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Hydrogen- and Fluorine-Bridged Disilyl Cations and Their Use in Catalytic C−F Activation

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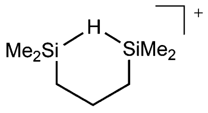
Abstract: The hydrogen-bridged disilyl cation **6** with an 1,8-naphthalenediyl backbone was synthesized and was characterized by NMR spectroscopy and X-ray crystallography, supported by quantum mechanical computations. The SiHSi linkage is symmetrical, corresponding to a single minimum potential, and the structural parameters are in agreement with the presence of a two electron−three center bond in **6**. Treatment of disilyl cation **6** with alkyl fluorides yields the disilylfluoronium ion **10**. The SiFSi group in the disilyl fluoronium ion **10** is symmetrical with an average SiF bond length of 175.9(8) and a bent angle $\beta = 130°$. Both cations catalyze the hydrodefluorination reaction of alkyl and benzyl fluorides to give alkanes.

Introduction

Multiple-center bonding is a common feature in the chemistry of electron-deficient compounds of the early s- and p-block elements. For silicon this type of bonding is possible in low-valent species such as silylium ions. Recently, disilyl cation **1** with a symmetric SiHSi bridge was synthesized in our laboratories and was characterized by multinuclear NMR spectroscopy supported by the results of quantum mechanical calculations.[1] Consecutively, the group of Sekiguchi characterized silyl cation **2** by NMR spectroscopy[2] and Lickiss and co-workers report in a preliminary note selected details from the solid-state structure of the tetrakis(pentafluorophenyl)borate ($[B(C_6F_5)_4]^-$, TPFPB) salt of cation **3**.[3] Recently, Reed and colleagues were able to crystallize carborane salts of simple hydrogen-bridged disilyl cations, **4**.[4] A similar bonding situation to that in **1** was found in neutral silylated vinylboranes **5** which were described by Wrackmeyer and co-workers.[5] These authors also noticed an enhanced reactivity of the Si−H linkage toward CC multiple bonds in hydrosilylation reactions.[5a,d]



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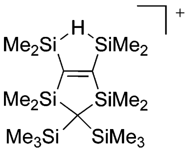

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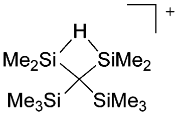

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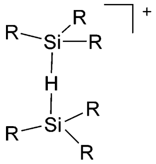

R = Me, Et

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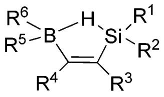

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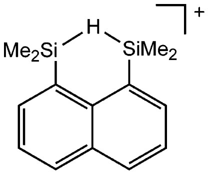
Although disilyl cation **1** is stable at room temperature, its high reactivity prevented a thorough study of its chemistry. In an attempt to increase the stability of the cation and to fix the two silyl groups spatially in a suitable conformation for the formation of the SiHSi linkage, we envisaged disilyl cation **6** with a naphthyl backbone as a target molecule. The close relation of cation **6** to the isolobal hydrogen-bridged boranate **7**, synthesized by Katz,[6] is obvious and opens intriguing possibilities[7] for the follow-up chemistry based on disilyl cation **6**. Here we describe the synthesis and structural characterization



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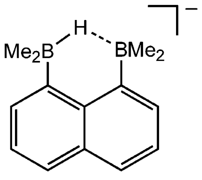

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[1] (a) Müller, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 3033. (b) Müller, T. In *Organosilicon Chemistry V*; Auner, N., Weis, J., Eds.; Wiley-VCH: New York, 2003, p 34.

[2] Sekiguchi, A.; Muratami, A.; Fukaya, N.; Kabe, Y. *Chem. Lett.* **2004**, *33*, 530.

[3] Lickiss, P. D.; Masangane, P. C. Sohal, W.; Veneziani, G. L. In *Organosilicon Chemistry V;* Auner, N., Weis, J., Eds.; Wiley-VCH: New York, 2003, p 45.

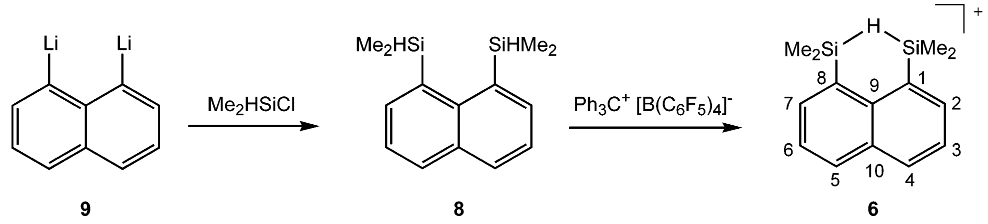
[4] Hoffmann, S. P.; Kato, T. Tham, F. S.; Reed, C. A. *Chem. Commun*. **2006**, 767.

[5] (a) Wrackmeyer, B.; Tok, O. L.; Bubnov, Y. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 124. (b) Wrackmeyer, B.; Tok, O. L. *Magn. Reson. Chem.* **2002**, *40*, 406. (c) Wrackmeyer, B.; Milius, W.; Tok, O. L. *Chem. Eur. J.* **2003**, *9*, 4732. (d) Wrackmeyer, B.; Tok, O. L.; Bubnov, Y. N. *Appl. Organomet. Chem.* **2004**, *18*, 43. (e) Wrackmeyer, B.; Tok, O. L.; Khan, A.; Badshah, A. *Appl. Organomet. Chem.* **2005**, *19*, 1249. (f) Wrackmeyer, B.; Tok, O. L.; Khan, A.; Badshah, A. *Appl. Organomet. Chem.* **2006**, *20*, 99.

[6] (a) Katz, H. E. *J. Am. Chem. Soc.* **1985**, *107*, 1420. (b) Katz, H. E. *J. Org. Chem*. **1985**, *50*, 5027.

10.1021/ja061800y CCC: $33.50

Scheme 1. Synthesis of Disilyl Cation **6**



of cation **6**, the transformation of cation **6** to an unusual disilylated fluoronium ion, and the use of both cations in a catalytic hydrodefluorination reaction.[8]

Results and Discussion

The precursor naphthyl silane **8** was obtained in satisfactory yield from the reaction of 1,8-dilithionaphthalene **9** [9] with dimethylchlorosilane and characterized by standard techniques (see Scheme 1 and, for details, the Experimental Section). Hydridobridged disilyl cation **6** was prepared by reaction of **8** with trityl cation in benzene or toluene as described previously for cation **1** (see Scheme 1).[1] The counteranion in this reaction was TPFPB. The salt **6**·TPFPB was isolated as a white-brown glassy amorphous solid, which was recrystallized from C_6F_6 to obtain colorless crystals.

The 1,8-naphthalenediyl backbone confers to cation **6** high stability, that is, while the cyclic cation **1** decomposes at temperatures higher than room temperature, cation **6** is stable for 3 days in toluene at 90 °C. This increased stability greatly simplifies the manipulation of the compound and allows studying its reactivity in detail.

Cation **6** is clearly identified by its characteristic ^{1}H and ^{29}Si NMR resonances, which closely resemble those found for the cation **1** and the related cation **2**.[1,2] The unusually shielded ^{1}H NMR signal for the SiH group in **6** (δ ^{1}H = 3.34, $\Delta\delta$ ^{1}H = −1.85 compared to silane **8**)[10] indicates its hydrogen-bridged structure. In addition, the deshielded ^{29}Si NMR resonance at δ ^{29}Si = 54.4 splits in the ^{1}H-coupled ^{29}Si INEPT spectra into a doublet of multiplets with a ^1J(SiH) coupling constant of 46 Hz, which was also identified in the ^{1}H NMR spectra. This remarkably small ^1J(SiH) coupling constant must be compared to ^1J(SiH) = 193 Hz found for the precursor silane **8** and it is characteristic for the SiHSi linkage in disilyl cations.[1,2] A similar reduction is found for the ^3J(HSiCH$_3$) coupling constant between the methyl protons and the bridging hydrogen atom (^3J(HSiCH$_3$) = 1.8 Hz in **6**, compared to 3.3 Hz found for silane **8**). The NMR spectroscopic parameters are independent from the solvent, as indicated by the nearly identical chemical shifts detected in benzene-d_6 and in toluene-d_8 (see Table 1).[11] Therefore, the interactions between solvent and cation are small as long as arenes are used as solvents.[11b]

Table 1. Selected NMR Parameter for Cations **6** and **10**

compd	X	δ^{29}Si	$\lvert ^1J(\mathrm{SiXSi})\rvert$, Hz	δ X	$^3J(\mathrm{XSiC}H_3)$, Hz
6[a]	H	54.4	45.7	3.34	1.8
6[b]	H	62.5	42.3	4.06	2.1[c]
6[d]	H	54.4		3.33	
10[a]	F	77.2	243.0	−144.0	13.7
10[d]	F	77.2	243.0	−144.2	

[a] In benzene-d_6 at 303 K. [b] Computed at GIAO/B3LYP/6-311G(2d,p)//MP2/6-31G(d,p). Chemical shifts δ reported relative to computed σ(^{29}Si, TMS) = 329.14 and σ(^{1}H, TMS) = 32.06. [c] Mean value of three ^3J(HH) values: 4.7, 0.6, and 1.1 Hz. [d] In toluene-d_8 at 303 K.

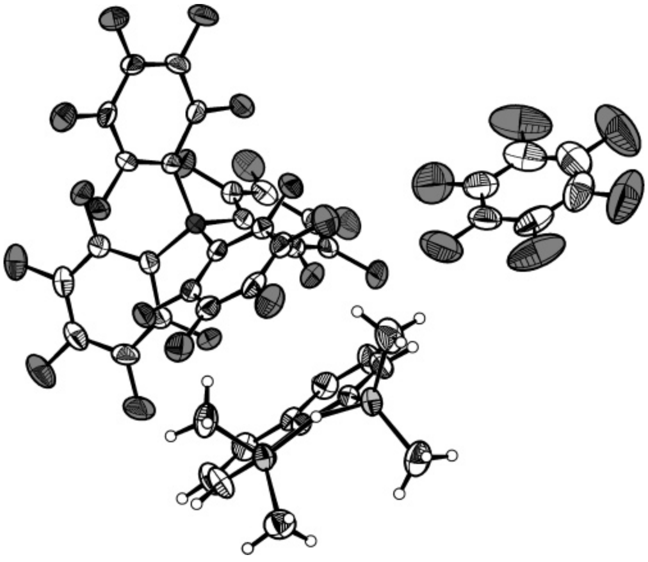


Figure 1. Ortep plot of the asymmetric unit of **6**·TPFPB·C_6F_6. (Color code: B, dark gray, F, medium gray; Si, light gray; C, white. Thermal ellipsoids are drawn at the 50% probability level).

Colorless crystals suitable for X-ray analysis were obtained by recrystallization of **6**·TPFPB from C_6F_6. The solid-state structure of the salt reveals an asymmetric unit that contains the cation **6** and the TPFPB anion along with one molecule of the solvent C_6F_6 (see Figure 1). The cation is well-separated from the anion and from the C_6F_6 molecule. The nearest approach between the cation **6** and C_6F_6 is 325.0(8) pm (between F and C^2), while the closest contact between **6** and the TPFPB anion is 326.6(5) pm (between F and C^1).[14]

The two silicon atoms in cation **6** are tetracoordinated. The relatively small sum of bonding angles α involving silicon and

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(7) See, for example, the chemistry of the 1,8-substituted boranes and gallanes: (a) Hoefelmeyer, J. D.; Schulte, M.; Tschinkl, M.; Gabbaï, F. P. *Coord. Chem. Rev.* **2002**, *235*, 93. (b) Melaimi, M.; Gabbaï, F. P. *Adv. Organomet. Chem.* **2005**, *53*, 61.

(8) Scott, V. J. Çelenligil-Çetin, R.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 2852.

(9) Neugebauer, W.; Clark, T.; Schleyer, P. v. R. *Chem. Ber.* **1983**, *116*, 3283.

(10) $\Delta\delta$ is calculated as $\Delta\delta = \delta(\mathbf{6}) - \delta(\mathbf{8})$.

(11) (a) For R$_3$Si$^+$ solvent effects on δ ^{29}Si up to 10 ppm are reported (R = alkyl), e.g. R = Et: δ ^{29}Si (Et$_3$SiC$_6$H$_6$)$^+$ = 92; δ ^{29}Si (Et$_3$SiC$_7$H$_8$)$^+$ = 82.[12,13] (b) Addition of solvents of higher nucleophilicity leads to reactions between the cation and the solvent. For example, in the presence of pivaloyl nitrile the corresponding iminium ion is formed as indicated by NMR spectroscopy.

(12) For a recent review on organometallic cations of group 14 elements including silylium ions, see: Müller, T. *Adv. Organomet. Chem.* **2005**, *53*, 155.

(13) (a) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917. (b) Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430.

(14) The distances between the silicon atoms and this fluorine atom are 351.6(5) and 389.9(6) pm, well beyond the sum of the van der Waals radii of the elements Si and F (320 pm).

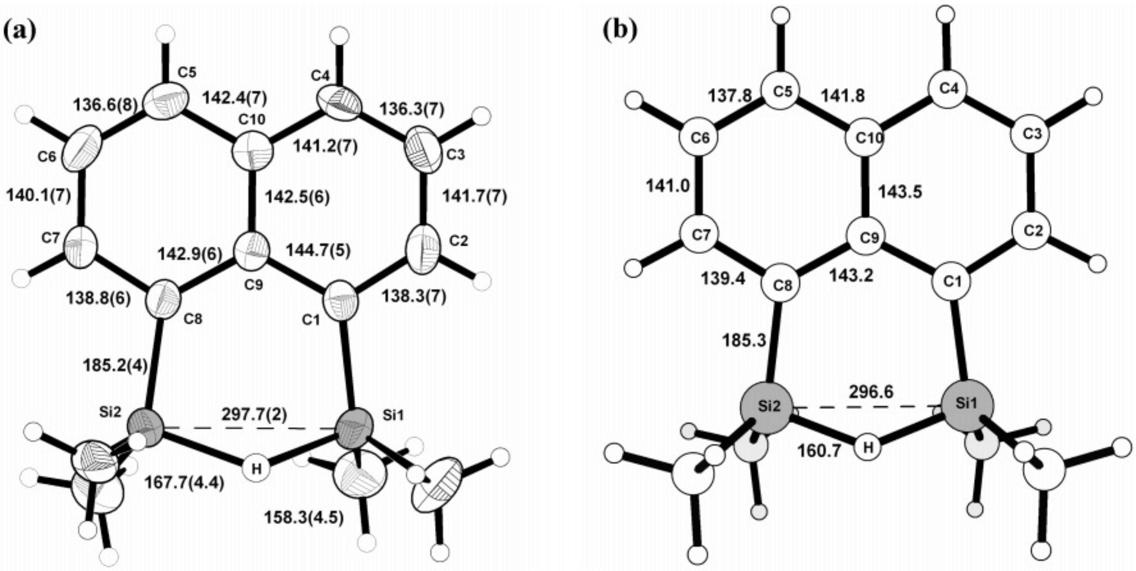

Figure 2. (a) Experimental molecular structure of disilyl cation **6**. Thermal ellipsoids are drawn at the 50% probability level. (b) Computed structure of disilyl cation **6** (at MP2/6-31G(d,p), molecular point group C_s; bond lengths are given in picometers).

its carbon neighbors for both silyl groups, $\sum\alpha$, indicates, however, considerable variations toward planarity ($\sum\alpha = 345.5°$ and 346.7°, which must be compared to the value for ideal tetrahedral environment $\sum\alpha = 328.4°$ and for trigonal planar coordination $\sum\alpha = 360°$). Such relative large $\sum\alpha$ values are reported for complexes between silylium ions with solvent molecules [e.g., $\sum\alpha = 341.4(5)°$ and 342.6(5)° for $[Et_3SiC_7H_8]^+$]^{12,13,15}, with anions [e.g., $\sum\alpha = 345.0(10)°$ and 349.0(9)° for $[Et_3Si][Br_6CB_{11}H_6]$]^{12,15,16} and, quite recently, also for the hydrogen-bridged disilyl cation **4** ($\sum\alpha = 350.1°$).[4] The silicon atoms are slightly bent out of the plane defined by the naphthyl ring [$\vartheta(Si^1C^1C^9C^{10}) = 4°$ and ($\vartheta(Si^2C^8C^9C^{10}) = 11°$]. They form a six-membered ring in a distorted half-chair conformation with the bridging hydrogen atom.

Although the position of the bridging hydrogen atom in **6** was detected in the differential Fourier analysis and the coordinates of the hydrogen atom were refined, the exact bonding parameters of the SiHSi linkage in cation **6** are subject to appreciable errors. Within the error margins the SiHSi bond is symmetrical with an SiHSi bond angle $\beta = 132(3)°$ (see Figure 2). A slightly unsymmetrical structure, however, cannot be excluded on the basis of these experimental data. In contrast, the heavy atom distances in cation **6** are well-defined and can be used to gauge the quality of geometries predicted by quantum mechanical calculations.[17] Ab initio calculations at the MP2/6-31G(d,p) level of theory predict for cation **6** a geometry that is very similar to the experimental structure (see Figure 2).[18] In particular, nearly all heavy atom distances predicted by the calculations are within the error margins of the experimental structure. In addition, the computations predict a symmetric SiHSi bridge with a long Si−H distance of 160.7 pm. The close accordance between theory and experiment is further substantiated by the comparison of the computed δ ^{29}Si NMR chemical shift[20] and the $^1J(SiH)$ coupling constant[22] for cation **6** with the experimental data (see Table 1).[1,12,23,24] A further analysis of the computed spin−spin coupling constants[22] for cation **6** reveals that the unusually small $^1J(SiH)$ coupling (calculated, 42.3 Hz; experimental, 45.7 Hz) is a consequence of the strongly reduced Fermi contact (Fc) term.[25] This result suggests a very small 3s(Si)-orbital contribution for the Si−H bonds, in agreement with a natural bond order (NBO) analysis at the HF/6-311G(d,p) level of theory[26] that indicates a contribution of the 3s(Si) orbitals to the Si−H−Si bond of less than 10%. Therefore, the accumulated experimental and theoretical data suggest for cation **6** a hydrogen-bridged structure with a *symmetrical* two electron−three center SiHSi bond similar to that found previously for

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(15) In the crystal structure of the salts $[Et_3SiC_7H_8]^+$·TPFPB and $[Et_3Si][Br_6CB_{11}H_6]$ two independent cations were found.

(16) Xie, Z.; Bau, R.; Benesi, A.; Reed, C. A. *Organometallics* **1995**, *14*, 3933.

(17) All computations were done with Gaussian 03, Revision B.03 (Frisch, M. J. et al. Gaussian, Inc., Pittsburgh, PA, 2003).

(18) Cation **6** was initially optimized using C_s symmetry at the hybrid density functional B3LYP level of theory[19] in connection with the 6-31G(d,p) basis. A subsequent frequency calculation was used to verify the nature of the stationary point as a minimum. This structure was used as a starting point for the subsequent MP2/6-31G(d,p) optimization. The geometry (see Supporting Information) obtained at the B3LYP/6-31G(d,p) level is very close to that obtained at the MP2 level; i.e., $d(SiSi) = 301.2$ pm, $d(SiH) = 162.1$ pm and $\alpha(SiHSi) = 136.5°$. A second minimum structure of **6** at B3LYP/6-31G(d,p) has C_2 symmetry. **6**(C_2) is not only very close in energy to **6**, but it is also geometrically nearly identically to **6** (see Supporting Information for further details).

(19) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (d) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612.

(20) NMR parameters were calculated for the MP2/6-31G(d,p)-optimized geometry using the gauge independent atomic orbital (GIAO) method[21] and a 6-311G(2d,p) basis set.

(21) (a) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. (b) Wolinski, K.; Hilton J. F.; Pulay, P. *J. Am. Chem. Soc.* **1982**, *104*, 5667. (c) Cheeseman, J.; Trucks, G. W.; Keith, T. A.; Frisch, M. *J. Chem. Phys.* **1996**, *104*, 5497.

(22) (a) Helgaker, T.; Watson, M.; Handy, N. C. *J. Chem. Phys*. **2000**, *113*, 9402. (b) Sychrovsky, V.; Gäfenstein, J.; Cremer, D. *J. Chem. Phys*. **2000**, *113*, 3530.

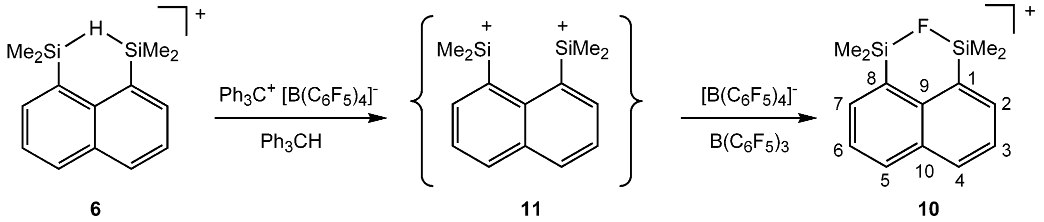
(23) ^{29}Si NMR computations for silylium ions and related compounds: (a) Maerker, C.; Schleyer, P. v. R. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, p 513. (b) Müller, T.; Zhao, Y.; Lambert, J. B. *Organometallics* **1998**, *17*, 278. (c) Kraka, E.; Sosa, C. P.; Gräfenstein, J.; Cremer, D. *Chem. Phys. Lett.* **1997**, 9 (279).

(24) For a monograph on the methodology, see*: Calculation of NMR and EPR Parameter;* Kaupp, M., Malkin, V. G., Bühl, M., Eds; Wiley-VCH: Weinheim, 2004.

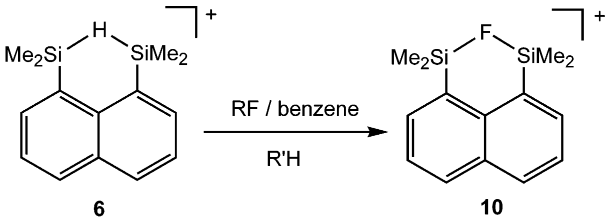
(25) The FC contribution to the $^1J(SiH)$ for **6** is calculated to be 40.2 Hz. This results in an overall $^1J(SiH) = 42.3$ Hz. These values must be compared with an FC contribution of 177.4 Hz predicted for silane **8** and an overall $^1J(SiH)$ coupling of $^1J(SiH) = 177.0$ Hz. (B3LYP/6-311G(2d,p)//MP2/6-31G(d,p)).

(26) (a) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO 4.0*; Theoretical Chemistry Institute, University of Wisconsin: Madison, WI, 1996. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

Scheme 2. Reaction of Cation **6** with Trityl Cation To Give Fluoronium Ion **10**



Scheme 3. Reaction of Cation **6** with Alkyl and Benzyl Fluorides To Give Fluoronium Ion **10**



R = $C_{10}H_{21}$, $C_6H_5CF_2$; R' = $C_{10}H_{21}$, $C_6H_5CH_2$

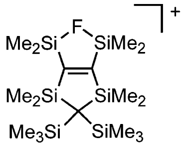
cation **1**.[1,27] The geometric parameters of the SiHSi linkage in **6** resemble that reported for the cations **3** and **4**. That is, the experimental SiH bond length in all three cations is very similar [165.5 pm (**3**), 163 pm (**6**) and 161 pm (**4**, R = Me)][28] and it slightly decreases with increasing SiHSi bent angle β [$\beta = 97.6°$ (**3**), 132(3)° (**6**), 160.1° (**4**, R = Me)].[3,4] Obviously the SiHSi bent angle β is a function of the ring size, steadily increasing from the four-membered cyclic cation **3** to the six-membered **6** and the acyclic cations **4**. In agreement, computations at the MP2/6-311G(d,p) level for cation **4** (Me), valid strictly only for the gas phase, predict a linear SiHSi linkage [r(SiH) = 160.8 pm, $\beta = 180°$].[29]

Hydride abstraction from cation **6** by trityl cation is an extremely slow process and it results in the exclusive formation of fluoronium ion **10** after 9 h at 75 °C in benzene. A possible intermediate in this reaction is the disilyl dication **11**, which instantaneously reacts with the weakly coordinating anion TPFPB with formation of **10**.[30] The only detectable byproducts in this reaction are $B(C_6F_5)_3$ and triphenylmethane, Ph_3CH (Scheme 2). After washing with pentane, the salt **10**·TPFPB was crystallized from toluene.

The same cation **10** is obtained under much milder conditions, when fluorodecane is used in the reaction with cation **6**. In this way, cation **10** is obtained nearly quantitatively from cation **6** along with decane after 3 h of stirring at 60 °C (Scheme 3). With benzyl trifluoride the reaction proceeds even at room temperature very fast and the only product detected besides the salt **10**·TPFPB is toluene. Interestingly, hexafluorobenzene, C_6F_6, is not reactive toward cation **6** and no conversion is observed, even after prolonged heating in toluene.

Therefore, there is a qualitative discrimination in the reactivity of cation **6** toward compounds with different kinds of C−F bonds, with benzylic C−F bonds being most reactive, intermediate reactivity versus C(sp^3)−F groups, and no reactivity versus C(aromatic)−F functionalities.

The ^{29}Si NMR chemical shift of δ ^{29}Si = 77.2, which is detected for cation **10**, indicates considerable charge accumulation at the silicon atoms. This chemical shift and the doublet splitting [^1J(SiF) = 243 Hz] are characteristic for the bissilylated fluoronium ions, and similar values are reported for fluoronium ion **12**.[2] The corresponding ^{19}F NMR [δ ^{19}F = −144.0; ^1J(FSi) = 243 Hz] and ^{13}C NMR data of oniumion **10** provide further evidence for its constitution (see Table 1 and Experimental Section). The ^{19}F NMR data might be compared to that of the neutral compound **13** (δ ^{19}F = −113.8), which shows at 240 K a degenerate fluorine exchange that is fast on the NMR time scale[31], and to that of the unsymmetrical fluorine bridged silicate anion **14** (δ ^{19}F = −70).[32,33] It is noteworthy that the fluorine atom in cation **10** is the most shielded along this series and that the ^1J(FSi) coupling constant is only slightly reduced compared to that of $PhSiMe_2F$ [^1J(FSi) = 278 Hz][34] in contrast to that found for the dynamic molecule **13** [^1J(FSi) = 127 Hz].[31] As already found for cation **6**, no solvent effects on the NMR chemical shifts of cation **10** were detected when the solvent was varied from benzene-d_6 to toluene-d_8 (see Table 1). This indicates also in this case negligible cation/solvent interactions at room temperature in solution.



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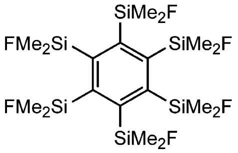

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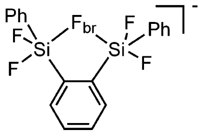

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Colorless crystals from the salt **10**·TPFPB were obtained from toluene solution. One molecule of the solvent toluene is found along with the cation **10** and the TPFPB anion in the asymmetric unit (see Figure 3a). While the cation and solvent molecule are well-separated [smallest C(toluene)−Si distance r(C^{meta}/Si) = 460.1(1.2) pm; smallest C(toluene)−F(**10**) distance r(C^{para}/F) = 550.3(1.0) pm], several relatively close contacts between the anion and cation can be detected (see Figure 3b). However, all contacts are beyond the sum of the van der Waals radii,

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(27) IR spectroscopy could be used to further characterize cation **6** and would give additional insight on the bonding. Computations predict an intensive band corresponding to ν_{as}(Si−H−Si) = 1966 cm^{-1} (at B3LYP/6-31G(d,p), unscaled harmonic frequency). All attempts however to record an IR spectrum of **6**·TPFPB, either dissolved in benzene-d_6 or without solvent, led to inconclusive results, most probably due to decomposition of **6** in the IR cell.

(28) The average SiH bond length for each cation is reported.

(29) Optimized structure at D_{3d} symmetry (see Supporting Information). Similar theoretical results are reported at the density functional level in ref 4.

(30) Preliminary evidence for the intermediate formation of disilyl dication **11** is provided by the reaction kinetics as obtained from ^{29}Si NMR spectroscopy. The disappearance of the NMR signal of the cation **6** follows a first-order rate law, while the appearance of the NMR signals of cation **10** is independent from the concentrations of cation **6** and **10** (zero-order rate law). This is in agreement with the existence of a short-living intermediate **11**.

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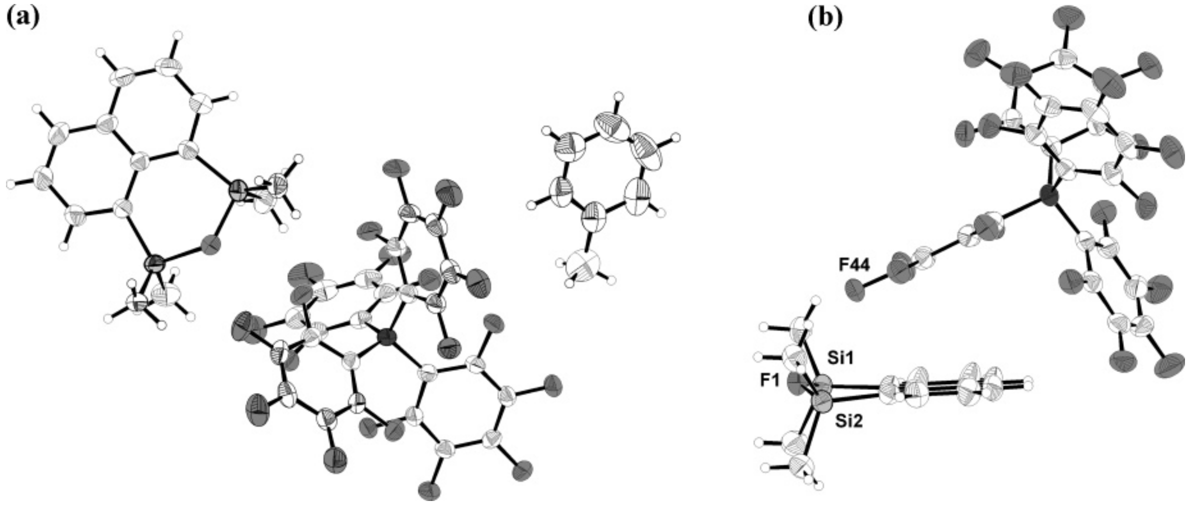


Figure 3. (a) Ortep plot of the asymmetric unit of **10**·TPFPB·C_7H_8. (Color code: B, dark gray; F, medium gray; Si, light gray; C, white. Thermal ellipsoids are drawn at the 50% probability level). (b) Closest contacts between the cation **10** and the TPFPB anion in the solid-state structure of **10**·TPFPB [Si1···F44 = 334.1(1.3) pm; Si2···F44 = 336.8(1.1) pm; F1···F44 = 293.8(8) pm].

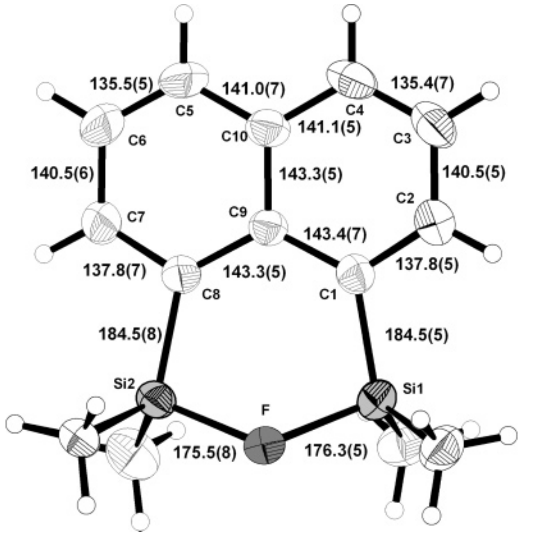
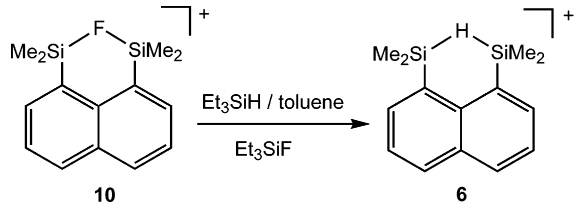


Figure 4. Ortep plot of cation **10** (bond lengths are given in picometers; color code: F, medium gray; Si, light gray; C, white. Thermal ellipsoids are drawn at the 50% probability level).

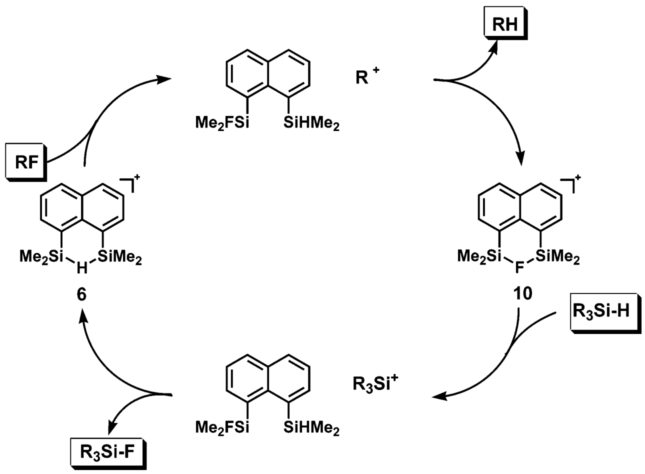
suggesting the absence of covalent interactions between anion and cation.[11,35]

The molecular structure of cation **10** reveals for the six-membered silicon-containing heterocycle a twisted half-chair conformation with tetrahedral coordinated silicon atoms (see Figure 4). Just as in the case of the hydrogen-bridged cation **6**, both silicon atoms show, however, strong variations toward a trigonal planar coordination, as measured by $\sum\alpha = 345.9°$ and 347.7°. The most prominent feature of the cation **10** is a symmetric bent Si−F−Si linkage (bent angle $\beta = 129.9°$) with SiF bond lengths that are clearly elongated compared to Si−F bonds in organosubstituted silyl fluorides (175.5 and 176.3 pm in cation **10** compared to 159.4 pm as the average Si−F bond length for tetracoordinated silicon fluorides,[36] see also Figure 4). The SiF bond lengths in cation **10** are intermediate between that found in the neutral compound **13** (168.4 pm) and the shorter SiF_{br} bond in the unsymmetrical fluorine-bridged silicate anion **14** (189.8 pm).

Scheme 4. Reaction of Fluoronium Ion **10** with Triethylsilane To Give Cation **6**



Scheme 5. Suggested Catalytic Hydrodefluorination Reaction



Interestingly, the fluoronium ion **10** is converted to the hydrogen-bridged cation **6** in 1 h by reaction with excess of triethylsilane in toluene at 50 °C (Scheme 4). The byproduct formed in this reaction is triethylsilyl fluoride. This result opens the possibility for the catalytic cycle, shown in Scheme 5, by which fluoroalkanes, RF, are converted to hydrocarbons, RH, by treatment with excess of Et_3SiH in the presence of catalytic amounts of either cation **6** or **10**. A quite similar catalytic C−F activation was recently described by Ozerov and co-workers, which utilized as catalyst a cationic silicon compound, generated from triethylsilane and the precatalyst trityl TPFPB.[8]

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(35) Sum of van der Waals radii: FF = 270 pm.

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Table 2. Catalytic Hydrodefluorination Reactions

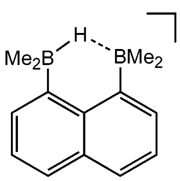
entry	RF	RH	*T*, °C	mol %	TON[a]
1	$C_{10}H_{21}F$	$C_{10}H_{22}$	25	2.2 (**6**)	45
2	$C_{10}H_{21}F$	$C_{10}H_{22}$	25	2.9 (**10**)	35
3	$C_6H_5CF_3$	$C_6H_5CH_3$	−15 to 25	4.7 (**6**)[b]	19

[a] Turnover numbers. [b] Addition of **6**·TPFPB at −15 °C.

Preliminary test reactions were performed with fluorodecane and benzyl trifluoride as substrates, and the results are summarized in Table 2. In a typical reaction equimolar amounts of fluorodecane and triethylsilane were dissolved in toluene and a small quantity of the salt **6**·TPFPB was added at room temperature. After 30 min at room temperature, the alkyl fluoride was consumed and the reaction was completed. Fluoronium cation **10** shows comparable reactivity in this hydrodefluorination reaction. With benzyl trifluoride the reaction is highly exothermic and therefore the catalyst was added at −15 °C and then the temperature was allowed to rise to room temperature. Interestingly, when this reaction was monitored by NMR spectroscopy, no other fluorine-containing compound but benzyl trifluoride and triethylfluorosilane were observed.

Conclusions

The synthesis and structural characterization of bissilylated onium salts **6**·TPFPB and **10**·TPFPB are reported. In the absence of nucleophiles, these cations are persistent, even in boiling toluene. Both cations, hydronium ion **6** and fluoronium ion **10**, are characterized by a symmetric bent SiXSi linkage (X = H, F). Although structurally closely related, the bonding in both cations is different. That is, while in **6** and related cations[2−4] electrondeficient multicenter bonding prevails,[1] Lewis acid base interactions seem to dominate in fluoronium ion **10**. Noteworthy, in contrast to related boron and carbon systems e.g. **7** and **15**, **16**,[5,37,38] in which unsymmetrical E−X···E groups (E = B, C; X = H, F) corresponding to double minimum potentials were found, the disilyl cations **6** and **10** prefer a symmetric structure equivalent to a single minimum potential. A full account on the bonding in bridged disilyl cations and the differences in the carbon systems will be given elsewhere.



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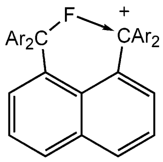

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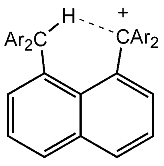

16

The disilyl cations **6** and **10** can be easily interconverted by reaction with alkylfluorides or silanes; thus, there is potential for a catalytic dehydrofluorination process of environmentally important fluoroalkanes to give hydrocarbons. This is shown here for some selected examples, and the scope and limitations of these processes are currently being tested in our laboratories.

Experimental Section

General. Diethyl ether and hexane were distilled from sodium/benzophenone. Benzene, benzene-d_6, toluene, toluene-d_8, and pentane were distilled from sodium. TMEDA, dimethylchlorosilane, and triethylsilane were distilled freshly from calcium hydride. Fluorodecane, hexafluorobenzene, and trifluorotoluene were distilled from P_4O_{10}. All reactions were carried out under inert conditions. Trityl TPFPB was prepared according to modified literature procedures.[39,40] IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. Elemental analyses were carried out on a Foss-Heraeus CHN-O-RAPID. NMR spectra were recorded on a Bruker DPX-250 spectrometer at 303 K. ^{1}H and ^{13}C NMR spectra were calibrated using residual solvent signals δ ^{1}H(C_6D_5H) = 7.20, δ ^{13}C(C_6D_6) = 128.0, δ ^{1}H($C_6D_5CD_2H$) = 2.03, δ ^{13}C($C_6D_5CD_3$) = 22.4. ^{19}F NMR spectra were calibrated using external δ ^{19}F(C_6F_6) = −162.9 vs $CFCl_3$. ^{29}Si NMR spectra were calibrated using external Me_2SiHCl (δ ^{29}Si = 11.1 vs TMS). ^{29}Si NMR spectra were recorded using the INEPT pulse sequence.

Compound 8.[9] *n*-Butyllithium (12.5 mmol, 2.5 M, 5 mL) was added slowly to a stirred solution of 10 mmol (2.07 g) of 1-bromonaphthalene in 30 mL of dry diethyl ether at −40 °C, and the mixture was stirred for a further 30 min. Stirring was stopped and the supernatant clear solution was decanted off via a flexible Teflon tube. The precipitate was washed three times with 50 mL portions of dry hexane. Then 14 mmol of *n*-butyllithium (2.5 M, 5.2 mL) in hexanes and 14 mmol (1.6 g) of TMEDA were added to the resulting white precipitate. The reaction mixture was heated to reflux for 3 h. The resulting brown suspension was cooled to −30 °C and was diluted with 30 mL of diethyl ether. Then 25 mmol (2.5 g) of dimethylchlorosilane was added. The dark brown suspension was allowed to warm to room temperature and heated to reflux for 1 h. Excess dimethylchlorosilane was removed at reduced pressure. After usual aqueous workup, the crude product was purified by column chromatography on silica using hexane as eluent (R_f = 0.64) to yield 2 g (8.2 mmol) of **2** as a colorless oil (82% yield). ^{1}H NMR (250.131 MHz, C_6D_6): δ 0.42 (d, $^3J_{HH}$ = 3.6 Hz, 12H, SiMe$_2$), 5.29 (sept, $^3J_{HH}$ = 3.6 Hz, $^1J_{Si-H}$ = 193 Hz, 2H, Si−H), 7.27−7.33 (m, 2H), 7.69−7.76 (m, 4H). ^{13}C{^{1}H} NMR (62.902 MHz, C_6D_6): δ −0.7 (CH$_3$), 124.7 (C-3/6), 131.5 (C-2/7), 134.3 (C-10), 136.0 (C-4/5), 138.3 (C-1/8), 142.0 (C-9). ^{29}Si NMR (49.696 MHz, C_6D_6): δ −19.63 (d, $^1J_{Si-H}$ = 193 Hz, $^2J_{Si-H}$ = 6.7 Hz, $^3J_{Si-H}$ = 2.3 Hz). Elemental analysis calcd/found ($C_{14}H_{20}Si_2$): C 68.78, H 8.25/C 68.58, H 8.37. IR: ν_{Si-H} = 2166 cm^{-1} (film).

6·TPFPB. Method a: From 8 by Reaction with Trityl TPFPB. A solution of 0.5 mmol (460 mg) of trityl TPFPB in benzene was slowly added to a stirred solution of 0.5 mmol (122 mg) of 1,8-bis-(dimethylsilyl)naphthalene in 2 mL of benzene at room temperature. The reaction was monitored by the disappearance of the orange color of the trityl cation. Stirring was stopped and the two phases were allowed to separate. The lower phase was transferred into an NMR tube and investigated by NMR spectroscopy. The brown salt was purified by washing with pentane to obtain 415 mg (0.45 mmol, 90% yield) **6**·TPFPB as a glassy solid.

Method b: From 10·TPFPB by Reaction with Triethylsilane. Triethylsilane (1.4 mmol, 167 mg) was added at room temperature to a stirred solution of 0.5 mmol of **10**·TPFPB in benzene. After 1 h at 50 °C the reaction mixture was transferred to an NMR tube and investigated by NMR spectroscopy. After evaporation of the solvent and washing with small portions of pentane, 304 mg (0.33 mmol, 66% yield) of **6**·TPFPB was obtained as brown glassy powder. Colorless crystals could be obtained by crystallization of the crude product from hexafluorobenzene at 7 °C. ^{1}H NMR (250.131 MHz, C_6D_6): δ 0.39 (d, $^3J_{H-H}$ = 1.8 Hz, 12H, SiMe$_2$), 3.34 (sept, $^3J_{H-H}$ = 1.8 Hz, $^1J_{Si-H}$ = 45.7 Hz, 1H, μ-H), 7.18−7.23 (m, 2H, H2/7), 7.32−7.38 (m, 2H, H3/6), 7.74−7.82 (m, 2H, H4/5). ^{13}C NMR (62.902 MHz, C_6D_6): δ −2.8 (SiMe$_2$), 126.4 (C1/8), 126.6 (C3/6), 133.2 (C10), 133.8 (C2/7), 134.3 (C4/5), 137.0 (d, $^1J_{C-F}$ = 244.1 Hz, CF, [B(C_6F_5)]$_4$), 137.6 (C9), 138.9 (d, $^1J_{C-F}$ = 246.3 Hz, CF, [B(C_6F_5)]$_4$), 149.1 (d, $^1J_{C-F}$ = 240.4 Hz, CF, [B(C_6F_5)]$_4$). ^{29}Si NMR (49.696 MHz, C_6D_6): δ 54.4 (dm, $^1J_{Si-H}$

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= 45.7 Hz, $^2J_{\mathrm{Si-H}}$ = 7.2 Hz). ^{19}F NMR (235.334 MHz, $C_6D_5CD_3$): δ −166.7 (t, $^3J_{\mathrm{FF}}$ = 18 Hz, 8F), −162.7 (t, $^3J_{\mathrm{FF}}$ = 20.5 Hz, 4F), −132.0 (m, 8F).

10 TPFPB. Method a: From the Reaction of 6·TPFPB with Trifluorotoluene. A solution of 0.5 mmol of **6**·TPFPB in benzene was cooled to 8 °C. After slowly adding 0.17 mmol (25 mg) of neat trifluorotoluene, the cooling was removed. The reaction mixture was stirred at room temperature for 30 min. After the stirring was stopped, a two-phase reaction mixture was obtained. The lower phase was transferred into an NMR tube and investigated by NMR spectroscopy. The dark red TPFPB salt of cation **10** was purified by washing with pentane to yield 460 mg (0.49 mmol, 98% yield) of **10**·TPFPB.

Method b: From the Reaction of 6·TPFPB with Fluorodecane. As described in method a, but upon adding 0.5 mmol (62 mg) of neat fluorodecane at room temperature, the reaction mixture was warmed to 60 °C for 3 h to yield 432 mg (0.46 mmol, 92% yield) of **10**·TPFPB.

Method c: From the Reaction of 6·TPFPB and Trityl TPFPB. Trityl TPFPB (0.3 mmol, 275 mg) in 2 mL of benzene was added to a stirred solution of 0.3 mmol of preformed **6**·TPFPB in 1 mL of benzene, and the mixture was heated to 75 °C for 9 h. Stirring was stopped and the two phases were allowed to separate. The lower phase was transferred into an NMR tube and investigated by NMR spectroscopy. Colorless crystals from **10**·TPFPB could be obtained by crystallization of the crude product from toluene at −35 °C to yield 220 mg (0.23 mmol, 78% yield) of **10**·TPFPB. ^{1}H NMR (250.131 MHz, C_6D_6): δ 0.36 (d, $^3J_{\mathrm{H-F}}$ = 13.7 Hz, 12H), 7.12−7.17 (m, 2H), 7.30−7.37 (m, 2H), 7.75−7.79 (m, 2H). ^{13}C NMR (62.902 MHz, C_6D_6): δ −1.0 (d, $^2J_{\mathrm{C-F}}$ = 15.4 Hz, CH_3), 125.1 (d, $^2J_{\mathrm{C-F}}$ = 11.2 Hz, C-1/8), 126.3 (d, $^4J_{\mathrm{C-F}}$ = 2.8 Hz, C-3/6), 133.5 (C-10), 134.3 (d, $^3J_{\mathrm{C-F}}$ = 8.2 Hz, C-2/7), 135.1 (C-4/ 5), 136.4 (d, $^3J_{\mathrm{C-F}}$ = 6.0 Hz, C-9), 137.0 (d, $^1J_{\mathrm{C-F}}$ = 244.1 Hz, CF, $[B(C_6F_5)]_4$), 138.9 (d, $^1J_{\mathrm{C-F}}$ = 246.3 Hz, CF, $[B(C_6F_5)]_4$), 149.1 (d, $^1J_{\mathrm{C-F}}$ = 240.4 Hz, CF, $[B(C_6F_5)]_4$). ^{29}Si NMR (49.696 MHz, C_6D_6): δ 77.2 (d, $^1J_{\mathrm{Si-F}}$ = 243 Hz). ^{19}F NMR (235.334 MHz, C_6D_6): δ −166.7 (t, $^3J_{\mathrm{FF}}$ = 18 Hz, 8F), −162.7 (t, $^3J_{\mathrm{FF}}$ = 20.5 Hz, 4F), −144.0 (s, $^1J_{\mathrm{Si-F}}$ = 243 Hz, Si−F, 1F), −132.0 (m, 8F).

Typical Procedure for the Catalytic Hydrodefluorination of Fluorohydrocarbons. A mixture of 4.5 mmol (720 mg) of fluorodecane, 4.5 mmol (520 mg) of triethylsilane, 0.6 mL of toluene, and hexafluorobenzene as internal standard was stirred at room temperature. **6**·TPFPB (0.1 mmol) in 1 mL of benzene was added via a flexible Teflon tube. The progress of the reaction was followed by NMR spectroscopy. After 1 h at room temperature fluorodecane and triethylsilane were completely consumed, and only triethylsilyl fluoride was formed, as indicated by ^{19}F and ^{29}Si NMR. Decane was identified by ^{13}C NMR and GC/MS. In the case of benzyl trifluoride as starting material, the reaction was done in benzene and the product toluene was detected by ^{1}H NMR. Et_3SiF: ^{19}F NMR (235.334 MHz, C_6D_6) δ −175.2 (s, $^1J_{\mathrm{Si-F}}$ = 288.7 Hz). ^{29}Si NMR (49.696 MHz, C_6D_6): δ 31.6 (d, $^1J_{\mathrm{Si-F}}$ = 288.7 Hz). Decane: ^{13}C NMR (62.902 MHz, C_6D_6): δ 13.9 (CH_3), 22.7, 33.3, 29.7, 30.2 (4×CH_2). GC/MS (EI) *m/e* (%): 142 (5), 113 (3), 99 (4), 98 (4), 85 (15), 84 (6), 71 (30), 70 (13), 57 (88), 55 (27), 43 (100), 41 (82), 29 (50), 27 (30). Toluene: ^{1}H NMR (250.131 MHz, C_6D_6): δ 2.16.

X-ray Crystallographic Analysis. A single crystal of **6**·TPFPB suitable for X-ray crystallographic analysis was grown by recrystallization from hexafluorobenzene, whereas that of **10**·TPFPB was grown by recrystallization from toluene. X-ray crystal structure analyses were performed on a STOE IPDS [Mo Kα radiation, λ = 71.073 pm, graphite monochromator at 173(2) K].

Crystal data for (6·TPFPB·C_6F_6): $C_{44}H_{19}BF_{26}Si_2$, MW = 1108.58, crystal dimension 0.17 × 0.17 × 0.09 mm^3, monoclinic, space group *P*21/c, a = 1498.08(8) pm, b = 1071.69(4) pm, c = 2741.62(17) pm, β = 93.974(5)°, V = 4.3910(4) nm^3, Z = 4, D_{calc} = 1.590 Mg m^{-3}. F(000) = 2200, $2\Theta_{\max}$ = 52.12°, 60 772 reflections measured, of which 8603 were unique [R(int) = 0.0951].The final R factor was 0.0753 with wR2 = 0.1143 for 8603 observed reflections with $I > 2\sigma(I)$. (R_W = 0.1416 all data, 60 772 reflections), GOF = 1.060. The Cambridge database file is CCDC 600351.

Crystal data for (10·TPFPB·C_7H_8): $C_{45}H_{26}BF_{21}Si_2$, MW = 1032.65, crystal dimension 0.33 × 0.30 × 0.26 mm^3, triclinic, space group *P*-1, a = 1035.20(10) pm, b = 1386.04(13) pm, c = 1564.53(15) pm, α = 85.862(8)°, β = 85.879(8)°, γ = 74.786(7)°, V = 2.1572(4) nm^3, Z = 2, D_{calc} = 1.590 Mg m^{-3}. F(000) = 1036, $2\Theta_{\max}$ = 50.8°, 26 358 reflections measured, of which 7842 were unique [R(int) = 0.0540]. The final R factor was 0.0334 with wR2 = 0.0812 for 7842 observed reflections with $I > 2\sigma(I)$. (R_W = 0.0493 all data, 26 358 reflections), GOF = 0.914. The Cambridge database file is CCDC 600350.

Acknowledgment. This paper is dedicated to Prof. H.-U. Siehl on the occasion of his 60th birthday. This work was supported by a scholarship of the Fonds der chemischen Industrie to R.P.

Supporting Information Available: Complete description of the computations including optimized geometries of cations **4** (Me) and **6** at different levels of theory and full citation of ref 17; correlation between computed and experimental ^{13}C NMR chemical shifts for cation **6**; ^{1}H, ^{13}C, ^{29}Si, ^{19}F NMR spectra of **6**·TPFPB and **10**·TPFPB; NMR spectra for the catalytic hydrodefluorination of trifluorotoluene; and CIF files for **6**·TPFPB and **10**·TPFPB. This material is available free of charge via the Internet at http://pubs.acs.org.

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