
Pb	-8.8	-8.7	





<sup>a</sup> Reagents and conditions: (a) HCCCH<sub>2</sub>SiMe<sub>3</sub>, CuI, PdCl<sub>2</sub>(Ph<sub>3</sub>P), Et<sub>3</sub>N; (b) H<sub>2</sub>, Pd 10% on carbon, MeOH; (c) MeI.



Figure 4. Thermal ellipsoid plot for  $17aH^+$  picrate. Ellipsoids are shown at the 20% probability level. The picrate counterion has been omitted for clarity.



Figure 5. LTQ low-energy CID spectra of (A) N-CH<sub>3</sub>-2-trimethylsilylpropylpyridine 15 and (B) N-CH<sub>3</sub>-4-trimethylsilylmethylpyridinium 16. The red star denotes the mass-selected precursor ion.

(IMC). CID of ion m/z 180 derived from 16, assigned as 2a, gives rise to similar types of fragment ions at m/z 108 and 106 (paths a and b), identified as 27 and 28, in addition to Me<sub>3</sub>Si<sup>+</sup> ion and its H<sub>2</sub>O addition peak at m/z 73 and 91, respectively (path c), which arise from the ion-molecule complex (Scheme 3); in addition, the radical cation 29 arises directly by loss of CH<sub>3</sub> radical from 2a (path d).

Isolation and CID of the ions m/z 208 derived from 15a and 16a give ions at m/z 180 which correspond to the trimethylsilylmethyl-substituted pyridinium ions 1a and 2a. In addition, ions at m/z 108, 73, and 91 are isolated, which must arise directly as a result of excitation of the parent ions m/z 208. To accommodate these observations, we propose that CID of the parent ion m/z 208 for 15a results in the formation of ion-molecule complex 1 (IMC1; Scheme 4, path a, with an analogous ionmolecule complex being formed from 16b), consisting of the enamine 26 and the stabilized  $\beta$ -silylethyl cation (as either an open or bridged cation); notably this ion-molecule complex



**Figure 6.** LTQ low-energy CID spectra of (A) *N*-CD<sub>3</sub>-2-trimethylsilylpropylpyridine **15d** and (B) *N*-CD<sub>3</sub>-4-trimethylsilylmethylpyridinium **16d**. The red star denots the mass-selected precursor ion.



**Figure 7.** LTQ low-energy MS<sup>3</sup> CID spectra of (A) *N*-CH<sub>3</sub>-2-trimethylsilylpropylpyridine and (B) *N*-CH<sub>3</sub>-4-trimethylsilylpropylpyridinium. The red star denotes the mass-selected precursor ion. The water adduct  $[73 + H_2O]$  is denoted by  $\bigstar$ .

resembles the resonance form **15a** (Figure 3), which characterizes the through-bond interaction between the Si-CH<sub>2</sub> bond and the pyridine  $\pi^*$  orbital. Loss of ethylene from the  $\beta$ -silylethyl cation within IMC1 could in principle give IMC2 (path b),





Scheme 3. Suggested Pathway for the CID Reaction of N-Methyl-4-trimethysilylpropylpyridinium Ion 16



Scheme 4. Potential Fragmentation Pathways of N-Methyl-2-trimethylsilylpropylpyridinium Ion 15a



consisting of Me<sub>3</sub>Si<sup>+</sup> ion, ethylene, and the enamine **26**; however, if IMC2 is formed, then it is unlikely that it has a sufficient lifetime for further reaction within this complex before dissociation occurs to give the Me<sub>3</sub>Si<sup>+</sup> ion and its H<sub>2</sub>O adduct at m/z 73 and 91, respectively, otherwise the ion **25** at m/z 106 should have been observed (by analogy with Scheme 2). Thus, we also believe that neither the ion **1a** at m/z 180 nor the ion **24** at m/z 108 arise from IMC2. There are plausible pathways for the formation of

Scheme 5. Proposed  $\pi$ -Ligand Exchange between Enamine 26 and Ethylene



Scheme 6. Grob Fragmentation of Pyridinium Ion 15



these two ions by reaction within IMC1. Thus, ion **24** (m/z 108) can arise by proton transfer from the trimethylsilylethyl cation to the basic enamine **26** with the formation of vinyltrimethylsilane (path c), while the ion at m/z 180 (**1a**) can arise by formal  $\pi$ -ligand exchange of Me<sub>3</sub>Si<sup>+</sup> between ethylene and the enamine **26** (path d), as shown in Scheme 5.

We also cannot discount direct conversion of the parent ion 15 at m/z 208 into the IMC2 (Scheme 4, path e) by Grob fragmentation (Scheme 6) with subsequent dissociation to give ion m/z 73.

#### CONCLUSION

Computational studies on the pyridinium ions 15 and 16 (M =Si, Ge, Sn, Pb) provide evidence for a weak through-bond (double hyperconjugative) interaction between the  $M-CH_2$  bond and the low-lying  $\pi^*$  orbital of the pyridinium ion. The strength of this interaction increases in the order Si < Ge < Sn < Pb, in line with the  $\sigma$ -donor abilities of the C–M bond. Some evidence for the through-bond interaction for M = Si in solution is provided by <sup>13</sup>C and <sup>29</sup>Si NMR studies; although the changes in the <sup>29</sup>Si chemical shift are measurable, the changes in the <sup>13</sup>C-<sup>29</sup>Si coupling constants are barely so. Fragmentation pathways followed by the ions 15 and 16 in the gas phase under CID, however, are strongly influenced by the throughbond interaction, such that the bonds which are weakened by this interaction are the most readily fragmented. This is consistent with the expectation that hyperconjugative effects on transition states are substantially larger than the effects on the ground state.

#### EXPERIMENTAL SECTION

**Synthesis.** All reactions were conducted in oven-dried glassware under a nitrogen atmosphere. Solvents were anhydrous ,and all fine chemicals were used as received from Sigma-Aldrich Chemical Co. Petroleum spirit refers to the fraction that boils at 40-60 °C. Analytical thin layer chromatography (TLC) was carried out using aluminumbacked 2 mm thick Merck silica gel 60 GF256. Compounds were visualized under UV 365 nm light or by iodine. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded as solutions in solvents indicated on an Inova 400 or Inova 500 spectrometer. <sup>1</sup>H and <sup>13</sup>C spectra were reported as chemical shift (ppm), followed by (in parentheses, where applicable) integration, multiplicity, coupling constant, and peak assignment.

2-Trimethylsilyl(propargyl)pyridine (22). To a solution of 2-bromopyridine (0.32 g, 2.02 mmol) in dry triethylamine (10 mL) and trimethyl(propargyl)silane (0.25 g, 2.23 mmol) at 0 °C under N<sub>2</sub> were added copper iodide (0.10 mmol, 0.02 g) and dichloro[bis(triphenylphosphine)]Pd(II) (0.03 g, 0.04 mmol), and the resulting solution was stirred for 1 h. The reaction mixture was then warmed to room temperature and stirred for 3 days. The mixture was diluted with  $H_2O(20 \text{ mL})$ and extracted with ether (2  $\times$  50 mL). The organic layer was washed with  $H_2O$  (3  $\times$  30 mL) and then with saturated ammonium chloride solution. The solution was dried (MgSO<sub>4</sub>), and the solvent was removed under reduced pressure and the product purified by dry-flash column chromatography (n-hexane/ether) to yield 2-trimethyl(propargyl)pyridine (22; 0.10 g, 0.5 mmol, 25% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.52 (1H, d, J = 4.9 Hz), 7.59 (1H, ddd, J = 7.8, 7.7, 2.0), 7.14 (1H, m), 7.3  $(1H, d, J = 7.8 \text{ Hz}), 1.75 (2H, s), 0.18 (9H, s, Si(CH_3)_3).$ <sup>13</sup>C NMR (125) MHz, CDCl<sub>3</sub>): δ 149.8, 143.9, 136.0, 126.6, 122.3, 86.7, 79.6, 4.3, 1.3. ESI/MS:  $[M + CH_3]^+$  204.120 30 (calculated for  $C_{12}H_{18}SiN^+$ 204.120 85).

4-Trimethylsilyl(propargyl)pyridine (23). To a solution of 4-bromopyridine-HCl (0.64 g, 4.04 mmol) in water (20 mL) was added NaOH until the solution was basified. The resulting 4-bromopyridne was then extracted into ether (2  $\times$  20 mL) and dried (MgSO<sub>4</sub>) and the solvent removed under reduced pressure. The 4-bromopyridine was then added to dry triethylamine (10 mL), and trimethyl(propargyl)silane (0.5 g, 4.43 mmol, 0.66 mL) under N2, copper iodide (0.20 mmol, 0.04 g), and dichloro[bis(triphenylphosphine)]palladium(II) (0.06 g, 0.08 mmol) were added at 0 °C, and the resulting mixture was stirred for 1 h. The reaction mixture was then warmed to room temperature and stirred for 3 days. The solution was quenched with H<sub>2</sub>O (20 mL) and extracted with ether (50 mL). The organic layer was washed with  $H_2O(3 \times 30 \text{ mL})$ and then with saturated ammonium chloride solution. The solution was dried (MgSO<sub>4</sub>), and the solvent was removed under reduced pressure and the compound purified by dry-flash column chromatography (nhexane/ether) to yield 4-trimethyl(propargyl)pyridine (23; 0.15 g, 0.8 mmol, 20% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.49 (2H, d, J = 5.2 Hz), 7.47 (2H, m), 1.73 (2H, s), 0.16 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 150.7, 149.4, 127.2, 74.4, 64.7, 7.7, -2.03. ESI/MS:  $[M + H]^+$  190.104 44 (calculated for  $C_{11}H_{16}SiN^+$  190.104 65).

2-Trimethylsilylpropylpyridine (**17**). To a solution of 2-trimethylsilyl(propargyl)pyridine (**22**; 0.10 g, 0.5 mmol) in methanol (50 mL) was added a catalytic amount of Pd (10 wt % on carbon) and the system stirred under an atmosphere of H<sub>2</sub> for 48 h. The solution was filtered through Celite, the solvent was removed under reduced pressure, and the compound was purified via an acid—base extraction to yield 2-trimethylsilylpropylpyridine (17; 0.04 g, 0.2 mmol, 41% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.50 (1H, d, *J* = 4.5 Hz), 7.57 (1H, ddd, *J* = 7.5, 7.5, 2.0 Hz), 7.12 (1H, d, *J* = 7.5 Hz), 7.08 (1H, m), 2.78 (2H, t, *J* = 8.0, 7.5 Hz), 1.72 (2H, m), 0.55 (2H, m) –0.04 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  161.3, 149.1, 136.2, 127.8, 120.8, 42.2, 24.6, 16.7 (<sup>1</sup>*J*(*C*-*Si*(CH<sub>3</sub>)<sub>3</sub>) = 55.3 Hz), -1.75 (<sup>1</sup>*J*(*Si*(CH<sub>3</sub>)<sub>3</sub>) = 50.2 Hz). ESI/MS: [M + CH<sub>3</sub>]<sup>+</sup> 208.151 55 (calculated for C<sub>12</sub>H<sub>22</sub>NSi<sup>+</sup> 208.151 60). <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>):  $\delta$  1.25.

4-Trimethylsilylpropylpyridine (**18**). To a solution of 4-trimethylsilyl-(propargyl)pyridine (**23**; 0.15 g, 0.8 mmol) in methanol (50 mL) was added a catalytic amount of Pd (10 wt % on carbon) and the system stirred under H<sub>2</sub> for 48 h. The solution was filtered through Celite, the solvent was removed under reduced pressure, and the compound was purified via an acid—base extraction to yield 4-trimethylsilylpropylpyridine (**18**; 0.02 g, 0.11 mol, 13% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.48 (2H, broad doublet), 7.08 (2H, broad doublet), 2.6 (2H, m), 1.62 (2H, m), 0.51 (2H, m), -0.033 (9H, s). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  151.3, 149.3, 123.9, 39.0, 24.6, 16.3 (<sup>1</sup>*J*(*C*-*Si*(CH<sub>3</sub>)<sub>3</sub>) = 51.2 Hz), -1.67 (<sup>1</sup>*J*(*Si*(CH<sub>3</sub>)<sub>3</sub>) = 50.6 Hz). ESI/MS: [M + H]<sup>+</sup> 194.133 64 (calculated for C<sub>11</sub>H<sub>22</sub>NSi<sup>+</sup> 194.133 64). <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>):  $\delta$  1.36. *N-Methyl-2-trimethylsilylpropylpyridinium Tosylate* (**15**•**Ots**). A solution of the pyridine derivative 17 (50 mg) in deuteriochloroform (0.5 mL) was treated with neat methyl tosylate (1.05 equiv) and the solution left overnight. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.76 (1H, m), 8.34 (1H, t, *J* = 7.9, 7.8 Hz), 7.78 (2H, m), 3.05 (1H, m), 1.76 (1H, m), 0.63 (2H, m), -0.01, (9H, s). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  158.6, 146.6, 145.2, 128.1, 22.2, 16.4 (<sup>1</sup>*J*(*C*-*Si*(CH<sub>3</sub>)<sub>3</sub>) = 49.7 Hz), -2.1 (<sup>1</sup>*J*(*Si*(CH<sub>3</sub>)<sub>3</sub>) = 50.9 Hz), 45.6. <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>):  $\delta$  1.55.

*N*-*Methyl*-4-*trimethylsilylpropylpyridinium Tosylate* (**16**·**Ots**). A solution of the pyridine derivative **18** (50 mg) in deuteriochloroform (0.5 mL) was treated with neat methyl tosylate (1.05 equiv) and the solution left overnight. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.96 (2H, d, *J* = 6.5 Hz), 7.71 (2H, m), 7.56 (2H, d, *J* = 6.5 Hz), 7.30 (2H, m), 4.34 (3H, s, N-CH<sub>3</sub>), 3.67 (2H, s), 2.74 (2H, m), 2.39 (3H, s), 2.26 (3H, s), 1.58 (2H, m), 0.45 (2H, m), -0.08 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  162.0, 144.8, 131.8, 129.7, 128.4, 127.7, 127.4, 56.2, 48.0 (N-CH<sub>3</sub>). 39.4, 24.8, 21.6, 15.7 (<sup>1</sup>*J*(*C*-*Si*(CH<sub>3</sub>)<sub>3</sub>) = 50.3 Hz), -2.5 (<sup>1</sup>*J*(*Si*(CH<sub>3</sub>)<sub>3</sub>) = 50.8 Hz). <sup>29</sup>Si NMR (80 MHz, CDCl<sub>3</sub>):  $\delta$  1.42.

NMR Measurements To Determine the Influence of the Silicon  $\gamma$  Effect on <sup>29</sup>Si Chemical Shifts and <sup>29</sup>Si $^{-13}$ C Coupling Constants. Both <sup>13</sup>C and <sup>29</sup>Si NMR were run for 16 h for compounds 15a, 16a, 17a, and 18. The resolution of the spectra can be calculated by dividing the width (in Hz) by the square of the FT size. The square of the FT size is required because the FT is composed of real and imaginary points and the spectrum consists of real points only. Thus, for the <sup>13</sup>C NMR the digital resolution is 30 188.7/(131 072) × 2 = 0.46 Hz and for <sup>29</sup>Si the digital resolution is 59 612.5/(131 072) × 2 = 0.91 Hz.

**Crystallography.** Intensity data were collected with an Oxford Diffraction SuperNova CCD diffractometer using Cu K $\alpha$  radiation (graphite crystal monochromator,  $\lambda = 1.541$  84 Å); the temperature during data collection was maintained at 130.0(2) K using an Oxford Cryosystems cooling device.

The structure was solved by direct methods and difference Fourier synthesis.<sup>16</sup> Thermal ellipsoid plots were generated using the program ORTEP-3<sup>17</sup> integrated within the WINGX<sup>18</sup> suite of programs.

Crystal data for 17aH<sup>+</sup>(picrate):  $C_{17}H_{22}N_4O_7Si$ ,  $M_r = 422.48$ , T = 130.0(2) K,  $\lambda = 1.541$  84 Å, triclinic, space group  $P\overline{I}$ , a = 6.7542(10) Å, b = 11.2277(12) Å, c = 13.9266(16) Å,  $\alpha = 90.444(9)^\circ$ ,  $\beta = 98.291(11)^\circ$ ,  $\gamma = 94.511(10)^\circ$ , V = 1041.6(2) Å<sup>3</sup>, Z = 2,  $D_c = 1.347$  Mg M<sup>-3</sup>,  $\mu$ (Cu K $\alpha$ ) = 1.408 mm<sup>-1</sup>, F(000) = 444, crystal size  $0.22 \times 0.12 \times 0.06$  mm, 6822 reflections measured, 3757 independent reflections ( $R_{int} = 0.056$ ), final R = 0.0742 ( $I > 2\sigma(I)$ ),  $R_w(F^2) = 0.2148$  (all data).

Mass Spectrometry Experiments. Mass spectrometry experiments were carried out using a commercially available hybrid linear ion trap and Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer (Finnigan LTQ-FT, Bremen, Germany), which is equipped with an electrospray ionization source. Stock solutions were prepared using 1 mmol of the pyridine derivative in 1 mL of acetonitrile and methylated to form pyridinium ions, using 2-3 drops of iodomethane or deuterated iodomethane. The solutions were introduced into the electrospray source at a flow rate of 5 µL/min. Typical electrospray conditions were employed and involve a needle potential of 4.0-5.0 kV, a heated capillary temperature of 200 °C, sheath air, ca. 3-25. The pyridinum precursor ion was mass-selected with a window of m/z 1 and then subjected to CID using a corresponding normalized collision energy of 25-45% and an activation Q of 0.25 for a period of 30 ms. All high-resolution mass spectrometry experiments were carried out on the same instrument. The  $[M + CH_3]^+$  pyridinium ions were massselected in the LTQ using standard procedures and were then analyzed in the FT-ICR MS to generate the high-resolution tandem mass spectrum. Calibration was carried out via the automatic calibration function using the suggested LTQ calibration solution, consisting of caffeine, MRFA, and Ultramark solution.

#### ASSOCIATED CONTENT

**Supporting Information.** Full listings of geometries and energies (Gaussian Archive entries) for ground-state structures and a CIF file giving crystallographic data for 17aH<sup>+</sup>. This material is available free of charge via the Internet at http://pubs.acs.org. The crystal data have also been deposited at the Cambridge Crystallographic Data Centre and assigned CCDC code 845803.

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(19) Calculated structures for ions 15 and 16 (where M = Ge, Sn, Pb) which exist in similar conformations are given in the Supporting Information.