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Competition between π-Arene and Lone-Pair Halogen Coordination of Silylium Ions?

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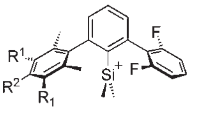
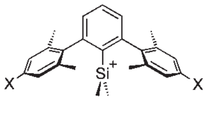
S *Supporting Information*

ABSTRACT: In 2,6-diarylphenylSiR_2 cations, the 2,6-diarylphenyl (*m*-terphenyl) scaffold blocks incoming nucleophiles and stabilizes the positive charge at silicon by lateral ring interactions. Direct ortho-halogen and π-electron-rich face coordination to silicon has been seen. For a series of cations bearing 2,6-difluoro-2′,6′-dimethyl-X_n-substituted rings, the relative contribution of these two modes of stabilization has been assessed. Direct coordination from an aryl fluoride is found to be comparable to that from the mesityl π-face.

The quest for stable silylium ions, R_3Si^+,[1] has led to the use of the 2,6-diarylphenyl (*m*-terphenyl) scaffold as a substituent, which can block incoming nucleophiles and stabilize the positive charge at silicon by lateral ring interactions. When the lateral rings are π-electron-rich because of methyl groups, single η^1 π coordination to the silicon center dominates.[1c] In contrast, halogen→Si interactions dominate when chlorine or fluorine atoms are at the ortho positions of the flanking rings (**I** and **II** in Figure 1).[2,3] Are the energetic details of these two modes of stabilization comparable? Would π effects compete or cooperate with the halogen→Si interactions? This study of a series of cations **1** bearing 2,6-difluoro- and 2,6-dimethyl-X_n-substituted rings indicates a "friendly" competition between the two modes of stabilization: lower-basicity xylyl and mesityl rings (**1a**, **1b**) contribute less than the F→Si interactions, whereas higher-basicity duryl and pentamethylphenyl rings (**1c**, **1d**) contribute more than the F→Si interactions.



	R^1	R^2
1a	H	H
1b	H	Me
1c	Me	H
1d	Me	Me



	X
2a	F
2b	Cl

Single Negishi coupling of triazene **3**[4] followed by treatment of **4** with iodine afforded biphenyl **5**. Hart-type coupling[5] of **5** and subsequent lithiation/silylation furnished silanes **7**. Cations **1** were prepared by hydride abstraction using $[Ph_3C][B(C_6F_5)_4]$ (Scheme 1).

NMR spectroscopy studies suggest analogies between **1a**/**1b** and **IIa** and between **1c**/**1d** and **Ia** (Figure 1). The experimental and calculated ^{29}Si NMR shift data (Table 1) show **1a** and **1b** ($\delta \approx 100$ ppm) to be more deshielded than **1c** and **1d** ($\delta \approx 60$ ppm). In **1a** and **1b**, the signal multiplicity for the $SiMe_2$ fragment (^{1}H, ^{13}C, ^{29}Si) indicates a dynamic equilibrium of tautomers in which Si–F coupling is detectable (Figure 2). The unresolved signals of **1c** and **1d** imply weak interactions with the ortho fluorine atoms, whereas an analysis of the ^{13}C NMR shifts of the lateral rings in these cations is consistent with η^1 π coordination by the C_{ortho} atoms of the methylated rings.[6] Thus evolves a picture for **1a**–**d** in which, among structures of an equilibrium that is fast on the NMR time scale, F→Si interactions contribute demonstrably in **1a** and **1b** but to a lesser extent in **1c** and **1d**.

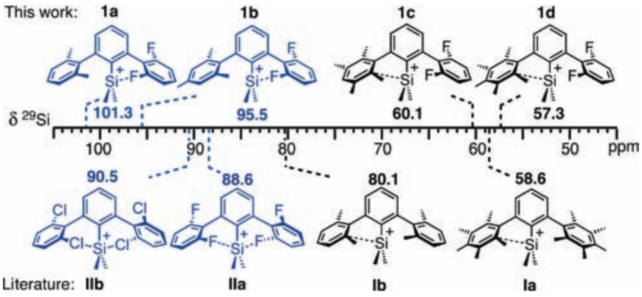
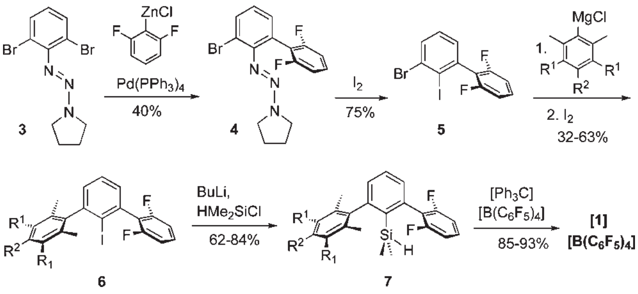


Figure 1. ^{29}Si NMR shifts of different terphenylsilylium ions: (black) molecules with preferential π-arene→Si interactions; (blue) molecules with preferential halogen→Si interactions. Solvent, C_6D_6; anion, $B(C_6F_5)_4^-$.

Scheme 1



M06-2X/Def2-TZVPP calculations predicted cations **1** to adopt a C_1-symmetric geometry with a low barrier to dynamic exchange of silicon among the preferential coordination sites.[7] In the specific cases, two minima were predicted for **1a** and **1b**, with halogen→Si preferred over π-arene→Si, whereas only a single π-arene→Si conformation was predicted for **1c** and **1d**.

Computational structural predictions fully matched the solid-state structures of **1a** and **1d** (Figure 3), which were obtained as

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Table 1. M06-L/Def2-TZVPP//M06-2X/Def2-TZVPP CSGT ^{29}Si NMR (ppm) Predictions for 1a, 1b, 1c, and 1d in Toluene

	1a	1b	1c	1d
exptl	101.3	95.5	60.1	57.3
calcd	98.9	97.6	61.6	56.2

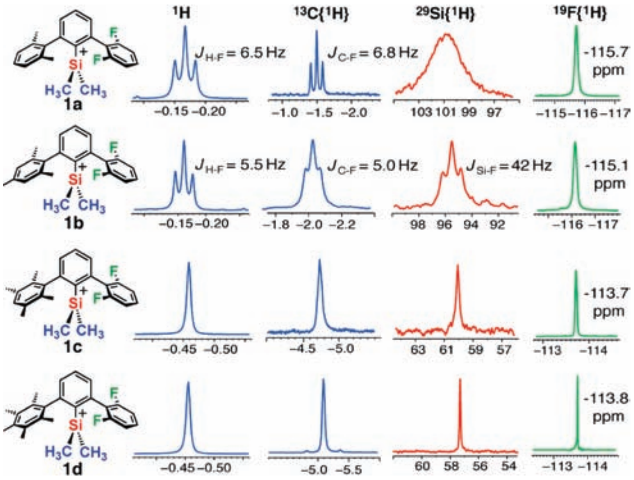


Figure 2. NMR analysis of **1a**, **1b**, **1c**, and **1d**: signals for methyl groups at silicon are shown in blue, signals for silicon in red, and signals for fluorine in green, each in the fast-exchange limit. Solvent, C_6D_6; anion, $B(C_6F_5)_4^-$.

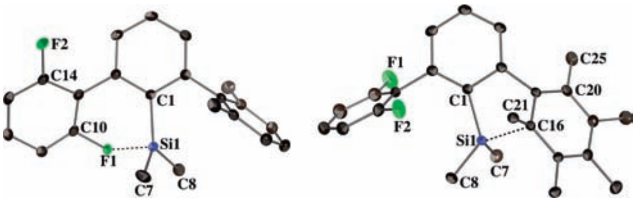


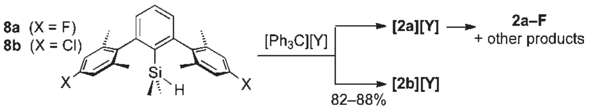
Figure 3. X-ray structures of (left) [**1a**][$CB_{11}H_6Cl_6$] and (right) [**1d**][$CB_{11}H_6Cl_6$] with 35% probability ellipsoids; anions and hydrogen atoms have been omitted. Dashed lines show the F→Si and π-arene→Si interactions.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Single-Crystal X-ray Structures and the Calculated C_1 Conformers of 1a and 1d

1a			1d		
parameter	exptl	calcd	parameter	exptl	calcd
F1→Si1	1.8658(8)	1.8880	C16→Si1	2.089(2)	2.1703
C10−F1	1.448(2)	1.4246	C16−C21	1.546(2)	1.5355
C14−F2	1.346(2)	1.3327	C20−C25	1.508(3)	1.5048
ΣC−Si−C	356.8(1)	356.58	ΣC−Si−C	345.5(2)	349.94
dfp-Si[a]	0.190(1)	0.198	dfp-Si[a]	0.413(1)	0.344
dihedral angle[b]	29.4(1)[c]	29.90	dihedral angle[b]	45.3(1)[d]	50.54

[a] Distance between the Si atom and the plane defined by the three C atoms bound to Si. [b] Angle between the least-squares planes of a flanking ring and the central ring. [c] Between the ring containing F1 and the central ring. [d] Between the ring containing C16 and the central ring.

Scheme 2



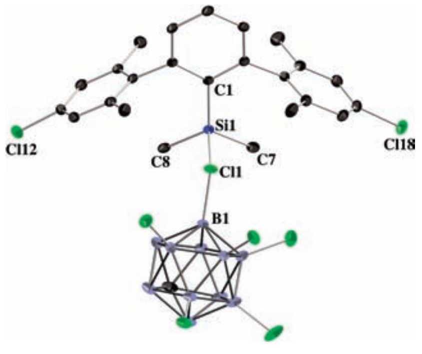


Figure 4. X-ray structure of **2b**−$CB_{11}H_6Cl_6$ with 35% probability ellipsoids; hydrogen atoms have been omitted.

solvent-free salts with the carborane anion $CB_{11}H_6Cl_6^-$.[8] **1a** exhibits fluorine coordination with a Si1−F1 distance of 1.8658(8) Å, which is longer than the Si−F bond length of 1.600(1) Å in Me_3SiF (Table 2).[9] X-ray analysis of **1d** revealed π coordination via C_{ortho} with a Si1−C16 distance of 2.089(2) Å, which is longer than the Si−C bond length of 1.875(2) Å in Me_4Si.[9] In both cations, the dihedral angle between the coordinating ring and the central ring deviates significantly from 90°, whereas the noninteracting ring adopts an almost perpendicular conformation relative to the central ring.

Aspirations to obtain a truly tricoordinate silylium ion led to the synthesis of cations **2** (Scheme 2). Hydride abstraction from **8a** with different trityl salts [Y = $B(C_6F_5)_4^-$, $CB_{11}H_6Cl_6^-$] showed the formation of Ph_3CH; however, cation **2a** was not observed. Instead, several decomposition products, including fluorosilane **2a**−F, were formed.[10,11] In contrast, **2b** was generated cleanly. ^{13}C NMR analysis[6] of [**2b**][$B(C_6F_5)_4$] revealed a C_{ortho}−Si π coordination comparable in strength to that of **Ib**, although their δ(^{29}Si) signals differed by ∼15 ppm.

Crystals of **2b** were obtained with the carborane anion $CB_{11}H_6Cl_6^-$. The X-ray analysis revealed an interaction between a lower-belt chlorine atom of the carborane and silicon (Figure 4). The Si1−Cl1 distance is 2.3130(5) Å, which is almost identical to that in iPr_3−$CB_{11}H_6Cl_6$;[12] coordination of **2b** by the anion causes a pyramidalization of the silicon center, as shown by the sum of angles around silicon [ΣC−Si−C = 351.40(12)°] and by the corresponding out-of-plane distance [dfp-Si = 0.3154(4) Å].[13]

Electron-rich arenes and aryl halides are donors for silylium ions. A delicate balance between these two coordination modes in silylium ions and a clear break point between mesityl- and duryl-substituted cations have been found. Arenes with reduced π basicity and no possible halogen→Si interactions (**2**) poorly accommodate the avidity of Si^+ for electron density, allowing coordination by anions as weakly basic as carborane ($CB_{11}H_6Cl_6^-$) to be observed in the crystal.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, computational details, and CIFs for [**1a**][$CB_{11}H_6Cl_6$], [**1d**][$CB_{11}H_6Cl_6$], and **2b**−$CB_{11}H_6Cl_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) For comparison of the ^{13}C NMR shifts for cations **1** and **2** with respect to the neutral silane precursors, see the Supporting Information.

(7) Details of the calculations are given in the Supporting Information.

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(10) Studies indicated that under the conditions given in Scheme 2, **2a** abstracts fluoride from **8a** (see the Supporting Information for details). **2a**−F was identified by GC−MS and ^{29}Si NMR spectroscopy.

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(13) Bond lengths and angles are listed in the Supporting Information.