

# Competition between $\pi$ -Arene and Lone-Pair Halogen Coordination of Silylium lons?

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Supporting Information

**ABSTRACT:** In 2,6-diarylphenylSiR<sub>2</sub> cations, the 2,6diarylphenyl (*m*-terphenyl) scaffold blocks incoming nucleophiles and stabilizes the positive charge at silicon by lateral ring interactions. Direct ortho-halogen and  $\pi$ -electronrich face coordination to silicon has been seen. For a series of cations bearing 2,6-difluoro-2',6'-dimethyl-X<sub>n</sub>-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  $\pi$ -face.

The quest for stable silylium ions, R<sub>3</sub>Si<sup>+,1</sup> 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  $\pi$ -electron-rich because of methyl groups, single  $\eta^{1} \pi$  coordination to the silicon center dominates.<sup>1c</sup> In contrast, halogen $\rightarrow$ Si interactions dominate when chlorine or fluorine atoms are at the ortho positions of the flanking rings (I and II in Figure 1).<sup>2,3</sup> Are the energetic details of these two modes of stabilization comparable? Would  $\pi$  effects compete or cooperate with the halogen $\rightarrow$ Si interactions? This study of a series of cations 1 bearing 2,6difluoro- and 2,6-dimethyl-X<sub>n</sub>-substituted rings indicates a "friendly" competition between the two modes of stabilization: lowerbasicity xylyl and mesityl rings (1a, 1b) contribute less than the  $F \rightarrow Si$  interactions, whereas higher-basicity duryl and pentamethylphenyl rings (1c, 1d) contribute more than the  $F \rightarrow Si$ interactions.



Single Negishi coupling of triazene  $3^4$  followed by treatment of 4 with iodine afforded biphenyl 5. Hart-type coupling<sup>5</sup> 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 <sup>29</sup>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<sub>2</sub> fragment (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si) indicates a dynamic equilibrium of



**Figure 1.** <sup>29</sup>Si NMR shifts of different terphenylsilylium ions: (black) molecules with preferential  $\pi$ -arene $\rightarrow$ Si interactions; (blue) molecules with preferential halogen $\rightarrow$ Si interactions. Solvent, C<sub>6</sub>D<sub>6</sub>; anion, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>.

Scheme 1



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 <sup>13</sup>C NMR shifts of the lateral rings in these cations is consistent with  $\eta^1 \pi$  coordination by the C<sub>ortho</sub> atoms of the methylated rings.<sup>6</sup> 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.

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.<sup>7</sup> In the specific cases, two minima were predicted for 1a and 1b, with halogen $\rightarrow$ Si preferred over  $\pi$ -arene $\rightarrow$ Si, whereas only a single  $\pi$ -arene $\rightarrow$ Si conformation was predicted for 1c and 1d.

Computational structural predictions fully matched the solidstate 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

 <sup>29</sup>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,  $B(C_6F_5)_4^{-1}$ .



**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 $\rightarrow$ Si and  $\pi$ -arene $\rightarrow$ Si interactions.

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<sub>3</sub>SiF (Table 2).<sup>9</sup> X-ray analysis of 1d revealed  $\pi$  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<sub>4</sub>Si.<sup>9</sup> 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<sub>3</sub>CH; however, cation **2a** was not observed. Instead, several decomposition products, including fluorosilane **2a**–F, were formed.<sup>10,11</sup> In contrast, **2b** was generated cleanly. <sup>13</sup>C NMR analysis<sup>6</sup> of [**2b** $][B(C_6F_5)_4]$  revealed a

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for the
Single-Crystal X-ray Structures and the Calculated C <sub>1</sub> Con-
formers of 1a and 1d

la			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
$\Sigma C-Si-C$	356.8(1)	356.58	$\Sigma C-Si-C$	345.5(2)	349.94
dfp-Si <sup>a</sup>	0.190(1)	0.198	dfp-Si <sup>a</sup>	0.413(1)	0.344
dihedral angle <sup>b</sup>	$29.4(1)^{c}$	29.90	dihedral angle <sup>b</sup>	$45.3(1)^d$	50.54

<sup>*a*</sup> Distance between the Si atom and the plane defined by the three C atoms bound to Si. <sup>*b*</sup> Angle between the least-squares planes of a flanking ring and the central ring. <sup>*c*</sup> Between the ring containing F1 and the central ring. <sup>*d*</sup> 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.

 $C_{ortho}$ –Si  $\pi$  coordination comparable in strength to that of Ib, although their  $\delta$ (<sup>29</sup>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  $iPr_3-CB_{11}H_6Cl_6$ ;<sup>12</sup> coordination of **2b** by the anion causes a pyramidalization of the silicon center, as shown by the sum of angles around silicon [ $\Sigma C-Si-C = 351.40(12)^\circ$ ] and by the corresponding out-of-plane distance [dfp-Si = 0.3154(4) Å].<sup>13</sup>

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  $\pi$  basicity and no possible halogen—Si interactions (2) poorly accommodate the avidity of Si<sup>+</sup> for electron density, allowing coordination by anions as weakly basic as carborane (CB<sub>11</sub>H<sub>6</sub>Cl<sub>6</sub><sup>-</sup>) 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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(13) Bond lengths and angles are listed in the Supporting Information.