Silyl Lewis Acids

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Synthesis of 2,6-Diarylphenyldimethylsilyl Cations: Polar-π Distribution of Cation Character**

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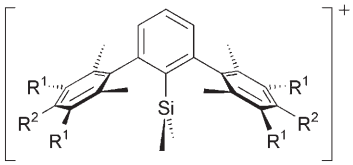
Dedicated to Kurt Mislow on the occasion of his 85th birthday

Discussion of the toluene solvate of the triethylsilyl cation brought to the fore the incredible reactivity of three-coordinate silyl cations and the ease with which they could be pacified by polar-π (p-π) interactions.[1,2] Isolation of the solvent-free trimesitylsilylium ion, prepared from allyltrimesitylsilane and an allyl abstraction reagent, demonstrated the relative thermodynamic stability of sterically sheltered naked silyl cations.[3] A combination of these seminal works provokes the synthesis of a new family of silyl cations, wherein the proximal environment rich in π electron density modulates the cation character at the silicon center,[4] and leads to a class of tunable silyl Lewis acids.

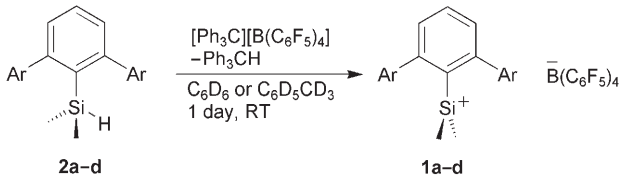
We chose **1** as our target class of cations.[5] The premise was that the 2,6-diarylphenyl scaffold would offer steric



	R^1	R^2
1a	H	H
1b	H	CH_3
1c	CH_3	H
1d	CH_3	CH_3

protection of the Si center, as well as a thermodynamic stabilization of the entire cation by p-π interactions.[6,7] The flanking rings, which have restricted rotation about the biaryl bonds in the 2- and 6-positions, should prevent anion and solvent molecules from interacting with the positively charged cavity. Donation of π(aryl) electron density into the empty 3p(Si) orbital was expected to lead to a reduced amount of positive charge on the silicon center and a decreased silyl Lewis acidity. The degree of π donation should be influenced by the varying number of electron-donating methyl groups on the flanking rings.[8]

Cations **1** were synthesized in three steps from 1,3-dichloro-2-iodobenzene. The Hart reaction enables the formation of crystalline iodoterphenyls.[9] Lithiation and reaction with chlorodimethylsilane gave hydrosilanes **2**.[10] Treatment of **2** with the trityl salt $[Ph_3C][B(C_6F_5)_4]$ in $[D_6]$benzene or $[D_8]$toluene at room temperature produced **1**-$B(C_6F_5)_4$ and triphenylmethane in approximately 90% yield, as determined by ^1H NMR integrals (Scheme 1).



Scheme 1. Synthesis of **1a–d**-$B(C_6F_5)_4$. Silane educts **2a–d** bear the same aryl substituents as **1a–d**.

Conformational analysis of cations **1** reveals a hierarchical set of symmetric conformers. Viewing down the Si–C_{aryl} bond, one can classify these conformers by the torsion angle of the aryl substituents (orthogonal (O) versus skewed (S)) and the position of the silyl group (central (C) versus lateral (L)). The OCO, OL–O, SCS, and SL–O conformers have C_{2v} C_s, C_2, and C_1 symmetry, respectively (Figure 1; Table 1).

Hybrid density functional computations (B3LYP/DZ-(2df,pd)) including full geometry optimizations and prediction of ^{29}Si NMR shifts were performed on the set of conformers over the class of cations **1**.[11] For all cations, the C_1 conformer is predicted to be the most stable geometry, and the C_2, C_s, and C_{2v} conformers have less stable geometries.[12] The calculated ^{29}Si NMR shifts are dramatically lower for the C_1 conformer, whereas those for the C_2, C_s, and C_{2v} structures are much higher, suggesting a specific silicon–arene interaction in the C_1 conformer; a short Si···C_{aryl} contact is predicted (2.11 Å). Increasing electron-donor character of the rings is reflected in the predicted ^{29}Si NMR shifts.

The ^1H and ^{13}C NMR spectra of **1a–d** display a signal degeneracy that cannot exclude a C_{2v} cation; however, signal isochrony is not conclusive because it may arise either from a static C_{2v} cation or a fast equilibrium among lower symmetry conformers. Therefore a detailed NMR analysis was undertaken.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.
CCDC 668197 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

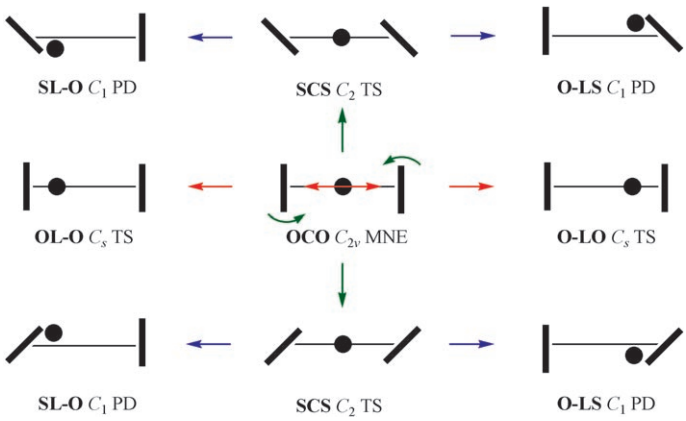


Figure 1. Idealized conformations of cations **1** viewed in plane and down the silyl to phenyl axis: Black dot = SiR_2; horizontal line = middle phenyl ring; vertical lines = flanking aryl groups. Conformation, symmetry and nature of the stationary point annotated below (PD = positive definite; TS = transition state; MNE = multiple negative eigenvalues).

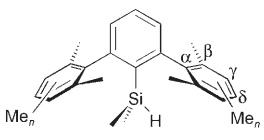
Table 1: B3LYP/DZ(2df,pd) calculated relative energies and ^{29}Si NMR shifts for **1a–d**.[a]

	SL-O (O-LS)	SCS	OL-O (O-LO)	OCO
1a	0.0 [74.2]	3.38 [192.4]	6.27 [138.9]	5.68 [248.6]
1b	0.0 [72.8]	4.07 [187.0]	7.15 [123.0]	10.51 [239.8]
1c	0.0 [54.2]	3.16 [169.9]	7.51 [130.0]	11.77 [240.8]
1d	0.0 [49.7]	3.48 [166.6]	7.82 [109.9]	12.34 [233.2]

[a] Energy units are in kcal mol^{-1} and NMR shift values shown in square brackets are in ppm relative to $SiMe_4$.

The ^{29}Si NMR shifts for **1a–d** in [D_6]benzene are $\delta = 80.1$, 79.1, 60.6, and 58.6 ppm, respectively, relative to tetramethylsilane (Table 2). The trend reflects the anticipated increase in shielding of the ^{29}Si nucleus with increasing electron-donor ability of the flanking rings as predicted in the computations; however, the magnitude of the shift is far from the predicted value of about $\delta = 200$ ppm predicted for the OCO C_{2v} conformer. The range of values ($\delta = 60$–80 ppm) implies a significant residual positive charge on the silicon center, similar to that predicted for the C_1 isomer ($\delta = 50$–75 ppm) or a Si^+–arene complex ($\delta = 70$–80 ppm).

Table 2: ^{29}Si and ^{13}C NMR shifts of **1** and **2**.[a]



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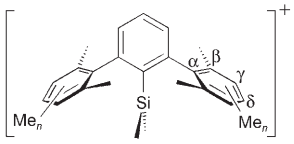

1

	Si	C_α	C_β	C_γ	C_δ
2a	−23.0	143.4	136.3	127.5	127.6
1a	80.1	153.4	130.1	139.4	131.0
2b	−23.0	140.7	136.1	128.3	136.7
1b	79.1	150.7	130.0	139.9	141.9
2c	−23.2	143.5	133.5	132.1	130.9
1c	60.6	155.2	124.4	151.6	133.8
2d	−23.2	141.3	132.1	131.7	133.8
1d	58.6	152.8	123.8	150.7	138.8

[a] Values in ppm in [D_6]benzene; ^{13}C signals referenced against solvent peak, ^{29}Si signals referenced against external $SiMe_4$.

For silyl cations interacting with aromatic solvents, a ^{29}Si NMR shift difference of $\Delta\delta > 10$ ppm has been observed upon solvent change from benzene to toluene.[1b] The ^{29}Si NMR shift of **1b**-B(C_6F_5)$_4$ is $\delta = 79.1$ ppm independent of whether the solvent is [D_6]benzene or [D_8]toluene, and ^{19}F NMR spectra of all **1**-B(C_6F_5)$_4$ species in [D_6]benzene are identical to free B(C_6F_5)$_4^-$ within 0.1 ppm. There appears to be little interaction of the cations with either solvent or counterion, and on the basis of ^{29}Si NMR shift values and the computational data, a C_1 structure for **1** would seem to be favored.

An analysis of the NMR signals of the lateral aryl carbon atoms was carried out to see if the differential shifts revealed any preferred interactions. Chemical shift assignments were determined by ^{1}H/^{13}C HSQC and ^{1}H/^{13}C HMBC spectroscopy (Table 2). The C_α, C_γ, and C_δ aryl carbon atoms in **1** are deshielded relative to those in precursors **2**, and the shift effects are greater than 10 ppm for the C_α and C_γ atoms; in contrast, the C_β atom is shielded by 6–9 ppm. In addition, ^{1}H/^{13}C and ^{1}H/^{29}Si HMBC spectra showed cross-peaks between C_β and SiCH_3 as well as between H_3C-C_β and the Si center, probably caused by $^3J_{C,H}$ and $^3J_{Si,H}$ coupling, respectively.

Wheland complexes display an upfield shift of the ^{13}C signal of the tetracoordinate atom relative to those of free arenes, whereas the other carbon atoms are more deshielded.[13] For the heptamethylbenzenium ion, for example, large signal shifts of 57 ppm (C_{ipso}), 198 ppm (C_{ortho}), 139 ppm (C_{meta}), and 191 ppm (C_{para}) are observed (hexamethylbenzene has a shift of $\delta = 133$ ppm).[14] Complex formation between Et_3Si^+ and toluene produces a similar but far less pronounced effect on the NMR shifts of the aryl carbon atoms.[1,15] Accordingly, the ^{13}C NMR data of **1** suggest a silicon–arene interaction primarily involving the C_β carbon atoms, with some of the positive charge residing on the aryl π systems, but weaker than in a full Wheland intermediate.

The ^{13}C $\Delta\delta$ patterns point to the C_β site on the flanking arene as the dominant site of the interaction, but do not resolve whether all four C_β sites interact simultaneously through the C_{2v} conformation or each C_β site contributes through an equilibrium of lower symmetry geometries with the silicon–arene interactions. The C_{2v} and C_s conformers seem geometrically unreasonable, as silicon would have to interact with two C_β atoms of the same ring without interacting with C_α atoms. On the other hand, the NMR data are consistent with either a C_2 or C_1 base geometry for **1**, and a dynamic equilibrium among two C_2 or four C_1 forms to account for the observed signal isochrony at room temperature.

Low-temperature NMR experiments carried out with **1b** in [D_8]toluene from 0 to −30 °C indicated an upper energy barrier limit of 51 kJ mol^{-1} for possible equilibrium processes. Below −30 °C, increased viscosity of the product solution foiled the acquisition of additional spectra. Thus, although the measured ^{29}Si NMR shifts are in good agreement with one silicon–arene interaction (for example [Et_3Si(toluene)]$^+$

shows a ^{29}Si shift of $\delta = 94$ ppm),[1] the presence of the C_2 conformer of **1** in solution could not be excluded rigorously.

Direct evidence for a specific and singular Si–C_β interaction comes from the solid state structure of **1c**. Crystals of composition **1c**-$B(C_6F_5)_4$·0.5 C_6H_5F were obtained from a C_6H_5F/C_6H_{14} solvent mixture at −20 °C. X-ray crystallographic analysis revealed the anion and solvent molecules to be well separated from the cation, which possesses the C_1 conformation predicted by computation and hypothesized from NMR data (Figure 2). The Si–C22 distance is

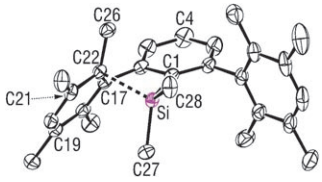

Figure 2. Molecular structure of **1c**-$B(C_6F_5)_4$·0.5 C_6H_5F in the crystal (anion, H atoms, and C_6H_5F omitted; displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: Si–C22 2.126(1), Si–C1 1.853(1), Si–C27 1.838(2), Si–C28 1.846(2); C1-Si-C27 114.53(8), C1-Si-C28 119.24(7), C27-Si-C28 112.3(1), C17-C22-C21 118.1(1), C17-C22-C26 117.7(1), C21-C22-C26 116.8(1), C19-C22-Si 102.79(6), C4-C1-Si 167.05(8).

2.126(1) Å, which is about 0.29 Å or 16% longer than an average Si–C bond (bond order is approximately 0.66). The geometry around the silicon atom is pyramidal; the sum of the covalent bond angles around Si is 346.1(1)°, and the Si center is about 0.40 Å out of the plane of the three covalently bound carbon atoms. In contrast, the ring interacting with silicon is less distorted; the sum of covalent bond angles around atom C22 is 352.6(2)°, and atom C22 exhibits a distance of only about 0.24 Å from the plane defined by atoms C17, C21, and C26. From the results of the X-ray crystallographic analysis, the structure of **1c** is best described as an η^1 π coordination of the tetramethylphenyl ring to the $SiArMe_2$ moiety, which possesses some, but by no means full, silyl cationic character.

The computational geometries for **1** are excellent. The predicted Si–C22 bond length (2.11 Å) lies close to the experimentally determined distance of 2.126(1) Å. A visual overlay of the calculated and experimental C_1 structures of **1c** is shown in Figure 3.

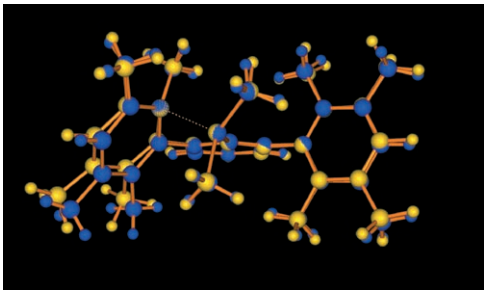

Figure 3. Overlay of calculated (yellow) and experimental (blue) structure of **1c**.

In light of the computational predictions, an outlook for future study is clear. According to theoretical predictions, cations **1** are best stabilized and silicon least positively charged when one unsymmetrical C_β–Si interaction is present; however, the energy differences between C_1 and the more symmetrical C_s and C_{2v} structures decreases with less electron-rich flanking aryl rings. Thus, cations with less Lewis basic aryl systems should favor C_2 or C_{2v} conformers, and observation of ^{29}Si NMR shifts above $\delta = 150$ ppm would provide strong evidence for their existence in solution.

In conclusion, a new class of pacified silyl cations has been developed and the structures examined in solution and, in one case, in the solid state. The housetop-like terphenyl scaffold provides the desired shroud for tunable π-electron donation and, therefore, silyl Lewis acid character. Variation of the 2,6-diarylphenyl fragment offers the possibility of an even more electron-deficient dimethylsilyl fragment and also enantiomerically pure and stereoisomerically stable structures through restricted rotation about the biaryl bonds at the 2- and 6-positions. Such efforts are ongoing.

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[10] Compounds **2a–d** are inert in air for months. Compounds **2b–d** were purified by recrystallization.
[11] Computational methods: Conformational analyses of **1a–d**, including structural, orbital, and property calculations, were carried out using the Gaussian98[11a] and GAMESS[11b] software packages. The computations employ a variety of levels of theory for comparative purposes. Wavefunction-based methods considered include Hartree–Fock, second order Møller–Plesset perturbation theory (MP2),[11c] and hybrid density functional theory (HDFT), using the B3LYP functional. The B3LYP functional uses the Becke's three-parameter functional[11a] in combination with nonlocal correlation provided by the Lee–Yang–Parr expression[11e,f] with both local and nonlocal terms, B3LYP. Dunning's double-ζ polarized sets, denoted DZ(2d,p) and DZ(2df,pd), were employed.[11g] Full geometry optimizations were performed and uniquely characterized by second derivatives (Hessian) analysis to determine the number of imaginary frequencies (0 = minima; 1 = transition state). Ionization potentials were predicted using Koopmans' theorem approximation[11h] as well as the more accurate ΔSCF computation.[11i,j] From the fully optimized structures, single-point NMR computations were performed, using the class III GIAO method.[11k,l] This method is most efficient in terms of convergence of chemical shift values as a function of basis set, and enables the most reliable predictions with relatively modest basis sets. In fact, comparisons of DZ(2d,p) vs DZ(2df,pd) reveal no significant advantage to the latter over the former. All predictions are calibrated with respect to TMS. Molecular orbital contour plots, used as an aid in the analysis of results, were generated and depicted using the programs 3D-PLTORB,[11m] and QMView[11n]: a) Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**; b) M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, S. T. Elbert, *J. Comput. Chem.* **1993**, *14*, 1347; c) C. Moøller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618; d) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; e) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; f) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200; g) T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007; h) T. Koopmans, *Physica* **1934**, *1*, 104; i) J. Almlof, B. Roos, U. Wahlgren, H. Johansen, *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 51; j) K. D. Jordan, M. N. Paddon-Row, *J. Phys. Chem.* **1992**, *96*, 1188; k) R. Ditchfield, *J. Chem. Phys.* **1972**, *56*, 5688; l) K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251; m) *3D-PLTORB*: San Diego, 3D version: **1997**; n) K. K. Baldridge, J. P. Greenberg, *J. Mol. Graphics* **1995**, *13*, 63.
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