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Activation of Pentafluorophenylsilanes by Weak Lewis Bases in Reaction with Iminium Cations

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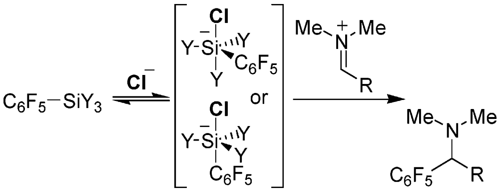

The Lewis base mediated carbon−carbon bond forming reactions between pentafluorophenylsilanes and iminium cations were studied theoretically and experimentally. The complexation of silanes with anionic Lewis bases was analyzed computationally using DFT methods at the B3LYP/6-31+G(d) level. The pentafluorophenyl group was found to exhibit a significant stabilizing effect on the formation of pentacoordinate silicon species, with $(C_6F_5)_3SiF$ and $C_6F_5SiF_3$ being the strongest Lewis acids. Comparison of geometrical isomers of trigonal bipyramidal siliconates $R_2(C_6F_5)SiXY^-$ (R = Me, F, Cl; X, Y = F, Cl, ClO_4) revealed that the heteroatoms and the C_6F_5 group prefer to occupy apical and equatorial positions, respectively. Calculations of C_6F_5 group transfer processes from silanes to *N*,*N*-dimethyliminium cation lead to the following conclusions: (1) when employing weak Lewis bases $X^- = Cl^-$, ClO_4^- as activators, $R_2(C_6F_5)SiF$ are more reactive than $R_2(C_6F_5)SiX$ (X = Cl, ClO_4); (2) the C_6F_5 group is much more reactive in an apical position than in an equatorial position of the siliconate; (3) a solvent greatly increases the reaction barrier by stabilizing the reactants; and (4) the efficiency of C−C bond formation can be improved by rendering the process intramolecular. It was shown experimentally that reactions of $(C_6F_5)_3SiF$ with $PhCH{=}NMe_2^+TfO^-$ can be promoted by a series of weak Lewis bases, from which the chloride anion was the most effective. Even more facile was the reaction of *N*-(silyloxyethyl)iminium ion $(C_6F_5)_3SiOCH_2CH_2N(Me){=}CHPh^+TfO^-$, likely proceeding via intramolecular transfer of a C_6F_5 group. The optimal conditions for pentafluorophenylation of iminium ions involved the use of benzyltriethylammonium chloride in refluxing dichloroethane.

Introduction

The major synthetic applications of organosilicon compounds correspond to the transfer of the organic group from the silicon atom to an electrophile.[1] However, the organosilanes are intrinsically moderately reactive, and an additional activator is required to initiate the electrophile−nucleophile coupling. One of the methods to effect such activation involves the employment of a Lewis base, which binds to the silicon atom, generating a five-coordinate siliconate intermediate.[2] In the latter species, the carbon−silicon bond becomes more polarized, rendering the nucleophilic leaving group more reactive (Scheme 1, path a).

The fluoride and alkoxide anions have turned out to be the most commonly used Lewis bases for activation of carbon−silicon bonds.[2a,3,4] Their efficiency originates from very strong bonds between silicon and fluoride and oxygen, respectively.

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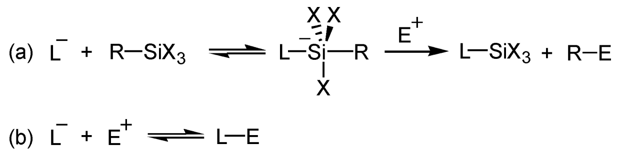
SCHEME 1



However, besides significant affinity toward silicon, these Lewis bases serve as extremely strong nucleophiles and therefore are incompatible with reactive electrophiles, such as carbocations (Scheme 1, path b). As a consequence, only poorly electrophilic neutral reagents, such as aldehydes, Michael acceptors, and imines, have been employed in Lewis base mediated C−C bond forming reactions.[3] In this regard, an important question arises: what are the optimal conditions for Lewis base activation of silicon reagents and for transferring a nucleophilic leaving group from the activated intermediate onto a carbocationic electrophile? To solve this problem for a specific combination of a leaving group and an electrophile, it is necessary to find a proper combination of silicon substituents and a Lewis base. In particular, the following criteria have to be fulfilled: (a) the silicon atom of the reagent should be prone to an interaction with the Lewis base for the formation of a five-coordinate siliconate; (b) the five-coordinate intermediate should readily transfer the leaving group to the electrophile; and (c) the reaction of the Lewis base with the silane must compete efficiently with its reaction with the electrophile. Correspondingly, a selection of a weaker Lewis base and increasing the silicon Lewis acidity appears as a major direction which should be pursued.

While considering trimethylsilyl derivatives, the acetate anion is the weakest competent activating Lewis base employed so far, as was demonstrated by Mukaiyama and co-workers for the transfer of a trifluoromethyl group onto aldehydes and electron-poor imines.[5−7] On the other hand, we have recently reported that an increase of silicon Lewis acidity can be achieved by introducing the electron-withdrawing pentafluorophenyl groups.[8−10] In this respect, it becomes interesting to find optimal conditions for the application of weak Lewis bases for activating silicon reagents in C−C bond forming reactions.

Herein we present our theoretical and experimental studies in an attempt to address the latter problem. The pentafluorophenyl silanes were selected as model compounds because the C_6F_5 group is a strong electron withdrawer and a variety of pentafluorophenyl silanes can be readily synthesized by conventional organometallic synthesis.[11] As electrophiles, the iminium cations were chosen since they constitute an important class of carbocationic electrophiles. The iminium cations can be obtained as stable isolable salts or can be generated in situ using known protocols.[12] Moreover, amines resulting from the addition of a C_6F_5 group onto an iminium cation may be interesting as potential pharmaceutical and agrochemical agents.[13]

We first performed quantum mechanical analysis of the C_6F_5 group transfer process in order to identify the most efficient combination of the reagents required for C−C bond forming reaction. Subsequently, the results of theory were verified experimentally.

Selection of the Theoretical Method

All computations were carried out using the Gaussian 03 program.[14] The stationary points were verified by vibrational analysis, and the thermodynamics was calculated at 298.15 K.

The B3LYP hybrid density functional method[15] and ab initio second-order perturbation theory[16] (MP2) were selected for the initial evaluation.[17,18] The interaction of fluorotrimethylsilane

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(4) At the same time, allylic trichlorosilanes undergo coupling with aldehydes in the presence neutral Lewis bases, such as amides, phosphoramides, and pyridine-*N*-oxides, but the efficiency of these reactions is likely associated with concerted character of transition state. See: (a) Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620. (b) Denmark, S. E.; Fu, J. *Chem. Commun.* **2003**, 167. (c) Malkov, A. V.; Dufkova, L.; Farrugia, L.; Kocovsky, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3674.

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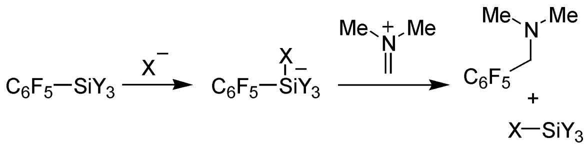
SCHEME 2



(Me$_3$SiF) with a fluoride anion to give difluorotrimethylsiliconate was selected as the reference for our calculations since, for this reaction, experimental thermochemical data in the gas phase are available ($\Delta H = -38.2$ kcal/mol, $\Delta G = -31.6$ kcal/mol).[19] Variation of method and basis set demonstrated that the B3LYP/6-31+G(d) level of theory is the most suitable ($\Delta H_{calc} = -40.4$ kcal/mol, $\Delta G_{calc} = -33.6$ kcal/mol). Further expanding the basis set to triple-ζ and addition of polarization functions did not lead to higher accuracy (see Supporting Information for details). Of special note is the fact that the use of diffuse functions is essential for reproducing the experimental results.[18] Accordingly, all further calculations were performed at the B3LYP/6-31+G(d) level.

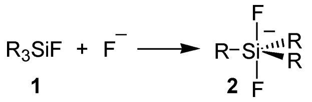
To take into account the solvent effect, the polarizable continuum model (PCM)[20] was employed as implemented in Gaussian 03. The single-point PCM calculations for gas-phase geometries were performed, and obtained solution energies were augmented with thermochemical corrections taken from gas-phase vibrational analysis. Dichloromethane was selected as a typical organic solvent of moderate polarity ($\epsilon = 8.93$), which is routinely used in synthesis.

Results and Discussion

Calculations. The C$_6$F$_5$ group transfer reaction between the silane and the iminium cation includes two steps: generation of the five-coordinate siliconate and the subsequent C−C bond forming event (Scheme 2). In principle, the formation of covalent species Me$_2$NCH$_2$X from the iminium ion and Lewis base may occur.[21] However, this is unlikely to affect our analysis of the reaction mechanism. Thus, iminium chlorides exist in solution as ionic hydrogen bonded aggregates R$_2$N=C(R)-H···Cl, whereas weaker counterions, which are most interesting from an experimental point of view, exist completely in the ionic form.[22]

The interaction of the silane with a Lewis base constitutes the first step of the process, and it is necessary to understand the effect of the C$_6$F$_5$ group on the efficiency of the generation of five-coordinate siliconate species. Table 1 lists the calculated energies for the reactions of fluorosilanes with a fluoride anion in the gas phase, as well as the calculated free energy in dichloromethane solution.

TABLE 1. Calculated Energies of Siliconate Formation (kcal/mol, at 298.15 K)[a]



entry	silane (R$_3$SiF)	ΔE	ΔH	ΔG	ΔG (CH$_2$Cl$_2$)
1	Me$_3$SiF	−39.8	−40.4	−33.6	1.8
2	Me$_2$(C$_6$F$_5$)SiF	−58.1	−58.7	−51.1	−7.5
3	Me(C$_6$F$_5$)$_2$SiF	−72.5	−73.0	−64.7	−16.0
4	(C$_6$F$_5$)$_3$SiF	−85.5	−86.1	−75.6	−23.6
5	Me$_2$SiF$_2$	−47.4	−48.0	−39.9	−6.9
6	MeSiF$_3$	−57.4	−58.0	−49.8	−17.9
7	SiF$_4$	−72.1	−72.7	−64.9	−32.2
8	C$_6$F$_5$SiF$_3$	−76.9	−77.5	−68.7	−26.5
9	PhSiF$_3$	−63.2	−63.8	−54.4	−18.3
10	Me$_2$(MeO)SiF	−42.2	−42.8	−34.8	0.0
11[b]	(CH$_2$)$_3$Si(Me)F	−44.5	−45.1	−37.1	−0.8
12[c]	Me$_2$(C$_6$F$_5$)$_2$Si	−58.0	−58.6	−50.2	1.2

[a] The two fluorines are located in apical positions of the trigonal bipyramidal structure of **2** unless mentioned otherwise. Δ = energy(**2**) − [energy(**1**) + energy (F$^-$)]. [b] One fluorine in apical and another in equatorial position of the siliconate. [c] Fluorine and C$_6$F$_5$ in the apical positions of the siliconate.

One can see that a C$_6$F$_5$ group significantly stabilizes the formation of the siliconate anion, and in the gas phase, this effect is noticeably stronger than that of fluoride substituent (cf. entries 2 and 5, $\Delta\Delta G = 11.2$ kcal/mol). However, solvent greatly reduces this difference, making them almost equally effective ($\Delta\Delta G_{sol} = 0.6$ kcal/mol). Not surprisingly, the C$_6$F$_5$ group is a more efficient stabilizing group than a methoxy substituent or a silacyclobutyl ring even in solution (entry 2 vs 10 and 11).

Of special note is the comparison of fluoride ion affinities of Me$_2$(C$_6$F$_5$)SiF and Me$_2$(C$_6$F$_5$)$_2$Si (entries 2 and 12). For these silanes, the gas-phase energies are similar, while in solution, they differ by 8.7 kcal/mol, with Me$_2$(C$_6$F$_5$)SiF furnishing a more stable siliconate. This effect is likely associated with significant charge delocalization within the C$_6$F$_5$ group compared to that in the small fluoride that causes a weaker solvation of Me$_2$(C$_6$F$_5$)$_2$SiF$^-$.

Among the studied silanes containing a C$_6$F$_5$ group, (C$_6$F$_5$)$_3$-SiF and C$_6$F$_5$SiF$_3$ produced the most stable pentacoordinate complexes in solution.[23]

Though fluoride is known to be the strongest activator with respect to silicon, weaker Lewis bases compatible with carbocationic electrophiles have to be considered. The anions of strong protic acids HX (e.g., X = OTf, ClO$_4$, CF$_3$CO$_2$, or Cl) would be attractive activators, relying on the greater bond energy of silicon−heteroatom versus carbon−heteroatom.[24] The silicon derivatives bearing such substituents are frequently employed as silylating agents and as Lewis acids.[25] Mechanistically, all these processes proceed through the nucleophilic substitution at the silicon atom, and the reactivity of silanes increases in the following order: R$_3$SiF < R$_3$SiOMe < R$_3$SiOAc < R$_3$SiCl ≈ R$_3$SiOC(O)CF$_3$ < R$_3$SiBr < R$_3$SiOTf ≈ R$_3$SiOClO$_3$.[25]

To evaluate the ability of a particular anion X to serve as Lewis base in the C$_6$F$_5$ group transfer reaction from a particular silyl group (e.g., R$_2$(C$_6$F$_5$)SiY), we have to compare various

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TABLE 2. Calculated Energies of Siliconate Formation (kcal/mol, at 298.15 K)[a]

	ΔE	ΔH	ΔG	ΔG (CH_2Cl_2)
$X^- + Me_2(C_6F_5)SiF \rightarrow Me_2(C_6F_5)Si(F)(X)^-$				
X^-				
MeO^-	−50.6	−51.2	−40.3	−11.5
AcO^-	−26.3	−26.9	−15.0	11.2
Cl^-	−17.7	−18.3	−12.0	13.9
$CF_3CO_2^-$	−15.8	−16.4	−4.7	16.1
ClO_4^-	−10.8	−11.4	−2.5	11.7
$X^- + Me_2(C_6F_5)SiX \rightarrow Me_2(C_6F_5)SiX_2^-$				
X^-				
MeO^-	−42.6	−43.2	−30.5	0.9
AcO^-	−27.5	−28.1	−16.6	11.8
Cl^-	−21.1	−21.7	−14.4	13.6
$CF_3CO_2^-$	−26.0	−26.6	−13.5	11.9
ClO_4^-	−17.7	−18.3	−8.1	13.9
$X^- + C_6F_5SiF_3 \rightarrow C_6F_5SiF_3X^-$				
X^-				
Cl^{-b}	−28.3	−28.9	−20.8	7.2
$CF_3CO_2^{-b}$	−28.5	−29.1	−15.8	4.0
ClO_4^{-b}	−13.5	−14.1	−2.6	15.8
$X^- + C_6F_5SiCl_3 \rightarrow C_6F_5SiCl_3X^-$				
X^-				
Cl^-	−25.9	−26.4	−18.7	11.9
$CF_3CO_2^{-c}$	−24.7	−25.3	−12.5	9.3
ClO_4^{-c}	−8.3	−8.9	2.4	22.9
$Cl^- + (C_6F_5)_3SiF^- \rightarrow (C_6F_5)_3SiFCl^-$	−34.7	−35.3	−24.2	10.8

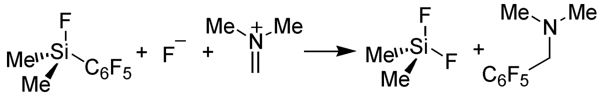
[a] Two heteroatomic substituents were located in apical positions of the trigonal bipyramidal structure of siliconate. $\Delta = \text{energy}(Me_2(C_6F_5)SiXY^-) - [\text{energy}(Me_2(C_6F_5)SiY) + \text{energy}(X^-)]$. [b] The most stable isomer with fluorine and X in apical positions. [c] Chlorine and X in apical positions.

TABLE 3. Relative Energies of Geometrical Isomers of $Me_2(C_6F_5)SiF_2^-$ (kcal/mol, at 298.15 K)

apical, apical	ΔE	ΔH	ΔG	ΔG (CH_2Cl_2)
F, F	0.0	0.0	0.0	0.0
F, C_6F_5	5.0	5.0	5.1	6.2
F, Me[a]	8.1	8.1	8.1	8.1
C_6F_5, Me[a]	9.9	9.9	10.0	10.0
Me, Me	10.9	10.9	10.7	10.7

[a] The data of constraint geometry optimization are given since on relaxed search the geometry spontaneously changes to a more stable isomer.

TABLE 4. Reaction Energies (kcal/mol, at 298.15 K)



	ΔE	ΔH	ΔG	ΔG (CH_2Cl_2)
reactants[a]	58.1	58.7	51.1	7.5
siliconate	0.0	0.0	0.0	0.0
local min	−76.8	−77.4	−66.3	3.9
TS1	−65.5	−66.1	−53.9	**24.4**
products	−130.8	−130.8	−129.8	−48.1

[a] $Me_2(C_6F_5)SiF + F^- + CH_2{=}NMe_2^+$.

siliconates of general formula $R_2(C_6F_5)SiYX^-$. If we select the perchlorate anion as the weakest Lewis base, then all siliconates are expected to fall within the range between two extreme structures possessing fluoride and perchlorate substituents, namely, $R_2(C_6F_5)SiFClO_4^-$ and $R_2(C_6F_5)Si(ClO_4)_2^-$. In general, for some anion X^-, the siliconate containing fluoride at silicon $R_2(C_6F_5)SiFX^-$ and symmetric species $R_2(C_6F_5)SiX_2^-$ have to be studied.

We first investigated computationally the interaction of silanes $Me_2(C_6F_5)SiY$, $C_6F_5SiY_3$, and $(C_6F_5)_3SiY$ with different Lewis bases (Table 2). In the gas phase, the complex formation is exothermic and is favored according to the negative Gibbs free energy for all calculated systems. However, in dichloromethane, the formation of five-coordinate siliconates with weak Lewis bases is unfavorable by about 10−15 kcal/mol. Even in the case of highly Lewis acidic $C_6F_5SiX_3$ and $(C_6F_5)_3SiX$ (X = F, Cl), complex formation should not occur owing to the loss of solvation energy of the smaller anion X relative to the solvation energy of larger siliconates. Nevertheless, pentacoordinate siliconate species may exist in very small equilibrium concentration and serve as competent nucleophiles.

Another important conclusion can be drawn from Table 2. Thus, comparison of the complexing abilities of pairs of silanes R_3SiF versus R_3SiX (i.e., $Me_2(C_6F_5)SiF$ vs $Me_2(C_6F_5)SiX$; $C_6F_5SiF_3$ vs $C_6F_5SiX_3$) suggests that in CH_2Cl_2 solution the fluorinated derivatives R_3SiF usually bind stronger the anionic Lewis bases (smaller positive free energy of complexation), thereby providing higher equilibrium concentrations of siliconates.

To compare the reactivity of siliconates, it is necessary to analyze the potential energy surface for their reactions with electrophiles. The difluorosiliconate $Me_2(C_6F_5)SiF_2^-$ was selected as a simplest hypercoordinate nucleophile, and its structure was examined in greater detail.

The trigonal bipyramidal arrangement of pentacoordinate silicon requires the consideration of five isomers differing in relative position of substituents (Table 3). The structure with two fluorines in apical positions is the most stable, whereas the molecule bearing, at apical sites, fluorine and a C_6F_5 group is 6.2 kcal/mol higher in energy. Other possible species are even higher in energy. It is interesting to note that solvent has only a very small effect on the relative energies of the geometrical isomers.

The interaction of the most stable isomer of difluorosiliconate $Me_2(C_6F_5)SiF_2^-$ with *N*,*N*-dimethyliminium ion was investigated as a model system. The calculated energies are referenced relative to the sum of energies of siliconate and iminium ions (Table 4). Figure 1 shows the free energy surfaces for the reaction in the gas phase and in dichloromethane solution.

The salient feature of this process is the extremely high thermodynamic driving force in the gas phase (overall $\Delta G = -180.9$ kcal/mol), which comes from the formation of strong Si−F and C−C bonds replacing a weak Si−C bond. As can be anticipated, the solvent dramatically reduces the exothermicity (by 125 kcal) since the reactants are charged, while the products are neutral. Furthermore, the solvation contributes to the increase of transition structure energy, making it higher than the sum of the reactants.

The transition structure and its key bond lengths and angles are given in Figure 2. A concerted transfer of the C_6F_5 group from silicon to the iminium carbon was observed with one imaginary frequency of $-249.0i$, which was validated by forward (to products) and backward (to the pentacoordinate silicon intermediate) IRC calculations. A σ-complex of the type characteristic for conventional aromatic electrophilic attack[26] could not be detected.

A local minimum preceding the transition structure was identified in the gas phase, representing a hydrogen bonded complex between the fluorine of difluorosiliconate and an

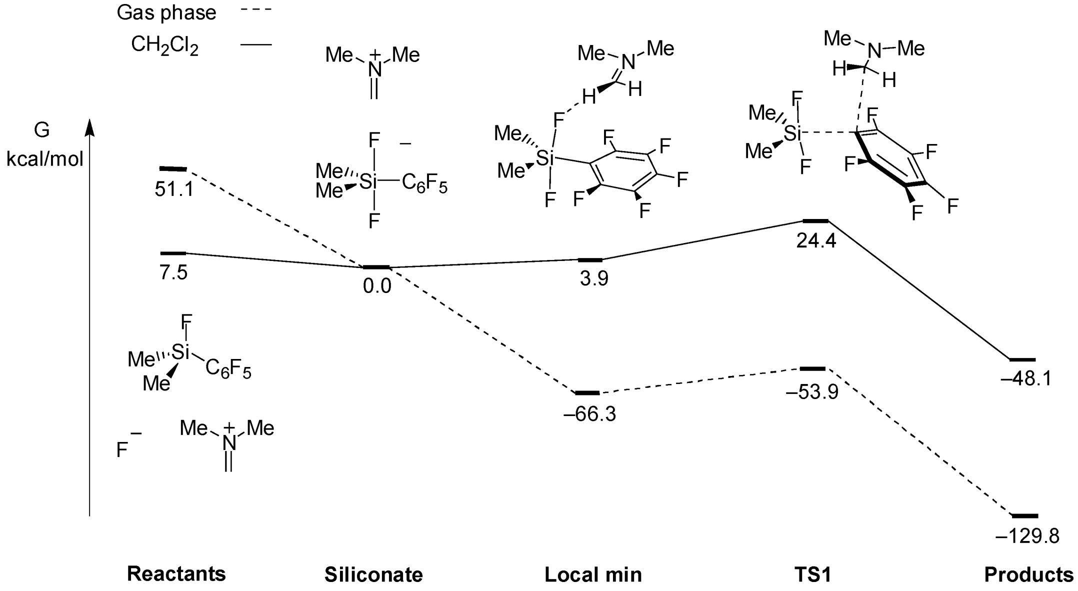


FIGURE 1. Free energy profiles of fluoride-activated reactions in the gas phase and dichloromethane solution.

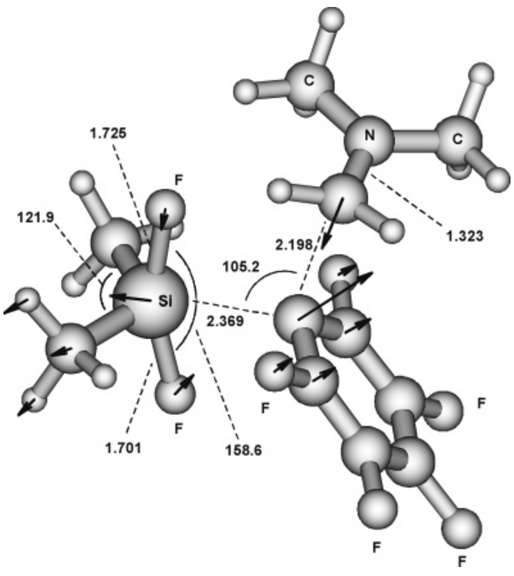


FIGURE 2. Transition structure TS1. Selected bond lengths (Å) and angles (deg).

iminium hydrogen. In solution, this complex is higher in energy than the parent siliconate and iminium ions and may not be a detectable intermediate.

It is interesting to analyze also the reaction of siliconate $Me_2(C_6F_5)SiF_2^-$ containing apical C_6F_5 and fluorine substituents. In this case, a barrierless transfer of the C_6F_5 fragment onto the electrophile was observed. The greater reactivity of the apical versus the equatorial group may be associated with higher polarization of the apical bonds. Thus, in the structure with an equatorial C_6F_5 group, the $Si-C_{C_6F_5}$ bond distance is 1.98 Å, while for the isomer with an apical C_6F_5 group it is 2.21 Å. In addition, the charge located on the C_6F_5 group is more negative in apical (−0.73 e) than in the equatorial isomer (−0.63 e; NAO charges[27]).

We next examined the performance of chloride and perchlorate anions as activators for the C_6F_5 group transfer from fluoro-, chloro-, and perchlorate-substituted dimethylpentafluorophenyl silanes $Me_2(C_6F_5)SiY$, Y = F, Cl, ClO_4. For the reaction of unsymmetrical siliconate $Me_2(C_6F_5)SiFCl^-$, two different transition structures were considered, corresponding to the approach of the electrophile to the C_6F_5 group from the fluorine side (TS2) or from the chlorine atom (TS3). The calculations show that the fluorine side approach is 1.4 kcal/mol lower in energy. Consequently, transition structures for reactions of other siliconates were calculated only for fluoride side approach. The intermediate hydrogen bonded local minima similar to that observed for $Me_2(C_6F_5)SiF_2^-$ were excluded from consideration since these stationary points do not affect the final conclusion, while their identification requires considerable computational resources. Table 5 shows the calculated energies referenced relative to the sum of starting silane, Lewis base, and iminium ions because in solution the formation of siliconates is energetically unfavorable. At the same time, the barriers for the generation of siliconates were not considered.[28]

It should be noted that the thermodynamics of chloride initiated reactions are very close, but the free energies of activation differ by 5.7 kcal/mol (i.e., TS2 vs TS4). This means that C_6F_5 group transfer triggered by a chloride ion will proceed approximately 10^4 times faster at room temperature when fluorosilane rather than chlorosilane is used! A similar trend was observed for perchlorate-activated processes, with $Me_2(C_6F_5)$-

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[26] (a) Taylor, R. *Electrophilic Aromatic Substitution*; John Wiley & Sons: Chichester, U.K., 1990. (b) Hubig, S. M.; Kochi, J. K. *J. Org. Chem.* **2000**, *65*, 6807. (c) For recent detailed computational studies of aromatic electrophilic addition, see: Esteves, P. M. Carneiro, J. W. M.; Cardoso, S. P.; Barbosa, A. G. H.; Laali, K. K.; Rasul, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **2003**, *125*, 4836.

[27] (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Foster J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.

[28] Indeed, the generation of siliconate from a reaction of the Lewis base and the silane is energetically favored (and barrierless) in the gas phase but is disfavored in solution (see Table 2). This means that in solution there exists an activation barrier which is probably due to solvent reorganization (a process which we have not studied). For a similar situation for S_N2 reaction, see: (a) Shaik, S. S.; Schlegel, H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry, The S_N2 Mechanism*; John Wiley and Sons: New York, 1992. (b) Chandrasekhar, J.; Smith, S. F.; Jorgensen W. L. *J. Am. Chem. Soc.* **1984**, *106*, 3049. (c) Chandrasekhar, J.; Smith, S. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 154. (d) Chandrasekhar, J.; Jorgensen W. L. *J. Am. Chem. Soc.* **1985**, *107*, 2974.

TABLE 5. Reaction Energies (kcal/mol, at 298.15 K)

reaction	Δ*E*	Δ*H*	Δ*G*	Δ*G* (CH_2Cl_2)
$Me_2(C_6F_5)SiF + Cl^- + CH_2{=}NMe_2^+$				
reactants	0.0	0.0	0.0	0.0
siliconate	−17.7	−18.3	−12.0	13.9
TS2 (F side)	−72.4	−73.6	−52.7	**52.7**
TS3 (Cl side)	−71.5	−72.7	−51.8	54.1
products	−139.2	−139.8	−131.3	−22.0
$Me_2(C_6F_5)SiCl + Cl^- + CH_2{=}NMe_2^+$				
reactants	0.0	0.0	0.0	0.0
siliconate	−21.1	−21.7	−14.4	13.6
TS4	−67.0	−68.2	−47.1	**58.4**
products	−138.6	−139.2	−130.6	−21.2
$Me_2(C_6F_5)SiF + ClO_4^- + CH_2{=}NMe_2^+$				
reactants	0.0	0.0	0.0	0.0
siliconate	−10.8	−11.4	−2.5	11.7
TS5	−51.6	−52.7	−30.0	**62.1**
products	−109.4	−110.0	−98.9	−3.7
$Me_2(C_6F_5)SiClO_4 + ClO_4^- + CH_2{=}NMe_2^+$				
reactants	0.0	0.0	0.0	0.0
siliconate	−17.7	−18.3	−8.1	13.9
TS6	−51.0	−52.2	−26.8	**68.4**
products	−107.5	−108.1	−96.5	−0.9

TABLE 6. Relative Energies of Geometrical Isomers of $C_6F_5SiY_3X^-$ (kcal/mol, at 298.15 K)

apical, apical	Δ*E*	Δ*H*	Δ*G*	Δ*G* (CH_2Cl_2)
$C_6F_5SiF_4^-$				
F, F	0.0	0.0	0.0	0.0
F, C_6F_5	1.9	1.9	2.1	3.6
$C_6F_5SiF_3Cl^-$				
F, Cl	0.0	0.0	0.0	0.0
F, F	1.7	1.7	2.3	2.0
F, C_6F_5	3.9	3.9	4.2	5.5
Cl, C_6F_5	2.5	2.5	2.9	3.9
$C_6F_5SiF_3ClO_4^-$				
F, ClO_4	0.0	0.0	0.0	0.0
ClO_4, C_6F_5	3.0	3.0	3.5	3.7
F, F	4.6	4.6	5.4	5.0
F, C_6F_5[a]	8.5	8.5	11.6	11.9
$C_6F_5SiCl_4^-$				
Cl, Cl	0.0	0.0	0.0	0.0
Cl, C_6F_5[a]	8.3	8.3	10.5	9.6

[a] The unconstrained optimization provided structure with one imaginary frequency corresponding to the movement toward the more stable isomer.

SiF being significantly more reactive than silyl perchlorate $Me_2(C_6F_5)SiClO_4$ ($\Delta\Delta G^{\ddagger}_{sol} = 6.3$ kcal/mol; see Table 5, TS5 vs TS6).

To verify the applicability of the B3LYP functional for the description of transition structures, the calculations for TS1−TS4 at the MP2/6-31+G(d)//B3LYP/6-31+G(d) level were performed and provided identical trends (see Supporting Information for details).

These computational results suggest a general guide for the synthetic work aimed at the application of weakly nucleophilic Lewis bases, which can be formulated as follows: *silyl fluorides should be used to provide fastest reactions; at the same time, silanes containing good leaving groups (such as ClO_4) will be less reactive*.

Since fluorine has such a profound activating effect on nucleophilic transfer of a C_6F_5 fragment, we decided to study the performance of a fully fluorinated derivative, namely, $C_6F_5SiF_3$.

First of all, the geometrical isomers of the trigonal bipyramid of five-coordinate complexes of $C_6F_5SiF_3$ with fluoride, chloride, and perchlorate anions were calculated (Table 6). The energy differences between geometrical isomers of these siliconates usually do not exceed 5 kcal/mol; that is lower than that in siliconates derived from $Me_2(C_6F_5)SiF$ (cf. Table 3). Consequently, if the barrier for the transition of the C_6F_5 group from an equatorial to an apical position is low, the reaction of such siliconates with an electrophile may be very fast owing to the significant elongation and polarization of the bond between silicon and the apical substituent.

The relative energies for the isomers of chlorinated siliconate $C_6F_5SiCl_4^-$ are also given in Table 6. The complex with the C_6F_5 group in an apical position corresponds to the transition structure toward rearrangement to a more stable isomer with a barrier height of about 10 kcal/mol. This means that, for a reaction of $C_6F_5SiCl_4^-$ requiring positioning of the C_6F_5 group in an apical arrangement, additional energy will be needed to reach the transition structure.

We attempted to locate the transition structure for the interaction of siliconates $C_6F_5SiY_3X^-$ (Y, X = F, Cl) with a dimethyliminium carbocation. Surprisingly, upon forming the C−C bond, the C_6F_5 group spontaneously moves from an equatorial to an apical position. The calculated data for a series of C−C bond forming reactions are given in Table 7. The energies were referenced to the species, which exist in high concentration, that is relative to the siliconate and iminium ions in the case of fluoride activation or relative to the starting silane, anion, and iminium cation for weaker Lewis bases.

Comparison of chloride ion promoted C_6F_5 group transfer reactions from $C_6F_5SiF_3$ and $C_6F_5SiCl_3$ suggests that in dichloromethane solution the transition structure for the trifluorosilyl derivative is 10.4 kcal/mol lower than that for the trichlorosilyl counterpart (TS8 vs TS9). A similar trend is observed for perchlorate-activated processes ($\Delta\Delta G^{\ddagger}_{sol} = 10.0$ kcal/mol, TS10 vs TS11). The trifluoroacetate anion showed similar reactivity to that of the chloride anion.

It is also interesting to compare the reactions of dimethylfluorosilyl and trifluorosilyl derivatives (Figure 3). In the case of fluoride activation, the methylated siliconate $Me_2(C_6F_5)SiF_2^-$ is more reactive than tetrafluorosiliconate $C_6F_5SiF_4^-$, even despite the fact that in the transition structures of the reaction of $Me_2(C_6F_5)SiF_2^-$ the C_6F_5 group is transferred from an equatorial position, while for $C_6F_5SiF_4^-$, it is from an apical position. On the other hand, for chloride- and perchlorate-initiated processes, the reverse trend is observed, with trifluorosilane $C_6F_5SiF_3$ being more reactive than dimethylsilane $Me_2(C_6F_5)SiF$. In the latter case, the faster reactions of trifluorosilane are associated both with more effective siliconate formation and with higher population of the isomer with an axial C_6F_5 group. Indeed, comparison of data from Tables 3 and 6 suggests that siliconates derived from $C_6F_5SiF_3$ have a smaller energy difference between geometrical isomers than those of $Me_2(C_6F_5)SiF_2^-$. Furthermore, the barrier for the apical/equatorial interconversion is known to be lower for more halogenated siliconates,[2b] thereby rendering the most reactive species with the axial C_6F_5 group more accessible for siliconates $C_6F_5SiF_3X^-$.

These data allow one to formulate an important generalization for the group transfer processes from a series of silanes R_2R_tSiX (R_t = transferable group, X = heteroatom, R = any substituent): *Upon employment of strong activators forming stable five-coordinate siliconates, those silanes with substituents providing the least stabilization of the siliconate species will be the more reactive. When using weak activators, thus*

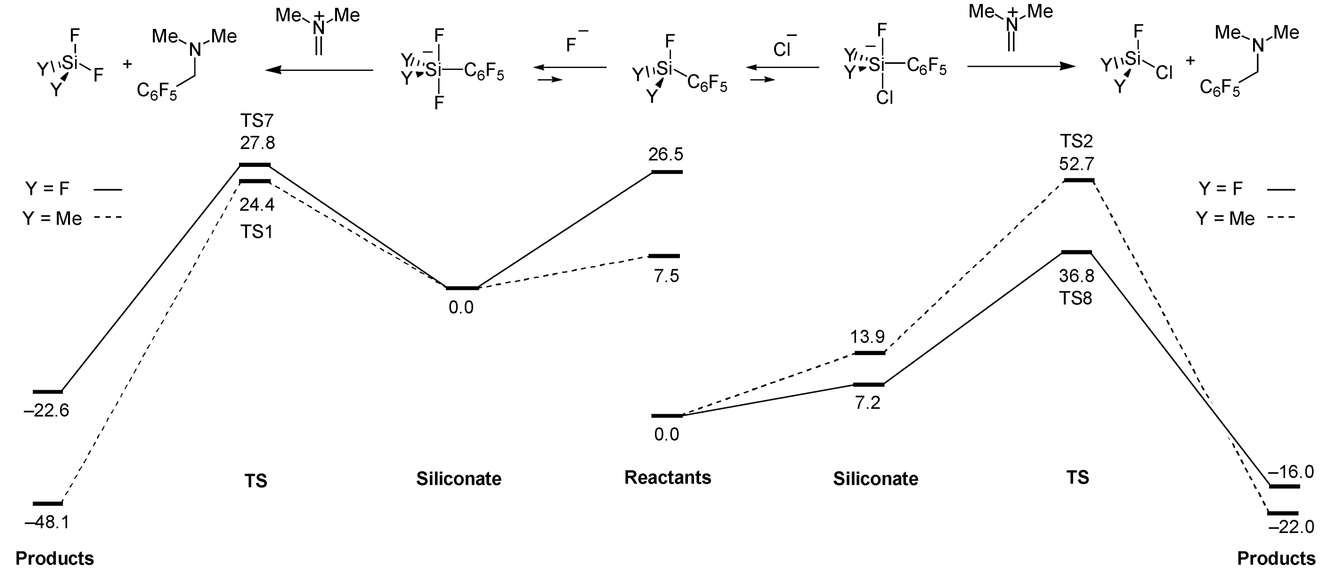
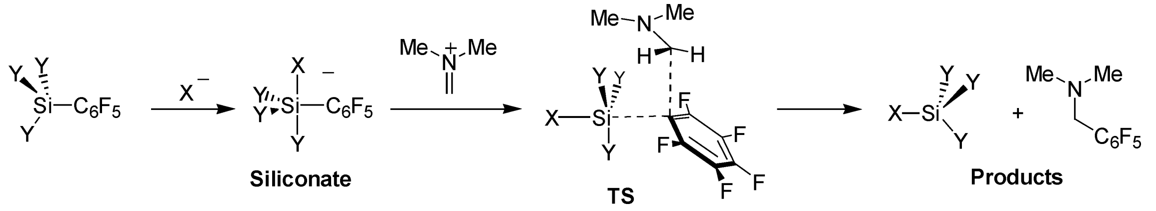


FIGURE 3. Free energy profiles of fluoride (left) and chloride (right) assisted reactions in dichloromethane solution (in kcal/mol).

TABLE 7. Reaction Energies (kcal/mol, at 298.15 K)

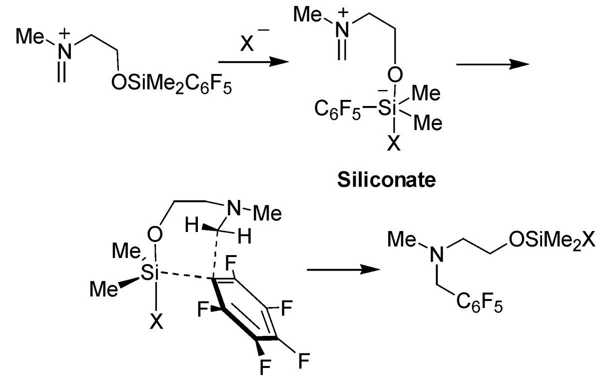


reaction	ΔE	ΔH	ΔG	ΔG (CH_2Cl_2)
$C_6F_5SiF_3 + F^- + CH_2{=}NMe_2^+$				
reactants	76.9	77.5	68.7	26.5
siliconate	0.0	0.0	0.0	0.0
TS7	−63.6	−64.1	−50.6	**27.8**
products	−108.2	−108.2	−106.5	−22.6
$C_6F_5SiF_3 + Cl^- + CH_2{=}NMe_2^+$				
reactants	0.0	0.0	0.0	0.0
siliconate	−28.3	−28.9	−20.8	7.2
TS8	−87.8	−89.0	−68.0	**36.8**
products	−134.8	−135.4	−126.0	−16.0
$C_6F_5SiCl_3 + Cl^- + CH_2{=}NMe_2^+$				
reactants	0.0	0.0	0.0	0.0
siliconate	−25.9	−26.4	−18.7	11.9
TS9	−74.5	−75.7	−55.5	**47.2**
products	−136.6	−137.2	−128.5	−18.8
$C_6F_5SiF_3 + ClO_4^- + CH_2{=}NMe_2^+$				
reactants	0.0	0.0	0.0	0.0
siliconate	−13.5	−14.1	−2.6	15.8
TS10	−62.1	−63.3	−37.7	**54.1**
products	−101.8	−102.4	−90.5	6.0
$C_6F_5SiCl_3 + ClO_4^- + CH_2{=}NMe_2^+$				
reactants	0.0	0.0	0.0	0.0
siliconate	−8.3	−8.9	2.4	22.9
TS11	−48.7	−49.9	−25.7	**64.1**
products	−104.6	−105.2	−93.6	2.5
$C_6F_5SiF_3 + CF_3CO_2^- + CH_2{=}NMe_2^+$				
reactants	0.0	0.0	0.0	0.0
siliconate	−28.5	−29.1	−15.8	4.0
TS12	−82.6	−83.8	−57.1	**35.5**
products	−123.7	−124.3	−110.9	−14.4

generating a five-coordinate intermediate in low equilibrium concentration, the silanes having substituents with the strongest anion-stabilizing effect will be the most reactive.

As was demonstrated in Table 1, among different substituents, fluoride and pentafluorophenyl groups provide the most significant stabilizing effect for the formation of siliconate anion. In this respect, the silanes of general formula $(C_6F_5)_nSiF_{4-n}$, $n = 1-4$, should be first evaluated experimentally in Lewis base mediated reactions. However, tetrakis(pentafluorophenyl)silane $(C_6F_5)_4Si$ is expected to be the least reactive in solution since,

TABLE 8. Energies for Intramolecular Reaction (kcal/mol, at 298.15 K)



	ΔE	ΔH	ΔG	ΔG (CH_2Cl_2)
$X^- = F^-$				
reactants	0.0	0.0	0.0	0.0
siliconate	−112.5	−113.1	−105.3	−3.8
TS13	−110.7	−111.3	−101.0	**11.3**
product	−182.7	−183.3	−176.2	−57.5
$X^- = Cl^-$				
reactants	0.0	0.0	0.0	0.0
siliconate	−65.3	−65.9	−58.7	22.1
TS14	−61.7	−62.3	−50.4	**43.1**
product	−134.3	−134.9	−127.3	−24.5

in its structure, there are no silicon−heteroatom bonds, necessary for the silicon to exhibit sufficient Lewis acidity for complexing weak Lewis bases.

The overall efficiency of Lewis base mediated processes results from the interplay of two steps: complexation of silicon reagent with Lewis base and C_6F_5 group transfer. The variation of environment around the silicon atom mainly facilitates the first step. At the same time, the C−C bond forming event can also be accelerated by rendering the process intramolecular. In particular, we have recently reported a method for the synthesis of pentafluorophenylated amino alcohols, where the key step involves the acetate ion induced C_6F_5 group transfer from *N*-(2-silyloxyethyl)iminium cation [$RCH{=}N^+(Me)CH_2CH_2OSi(C_6F_5)_3$].[9b]

Though no mechanistic studies to confirm the intramolecular character of the transformation have been performed, the reaction proceeded smoothly under very mild conditions.[9b] As a mechanistic probe to distinguish between inter- and intramolecular C_6F_5 group transfer, we calculated the energy profiles for the fluoride and chloride ion promoted reactions of *N*-methyl-*N*-(2-silyloxyethyl)methyleneiminium ion (Table 8).

Comparison of these data with those for the reaction of dimethyliminium cation with $Me_2(C_6F_5)SiF$ suggests that in solution both fluoride- and chloride-mediated reactions proceed considerably faster intramolecularly (F^-, $\Delta\Delta G^{\ddagger}_{sol} = 13.1$ kcal/mol, TS1 vs TS13; Cl^-, $\Delta\Delta G^{\ddagger}_{sol} = 9.6$ kcal/mol, TS2 vs TS14). This means that for intramolecular processes milder conditions may be used in synthetic experiments.

Experimental Studies. To validate the theoretical considerations, we performed a series of Lewis base promoted reactions between an iminium electrophile and various pentafluorophenylsilanes. *N*,*N*-Dimethylbenzylideneiminium triflate (**3**), obtained from benzylidenemethylamine and methyl triflate, was selected as model electrophile. As basic activators, the anions of protic acids were tested, which were employed either in the form of quaternary ammonium salts or generated in situ from acid and triethylamine. The standard ratio of reagents was used throughout (**3**:silane:activator = 1:1.1:1.2, [**3**] = 0.25 M), and reactions were performed either in methylene chloride at room temperature or in 1,2-dichloroethane at reflux (82 °C). After mixing the reagents and exposure for a certain period of time (45 min, 3 h, 15 h), the mixture was worked up and amine **4** was isolated by flash column chromatography. The results of variation of Lewis base and silane are presented in Table 9.

The mixture of acetic acid (pK_a = 4.76) and triethylamine induced the pentafluorophenylation of **3** with $(C_6F_5)_3SiF$, whereas $C_6F_5SiF_3$ proved to be noticeably less reactive. Lowering the Lewis basicity of the activator by using 3-cyanobenzoate anion (pK_a = 3.64) insignificantly affected the reaction efficiency furnishing amine **4** in 44% yield after 15 h at room temperature. Further decrease of anion basicity to 3,5-dinitro- and 2,4-dinitrobenzoates (pK_a 2.82 and 1.42, respectively) retarded the reaction, though the yields of 48−52% were achieved at elevated temperature (Table 9, entries 6 and 7).

Subsequently, we tested the anions of strong protic acids, such as trifluoroacetic (pK_a = −0.26), methanesulfonic (pK_a = −1.89), HBr (pK_a = −9.00), and HCl (pK_a = −8.00). It was rewarding to find that these activators are able to promote the pentafluorophenylation in refluxing dichloroethane (Table 9, entries 8−17). To the best of our knowledge, these are the first examples when the poorly nucleophilic trifluoroacetate, mesylate, chloride, and bromide anions trigger C−C bond formation by nucleophilic activation of a silicon atom! Of special note is the high yield of product (85%) in experiment with the chloride ion serving as Lewis base (Table 9, entry 17). Heating of iminium triflate **3** with $(C_6F_5)_3SiF$ without any additives did not give any product, thereby demonstrating that triflate anion (pK_a of TfOH equals −14) cannot be exploited as a competent Lewis base.

Different pentafluorophenylsilanes were combined with iminium salt **3** under optimal conditions (Table 9, entries 18−24). On the basis of the yield of the product, it can be concluded that the reactivity of silanes decreases in the order: $(C_6F_5)_3SiF > C_6F_5SiF_3 > (C_6F_5)_3SiOMe \gg$ other silanes. Fluorosilanes were considerably more active than analogous chlorosilanes (cf. entries 17 and 22; 18 and 19), which is in full agreement with theoretic predictions.

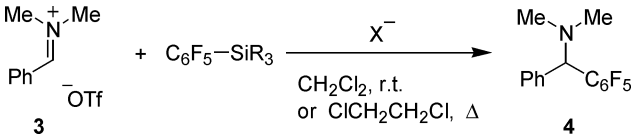
Concerning intramolecular reactions, iminium salt **5**, obtained from benzylidenemethylamine and 2-silyloxyethyltriflate according to our recent procedure,[9b] was treated with a series of Lewis bases to afford amino alcohol **6**, and the results are collected in Table 10.

All activators, which worked for salt **3**, also were applicable for the synthesis of amino alcohol **6**. As a rule, siloxyethyliminium salt **5** reacted more readily compared to the combination of **3**/$(C_6F_5)_3SiF$. For example, amino alcohol **6** can be obtained by using 3,5-dinitrobenzoate anion at room temperature (Table 10, entry 2), whereas system **3**/$(C_6F_5)_3SiF$ is absolutely ineffective under similar conditions (Table 9, entry 5). Employment of a chloride anion as activator also provided good yield of **6**. Interestingly, the latter reaction slowly proceeds even at room temperature (Table 10, entry 10). The efficiency of the C_6F_5 group transfer from salt **5**, as well as the results of calculations, testifies in favor of intramolecular mechanism of the process.

Conclusion

We demonstrated both theoretically and experimentally that a pentafluorophenyl group exerts a considerable stabilizing effect

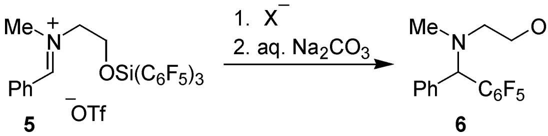
TABLE 9. Lewis Base Activated C_6F_5 Group Transfer Reactions



entry	silane	X⁻	solvent	temp	time	yield of **4** (%)[a]
1	$C_6F_5SiF_3$	AcOH/NEt_3	CH_2Cl_2	rt	45 min	<5
2	$(C_6F_5)_3SiF$	AcOH/NEt_3	CH_2Cl_2	rt	45 min	35
3	$(C_6F_5)_3SiF$	AcOH/NEt_3	CH_2Cl_2	rt	15 h	58
4	$(C_6F_5)_3SiF$	3-NC−BzOH/NEt_3	CH_2Cl_2	rt	15 h	44
5	$(C_6F_5)_3SiF$	3,5-$(NO_2)_2$−BzOH/NEt_3	CH_2Cl_2	rt	45 min	<5
6	$(C_6F_5)_3SiF$	3,5-$(NO_2)_2$−BzOH/NEt_3	$ClCH_2CH_2Cl$	82 °C	3 h	48
7	$(C_6F_5)_3SiF$	2,4-$(NO_2)_2$−BzOH/NEt_3	$ClCH_2CH_2Cl$	82 °C	3 h	52
8	$C_6F_5SiF_3$	CF_3CO_2H/NEt_3	$ClCH_2CH_2Cl$	82 °C	3 h	19
9	$(C_6F_5)_3SiF$	CF_3CO_2H/NEt_3	$ClCH_2CH_2Cl$	82 °C	3 h	35
10	$(C_6F_5)_3SiF$	CF_3CO_2 NBu_4	$ClCH_2CH_2Cl$	82 °C	3 h	41
11	$C_6F_5SiF_3$	CF_3CO_2 NBu_4	$ClCH_2CH_2Cl$	82 °C	3 h	12
12	$(C_6F_5)_3SiF$	MsO NBu_4	$ClCH_2CH_2Cl$	82 °C	3 h	48
13	$(C_6F_5)_3SiF$	Bu_4NBr	$ClCH_2CH_2Cl$	82 °C	3 h	65
14	$C_6F_5SiF_3$	Bu_4NBr	$ClCH_2CH_2Cl$	82 °C	3 h	38
15	$(C_6F_5)_3SiF$	−	$ClCH_2CH_2Cl$	82 °C	3 h	<5
16	$(C_6F_5)_3SiF$	$BnNEt_3Cl$	CH_2Cl_2	rt	15 h	8
17	**$(C_6F_5)_3SiF$**	**$BnNEt_3Cl$**	**$ClCH_2CH_2Cl$**	**82 °C**	**3 h**	**85**
18	$C_6F_5SiF_3$	$BnNEt_3Cl$	$ClCH_2CH_2Cl$	82 °C	3 h	39
19	$C_6F_5SiCl_3$	$BnNEt_3Cl$	$ClCH_2CH_2Cl$	82 °C	3 h	<5
20	$(C_6F_5)_3SiOMe$	$BnNEt_3Cl$	$ClCH_2CH_2Cl$	82 °C	3 h	21
21	$C_6F_5Si(OEt)_3$	$BnNEt_3Cl$	$ClCH_2CH_2Cl$	82 °C	3 h	<5
22	$(C_6F_5)_3SiCl$	$BnNEt_3Cl$	$ClCH_2CH_2Cl$	82 °C	3 h	<5
23	$(C_6F_5)_4Si$	$BnNEt_3Cl$	$ClCH_2CH_2Cl$	82 °C	3 h	<5
24	$(C_6F_5)_3SiMe$	$BnNEt_3Cl$	$ClCH_2CH_2Cl$	82 °C	3 h	15

[a] Isolated yield.

TABLE 10. Intramolecular Lewis Base Activated C_6F_5-group Transfer Reactions



entry	LB	solvent	temp	time	yield of **6** (%)[a]
1[b]	AcOH/NEt_3	CH_2Cl_2	rt	20 min	75
2	3,5-$(NO_2)_2$−BzOH/NEt_3	CH_2Cl_2	rt	45 min	64
3	2,4-$(NO_2)_2$−BzOH/NEt_3	CH_2Cl_2	rt	45 min	38
4	2,4-$(NO_2)_2$−BzOH/NEt_3	CH_2Cl_2	rt	3 h	53
5	Cl_2CHCO_2H/NEt_3	CH_2Cl_2	rt	3 h	31
6	CF_3CO_2 NBu_4	$ClCH_2CH_2Cl$	82 °C	3 h	50
7	Bu_4NOMs	$ClCH_2CH_2Cl$	82 °C	3 h	43
8	Bu_4NBr	$ClCH_2CH_2Cl$	82 °C	3 h	54
9	$BnNEt_3Cl$	$ClCH_2CH_2Cl$	82 °C	3 h	77
10	$BnNEt_3Cl$	CH_2Cl_2	rt	15 h	32
11	−	$ClCH_2CH_2Cl$	82 °C	3 h	<5

[a] Isolated yield. [b] From ref 9b.

on a pentacoordinate silicon intermediate, and the magnitude of this effect is comparable to that of fluorine. However, in addition to having the role of an electron-withdrawing group, a pentafluorophenyl substituent may also serve as a transferable nucleophilic group toward carbon electrophiles.

By varying the character of other substituents on silicon, it is possible to achieve a suitable energetic balance between the generation and subsequent reaction of the pentacoordinate silicon intermediate so that very weak Lewis base activators can be used. Indeed, under certain conditions, even chloride and trifluoroacetate anions exhibited noticeable activity as nucleophilic promoters for the transfer of a pentafluorophenyl group from silicon to the iminium carbocation. Given the ample opportunities for the generation of electrophilic species by protonation of organic substrates with hydrochloric or trifluoroacetic acids with concomitant appearance of corresponding conjugate bases, the data presented in this work pave the way for the development of new carbon−carbon bond forming processes employing silicon reagents. The results of our investigations along these lines will be reported in forthcoming publications.

Experimental Section

Fluorotris(pentafluorophenyl)silane was obtained according to modified procedure.[29] Fluorosulfonic acid (4.0 mL, 70 mmol) was added dropwise through the reflux condenser to a suspension of tris(pentafluorophenyl)phenylsilane[11a] (18.2 g, 30 mmol) in dichloroethane (20 mL). The exothermic reaction occurred accompanied by the dissolution of starting silane. After stirring for 10 min, the reaction flask was heated at 50 °C for additional 1.5 h, and the solvent was evaporated under vacuum (finally applying oil pump at 50 °C to ensure complete removal of dichloroethane). The residue was treated with hexane (40 mL) that provided a two-phase mixture. The upper layer containing most of the product was decanted, and the lower layer was extracted with hot hexane (10 mL). The combined hexane layers were heated to reflux, and sodium fluoride (0.25 g, 6 mmol) was added. The solution was filtered while hot and allowed to cool to 5 °C that caused precipitation of clear colorless needles. Filtration and drying in vacuum afforded 14.5 g of $(C_6F_5)_3SiF$ (88% yield).

Pentafluorophenyltrifluorosilane. The mixture of sodium hexafluorosiliconate (16.6 g, 50 mmol) and pentafluorophenyltrichlorosilane[30] (7.54 g, 25 mmol) was refluxed for 1 h and then distilled

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(29) Frohn, H. J.; Lewin, A.; Bardin, V. V. *J. Organomet. Chem.* **1998**, *568*, 233.

at 105−109 °C (ambient pressure) to give 5.36 g of $C_6F_5SiF_3$ (85% yield).

***N,N*-Dimethylbenzylideneiminium triflate (3).** Benzylidenemethylamine (2.5 g, 21 mmol) was added to the solution of methyl triflate (2.5 mL, 22.1 mmol) in benzene (15 mL) that caused an exothermic reaction and formation of a biphasic mixture. After stirring for 2 min, the mixture was allowed to cool slowly without stirring. After crystallization of the lower layer, the benzene was decanted, and the residue was washed with benzene (2 × 10 mL). Drying in vacuum provided 5.82 g of colorless crystals (98% yield). Mp 77−78 °C. ^{1}H NMR (300 MHz, CD_3CN) δ: 3.76 (d, 3H, J = 1.2 Hz, Me), 3.86 (d, 3H, J = 1.2 Hz, Me) 7.69−7.94 (m, 5H, Ph), 8.99 (s, 1H, CH). ^{13}C NMR (50 MHz, CD_3CN) δ: 45.1, 52.8, 131.2, 133.9, 137.3, 174.0.

Lewis Base Activated Reactions. To the iminium triflate (1 mmol) were successively added 4 mL of dry solvent, silane (1.1 mmol), and quaternary ammonium salt (1.2 mmol). The mixture was stirred either at room temperature or at gentle reflux for the time indicated in Table 9 or 10. For the workup, saturated aqueous Na_2CO_3 (0.8 mL) was added at 10 °C, and the resulting suspension was diluted with 15 mL of ether/hexane (1:1), filtered through anhydrous Na_2SO_4, and concentrated in vacuum. The residue was chromatographed on silica gel.

For experiments using an acid/NEt_3 mixture, 3 mL of solvent was added to the iminium triflate (1 mmol) followed by addition of silane (1.1 mmol) and a solution of acid (1.2 mmol) and triethylamine (167 μL, 1.2 mmol) in 1 mL of solvent. After completion, the mixture was worked up as described above.

Dimethyl(pentafluorophenylphenylmethyl)amine (4). Chromatography in hexanes−EtOAc, 10:1, R_f = 0.32; bp 144−150 °C/15 Torr (bath temperature). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.29 (s, 6H, NMe_2), 4.84 (s, 1H, CH), 7.24−7.39 (m, 3H, Ph), 7.47−7.55 (m, 2H, Ph). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ: 44.0, 66.0, 115.1 (tm, J = 15.3 Hz, *i*-C_6F_5), 127.3, 127.7, 128.6, 137.6 (dm, J = 252.6 Hz), 139.9, 140.2 (dm, J = 253.3 Hz), 144.8 (dm, J = 249.5 Hz). ^{19}F NMR (188 MHz, $CDCl_3$) δ: −162.79 (td, 2F, J = 22.2, 8.3 Hz, *meta*), −156.62 (t, 1F, J = 20.8 Hz, *para*), −140.14 (dm, 2F, J = 22.8 Hz, *ortho*). Anal. Calcd for $C_{15}H_{12}F_5N$: C, 59.80; H, 4.01; N, 4.65. Found: C, 59.64; H, 3.91; N, 4.53.

***N*-Methyl-*N*-(pentafluorophenylphenylmethyl)-2-aminoethanol (6).**[9b] Chromatography in hexane/EtOAc 3:1, R_f = 0.36.

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Supporting Information Available: Cartesian coordinates and absolute energies for calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0606812

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(30) Frohn, H. J.; Giesen, M.; Klose, A.; Lewin, A.; Bardin, V. V. *J. Organomet. Chem.* **1996**, *506*, 155.