J|A|C|S ARTICLES

Published on Web 07/07/2010

Selective Aromatic C−F and C−H Bond Activation with Silylenes of Different Coordinate Silicon

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Abstract: Herein we report on the reaction of stable two-coordinate silylene, L^1Si [L^1 = CH{(C═CH_2)(CMe)(2,6-*i*$Pr_2C_6H_3N)_2$}] (**1**) and three-coordinate silylene (Lewis base stabilized silylene), L^2SiCl [L^2 = $PhC(NtBu)_2$] (**2**) with aromatic compounds containing C−F and C−H bonds. The reaction of **1** and **2** with hexafluorobenzene (C_6F_6) affords the silicon(IV) fluorides, $L^1SiF(C_6F_5)$ (**3**) and $L^2SiFCl(C_6F_5)$ (**4**), respectively. The reaction proceeds through the unprecedented oxidative addition of one of the C−F bonds to the silicon(II) center without any additional catalyst. When **1** and **2** are treated with octafluorotoluene ($C_6F_5CF_3$), pentafluoropyridine (C_5F_5N) regioselective C−F bond activation occurs leading to the formation of $L^1SiF(4\text{-}C_6F_4CF_3)$ (**5**), $L^1SiF(4\text{-}C_5F_4N)$ (**6**), $L^2SiFCl(4\text{-}C_6F_4CF_3)$ (**7**), and $L^2SiFCl(4\text{-}C_5F_4N)$ (**8**), respectively. More interestingly, compounds **1** and **2** react with pentafluorobenzene (C_6F_5H) under formation of silicon(IV) hydride $L^1SiH(C_6F_5)$ (**9**) by chemoselective C−H bond activation, in the latter case producing silicon(IV) fluoride $L^2SiFCl(4\text{-}C_6F_4H)$ (**10**) by chemo- as well as regioselective C−F bond activation. Furthermore, the reaction of **1** with 1,3,5-trifluorobenzene ($1,3,5\text{-}C_6F_3H_3$) leads to the chemoselective formation of silicon(IV) hydride $L^1SiH(1,3,5\text{-}C_6F_3H_2)$ (**11**). The formation of compounds **9** and **11** occurs via oxidative addition of the aromatic C−H bond to the silicon(II) center instead of C−F bond activation. All reported reactions proceed without any additional catalyst. Compounds **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, and **11** were investigated by microanalysis and multinuclear NMR spectroscopy and compounds **3**, **7**, **8**, and **9** additionally by single crystal X-ray structural analyses.

Introduction

Divalent silicon compounds are known as silylenes, and they represent an indispensable synthon in organosilicon chemistry.[1] Since 1994, when West et al.[2] isolated the first silylene, it was known that stable silylenes are generally two-coordinate. In 2006 a three-coordinate base stabilized silylene L^2SiCl [L^2 = $PhC(NtBu)_2$] (**2**),[3] was prepared. Following that there were some reports on the synthesis of three-coordinate stable silylenes,[4] including NHC·$SiCl_2$[5] and NHC·$SiBr_2$[6] [NHC = C[N(2,6-*i*$Pr_2C_6H_3$)CH]$_2$]. Unlike carbenes, silylenes have invariably a singlet electronic ground state. Therefore they can act both as Lewis acids and as Lewis bases.[7,8] Consequently the silylenes are electronically and coordinatively unsaturated, and they are capable of a variety of insertion reactions into X−Y bonds (X−Y: C−H,[9] N−H,[10] O−H,[11] S−H,[10c] P−P,[12] N−Si,[13] C−Cl,[14] C−Br,[14] C−I,[14] and Si−Cl[14] bonds), to yield silanes with different substituents. To the best of our knowledge, there are no reports in literature on the insertion reactions of stable

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silylenes into aromatic C−H bonds or into any kind of C−F bond. Therefore we became interested in studying the reactivity of stable silylenes, L^1Si [L^1 = CH{(C═CH_2)(CMe)(2,6-iPr$_2$C$_6$H$_3$N)$_2$}] (**1**)[15] and L^2SiCl (**2**)[3,16] with aromatic compounds containing C−F and C−H bonds, namely, hexafluorobenzene (C_6F_6), octafluorotoluene ($C_6F_5CF_3$), pentafluoropyridine (C_5F_5N), pentafluorobenzene (C_6F_5H), and 1,3,5-trifluorobenzene (1,3,5-$C_6F_3H_3$). These compounds were selected with the intention to study whether they can form the oxidative addition products by insertion reactions into the aromatic C−F or C−H bond. Direct transformations of aromatic C−F and C−H bonds are a real challenge in chemistry. Specifically the C−F bond is in most cases thermally, photochemically, electrooxidatively, and often even chemically stable, so that it is in general not easy to cleave this bond for chemical modifications of organofluoro compounds. But still it is potentially useful for synthetic chemistry to utilize effective C−F bond activation of aryl fluorides. The organic compounds with fluorine-containing groups are important in pharmaceutical, agrochemical, and materials science.[17] Polyfluoroarenes are a representative class of such compounds, and thus the development of a selective C−F and C−H bond activation method is highly desired. In the literature one finds mostly reports on transition or lanthanide metals that are based on catalyzed or stoichiometric activated C−F and C−H bonds of polyfluoroarene compounds.[18−20] Some of these metal complexes are in high oxidation states and act through an electrophilic σ-metathesis pathway, while others are in low oxidation states and react by oxidative addition. Braun and Perutz et al. have reported that Ni(COD)$_2$ [COD = 1,5-cyclooctadiene] activates selectively C−F over C−H bonds of fluoropyridine substrates in the presence of triethylphosphine (PEt$_3$).[21] The reaction of Pt(PCy$_3$)$_2$ [Cy = cyclohexane] with pentafluoropyridine and 2,3,5,6-tetrafluoropyridine leads to C−F and C−H bond activation products, respectively; in the latter case a preference for C−H over C−F bond activation was observed.[22] Very recently Johnson et al. reported the selective C−F bond activation of tetrafluorobenzenes by Ni(0) with a nitrogen donor analogous to N-heterocyclic carbenes.[23] In 2008 Ozerov et al. described for the first time aliphatic C−F bond over aromatic C−F bond activation by using a silylium-carborane catalyst in the presence of a silicon(IV) hydride.[24] In the literature there are reports on C−H bond activation by compounds with low valent Group 14 elements (carbene, silylene, germylene, and stannylene)[25] and also on the silylene and germylene mediated C−H bond activation.[26] There is, however, only one report by Kuhn et al. on C−F bond activation of pentafluoropyridine by compounds with low valent Group 14 elements, namely, 1,3-dimethyl-4,5-dimethyl-2-ylidene and 1,3-diisopropyl-4,5-dimethyl-2-ylidene.[27] Very recently we have described the regioselective hydrodefluorination of carbonyl compounds containing aromatic C−F bonds including hexafluorobenzene by a tin(II) hydride.[28] Herein, we report on the regioselective activation of C−F bonds of fluoroarenes, the chemoselective activation of a C−H bond of partially fluorinated arenes using a silylene, L^1Si (**1**), and the regio and chemoselective activation of C−F over C−H bonds by three-coordinate silylene, L^2SiCl (**2**), without any additional catalyst. To the best of our knowledge this is the first stoichiometric main group system described that is able to activate the C−F bond of perfluoroarenes and simultaneously activates the C−H bond over the C−F bond of polyfluoroarenes. This demonstrates that the low valent silicon, congener of carbon, mimics transition metal complexes.[29]

Results and Discussion

The reaction of L^1Si [L^1 = CH{(C═CH_2)(CMe)(2,6-iPr$_2$C$_6$H$_3$N)$_2$}] (**1**) and L^2SiCl [L^2 = PhC(NtBu)$_2$] (**2**) with hexafluorobenzene (C_6F_6) leads to the pentafluorophenyl derivative of silicon(IV) fluoride, $L^1SiF(C_6F_5)$ (**3**) and $L^2SiFCl(C_6F_5)$ (**4**) (Scheme 1). The reaction proceeds through the unprecedented oxidative addition of one of the C−F bonds of C_6F_6 to the silicon(II) center.

Compounds **3** and **4** have been well-characterized by spectroscopic and analytic measurements, and compound **4** was in addition characterized by X-ray structural analysis. In the ^{19}F NMR spectra of **3** and **4** the Si−*F* resonances arise at δ −131.1 ppm and δ −63.4 ppm, respectively. These two chemical shifts are very much different due to the different coordination numbers at the silicon atoms. Compounds **3** and **4** display a

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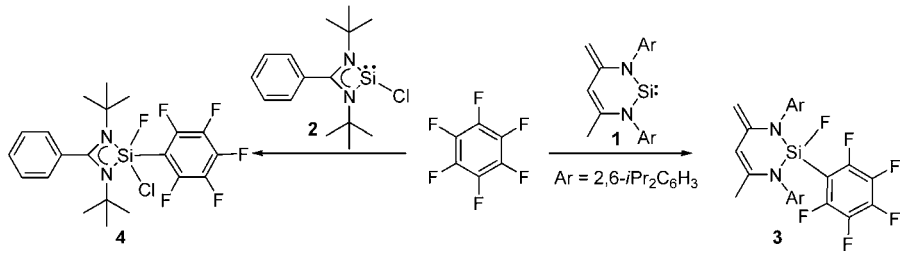
Scheme 1. Preparation of **3** and **4**



doublet in the ^{29}Si NMR spectrum (δ −54.3 ppm for **3** and δ −91.9 ppm for **4**) with a coupling constant of $^2J(^{29}\text{Si}-^{19}\text{F})$ = 262.58 Hz and $^2J(^{29}\text{Si}-^{19}\text{F})$ = 282.89 Hz, respectively. Compound **3** is soluble in benzene, THF, *n*-hexane, and *n*-pentane, which is in contrast to that of compound **4**, which is insoluble in nonpolar solvents, such as *n*-hexane and *n*-pentane, and both compounds are stable in the solid state as well as in solution for a long time without any decomposition under an inert atmosphere. Compound **3** crystallizes in the monoclinic space group *C*2/*c* from a saturated toluene solution at room temperature after one day, with one molecule in the asymmetric unit. X-ray crystal structure analysis afforded a monomeric structure as illustrated in Figure 1.

The coordination polyhedron around the silicon atom features a distorted tetrahedral geometry. The silicon is attached to two nitrogen atoms from the backbone of the chelating ligand, the terminal F atom, and a pentafluoro phenyl group. From the molecular structure of **3** we can see that the fluorine atom at silicon (F1) is closer to one of the two ortho fluorine atoms (F6) of the pentafluoro phenyl group (the distance between F1 and F6 is 2.665(5) Å, and the distance between F1 and F2 is 4.468(4) Å; see Figure 1). The Si1−N1 bond length and N1−Si1−N2 bond angle are 1.696(1) (Å) and 107.08(6)°, respectively. These data are comparable with those of related compounds.[30] A noteworthy feature of compound **3** is the SiF(C_6F_5) moiety; the Si−F bond length (Si1−F1 1.578(1) Å) can be compared with those of NHC·SiF_4 (av 1.577(2) Å) and those of NHC·SiF_4·NHC (av 1.66(2) Å) (NHC = C[N(2,6-*i*Pr$_2$C$_6$H$_3$)CH]$_2$), which are slightly longer.[31]

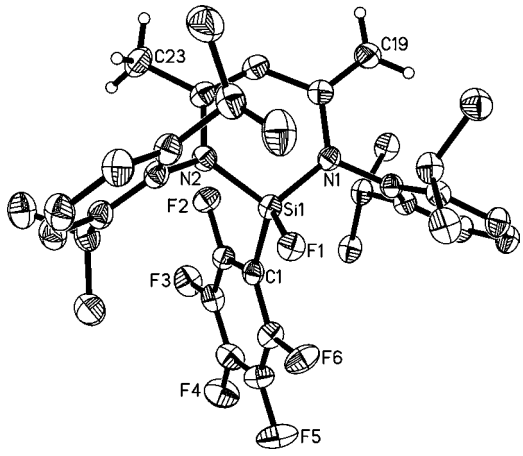


Figure 1. Molecular structure of **3**. Anisotropic displacement parameters are depicted at the 50% probability level. H atoms are omitted for clarity reasons except for H on C19 and C23. Selected bond lengths [Å] and angles [deg]: Si1−F1 1.5780(9), Si1−C1 1.8811(15), Si1−N1 1.6960(14); N1−Si1−C1 110.97(6), F1−Si1−N1 112.44(6), F1−Si1−C1 103.07(6), N1−Si1−N2 107.08(6).

Furthermore, we were interested in the selectivity of the oxidative addition of the C−F bond at the silicon(II) center. Therefore we selected other aromatic perfluoro compounds, namely, octafluorotoluene ($C_6F_5CF_3$) and pentafluoropyridine (C_5F_5N) (Scheme 2). Compounds **1** and **2** react with octafluoro toluene and pentafluoro pyridine in toluene at room temperature to form only one regioisomer with para-C−F bond activation relative to the CF_3 group and the nitrogen atom, respectively.

The CF_3 group of octafluoro toluene is not affected by the silicon(II) center, when it is reacted with any one of the mentioned silylenes (**1** or **2**) contrary to the reported C−F bond activation of this molecule.[24] This was confirmed by ^{19}F NMR measurement in benzene-d_6 solution, showing a triplet for the CF_3 group (δ −56.8 ppm; $^3J(^{19}\text{F}-^{19}\text{F})$ = 21.61 Hz for **5** and δ −56.1 ppm; $^3J(^{19}\text{F}-^{19}\text{F})$ = 21.75 Hz for **7**). The ^{1}H NMR spectra exhibit a singlet resonance (δ 5.45 and 5.44 ppm) which corresponds to the C−*H* protons of the ligand backbone of the fluorine substituted silane, L^{1}SiF(4-$C_6F_4CF_3$) (**5**) and L^{1}SiF (4-C_5F_4N) (**6**), respectively. It is also worth mentioning that in the ^{19}F NMR spectra of compounds **5**, **6**, **7**, and **8** the Si−*F* resonances arise at δ −131.5, −132.2, −63.7, and −64.4 ppm, respectively, which are almost similar when compared with those of **3** and **4** (δ −131.1 ppm for **3** and δ −63.4 ppm for **4**). In addition, the Si−F resonances of compounds **3**, **5**, and **6** exhibit doublets, with almost similar coupling constants (50.03 Hz for **3**, 49.71 for **5**, and 45.45 for **6**), due to coupling with only one of the ortho fluorines. The ^{29}Si NMR spectra of all four compounds (**5**, **6**, **7**, and **8**) show doublets (δ −55.2, −56.08, −97.2, and −97.9 ppm) with a coupling constant of $J(^{29}\text{Si}-^{19}\text{F})$ = 263.59, 263.66, 283.65, and 282.72 Hz, respectively. Compounds **5**, **6**, **7**, and **8** exhibit the base peak in the EI mass spectra at 665 [M$^+$−Me], 598 [M$^+$−Me], 530 [M]$^+$, and 428 [M$^+$−Cl], respectively.

In addition single crystal X-ray structural analysis was carried out for compounds **7** and **8**, confirming that only the para fluoride relative to the CF_3 group and N atom, respectively, is activated by the silylene **2**. Compounds **7** and **8** both crystallize in the triclinic space group $P\bar{1}$, with one monomer in the asymmetric unit. Compound **8** cocrystallizes with one disordered toluene molecule. Single crystals of **7** and **8** were obtained from a saturated toluene solution at room temperature (Table 1). The coordination polyhedron around the silicon atom features a distorted trigonal bipyramidal geometry with a terminal Si−F

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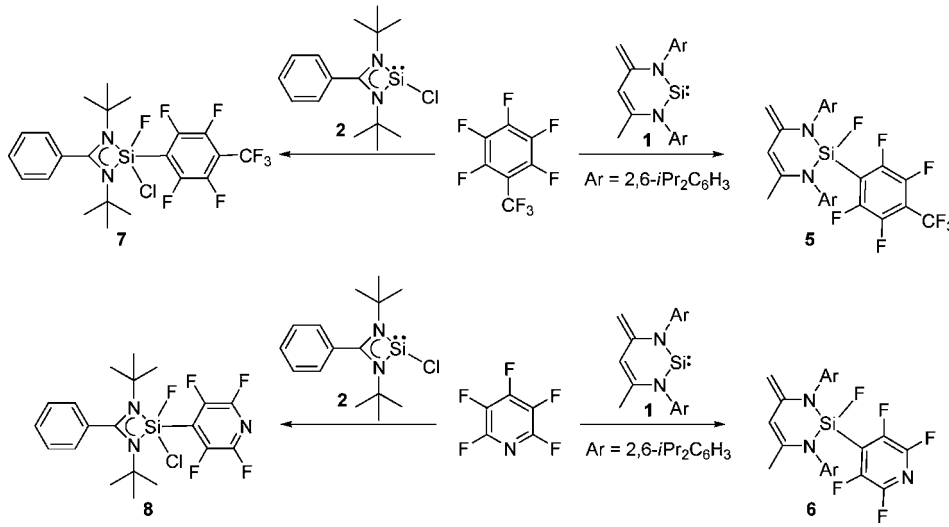
Scheme 2. Preparation of **5**, **6**, **7**, and **8**



bond (Figure 2 for **7** and Figure 3 for **8**). The Si−F bond lengths are almost similar (1.633(3) Å for **7** and 1.6394(19) Å for **8**), although they are longer compared to that of compound **3** (1.5780(9)Å), due to a different coordination number around silicon.

After the successful reaction of **1** and **2** with perfluoro aromatic compounds, we turned to partially fluorinated aromatic compounds, namely, pentafluoro benzene (C_6F_5H). The reaction of **1** and **2** with pentafluorobenzene leads to the chemoselective formation of silicon(IV) hydride $L^1SiH(C_6F_5)$ (**9**) and silicon(IV) fluoride $L^2SiFCl(4\text{-}C_6F_4H)$ (**10**), respectively, in good yields (Scheme 3).

The first reaction occurs via oxidative addition of the aromatic C−H bond to the silicon(II) center instead of C−F bond activation. This is most probably due to smaller C−H bond energy compared to that of the C−F bond. The second reaction proceeds via oxidative addition of the aromatic C−F bond to the silicon(II) center instead of C−H bond activation, although the C−F bond exceeds the C−H bond energy [$D(F-C_6F_5) - D(H-C_6H_5) = 16$ kJ mol^{-1}].[32] This is possible because the Si−F bond energy is higher, when compared with that of the Si−H bond. The ability of compound **2**, but not **1**, to undergo C−F bond activation rather than C−H bond activation demonstrates the effect of different coordination numbers around the silicon atoms to the resulting products **9** and **10**. In compound **9**, silicon has the coordination number 4, while **10** is 5-fold coordinated. In general silicon hydrides with high coordinate silicon are less

Table 1. Crystallographic Data at $T = 100$ [K] for the Structural Analyses of Compounds **3**, **7**, **8**, and **9**

	3	7	8·tol	9
empirical formula	$C_{35}H_{40}F_6N_2Si$	$C_{22}H_{23}ClF_8N_2Si$	$C_{27}H_{31}ClF_5N_3Si$	$C_{35}H_{41}F_5N_2Si$
molecular weight	630.78	530.96	556.09	612.79
T	100 K	100 K	100 K	100 K
CCDC-No.	770535	775969	775968	706622
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1$
a [Å]	20.810(4)	9.785(2)	9.832(2)	9.5252(19)
b [Å]	9.6243(19)	9.976(2)	10.142(2)	17.166(3)
c [Å]	33.923(7)	13.842(3)	14.530(3)	10.174(2)
α [deg]	90	89.57(3)	88.37(3)	90
β [deg]	104.28(3)	82.58(3)	88.69(3)	93.36(3)
γ [deg]	90	89.18(3)	71.03(3)	90
V [Å^3]	6584(2)	1339.8(5)	1369.4(5)	1660.7(6)
Z	8	2	2	2
ρ_{calc} [Mg m^{-3}]	1.273	1.316	1.349	1.225
μ [mm^{-1}]	0.132	0.255	0.239	0.125
$R1$ [$I > 2\sigma(I)$]	0.0350	0.0832	0.0550	0.0432
$wR2$ (all data)	0.0818	0.2396	0.1493	0.1087

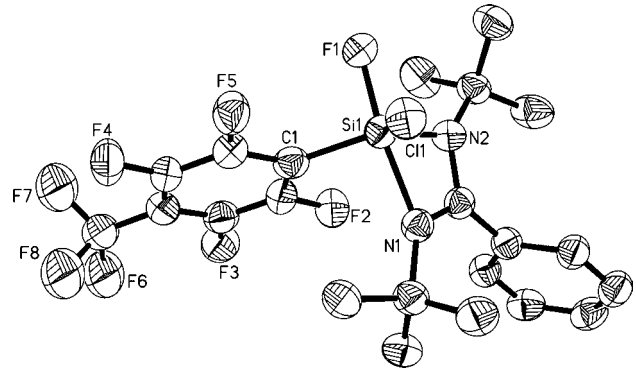


Figure 2. Molecular structure of **7**. Anisotropic displacement parameters are depicted at the 50% probability level. H atoms are omitted for clarity reasons. The CF_3 group is disordered, and only one of two orientations is shown. Selected bond lengths [Å] and angles [deg]: Si1−F1 1.633(3), Si1−Cl1 2.0705(16), Si1−C1 1.913(5), Si1−N1 1.938(3); N1−Si1−C1 91.73(16), F1−Si1−N2 97.92(15), F1−Si1−C1 92.57(16), F1−Si1−Cl1 94.56(11), N1−Si1−N2 69.94(15).

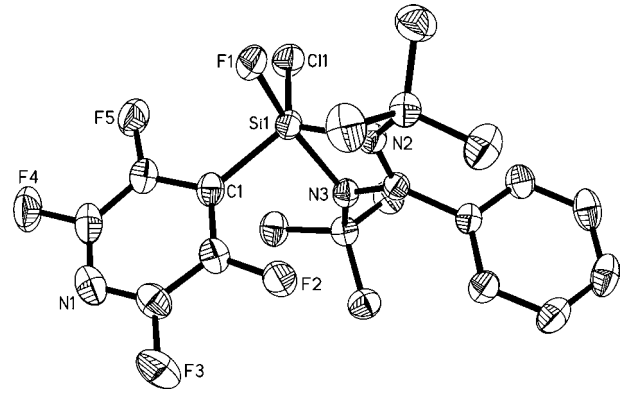
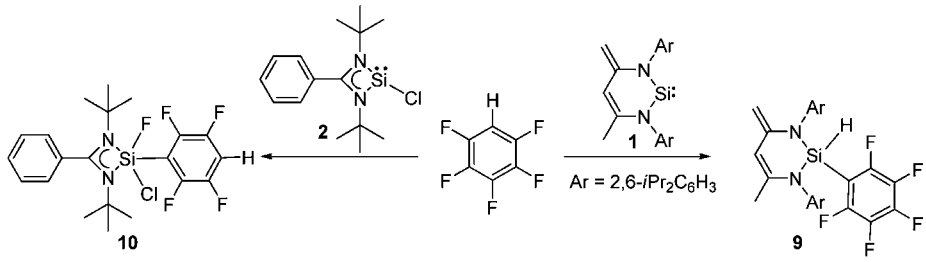


Figure 3. Molecular structure of **8**. Anisotropic displacement parameters are depicted at the 50% probability level. H atoms and cocrystallized toluene are omitted for clarity reasons. Selected bond lengths [Å] and angles [deg]: Si1−F1 1.6394(19), Si1−Cl1 2.0756(11), Si1−C1 1.905(3), Si1−N2 1.785(2); N2−Si1−C1 119.96(11), F1−Si1−N2 97.82(10), F1−Si1−C1 92.87(11), F1−Si1−Cl1 93.35(8), N2−Si1−N3 69.77(10).

Scheme 3. Preparation of **9** and **10**



stable than those of the corresponding fluoride analogues. This is the fundamental reason for the preferred formation of high coordinate silicon with fluorides and not with hydrides.

Single crystals of **9** were obtained from a saturated *n*-hexane solution at −32 °C after two days. Compound **9** crystallizes in the monoclinic space group $P2_1$, with one molecule in the asymmetric unit. X-ray crystal structural analysis revealed a monomeric structure as illustrated in Figure 4. The hydrogen on silicon is not involved in any kind of hydrogen bonding, whereas intramolecular hydrogen bonds are observed with both nitrogen atoms and the four CH protons of the *iso*-propyl groups. In addition there is an intermolecular hydrogen bond present between the terminal $=CH_2$ group of the ligand backbone and the fluorine F3 in para-position to silicon. This type of intermolecular interaction was also observed in the case of compound **3**. The hydrogen atom on silicon was found and refined without any restraints. Compound **9** is stable in the solid state as well as in solution for a long time without any decomposition under inert atmosphere. The coordination polyhedron around the silicon atom features a distorted tetrahedral geometry like that in compound **3**, only that the Si−F moiety is replaced by Si−H.

The ^{1}H, ^{19}F, and ^{29}Si NMR spectra revealed that **9** has a SiH(C_6F_5) moiety. The Si−H proton shows a resonance at δ 5.46 ppm. The fluorine NMR displays five different resonances, which are similar to those of compound **3**, but different when compared to those of $LSnC_6F_5$ [L = CH{(CMe)$_2$(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$}].[28] The reason is probably that compound **9** exists in solution in the same form as in the solid state, while in case of $LSnC_6F_5$ the pentafluoro phenyl group and the lone pair at

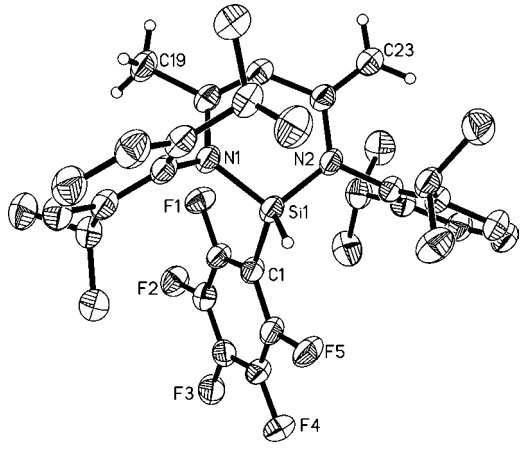
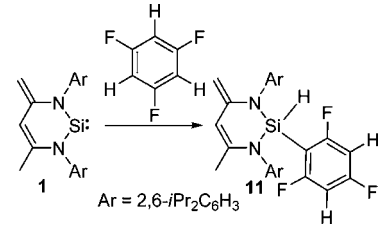


Figure 4. Molecular structure of **9**. Anisotropic displacement parameters are depicted at the 50% probability level. H atoms are omitted for clarity reasons except for H on silicon, which was found and refined freely, and H on C19 and C23. Selected bond lengths [Å] and angles [deg]: Si1−N1 1.7203(17), Si1−C1 1.890(2); N1−Si1−C1 113.01(9), N1−Si1−N2 105.79(9).

Scheme 4. Preparation of **11**



tin can rapidly interchange in solution. The ^{29}Si{^{1}H} decoupled proton spectrum of **9** exhibits a doublet resonance (δ −41.2 ppm) with a coupling constant of 18.28 Hz, due to the silicon atom (Si1) that couples with one of the ortho fluorine atoms (F1) of the pentafluoro phenyl group, while the proton coupled spectrum shows a doublet resonance with a coupling constant of $^2J(^{29}\text{Si}-^1\text{H}) = 261.63$ Hz. In addition the ^{1}H NMR spectrum exhibits the expected pattern for the ligand with four septets of the four *iso*-propyl groups.

^{1}H, ^{19}F, and ^{29}Si NMR spectroscopy confirmed that **10** has a SiF(4-C_6F_4H) moiety. The C−H proton shows a resonance at δ 6.48 ppm, and there is no indication for the formation of a Si−H bond. In the ^{19}F NMR, there is a Si−F resonance present at δ 59.2 ppm, which is attributed to ^{29}Si satellites with a coupling constant of $^2J(^{29}\text{Si}-^{19}\text{F}) = 288.84$ Hz. This is finally documented by measuring the ^{29}Si NMR, which exhibits a doublet (δ −96.03 ppm) with the same coupling constant. In the EI mass spectrum compounds **9** and **10** are showing the base peak at 597 [M$^+$−Me] and 427 [M$^+$−Cl], respectively.

Moreover, we reacted compound **1** with 1,3,5-trifluoro benzene (1,3,5-$C_6F_3H_3$) for checking whether the C−H or C−F bond activation has occurred. The reaction of **1** with 1,3,5-trifluoro benzene leads also to the chemoselective formation of silicon(IV) hydride L^1SiH(1,3,5-$C_6F_3H_2$) (**11**) in good yield (Scheme 4). The reaction occurs at 80 °C oil bath temperature, which is in contrast to the formation of compound **9**, which occurs at room temperature.

In the case of compound **11** the Si−H resonance appears at 5.42 ppm in the ^{1}H NMR spectrum, and the three fluorine atoms are displaying three different resonances in the ^{19}F NMR spectrum (δ −90.4 (*o*-F), −99.6 (*o*-F), and −103.9 (*p*-F) ppm). The ^{29}Si NMR spectrum exhibits a doublet of doublets (δ −40.1 ppm) with a coupling constant of $^1J(^{29}\text{Si}-^1\text{H}) = 256.3$ Hz and $^3J(^{29}\text{Si}-^{19}\text{F}) = 18.73$ Hz. In the EI mass spectrum compound **11** shows the base peak at 576 [M]$^+$ as the molecular ion.

Conclusion

In summary we have shown that aromatic C−F bond activation is possible with both silylenes L^1Si (**1**) and L^2SiCl (**2**), when they are reacted with perfluoroaromatic compounds in the absence of any additional catalyst. But the behavior of the two silylenes is very distinct when they are reacted with

partially fluorinated aromatic compounds. The two coordinate silylene of L^1Si (**1**) reacts via C−H bond activation, while the three-coordinate silylene of L^2SiCl (**2**) reacts via C−F bond activation. This is the first time that aromatic C−F bond activation has proved to be a useful tool for the preparation of silicon fluorine compounds. The stability of compounds **3**−**11** at room temperature favors their further functionalization. Currently, we are engaged in investigating other main-group reagents for selective C−F bond activation.

Experimental Section

All manipulations were performed under a dry and oxygen free atmosphere (N_2) using standard Schlenk techniques or inside a MBraun MB 150-GI glovebox maintained at or below 1 ppm of O_2 and H_2O. All solvents were distilled from Na/benzophenone prior to use. The starting materials **1**[15] and **2**[16] were prepared using literature procedures. Other chemicals were purchased commercially and used as received. ^{1}H, ^{19}F, and ^{29}Si NMR spectra were recorded on a Bruker Avance DRX instrument and referenced to the $SiMe_4$ in the case of the ^{1}H and ^{29}Si NMR and $CFCl_3$ for the ^{19}F NMR spectra, respectively. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument.

Synthesis of [CH(C═CH$_2$)(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$]SiF(C$_6$F$_5$) (3). An NMR tube was loaded with hexafluorobenzene (0.048 g, 0.25 mmol) and **1** (0.11 g, 0.25 mmol) at room temperature. After that toluene-d_8 (0.6 mL) was added, and the sealed NMR tube was kept in a hot oil bath at 120−130 °C. After 12 h the ^{1}H NMR spectrum was recorded and showed the formation of compound **3**. The solution from the NMR tube was transferred into a Schlenk flask, the solvent evaporated, and the residue extracted with toluene (2 mL). Storing this solution overnight at room temperature afforded colorless crystals, which were suitable for X-ray diffraction analysis. Yield 0.13 g (85%). Mp 156 °C. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 6.90−7.12 (m, 6H, Ar*H*), 5.46 (s, 1H, C*H*), 4.02 (s, 1H, CH_2), 3.77 (sept, 2H, CH(CH$_3$)$_2$), 3.46 (s, 1H, CH_2), 3.24 (sept, 1H, CH(CH$_3$)$_2$), 3.03 (sept, 1H, CH(CH$_3$)$_2$), 1.02−1.47 (m, 21H; CH_3 and CH(CH_3)$_2$), 0.40 (d, 6H, CH (CH_3)$_2$) ppm. ^{19}F NMR (188.29 MHz, C_6D_6): δ −123.92 (br, 1F, *o*-F), −125.41 (d, 1F, *o*-F), −131.13 (d, 1F, Si−*F*), −148.90 (t, 1F, *p*-F), −159.53 (br, 1F, *m*-F), −162.79 (br, 1F, *m*-F) ppm. ^{29}Si NMR (99.36 MHz, C_7D_8, 25 °C): δ −54.37 (^2J(^{29}Si−^{19}F) = 262.58 Hz) ppm. EI-MS (70 eV; *m*/*z* (%)): 630 (100) [M]$^+$. Anal. Calcd for $C_{35}H_{40}F_6N_2Si$ (630.29): C, 66.64; H, 6.39; N, 4.44. Found: C, 66.00; H, 6.51; N, 4.30.

Synthesis of [PhC(N*t*Bu)$_2$]SiFCl(C$_6$F$_5$) (4). An NMR tube was loaded with hexafluorobenzene (0.048 g, 0.25 mmol) and **2** (0.07 g, 0.25 mmol) at room temperature. Then toluene-d_8 (0.6 mL) was added, and the sealed NMR tube was kept in a hot oil bath at 120−130 °C. After 24 h the ^{1}H NMR spectrum was recorded and showed the formation of only compound **4**. The solution from the NMR tube was transferred into a Schlenk flask; after evaporation of the solvent compound **4** remained. Yield 0.09 g (76%). Mp 132 °C. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 6.81−7.04 (m, 5H, Ar*H*), 0.97 (s, 18H, C (CH_3)$_3$) ppm. ^{19}F NMR (188.29 MHz, C_6D_6): δ −63.4 (s, 1F, Si−*F*), −130.7 (br, 2F, *o*-*F*), −153.4 (t, ^3J(^{19}F−^{19}F) = 20.20 Hz, 1F, *p*-F), −161.3 (br, 2F, *m*-F) ppm. ^{29}Si NMR (99.36 MHz, C_7D_8, 25 °C): δ −91.9 (^1J(^{29}Si−^{19}F) = 282.89 Hz) ppm. EI-MS (70 eV; *m*/*z* (%)): 480 (25) [M]$^+$, 445 (100) [M$^+$−Cl]. Anal. Calcd for $C_{21}H_{23}ClF_6N_2Si$ (480.95): C, 52.44; H, 4.82; N, 5.82. Found: C, 53.04; H, 5.31; N, 6.18.

(32) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 67th ed.; CRC Press, FL, 1986, pp F186−F187.

Synthesis of [CH(C═CH$_2$)(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$]SiF(4-C$_6$F$_4$CF$_3$) (5). A solution of octafluorotoluene (0.23 g, 1.00 mmol in 5 mL of toluene) was added by cannula to a solution of **1** (0.44 g, 1.00 mmol in toluene 25 mL) at room temperature. After 12 h all volatiles were removed in vacuo, and the remaining residue was extracted with *n*-hexane (25 mL) to yield compound **5**. Yield 0.52 g (80%). Mp 61 °C. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 6.89−7.17 (m, 6H, Ar*H*), 5.46 (s, 1H; C*H*), 4.03 (s, 1H, CH_2), 3.72 (sept, 2H, CH(CH$_3$)$_2$), 3.47 (s, 1H, CH_2), 3.22 (sept, 1H, CH(CH$_3$)$_2$), 2.98 (sept, 1H, CH(CH$_3$)$_2$), 0.90−1.47 (m, 21H; CH_3 and CH(CH_3)$_2$), 0.38 (d, 6H, CH (CH_3)$_2$) ppm. ^{19}F NMR (188.29 MHz, C_6D_6): δ −56.8 (t, 3F, CF_3), −122.4 (br, 1F, *o*-F), −123.6 (d, 1F, *o*-F), −131.4 (d, 1F, Si−*F*), −138.3 (br, 1F, *m*-F), −141.0 (br, 1F, *m*-F) ppm. ^{29}Si NMR (99.36 MHz, C_6D_6, 25 °C): δ −55.2 (^2J(^{29}Si−^{19}F) = 263.59 Hz) ppm. EI-MS (70 eV; *m*/*z* (%)): 665 (100) [*M*−Me]$^+$. Anal. Calcd for $C_{36}H_{40}F_8N_2Si$ (680.28): C, 63.51; H, 5.92; N, 4.11. Found: C, 62.97; H, 6.02; N, 3.89.

Synthesis of [CH(C═CH$_2$)(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$]SiF(4-C$_5$F$_4$N) (6). A solution of pentafluoropyridine (0.17 g, 1.00 mmol in 5 mL of toluene) was added by cannula to a solution of **1** (0.42 g, 1.00 mmol in toluene 25 mL) at room temperature. After 12 h all the volatiles were removed in vacuo, and the remaining residue was extracted with *n*-hexane (20 mL) to yield compound **6**. Yield 0.54 g (88%). Mp 166 °C. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 6.85−7.17 (m, 6H, Ar*H*), 5.44 (s, 1H; C*H*), 4.04 (s, 1H, CH_2), 3.73 (sept, 2H, CH(CH$_3$)$_2$), 3.48 (s, 1H, CH_2), 3.26 (sept, 1H, CH(CH$_3$)$_2$), 2.96 (sept, 1H, CH(CH$_3$)$_2$), 0.90−1.45 (m, 21H; CH_3 and CH(CH_3)$_2$), 0.35 (d, 6H, CH (CH_3)$_2$) ppm. ^{19}F NMR (188.29 MHz, C_6D_6): δ −90.0 (br, 1F, *o*-F), −92.7 (d, 1F, *o*-F), −126.8 (br, 1F, *m*-F), −128.9 (br, 1F, *m*-F), −132.2 (d, 1F, Si−*F*) ppm. ^{29}Si NMR (99.36 MHz, C_6D_6, 25 °C): δ −56.08 (^2J(^{29}Si−^{19}F) = 263.66 Hz) ppm. EI-MS (70 eV; *m*/*z* (%)): 598 (100) [M$^+$−Me]. Anal. Calcd for $C_{34}H_{40}F_5N_3Si$ (613.29): C, 66.53; H, 6.57; N, 6.85. Found: C, 66.62; H, 6.64; N, 6.88.

Synthesis of [PhC(N*t*Bu)$_2$]SiFCl(4-C$_6$F$_4$CF$_3$) (7). A solution of octafluorotoluene (0.23 g, 1.00 mmol in 5 mL toluene) was added by cannula to a solution of **2** (0.29 g, 1.00 mmol in 25 mL of toluene) at room temperature. After 12 h all volatiles were removed in vacuo, and the remaining residue was extracted with toluene (20 mL), concentrated to about 5 mL and kept at room temperature. Colorless crystals of **7** suitable for X-ray diffraction analysis are formed after two days. Yield 0.37 g (70%). Mp 72 °C. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 6.94−7.08 (m, 5H, Ar*H*), 0.98 (s, 18H, C (CH_3)$_3$) ppm. ^{19}F NMR (188.29 MHz, C_6D_6): δ −56.1 (t, ^4J(^{19}F−^{19}F) = 21.75 Hz, 3F, CF_3), −63.7 (s, 1F, Si−*F*), −128.9 (br, 2F, *o*-*F*), −140.2 (br, 2F, *m*-F) ppm. ^{29}Si NMR (99.36 MHz, C_6D_6, 25 °C): δ −97.2 (^1J(^{29}Si−^{19}F) = 283.65 Hz) ppm. EI-MS (70 eV; *m*/*z* (%)): 530 (100) [M]$^+$. Anal. Calcd for $C_{22}H_{23}ClF_8N_2Si$ (530.96): C, 49.77; H, 4.37; N, 5.28. Found: C, 50.77; H, 5.37; N, 5.92.

Synthesis of [PhC(N*t*Bu)$_2$]SiFCl(4-C$_5$F$_4$N) (8). A solution of pentafluoropyridine (0.17 g, 1.00 mmol in 5 mL of toluene) was added by cannula to a solution of **2** (0.29 g, 1.00 mmol in 25 mL of toluene) at room temperature. After 12 h all volatiles were removed in vacuo, and the remaining residue was extracted with toluene (20 mL), concentrated to about 10 mL, and stored at room temperature. Colorless crystals of **8** suitable for X-ray diffraction analysis are formed after one day. Yield 0.38 g (82%). Mp 137 °C. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 7.02−7.09 (m, 5H, Ar*H*), 0.96 (s, 18H, C (CH_3)$_3$) ppm. ^{19}F NMR (188.29 MHz, C_6D_6): δ −64.4 (s, 1F, Si−*F*), −92.1 (br, 2F, *o*-*F*), −133.2 (br, 2F, *m*-F) ppm. ^{29}Si NMR (99.36 MHz, C_6D_6, 25 °C): δ −97.9 (^1J(^{29}Si−^{19}F) = 282.72 Hz) ppm. EI-MS (70 eV; *m*/*z* (%)): 463 (35) [M]$^+$, 428 (100) [M$^+$−Cl]. Anal. Calcd for $C_{20}H_{23}ClF_5N_3Si$ (463.95): C, 51.78; H, 5.00; N, 9.06. Found: C, 51.96; H, 5.29; N, 8.97.

Synthesis of [CH(C═CH$_2$)(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$]SiH(C$_6$F$_5$) (9). A solution of pentafluorobenzene (0.17 g, 1.00 mmol in 5 mL of toluene) was added by cannula to a solution of **1** (0.490 g, 1.00 mmol in 25 mL of toluene) at room temperature. After 12 h all the

volatiles were removed in vacuo, and the remaining residue was extracted with *n*-hexane (15 mL), concentrated to about 5 mL, and stored in a freezer at −30 °C. Colorless crystals of **9** suitable for X-ray diffraction analysis are formed after one day. Yield 0.54 g (90%). Mp 152 °C. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 6.77−7.15 (m, 6H, Ar*H*), 5.46 (br, 2H; C*H* and Si*H*), 4.02 (s, 1H, CH_2), 3.74 (sept, 1H, C*H*$(CH_3)_2$), 3.63 (sept, 1H, C*H*$(CH_3)_2$), 3.45 (s, 1H, CH_2), 3.24 (sept, 1H, C*H*$(CH_3)_2$), 3.10 (sept, 1H, C*H*$(CH_3)_2$), 1.01−1.67 (m, 21H; CH_3 and CH$(CH_3)_2$), 0.41 (d, 6H, CH $(CH_3)_2$) ppm. ^{19}F NMR (188.29 MHz, C_6D_6): δ −122.8 (d, 1F, *o*-F), −131.8 (d, 1F, *o*-F), −149.6 (t, 1F, *p*-F), −160.2 (t, 1F, *m*-F), −161.7 (t, 1F, *m*-F) ppm. ^{29}Si NMR (99.36 MHz, C_7D_8, 25 °C): δ −41.2 ($J(^{29}Si-^1H)$ = 261.63 Hz) ppm. EI-MS (70 eV; *m*/*z* (%)): 597 (100) [M^+−Me].

Synthesis of [PhC(N*t*Bu)$_2$]SiFCl(4-C_6F_4H) (10). A solution of pentafluorobenzene (0.17 g, 1.00 mmol in 5 mL of toluene) was added by cannula to a solution of **2** (0.29 g, 1.00 mmol in 25 mL of toluene) at room temperature. After 12 h all the volatiles were removed in vacuo, and the remaining residue was extracted with toluene (15 mL) to yield compound **10**. Yield 0.34 g (75%). Mp 126 °C. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 6.97−7.05 (m, 5H, Ar*H*), 6.48 (m, C*H*), 0.99 (s, 18H, C $(CH_3)_3$) ppm. ^{19}F NMR (188.29 MHz, C_6D_6): δ −59.2 (s, 1F, Si−*F*), −126.3 (br, 2F, *o*-*F*), −133.4 (br, 2F, *m*-F) ppm. ^{29}Si NMR (99.36 MHz, C_6D_6, 25 °C): δ −96.0 ($^1J(^{29}Si-^{19}F)$ = 288.84 Hz) ppm. EI-MS (70 eV; *m*/*z* (%)): 462 (20) $[M]^+$, 427 (100) [M^+−Cl].

Synthesis of [CH(C=CH$_2$)(CMe)(2,6-*i*Pr$_2$C$_6$H$_3$N)$_2$]SiH(1,3,5-$C_6F_3H_3$) (11). An NMR tube was loaded with 1,3,5-trifluorobenzene (0.033 g, 0.25 mmol) and **1** (0.11 g, 0.25 mmol) at room temperature. After that benzene-d_6 (0.6 mL) was added, and the sealed NMR tube was kept in an oil bath at 60−70 °C. After 12 h the ^{1}H NMR spectrum was recorded showing the formation of compound **11**. The solution from the NMR tube was transferred into a Schlenk flask; after that all volatiles were removed from the solution to yield compound **11**. Yield 0.120 g (82%). Mp 208 °C. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 7.03−7.15 (m, 6H, Ar*H*), 6.33 (m, 1H, Ar-*H*), 5.85 (m, 1H, Ar-*H*), 5.54 (s, 1H, C*H*), 5.42 (br, 1H, Si*H*), 3.99 (s, 1H, CH_2), 3.84 (sept, 1H, C*H*$(CH_3)_2$), 3.67 (sept, 1H, C*H*$(CH_3)_2$), 3.36 (br, 2H, CH_2 and C*H*$(CH_3)_2$), 3.16 (sept, 1H, C*H*$(CH_3)_2$), 3.10 (sept, 1H, C*H*$(CH_3)_2$), 1.62 (s, 3H, CH_3), 1.14−1.43 (m, 18H, CH$(CH_3)_2$), 0.49 (d, 6H, CH $(CH_3)_2$) ppm. ^{19}F NMR (188.29 MHz, C_6D_6): δ −90.4 (br, 1F, *o*-F), −99.6 (br, 1F, *o*-F), −103.9 (m, 1F, *p*-F). ^{29}Si NMR (99.36 MHz, C_6D_6, 25 °C): δ −40.1 ($J(^{29}Si-^1H)$ = 256.3 Hz) ppm. EI-MS (70 eV; *m*/*z* (%)): 576 (100) $[M]^+$.

Crystallographic Details for Compounds 3, 7, 8, and 9. Suitable crystals of **3**, **7**, **8**, and **9** were mounted on a glass fiber, and data was collected on an IPDS II Stoe image-plate diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at 133(2) K. The data was integrated with X-area. The structures were solved by Direct Methods (SHELXS-97)[33] and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[33] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model except hydrogen bound to silicon, which was found and refined freely.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Supporting Information Available: X-ray data for **3**, **7**, **8**, and **9** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA103988D

(33) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.