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The first metal free selective C–F bond activation of a CF₃ group was observed with *N*-heterocyclic silylenes [PhC(N ι Bu)₂SiCl] (1) and [CH{(C=CH₂)(CMe)(2,6-*i*Pr₂C₆H₃N)₂Si}] (2) with PhN=C(CF₃)₂. The reaction proceeds in a 1 : 1 molar ratio to yield the mono C–F bond activated products 3 and 4 with each containing a CF₂ group. Both the reactions proceed through an unprecedented selective activation of one of the C–F bonds rather than forming the [1+2] cycloaddition product containing the three-membered SiNC rings.

Bifluorinated organic compounds such as 1,1-difluoro-1-alkenes find increasing application in chemical, material and biological processes because of their unique activity.¹ These bifluorinated compounds are generally prepared by the selective defluorination of a trifluoromethyl group from a commercially available trifluoromethyl group containing compounds in the presence of a metal center.² These 1,1-difluoro-1-alkene containing compounds exhibit exceptional chemical reactivities toward addition reactions,³ and they can also be reduced to monofluoroalkenes. Therefore they are considered as important intermediates for other classes of fluorinated organic compounds.⁴ They are also used as potential inhibitors.⁵

In general the activation of the C–F bond is a subject of interest because it is the strongest single bond that carbon can form due to the high electronegativity of fluorine.⁶ Recently Ozerov *et al.* reported the hydrodefluorination of a C(sp³)–F bond using carborane supported, highly electrophilic silylium compounds as a catalyst.^{6b,c} Moreover, the selective activation of one of the C–F bonds is difficult to achieve.⁷

Silylenes contain a divalent silicon atom and they are very important synthons in organosilicon chemistry.⁸ The first isolable *N*-heterocyclic silylene (NHSi) was reported by West *et al.*,⁹ after which many stable *N*-heterocyclic silylenes (NHSis) have been documented.^{8,10} They are considered to be the

silicon analogues of *N*-heterocyclic carbenes (NHCs), where the latter find widespread applications in chemistry.^{11,12} They have two non-bonding electrons in the HOMO and an empty p-orbital as the LUMO which feature both nucleophilic as well as electrophilic reactive sites at the same silicon center and tend to possess an ambiphilic character and behave as Lewis acids as well as Lewis bases.¹³ The silylenes are electronically and coordinatively unsaturated and they are capable of undergoing a variety of reactions.^{14–16}

Recently we reported the C–H as well as C–F bond activation of fluoroarenes with [PhC(N ι Bu)₂SiCl] (1) and [CH{(C=CH₂)(CMe)(2,6-*i*Pr₂C₆H₃N)₂Si}] (2).¹⁷ With the target of synthesizing difluorinated compounds by utilizing 1 and 2, we selected PhN=C(CF₃)₂ which contains two CF₃ groups. The treatment of 1 and 2 with PhN=C(CF₃)₂ resulted in difluorinated alkene products 3 and 4 formed by the selective activation of one of the carbon–fluorine bonds without any metal catalyst rather than giving the SiNC three-membered ring by [1+2]-cycloaddition reaction.

Compounds 3 and 4 were obtained in good yields when PhN=C(CF₃)₂ was treated with 1 and 2 in a molar ratio of 1 : 1 as shown in Scheme 1. Both reactions involve the selective and facile C–F bond activation of one CF₃ group. Compounds 3 and 4 are soluble in common organic solvents. They are stable, both in the solid state as well as in solution without any decomposition under an inert gas atmosphere. Both the compounds were fully characterized by NMR spectroscopy, EI-MS and elemental analysis. The molecular structures of the compounds 3 and 4 were unambiguously established by single crystal X-ray structural analyses.

The ²⁹Si NMR spectrum of 3 shows a double resonance centered at δ –106.9 ppm ($J_{\text{Si-F}}$ = 251 Hz), which is upfield shifted when compared with that of 1 (δ 14.6 ppm).^{10a} Compound 3 exhibits four ¹⁹F NMR resonances at δ –60.81 to –60.95 (m, 3F, CF₃), –72.89 (b, 1F, SiF), –83.60 to –83.78 (m, 1F, CF₂), and –84.52 to –84.73 (m, 1F, CF₂) ppm. The assignment of the Si–F resonance was confirmed by the HSQC (¹⁹F–²⁹Si) technique. The ι Bu protons of compound 3 in the ¹H NMR spectrum exhibit a double resonance of equal intensity for the ι Bu groups that reside on nitrogen atoms (δ 0.79 and 1.15 ppm). In addition,

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

compound **3** shows its fragment ion $[M^+ - F]$ in the mass spectrum at m/z 516.

Compound **3** crystallizes in the monoclinic space group $P2_1/n$, the molecular structure of which is shown in Fig. 1. The silicon atom is five coordinate and the coordination environment is made up of three nitrogen atoms (two from the amidinato ligand and one from the amino moiety), one chlorine atom and a fluorine atom.

The structural index τ which defines the extent of deviation from trigonal bipyramidal to square pyramidal geometry ($\tau = 1$ for perfect trigonal bipyramidal; $\tau = 0$ for perfect square based pyramid)¹⁸ is 0.69 indicating strong deviation from the square pyramidal geometry and closer to regular trigonal bipyramidal geometry. The Si1–F6 bond length is 1.6476(13) Å, which is quite comparable to that in $\text{PhC}(\text{N}t\text{Bu})_2\text{SiF}_3$.¹⁹ The N1–Si1–N2 bite angle between the silicon atom with the backbone ligand is 69.51(8)°. The bond length between the Si and the amino nitrogen atom is 1.7470(18) Å. The Si–Cl bond length in **3** is 2.0935(8) Å, which is shorter when compared with that in **1**

(Si–Cl in **1** is 2.156(1) Å).^{10a} The bond length of C22–C23 is 1.492(3) Å and C22–C24 is 1.311(3) Å which indicates both single and double bond character.

Like **3**, compound **4** also shows a double resonance centered at $\delta -65.1$ ppm ($J_{\text{Si-F}} = 286$ Hz), in its ^{29}Si NMR spectrum, which is upfield shifted when compared with that of **2** (δ 88.4 ppm).^{10b} Compound **4** also exhibits four ^{19}F NMR resonances $\delta -62.08$ to -62.51 (m, 3F, CF_3), -77.19 to -77.34 (m, 1F, CF_2), -80.51 to -80.93 (m, 1F, CF_2), and -137.35 (s, 1F, SiF) (by the HSQC (^{19}F – ^{29}Si) technique) ppm. The γ -CH proton for compound **3** in the ^1H NMR spectrum is observed at δ 5.40 ppm and is upfield shifted when compared with that of **2** (δ 5.44 ppm).^{10b} The NCCH_2 protons in **4** exhibit sharp singlets at 3.37 and 4.01 ppm (δ for **2** 3.32 and 3.91 ppm). In addition **3** shows its molecular ion in the mass spectrum at m/z 685.

Compound **4** crystallizes in the orthorhombic space group $Pnma$ with half a molecule in the asymmetric unit. The structure is depicted in Fig. 2. In **4** the silicon atom is four coordinate and displays a distorted tetrahedral geometry comprising three nitrogen atoms (two from the amidinato ligand and one from the amino moiety) and one fluorine atom. The crystallographic mirror plane through the molecule leads to disorder between the CF_2 and the CF_3 group and between a CCH_3 and a $\text{C}=\text{CH}_2$ group. There is shortening of bonds observed between the Si atom and the nitrogen atoms of the supporting ligand. The Si–N bond length from the backbone ligand in **4** is 1.708(2) Å, whereas in **2** it is 1.7345(10) Å.²⁰ The bite angle (N–Si–N) at the silicon atom with the backbone ligand is 106.39(16)° compared to 99.317(54)° in **2**.^{10b}

Herein, we report the first metal free selective and facile C–F bond activation of a bound CF_3 group by the *N*-heterocyclic silylenes $[\text{PhC}(\text{N}t\text{Bu})_2\text{SiCl}]$ (**1**) and $[\text{CH}\{(\text{C}=\text{CH}_2)(\text{CMe})(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3\text{N})_2\}\text{Si}]$ (**2**). The reaction of **1** and **2** with $\text{PhN}=\text{C}(\text{CF}_3)_2$ yielded the five coordinate silicon containing compound **3** and the four coordinate silicon containing product **4**, respectively. These reactions proceed

Fig. 1 Molecular structure of **3**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–Si1 1.7959(18), N2–Si1 1.9507(18), N3–Si1 1.7470(18), F6–Si1 1.6476(13), Cl1–Si1 2.0935(8), C22–N3 1.423(3), C22–C23 1.492(3), C22–C24 1.311(3), C24–F1 1.318(3), C23–F3 1.322(3), C22–N3 1.423(3); N1–Si1–N2 69.51(8), N2–Si1–N3 96.62(8), Cl1–Si1–F6 91.67(5), F6–Si1–N2 165.53(8), F6–Si1–Cl1 118.08(6), N3–Si1–N1 124.17(8).

Fig. 2 Molecular structure of **4**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): N1–Si1 1.708(2), N2–Si1 1.727(3), F1–Si1 1.584(3), N2–C22 1.429(5), C22–C23 1.397(4), C(1)–C(2) 1.398(3), C(2)–C(3) 1.415(4), N1–Si1–N1' 106.39(16), F1–Si1–N2 98.61(14).

without any catalyst with selective activation of one of the carbon–fluorine bonds rather than complete defluorination of the CF₃ group. Furthermore no [1+2]-cycloaddition products were observed by oxidative addition of PhN=C(CF₃)₂ at the low valent silicon atoms of **1** and **2**, respectively.

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