

Published on Web 05/25/2010

## Intramolecular Halogen Stabilization of Silylium Ions Directs Gearing Dynamics

Paola Romanato, Simon Duttwyler, Anthony Linden, Kim K. Baldridge,\* and Jay S. Siegel\* Organic Chemistry Institute, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland

Received December 30, 2009; E-mail: kimb@oci.uzh.ch; jss@oci.uzh.ch

Silicon cations<sup>1</sup> are highly reactive Lewis acids that are useful in chemical synthesis.<sup>2,3</sup> Even relatively weak Lewis bases, such as the  $\pi$ -basic solvent toluene, form tetrahedral complexes with silylium ions.<sup>4,5</sup> Intramolecular  $\pi$  coordination in cationic silicon species with a 2,6-diarylphenyl scaffold distorts the ideal  $C_{2\nu}$ -symmetric geometry to adopt the  $C_1$ -symmetric geometry of a Wheland-like complex.<sup>6</sup> The energy difference between the  $C_{2\nu}$  and  $C_1$  forms decreases with lateral rings having lower basicity than benzene are likely candidates for cations without internal  $\pi$  coordination. On the basis of this idea, silyl cations 1 bearing 2,6-dihalophenyl substituents were synthesized. However, instead of free tricoordinate ions, NMR and X-ray crystallographic studies revealed a trigonal-bipyramidal geometry with bridging halogen atoms as the apical ligands.<sup>7</sup>



Double Negishi coupling on triazene  $5^8$  led to diarylphenyltriazene **4**, which gave the corresponding iodoterphenyl **3a** when treated with iodine.<sup>9</sup> Lithiation of  $3^{10}$  followed by reaction with chlorodimethylsilane afforded the silanes **2**. Hydride abstraction by [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] gave the silylium ions [**1**][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Scheme 1).

The <sup>29</sup>Si NMR resonances of **1a** (89 ppm) and **1b** (91 ppm) are downfield-shifted relative to their neutral precursors (-20 ppm), an indication that species with partial positive charge on silicon are formed. While these values are still far from that of a free silylium ion,<sup>11</sup> they indicate deshielding in comparison with classical silanium ions.<sup>12</sup>

<sup>1</sup>H and <sup>29</sup>Si NMR spectra of **1a** revealed magnetic coupling to the fluorine substituents (Figure 1). The signal of the methyl groups attached to silicon in **1a** appeared as a quintet, and the same multiplicity was maintained upon cooling to 223 K. Additionally, the silicon signal, which appeared as a broad resonance at room temperature, was resolved into a quintet at lower temperature.<sup>13</sup> Coordination by fluorine can explain the multiplicity and the coupling constant (J = 32 Hz) of the silicon signal; the effect of this interaction reached the methyl groups covalently bonded to silicon. <sup>19</sup>F NMR spectroscopy revealed signal isochrony for the fluorine substituents over the temperature range 293–223 K. Computational analysis of a conformational graph showed that this equivalence originated from a dynamic exchange of lower-symmetry conformations rather than a static conformer having  $C_{2\nu}$  symmetry.

Eight conformations of **1** can be arranged into a bipartite graph  $(K_{4,4})$  with conrotatory or disrotatory (correlated one-ring-flip) connections (Figure 2).<sup>14</sup> Calculations at the density functional theory level favored a  $C_2$  ground state  $(B_1-C_2)$  for **1a** and **1b** in which the silicon interacts with one halogen atom from each of the opposing flanking rings (Table 1);<sup>15</sup> the experimental <sup>29</sup>Si NMR values matched well the computed values for the B<sub>1</sub>- $C_2$  conformers



 $(\Delta \delta \approx 3 \text{ ppm})$ . Computations further predicted that cation **1a** should undergo fluorine exchange at silicon via a disrotatory gearing of the lateral aryl rings (Figure 3); the circuit  $(B_1-A_2)_2$  was predicted to require only 4.5 kcal mol<sup>-1</sup>. In contrast, cation **1b** was predicted to exchange chloro substituents at silicon via a  $B_1-A_1-B_1$ conrotatory librational process.

Crystals of composition [**1a**][CB<sub>11</sub>H<sub>6</sub>Cl<sub>6</sub>] were obtained from a C<sub>6</sub>H<sub>5</sub>Cl/C<sub>6</sub>H<sub>14</sub> mixture using the carborane CB<sub>11</sub>H<sub>6</sub>Cl<sub>6</sub><sup>-</sup> as the counterion.<sup>16,17</sup> X-ray crystallographic analysis revealed the cation structure to be essentially the  $C_2$  trigonal-bipyramidal B<sub>1</sub>- $C_2$  form



Figure 1. Variable-temperature <sup>1</sup>H and <sup>29</sup>Si NMR analysis of 1a.



*Figure 2.* Bipartite conformational graph of 1 viewed along the  $Si-C_{aryl}$  axis. Blue paths, disrotatory; red paths, conrotatory; bold blue path, gearing circuit. GS, ground state; TS, transition state; HSP, higher-order stationary point. Bold black lines, lateral aryl rings; wedges, methyl groups at silicon.

Table 1. B98/DZ(2df,pd)-Calculated Relative Gas-Phase Energies (kcal mol<sup>-1</sup>) and B98/DZ+(2df,pd) <sup>29</sup>Si NMR Shifts (ppm)<sup>a</sup> for **1a** and 1b<sup>b</sup>

		1a			1b		
		<sup>29</sup> Si NMR shift			<sup>29</sup> Si NMR shift		
	$E_{\rm rel}$	calcd	exptl	E <sub>rel</sub>	calcd	exptl	
$A_1 - C_{2v}$	13.2	272.2	-	9.3	208.3	_	
$A_2-C_s$	4.5	160.3	_	16.6	195.5	_	
$A_3-C_{2v}$	22.0	33.6	_	79.8	13.6	_	
$B_1-C_2$	0.0	87.6 <sup>c</sup>	88.6	0.0	<b>93.8</b> <sup>c</sup>	90.5	
$B_2-C_s$	9.6	69.2	_	21.4	66.3	_	

<sup>a</sup> NMR shift data calibrated relative to TMS. <sup>b</sup> For additional computational details, see the Supporting Information. <sup>c</sup> B98/ DZ+(2df,pd) calibrated <sup>29</sup>Si NMR shifts in toluene: **1a**, 87.2; **1b**, 93.7.



Figure 3. Proposed conformational gearing circuit.



Figure 4. ORTEP plot of [1a][CB<sub>11</sub>H<sub>6</sub>Cl<sub>6</sub>] with 30% probability ellipsoids; the anion and hydrogen atoms have been omitted. Dashed lines show the Si-F interactions. The conformation is consistent with the  $B_1$ - $C_2$  form (cf. Figure 1).

Table 2. Selected Bond Lengths (Å) and Dihedral Angles (deg) for the Calculated C<sub>2</sub> Conformer and the Single-Crystal X-Ray Structure of 1a

	$C_2$ calc	:d		
parameter	gas-phase <sup>a</sup>	in toluene <sup>b</sup>	exptl	
$F2 \rightarrow Si$	2.118 [2.126]	2.133	2.151(2)	
F4 → Si	2.118 [2.126]	2.133	2.065(2)	
C14-F2	1.397 [1.397]	1.394	1.410(3)	
C20-F4	1.397 [1.397]	1.394	1.421(3)	
C10-F1	1.331 [1.332]	1.336	1.352(3)	
C16-F3	1.331 [1.332]	1.336	1.351(3)	
dihedral angle <sup>c</sup>	35.14	36.25	$38.28(13)^d$	
-	35.14	36.25	$31.14(13)^{e}$	
dfp-Si <sup>f</sup>	0.0	0.0	0.0184(7)	

<sup>a</sup> B98/DZ(2df,pd) [B98/DZ+(2df,pd)]. <sup>b</sup> B98/DZ+(2df,pd) in toluene. <sup>c</sup> Angle between the least-squares planes of a flanking ring and the central ring.<sup>d</sup> Between the ring containing F2 and the central ring.<sup>e</sup> Between the central ring and the ring containing F4. <sup>f</sup> Distance between the Si atom and the plane defined by the three C atoms bound to Si.

predicted computationally (Figure 2; cf. Figure 2). The F2-Si and F4-Si distances are longer than a typical F-Si bond by 0.55 and 0.46 Å, respectively (Table 2).<sup>18</sup> The sum of C-Si-C angles, 359.9(1)°, and the F2-Si-F4 angle, 174.20(6)°, indicate that the fluorine atoms occupy the apical positions of a trigonal bipyramid.

Spectroscopic data and computations support similar ground states for 1a and 1b. The observed <sup>29</sup>Si NMR shifts for 1a and 1b indicate a slightly weaker electron donation to silicon by 1b. Comparison of the differences in the <sup>13</sup>C NMR shifts of the flanking rings in silanes 2 versus cations 1 suggests a similar coordination mode in **1a** and **1b**.<sup>19</sup> For the favored  $C_2$  conformation of **1b**, the Si-Cl distance (coordinating chlorine atoms) was predicted to be 2.661 Å,  $\sim 0.61$  Å longer than in a single Si–Cl bond.<sup>20</sup>

This new class of silylium ions, coordinated by neutral halogen atoms that are part of C(Ar)-X bonds, displays binding to  $SiR_3^+$ that is energetically comparable to that of a  $\pi$ -basic ligand such as benzene. Desymmetrization of the meta-terphenyl scaffold via replacement of one halogenated ring with a methylated ring can refine the energetic details of lone-pair (halogen) or  $\pi$  (aryl) donor stabilization of silyl cations.

Acknowledgment. This work was supported by the Swiss National Science Foundation.

Supporting Information Available: Experimental procedures, details, and CIFs for computational  $[1a][CB_{11}H_6Cl_6],$  $[1a \cdot THF][B(C_6F_5)_4]$ ,<sup>16</sup> and  $[1a \cdot Et_2O][B(C_6F_5)_4]$ .<sup>16</sup> This material is available free of charge via the Internet at http://pubs.acs.org.

## References

- (1) (a) Kochina, T. A.; Vrazhnov, D. V.; Sinotova, E. N.; Voronkov, M. G. Russ. Chem. Rev. 2006, 75, 95. (b) Reed, C. A. Acc. Chem. Res. 1998, 31, 325. (c) Lambert, J. B.; Zhao, Y.; Zhang, S. M. J. Phys. Org. Chem. 2001, 14, 370.
- For catalytic activation of carbonyl groups, see: (a) Klare, H.; Bergander, K.; Oestreich, M. Angew. Chem., Int. Ed. 2009, 48, 9077. (b) Hara, K.; Akiyama, R.; Sawamura, M. Org. Lett. 2005, 7, 5621.
   For Lewis base activation of silicon Lewis acids, see: Denmark, S. E.; Chung, W. J. Org. Chem. 2008, 73, 4582.
- (4) This paper uses current IUPAC recommendations for cationic species (see: Powell, W. H. Pure Appl. Chem. 1993, 65, 1357). The term silvlium ion refers to a tricoordinate silicon cation. A silanium ion is a pentacoordinate species with a formal positive charge at silicon. The expression silyl cation
- is used for species without specification of the coordination number.
  (5) Lambert, J. B.; Zhang, S.; Ciro, S. M. Organometallics 1994, 13, 2430.
  (6) Duttwyler, S.; Do, Q.; Linden, A.; Baldridge, K. K.; Siegel, J. S. Angew. Chem., Int. Ed. 2008, 47, 1719.
  (7) For halogen → Si coordination in silylium ions, see: (a) Lehmann, M.;
- Schulz, A.; Villinger, A. Angew. Chem., Int. Ed. 2009, 48, 7444. (b) Panisch, Schutz, A.; Villinger, A. Angew. Chem., Int. Ed. 2009, 48, 1444. (b) Panisch,
  R.; Bolte, M.; Müller, T. J. Am. Chem. Soc. 2006, 128, 9676. (c) Küppers,
  T.; Bernhardt, E.; Eujen, R.; Willner, H.; Lehmann, C. W. Angew. Chem.,
  Int. Ed. 2007, 46, 6346. (d) Hoffmann, S. P.; Kato, T.; Tham, F. S.; Reed,
  C. A. Chem. Commun. 2006, 767. (e) Xie, Z.; Manning, J.; Reed, R. W.;
  Mathur, R.; Boyd, P. D. W.; Benesi, A.; Reed, C. A. J. Am. Chem. Soc.
  1996, 118, 2922.
  Liu, C.-Y.; Knochel, P. Org. Lett. 2005, 7, 2543.
- (9) Moore, J. S. Tetrahedron Lett. 1994, 35, 5539.
- (10) For the synthesis of 3b, see: Saednya, A.; Hart, H. Synthesis 1996, 1455.
- A typical value would be 225 ppm, as for trimesitylsilylium ion. See: Kim, K.-C.; Reed, C. A.; Elliot, D. W.; Mueller, L. J.; Tham, F.; Lin, L.; Lambert, (11)J. B. Science 2002, 297, 825.
- (12) For silanium ions, see: (a) Kost, D.; Kalikhman, I. Acc. Chem. Res. 2009, 42, 303. (b) Chauhan, M.; Chuit, C.; Corriu, R. J. P.; Mehdi, A.; Reyé, C. Organometallics 1996, 15, 4326. (c) Belzner, J.; Schär, D.; Kneisel, B. O.; Herbst-Irmer, R. Organometallics 1995, 14, 1840. (d) Berlekamp, U.-H.; Jutzi, P.; Mix, A.; Neumann, B.; Stammler, H.-G.; Schoeller, W. W Angew. Chem., Int. Ed. 1999, 38, 2048. (e) Ebata, K.; Inada, T.; Kabuto, C.; Sakurai, H. J. Am. Chem. Soc. 1994, 116, 3595.
- (13) For an earlier example of a rapidly exchanging F–Si system, see: Olah, G. A.; Mo, Y. K. J. Am. Chem. Soc. 1971, 93, 4942.
  (14) Mislow, K. Chemtracts: Org. Chem 1989, 2, 151.
  (15) The C<sub>1</sub> starting geometry converged to the C<sub>2</sub> structure.

- (16) Initial attempts to crystallize 1a showed that traces of THF and Et<sub>2</sub>O had coordinated to the silicon center. Cocrystals containing  $[1a \cdot THF][B(C_6F_5)_4]$ and [1a·Et<sub>2</sub>O][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] were obtained, and X-ray analysis displayed a distorted-tetrahedral arrangement around silicon (see the Supporting Information).
- (17) For the carborane CB<sub>11</sub>H<sub>6</sub>Cl<sub>6</sub><sup>-</sup>, see: Reed, C. A. Acc. Chem. Res. 1998, 31, 133.
- (18) The Si-F bond length of 1.600(1) Å in Me<sub>3</sub>SiF (see: Rempfer, B.; Oberhammer, H.; Auner, N. J. Am. Chem. Soc. 1986, 108, 3893) was used as a reference.
- (19) For comparison of the <sup>13</sup>C NMR shifts in cations 1, see the Supporting Information. Analysis of the <sup>13</sup>C NMR shifts of analogues with methylated flanking rings revealed  $\pi$  coordination via C<sub>ortho</sub> with a resonance pattern typical of Wheland intermediates (ref 6). The data for cations 1 are not consistent with this kind of electron donation.
- (20) Reference 7a indicates a Si-Cl bond length of 2.055(2) Å for Me<sub>3</sub>SiCl.
- JA9109665