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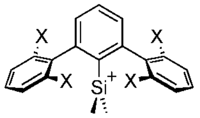
Intramolecular Halogen Stabilization of Silylium Ions Directs Gearing Dynamics

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[1] are highly reactive Lewis acids that are useful in chemical synthesis.[2,3] Even relatively weak Lewis bases, such as the π-basic solvent toluene, form tetrahedral complexes with silylium ions.[4,5] Intramolecular π coordination in cationic silicon species with a 2,6-diarylphenyl scaffold distorts the ideal C_{2v}-symmetric geometry to adopt the C_1-symmetric geometry of a Wheland-like complex.[6] The energy difference between the C_{2v} and C_1 forms decreases with decreasing π basicity of the flanking aromatic rings. Systems with lateral rings having lower basicity than benzene are likely candidates for cations without internal π 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.[7]



	X
1a	F
1b	Cl

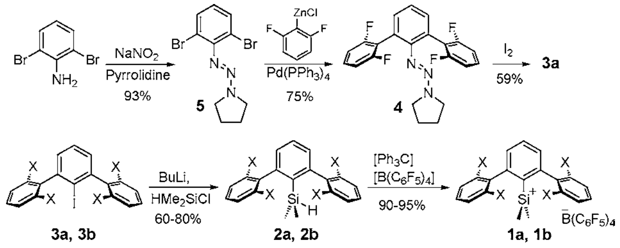
Double Negishi coupling on triazene **5**[8] led to diarylphenyltriazene **4**, which gave the corresponding iodoterphenyl **3a** when treated with iodine.[9] Lithiation of **3**[10] followed by reaction with chlorodimethylsilane afforded the silanes **2**. Hydride abstraction by $[Ph_3C][B(C_6F_5)_4]$ gave the silylium ions $[\mathbf{1}][B(C_6F_5)_4]$ (Scheme 1).

The ^{29}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,[11] they indicate deshielding in comparison with classical silanium ions.[12]

^1H and ^{29}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.[13] 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. ^{19}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_{2v} 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).[14] 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);[15] the experimental ^{29}Si NMR values matched well the computed values for the B_1-C_2 conformers ($\Delta\delta \approx 3$ 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^{-1}. In contrast, cation **1b** was predicted to exchange chloro substituents at silicon via a $B_1{-}A_1{-}B_1$ conrotatory librational process.

Scheme 1



Crystals of composition $[\mathbf{1a}][CB_{11}H_6Cl_6]$ were obtained from a C_6H_5Cl/C_6H_{14} mixture using the carborane $CB_{11}H_6Cl_6^-$ as the counterion.[16,17] X-ray crystallographic analysis revealed the cation structure to be essentially the C_2 trigonal-bipyramidal B_1-C_2 form

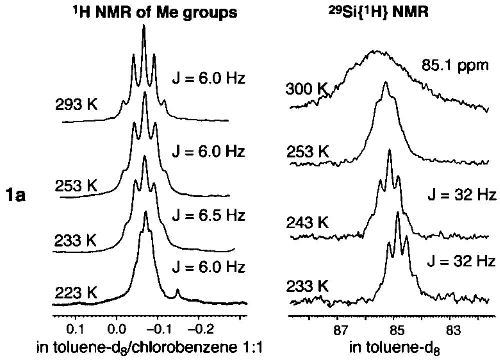


Figure 1. Variable-temperature ^1H and ^{29}Si NMR analysis of **1a**.

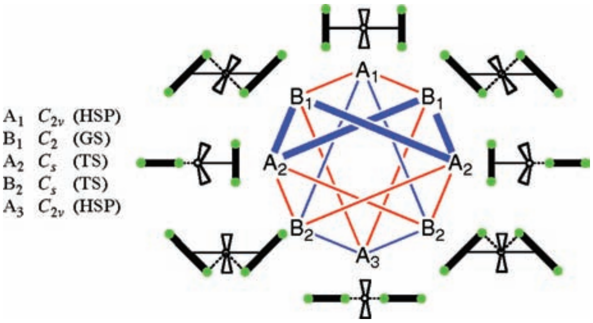


Figure 2. Bipartite conformational graph of **1** viewed along the Si−C$_{aryl}$ axis. Blue paths, disrotatory; red paths, conrotatory; bold blue path, gearing circuit. GS, ground state; TS, transition state; HSP, higher-order stationary point. Bold black lines, lateral aryl rings; wedges, methyl groups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

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Table 1. B98/DZ(2df,pd)-Calculated Relative Gas-Phase Energies (kcal mol^{-1}) and B98/DZ+(2df,pd) ^{29}Si NMR Shifts (ppm)[a] for **1a** and **1b**[b]

	1a			**1b**		
		^{29}Si NMR shift			^{29}Si NMR shift	
	E_{rel}	calcd	exptl	E_{rel}	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**[c]	**88.6**	**0.0**	**93.8**[c]	**90.5**
B_2-C_s	9.6	69.2	–	21.4	66.3	–

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

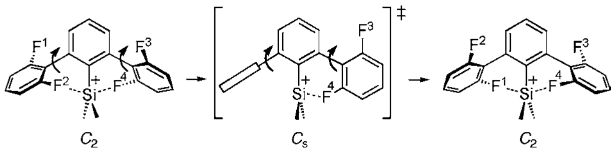

Figure 3. Proposed conformational gearing circuit.

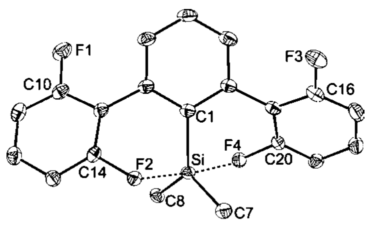

Figure 4. ORTEP plot of [**1a**][$CB_{11}H_6Cl_6$] with 30% probability ellipsoids; the anion and hydrogen atoms have been omitted. Dashed lines show the Si−F interactions. The conformation is consistent with the B_1-C_2 form (cf. Figure 1).

Table 2. Selected Bond Lengths (Å) and Dihedral Angles (deg) for the Calculated C_2 Conformer and the Single-Crystal X-Ray Structure of **1a**

	C_2 calcd		
parameter	gas-phase[a]	in toluene[b]	exptl
F2 → 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[c]	35.14	36.25	38.28(13)[d]
	35.14	36.25	31.14(13)[e]
dfp-Si[f]	0.0	0.0	0.0184(7)

[a] B98/DZ(2df,pd) [B98/DZ+(2df,pd)]. [b] B98/DZ+(2df,pd) in toluene. [c] Angle between the least-squares planes of a flanking ring and the central ring. [d] Between the ring containing F2 and the central ring. [e] Between the central ring and the ring containing F4. [f] 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).[18] 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 ^{29}Si NMR shifts for **1a** and **1b** indicate a slightly weaker electron donation to silicon by **1b**. Comparison of the differences in the ^{13}C NMR shifts of the flanking rings in silanes **2** versus cations **1** suggests a similar coordination mode in **1a** and **1b**.[19] For the favored C_2 conformation of **1b**, the Si−Cl distance (coordinating chlorine atoms) was predicted to be 2.661 Å, ~0.61 Å longer than in a single Si−Cl bond.[20]

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 π-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 π (aryl) donor stabilization of silyl cations.

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

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(15) The C_1 starting geometry converged to the C_2 structure.

(16) Initial attempts to crystallize **1a** showed that traces of THF and Et_2O had coordinated to the silicon center. Cocrystals containing [**1a**·THF][$B(C_6F_5)_4$] and [**1a**·Et_2O][$B(C_6F_5)_4$] were obtained, and X-ray analysis displayed a distorted-tetrahedral arrangement around silicon (see the Supporting Information).

(17) For the carborane $CB_{11}H_6Cl_6^-$, see: Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133.

(18) The Si−F bond length of 1.600(1) Å in Me_3SiF (see: Rempfer, B.; Oberhammer, H.; Auner, N. *J. Am. Chem. Soc.* **1986**, *108*, 3893) was used as a reference.

(19) For comparison of the ^{13}C NMR shifts in cations **1**, see the Supporting Information. Analysis of the ^{13}C NMR shifts of analogues with methylated flanking rings revealed π coordination via C_{ortho} 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_3SiCl.

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