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Silicon-fluorine chemistry: from the preparation of SiF_2 to C–F bond activation using silylenes and its heavier congeners†

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This feature article is intended to provide a background to the history of the isolation of silicon(II) fluorides and the different synthetic methodologies used to generate them. Although first detected in the 1970s, the chemistry of silicon(II) fluorides has not encountered serious research efforts for a rather long period of time. This is somewhat surprising given the fact that the chemistry of compounds with divalent silicon has undergone a renaissance during last three decades. Recently, the interest in silicon(II) fluorides have been resparked with tremendous progress being achieved in this area, in particular, with respect to their synthesis and structural characterisation. The successful isolation of cyclic alkyl amino carbene (cAAC) stabilized silicon difluoride has completed the classic progression of SiF_2, from a transient intermediate to spectroscopically detected molecule to a stable compound. The related germanium(II), tin(II), and lead(II) fluoride chemistry will also be discussed. Apart from the isolation of tetrel(II) fluorides, the use of compounds with low valent group 14 elements for the selective activation and functionalisation of C–F bonds has witnessed some remarkable advances, which will also be summarized in this feature article.

Introduction

"*Oh threats of hell and hopes of paradise!*
One thing at least is certain – This Life flies"
– Omar Khayyám, Rubaiyat of Omar Khayyam

The austere insight of Khayyám about life bears a striking resemblance to the present day silicon chemistry. Despite the ever-looming threat of instability and high reactivity of organosilicon compounds, especially in the low oxidation state, and the hope of taming them using chemical tricks (bulky ligands, donor–acceptor approach), the only certain thing is that the present day silicon chemistry is propelling in fifth gear. Starting from the seminal report on the synthesis of a compound with a Si=Si double bond by West and co-workers[1] that toppled the then much venerated "double bond rule", to a stable silanone,[2] which was "F. S. Kipping's dream", organosilicon chemistry has traversed a long journey, witnessing a catalogue of esteemed discoveries made across the world.[3] Such realisation of novel organosilicon compounds has allowed us to analyze their structures, elucidate their bonding properties and study their reactivities, which eventually revealed the marked differences between silicon and carbon, and led W. Kutzelnigg to comment "*the heavier main-group elements, Si to Pb, actually exhibit 'normal' chemical behaviour while carbon should be considered the 'unusual' member of the group 14 elements rather than the prototype*".[4] The remarkable progress of organosilicon chemistry over the last three decades has been closely monitored by the chemistry community, which has resulted in numerous elegant reviews.[5]

Even before the beginning of the chemistry of compounds with multiple-bonds between silicon atoms, the chemistry of silicon(II) halides has attracted considerable attention. The confirmation of the: CCl_2 intermediate in the Reimer–Tiemann reaction,[6a] as well as Nef's pioneering work[6b,c] on divalent carbon compounds have led silicon chemists to undertake the synthesis of dihalosilylenes. Another impetus originated from the realisation that silicon(II) halides are the intermediates in many important reactions, such as the Rochow Müller process,[7a] where methylchlorosilanes are prepared from methyl chloride in an easy and inexpensive way. The Rochow Müller process has resulted in the huge growth of the silicone polymer area. Spectral evidence has been obtained in the formation of unstable silylenes ($SiCl_2$ and MeSiCl) during the reaction. Such silicon(II) compounds can be used as synthons to prepare new compounds, which are otherwise inaccessible. In their recent feature article on the readily available $SiCl_2/[SiCl_3]^-$ system, Teichmann and Wagner elegantly highlighted the classical high-temperature protocols used for the

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† Dedicated in the memory of Professor George A. Olah and on the occasion of the 60th birthday of Professor Dr Alexander C. Filippou.

generation of $SiCl_2$ and their utility as synthons for making unusual silicon compounds.[7b]

Following the syntheses of $[SiBr_2]_x$ and $[SiCl_2]_x$ by the Schmeißer group,[8] chemists have turned their attention towards $[SiF_2]_x$. The interest has been stimulated by the fact that the divalent fluoride of carbon is more stable than its parent carbene. For example, carbene ($:CH_2$) has a half-life of 1 ms in the gas phase, while carbon difluoride has a half-life of 1 s.[9a,b] The half-life of gaseous SiF_2 is 150 s at 0.2 Torr and ambient temperature.[9c] Moreover, neither CF_4 nor SiF_4 react with glass, which is a usual problem for other fluorides. The preparation of SiF_2 from magnesium and dibromofluorosilane by Schmeißer goes back as early as 1954.[10] Since then, the divalent fluorides of silicon have become a major research area especially at Rice University, USA where the Timms and Margrave groups have performed an extensive and systematic study of the properties of silicon difluoride.[11] Nevertheless, no monomeric SiF_2 has been isolated under synthetically useful conditions until very recently, when we reported cyclic alkyl amino carbene (cAAC) coordinated silicon difluoride from the reduction of cAAC·SiF_4 with KC_8.[12] In this review, we provide a comprehensive coverage of the synthesis and reactions of silicon(II) fluorides. The fluorides of other heavier group 14 elements such Ge(II), Sn(II) and Pb(II) will be covered. It will also summarize the recent efforts, by our group and others, on the activation of the C–F bond using compounds with low valent silicon atoms. We extend into other classes of reactivity that are closely related and of particular interest such as germylene and stannylene assisted C–F activation. Finally, the recent studies on the hydrodefluorination of C–F bonds using silylium cations are also presented.

Early preparations of silicon difluoride

Table 1 lists some key milestones in the development of group 14-fluoride chemistry. Although the groups of Timms and Margrave at Rice University, Houston, USA are generally credited for preparing SiF_2 for the first time, Schmeißer prepared polymeric silicon(II) fluoride from the reaction of dibromofluorosilane and magnesium in 1954.[10] In 1958, Pease found that silicon difluoride could be formed from the reaction of SiF_4 and Si at high temperature, which condenses below −80 °C.[13] Another effort from Schmeißer and Ehlers involved the cleavage of the Si–Si bond in Si_2F_6 at 700 °C that led to the formation of SiF_4 along with SiF_2,[14] which condensed as a yellow solid in liquid air. Above −80 °C, SiF_2 polymerizes to yield a colorless, rubbery solid $[SiF_2]_x$, which catches fire in moist air.

All the aforementioned reactions in fact deal with polymeric silicon difluoride but indicate the formation of monomeric SiF_2 as an intermediate. Moreover, no physical properties of SiF_2 were measured. To unequivocally prove the existence of monomeric SiF_2, Timms *et al.* constructed a special apparatus (Fig. 1). SiF_4 was passed into a reservoir and subsequently, using the needle valves, passed over chunks of heated silicon at 1200 °C, which afforded 50% SiF_2.[15] To avoid the disproportionation reaction, as soon as the SiF_2 is formed, it is swept through the vacuum line to a point where it's physical properties or chemical reactivities could be measured.

Ehlert and Margrave performed a mass spectrometric experiment of SiF_2.[16a] SiF_4 was passed through a Si column at very high temperature and subsequently passed into a mass spectrometer, which detected only SiF_4 and monomeric SiF_2; no

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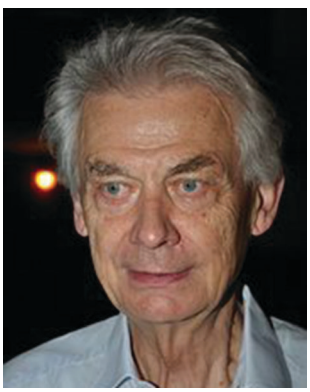
Sakya S. Sen received his PhD from the University of Göttingen, Germany under the supervision of Professor Herbert W. Roesky and subsequently joined the laboratory of Professor Holger Braunschweig at the University of Würzburg, Germany as an AvH postdoctoral fellow. Since 2014 he has worked in the CSIR-NCL, Pune, India as a senior scientist. His research interests are the synthesis and application of compounds with low valent main group elements. Sakya is the recipient of the CSIR-young scientist award in 2017 and young associate of Indian Academy of Sciences.



Herbert W. Roesky

Herbert W. Roesky obtained his doctorate from the University of Göttingen. After working at DuPont in the United States, he returned to Göttingen and finished his habilitation. He then became a Professor at the Johann-Wolfgang-Goethe-Universität, Frankfurt am Main in 1971. He moved to the University of Göttingen in 1980 and was the director of the Institute for Inorganic Chemistry until 2004. He is primarily known for his pioneering work on fluorides of both transition and main group elements. His current research interest is focused on the synthesis and reactivity of compounds with heavier group 13 and 14 elements in low oxidation states. More than 1250 peer-reviewed papers, articles, patents, and books record his research activities in the areas of inorganic chemistry and materials science. He is also the recipient of several prizes, i.e. Gottfried Wilhelm Leibniz Prize, the Alfred Stock Memorial Prize, the Grand Prix de la Foundation de la Maison de la Chimie, the Wilkinson Prize, Moissan award and ACS awards in Inorganic and Fluorine Chemistry.

Table 1 The important milestones in the chemistry of silicon fluorides

Year	Comment
1964	Schmeißer and Ehlers observed the formation of SiF_2 at −80 °C
1965	Timms *et al.* prepared SiF_2 from SiF_4, measured its half-life, and studied its reactivity
2001	Roesky and co-workers structurally characterized Ge(II) fluoride
2008	Roesky and co-workers structurally characterized Sn(II) fluoride
2005	Ozerov and co-workers used silylium cation for the hydrodefluorination reaction
2010	Compounds with low valent silicon atom can activate C–F bonds
2011/2012	By coordinating the lone pair of silylene to BH_3 or a transition metal fragment, the first compound featuring an Si(II)–F bond was realized
2018	Using cAAC carbene, the SiF_2 moiety is stabilized and structurally validated

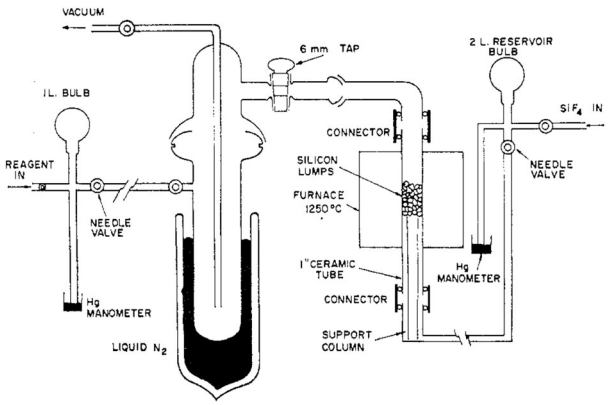
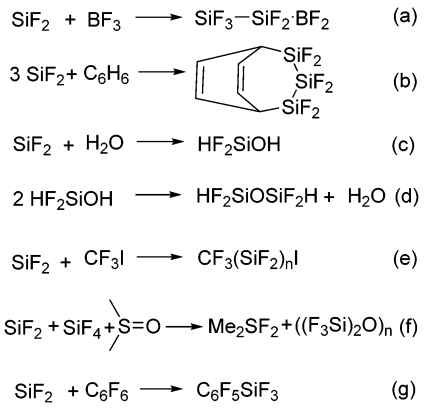


Fig. 1 The apparatus used for the preparation and reaction of SiF_2. Reproduced with permission from ref. 17.



Scheme 1 The reactions of a SiF_4–SiF_2 mixture with various substrates.

polymeric species of SiF_2 were observed. It was estimated that SiF_2 has a half-life of 120 seconds. The infrared spectrum of gaseous SiF_2 has been recorded from 1050 to 400 cm^{-1}. Two absorption bands centered at 855 and 872 cm^{-1} were assigned to the symmetric and anti-symmetric stretching modes, respectively.[16b]

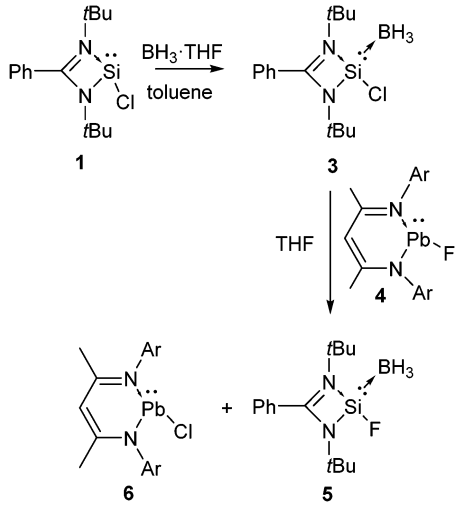
The relatively easy generation of SiF_2 by the Timms' group saw a flurry of research activity into their properties and reactivity in the early 1970s. The reactivity of polymeric SiF_2 was investigated with various substrates such as BF_3, benzene, hexafluorobenzene, and water (Scheme 1).[17] The general strategy of the reactions was to condense the reactant and SiF_4–SiF_2 mixture together and characterize the condensate. Multi-nuclear NMR spectroscopy, IR spectroscopy, mass spectrometry, and elemental analysis were performed to characterize the condensates. As none of the product was characterized by single crystal X-ray diffraction, the structural authentication of the SiF_2 unit remained elusive. In the following years, publications on silicon difluoride trickled out and there were not many significant advances. In fact, the research interest in silicon difluoride never again reached the heights that were attained in the 1960s and 70s.

The efforts to prepare stable compounds with an Si(II)–F bond: structural validation

The facile isolation of stable silicon(II) chlorides[18] such as [LSi(II)Cl, L = $\{PhC(NtBu)_2\}^-$] (**1**) and N-heterocyclic carbene (NHC)-stabilized dichlorosilylene (L′Si(II)Cl_2, L′ = 1,3-bis(2,6-$iPr_2C_6H_3$)imidazol-2-ylidene) (**2**) renewed the interest in making a compound with a Si(II)–F bond. However, due to the high propensity of silicon(II) fluoride toward polymerization or disproportionation, attempts to isolate "$[PhC(NtBu)_2]SiF$" or "IDipp·SiF_2" were not successful. In line with our observations, Jutzi and co-workers also found that Me_5C_5SiF was unstable and dimerized into the corresponding disilene, $Me_5C_5(F)Si{=}Si(F)C_5Me_5$. The latter was also found to be unstable and underwent a [2+2]-cycloaddition to form cyclotetrasilane.[19]

"*We must accept finite disappointment, but never lose infinite hope.*"
– Martin Luther King, Jr.

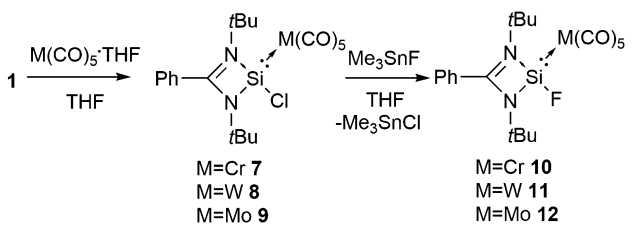
We imagined that the presence of the stereoactive lone pair of electrons on the silicon atom of silicon difluoride impedes its isolation. To prevent this feisty nature of silicon(II) difluoride, we reacted **1** with BH_3 to coordinate the lone pair of electrons of silicon to the electron deficient boron center (Scheme 2).[20] The reaction led to the formation of an adduct, **3**. The latter was subsequently reacted with L_1PbF, [L_1 = CH{(CMe)(2,6-$iPr_2C_6H_3N$)}$_2$] (**4**),[20] which resulted in the formation of compound **5** along with the formation of L_1PbCl (**6**). **5** features a formal Si(II)–F bond. The ^{19}F NMR spectrum displayed a resonance at δ −121.59 ppm accompanied by ^{29}Si satellite signals (J = 438.17 Hz). The ^{29}Si NMR spectrum revealed a doublet of quartets (δ 23.63 ppm and $J_{(29Si–11B)}$ = 66.78 Hz), which underpinned the presence of Si–B and Si–F bonds. Although the spectroscopic data unambiguously affirmed the formation of a compound with a Si(II)–F bond, its structural characterization by X-ray diffraction was still missing.



Scheme 2 The synthesis of amidinato stabilized Si(II) fluoride in the coordination sphere of borane; Ar = 2,6-iPr$_2$-C$_6$H$_3$.

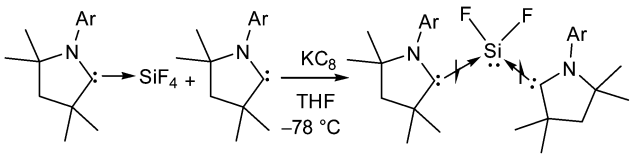
The unraveling of an efficient synthetic pathway to access formal Si(II) fluorides using a donor–acceptor approach furthered us to bring transition metals into play instead of borane. A very common strategy that has often been applied in organometallic chemistry for isolating reactive compounds is to bind those species to transition metals.[21] Moreover, the presence of a transition metal in a compound usually allows the growth of better quality single crystals suitable for X-ray analysis. Silylenes are known to coordinate with transition metals. Prior to us Rivard and co-workers described the generation of stable M(II)H$_2$ (M = Si, Ge, and Sn) and H$_2$SiEH$_2$ (E = Ge and Sn) under the coordination sphere of late transition metals.[22] By applying the same synthetic protocol, we prepared three silicon(II) fluoride compounds, PhC(NtBu)$_2$(F)Si·M(CO)$_5$ {M = Cr (**10**), Mo (**11**), and W(**12**)},[23] using a metathesis reaction of the corresponding chlorides (**7**–**9**) with Me$_3$SnF, a versatile fluorinating agent (Scheme 3). **10** and **12** were structurally characterized. There is a small variation in the Si–M bond lengths in **10** (2.3398(4) Å) and **12** (2.4990(8) Å) when compared to the corresponding chloride analogues **7** (2.3458(7) Å) and **9** (2.5086(11) Å). The Si–F bond lengths in **10** and **12** are 1.6168(8) and 1.6245(14) Å, respectively. A comparison of the Si–F bond lengths in **10** and **12** with that in gaseous SiF$_2$ (1.59 Å) indicates an increase in the bond length by only 0.03 Å.

"*It's kind of fun to do the impossible*."
– Walt Disney



Scheme 3 The synthesis of amidinato stabilized Si(II) fluorides in the coordination sphere of transition metals.

Although, **5** and **10**–**12** possess a formal Si(II)–F bond, access to a silicon difluoride that is stable at room temperature remained elusive. Therefore, the question arose whether it is viable to isolate a stable compound featuring a silicon(II) difluoride moiety. Since NHCs were found inappropriate for stabilizing the silicon(II) difluoride moiety, we turned our attention towards cAAC. According to the calculations,[24] the singlet–triplet energy gap of cAAC (46 kcal mol^{-1}) is much smaller than that of NHC (68 kcal mol^{-1}), and as a result, the HOMO of cAAC (−5.0 eV) is higher in energy than that of NHC (−5.2 eV). Following the isolation of stable cAAC by the Bertrand group,[25] it has been widely used for the stabilisation of a plethora of unprecedented silicon compounds that could be prepared in no other way.[26] The attempts to synthesize cAAC supported SiF$_2$ from the reactions of (cAAC)$_2$SiCl$_2$ with various fluorinating agents (Me$_3$SnF, CsF, and C$_5$F$_5$N) were unsuccessful. Hence, a conventional reduction method was employed. The reduction of the cAAC–SiF$_4$ adduct (**13**) with KC$_8$ in the presence of another equivalent of cAAC resulted in (cAAC)$_2$SiF$_2$ (**14**) as a purple solid (Scheme 4).[12] The ^{29}Si and ^{19}F NMR spectra of **14** display no resonance at room temperature due to their rapid exchange on the NMR timescale. However, a low temperature NMR experiment exhibited a triplet at δ 29.73 ppm in the ^{29}Si NMR spectrum and a broad singlet at δ −123.47 ppm in the ^{19}F NMR spectrum. The UV-vis spectrum of **14** showed an absorption band at 529 nm that was in good accordance with the TD-DFT calculations. This absorption can be attributed to ligand to silicon charge transfer. An X-ray crystal structure of **14** (Fig. 2) revealed that the SiF$_2$ unit was coordinated by two cAAC moieties with Si–F bond lengths of 1.592(1) and 1.593(1) Å, which are within the range of those reported for **10**. Subsequent theoretical studies showed that **14** possesses an open shell singlet configuration, which is 4.9 kcal mol^{-1} lower in energy than the triplet



Scheme 4 The synthesis of cAAC supported SiF$_2$ (**14**) (Ar = 2,6-iPr$_2$C$_6$H$_3$).

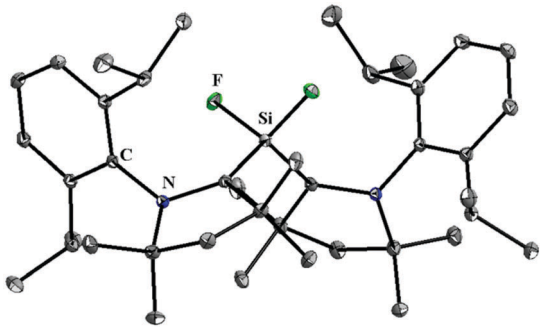
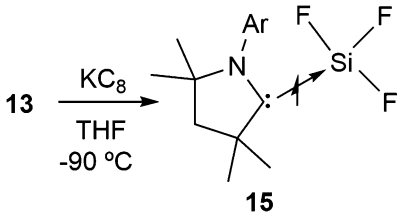


Fig. 2 The molecular structure of **14**.



Scheme 5 The synthesis of a cAAC supported SiF_3 radical (**15**).

configuration and 10.2 kcal mol^{-1} lower in energy than the closed-shell singlet configuration. The large energy difference between the open shell singlet configuration and the triplet configuration underpins why **14** was EPR silent.

"*There is no end. There is only the infinite passion of life*"
–Federico Fellini (Italian Film Director)

Once we accomplished the isolation of a compound with a silicon(II) difluoride moiety, we wished to prepare a compound with a SiF_3 radical unit. Gratifyingly, the reduction of **13** with one equivalent of KC_8 in the absence of any free cAAC resulted in a monoradical product, (cAAC)SiF_3 (**15**), which was the first stable radical containing a SiF_3 group (Scheme 5).[12] The monomeric nature of **15** was characterized using a single crystal X-ray diffraction study (Fig. 3). The EPR spectrum of **15** was recorded in *n*-hexane at room temperature (Fig. 4), which showed a very large ^{19}F coupling parameter. According to the McConnell spin polarisation model, this high coupling parameter is due to the high polarity of the Si–F bond and its interaction with the carbon radical center.

Germanium, tin and lead(II) fluorides

Due to the inert-pair effect, GeF_2 and SnF_2 are more stable than their lower homologues. GeF_2 is a strongly fluorine-bridged chain polymer in which the parallel chains are cross-linked by weak fluorine bridges. SnF_2 exists as a tetramer containing a puckered eight-membered ring in which the Sn and F atoms are alternately arranged. SnF_2 has been widely used in toothpaste as a source of fluoride to harden the dental enamel. However, due to their polymeric structures GeF_2 and SnF_2 have low

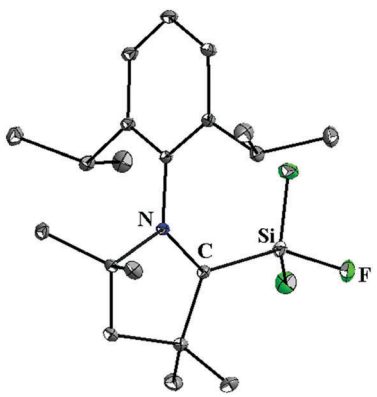


Fig. 3 The molecular structure of **15**.

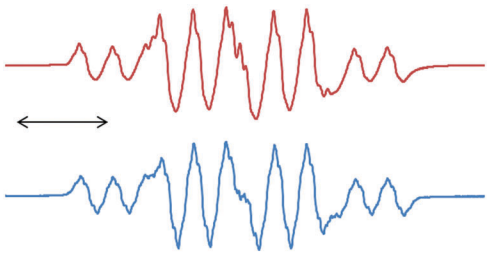
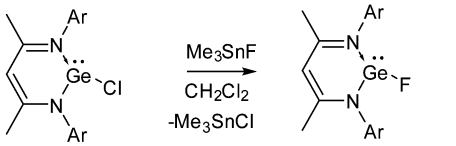


Fig. 4 The experimental EPR spectrum of **15** (below) at room temperature recorded in hexane and the simulated spectrum (above) with $a(^{14}N)$ = 6.9 G, $a(^{29}Si)$ = 10 G, $a(^{19}F, 3F)$ = 16.8 G and $a(^{1}H, 3H)$ = 1.2 G.



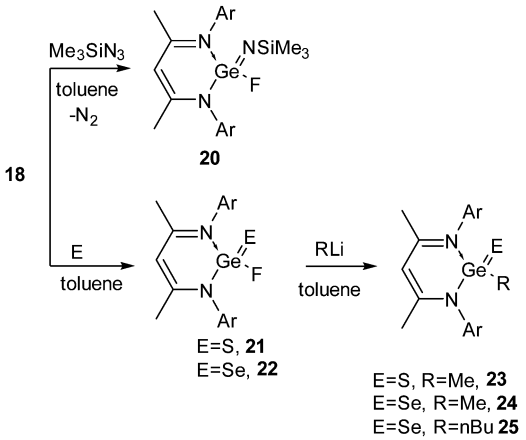
Ar=2,6-*i*-$Pr_2C_6H_3$ **16**
Ar=2,6-$Me_2C_6H_3$ **17**
Ar=2,6-*i*-$Pr_2C_6H_3$ **18**
Ar=2,6-$Me_2C_6H_3$ **19**

Scheme 6 The synthesis of Ge(II) fluorides **18** and **19**.

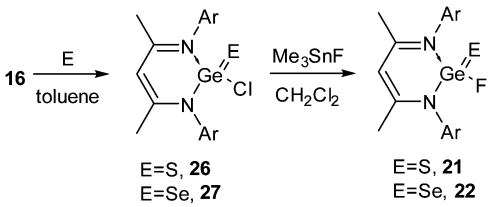
solubilities in common organic solvents and hence, it is difficult to study their reactions in the solution state.

The preparation of compounds containing a Ge(II)–F bond was achieved with relative ease. Ge(II) fluorides, **18** and **19**, were synthesized in our group from the reaction of Ge(II) monochlorides, L_1GeCl (**16**) and L_2GeCl [L_2 = CH{(CMe)(2,6-$Me_2C_6H_3N$)}$_2$] (**17**) with Me_3SnF in dichloromethane (Scheme 6).[27] The ^{19}F NMR spectra of **18** and **19** display a singlet resonance at δ 50.6 and 54.5 ppm, respectively. Single crystal X-ray diffraction studies showed that the Ge–F bond in **18** is 1.805(17) Å, which is in good accordance with the Ge–F bond in Inoue's [Ge(F)(NSIPr)$_2$Ge][BF_4] (SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) (1.800(4) Å).[28]

The syntheses of **18** and **19** permitted us to investigate their oxidation reactions with organoazide and elemental sulfur. Refluxing a toluene solution of **18** and Me_3SiN_3 for 3 h resulted in the oxidative addition product **20** (Scheme 7).[27] The oxidation of the Ge(II) center was accompanied by a downfield shift in the ^{19}F NMR spectrum of **20** (δ 71.1 ppm). Treatment of **18** with elemental sulfur and selenium afforded {HC(CMeNAr)$_2$}Ge(E)F (E = S (**21**)[29a] and Se (**22**),[29b] Ar = 2,6-i$Pr_2C_6H_3$) (Scheme 7). Alternatively, oxidation of **16** with elemental sulfur and selenium resulted in {HC(CMeNAr)$_2$}Ge(E)Cl (E = S (**26**), Se (**27**)), which upon fluorination with Me_3SnF furnished **21** and **22** (Scheme 8), respectively.[29] The Ge–F bond length in **21** and **22** is 1.848(2) Å and 1.758(3) Å. The Ge–S bond distance in **21** is 2.050(9) Å, which is shorter than the reported Ge–S bond lengths in [{PhC(N*t*Bu)$_2$}$_2$Ge$_2$(μ-S)$_2$Cl$_2$] (2.2090(4) and 2.2978(4) Å)[30] and the other reported Ge–S single bonds (2.17–2.25 Å)[31] but comparable with those in **26** (2.050(9) Å) and germanethione, Tbt(Tipp)Ge=S (2.049(3) Å) [Tbt = 2,4,6-tris{bis(trimethylsilyl)methyl}phenyl and Tipp = 2,4,6-triisopropylphenyl].[32] The Ge–Se bond length in **22** (2.176(7) Å) is very close to those in Tbt(Tipp)Ge=Se (2.180(2) Å)[33]



Scheme 7 The oxidation reactions of Ge(II) fluoride **18** with sulfur and azide (Ar = 2,6-iPr$_2$C$_6$H$_3$).

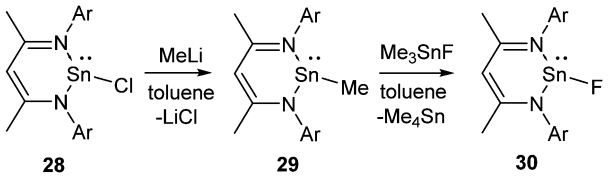


Scheme 8 The alternative synthesis of **21** and **22** (Ar = 2,6-iPr$_2$C$_6$H$_3$).

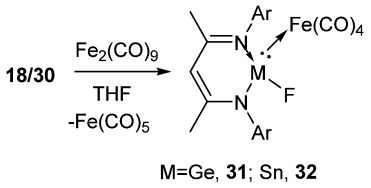
reported by Okazaki *et al.* and [(iBu)$_2$ATI]Ge(=Se)Cl (2.198(1) Å) (ATI = aminotroponiminate) reported by Nagendran and co-workers,[34] but substantially shorter than the reported Ge–Se single bond lengths (2.337–2.421 Å).[33,35] Treatment of alkyl lithium (Ar = Me, nBu) with **21** and **22** resulted in the dehalogenated derivatives [{HC(CMeNAr)$_2$}Ge(E)R] (E = S, R = Me (**23**); E = Se, R = Me (**24**), nBu (**25**)) (Scheme 7).[29]

The metathesis between the group 14 chlorides and trimethyltin fluoride was not successful towards synthesizing the corresponding Sn(II) fluorides and no reaction was observed between L$_1$SnCl (**28**) and Me$_3$SnF even after refluxing for several days. Therefore, the synthetic protocol was modified. Treatment of **28** with MeLi afforded L$_1$SnMe (**29**), which was subsequently converted to the desired compound, **30** upon refluxing with Me$_3$SnF in toluene for 3 h (Scheme 9).[36] The ^{19}F NMR spectrum of **30** shows a singlet at δ −125.29 ppm and the ^{119}Sn NMR spectrum exhibits a doublet at δ −371.52 ppm. The existence of **30** as a monomer was corroborated by single crystal X-ray diffraction studies. The terminal Sn–F bond in **30** was determined to be 1.988(2) Å, which was shorter when compared to the bridging Sn–F–Sn (2.156 (3) Å) bond in *trans*-[Sn(μ-F)$_2$NC(Me$_2$)(CH$_2$)$_3$CMe$_2$]$_2$ reported by Lappert's group.[37]

The complexation reactions of Ge(II) and Sn(II) compounds with terminal fluoride atoms are not known. In order to shed light in this area, **18** and **30** were reacted with diiron nonacarbonyl, Fe$_2$(CO)$_9$, at room temperature resulting in the iron carbonyl complexes of germanium(II), L$_1$Ge(F)Fe(CO)$_4$ (**31**) and tin(II), L$_1$Sn(F)Fe(CO)$_4$ (**32**), respectively (Scheme 10).[38] The Ge–Fe and Sn–Fe bonds were dative in nature. The Ge–Fe bond



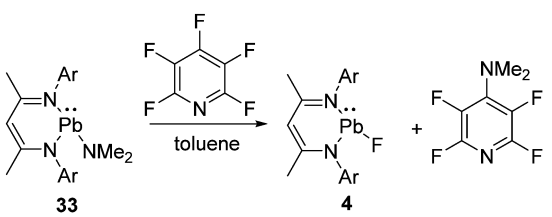
Scheme 9 The synthesis of Sn(II) fluoride (Ar = 2,6-iPr$_2$C$_6$H$_3$).



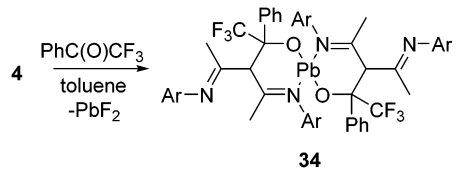
Scheme 10 The reactions of **18** and **30** with Fe$_2$(CO)$_9$ (Ar = 2,6-iPr$_2$C$_6$H$_3$).

length in **31** (2.3262(7) Å) is comparable to that in L$_1$Ge(OH)-Fe(CO)$_4$[39] (2.330(1) Å). Similarly, the Sn–Fe bond distance in **32** was found to be 2.4577(6) Å, which is comparable to that in L$_1$Sn(OH)Fe(CO)$_4$ (2.4832(7) Å).[40] The Ge–F bond length in **31** (1.868(2) Å) was found to be longer than that in **18** (1.805(17) Å) and **21** (1.848(2) Å), while the Sn–F bond length was reduced in **32** (1.9497(19) Å) than that present in **30** (1.988(2) Å).

We have mentioned the use of Pb(II) fluoride before (*vide supra*, Scheme 2) as a fluorinating agent for the metathesis reaction of Si(II) chloride to fluoride. However, the preparation of Pb(II) fluoride was found to be more challenging than its lighter congeners, which could be attributed to the insolubility associated with the lead compounds. The synthetic strategies applied for the preparation of Ge(II) and Sn(II) fluorides did not furnish the analogous Pb(II) fluoride, and instead, the formation of metallic lead was observed in each reaction. These findings left an impression that Me$_3$SnF should be substituted by another mild fluorinating agent. Moreover, the by-product formed while using Me$_3$SnF as a fluorinating agent is Me$_3$SnCl, which is highly toxic. Therefore, pentafluoropyridine was chosen as a fluorinating agent and reacted with L$_1$Pb(II)NMe$_2$ (**33**) to afford the β-diketiminatolead(II) monofluoride, L$_1$Pb(II)F (**4**), together with 4-dimethylaminotetrafluoropyridine (Scheme 11).[20] The driving force of this reaction is the formation of a C–N bond, which compensated the energy required for the C–F bond cleavage. The Pb–F bond length in **4** (2.088(17) Å) is expectedly longer than those of Ge–F (1.805(17) Å) in **18** and Sn–F (1.988(2) Å) in **30**. The low temperature ^{19}F NMR spectrum of **20** exhibits a resonance at



Scheme 11 The synthesis of Pb(II) fluoride (Ar = 2,6-iPr$_2$C$_6$H$_3$).



Scheme 12 The reaction of **4** with trifluoroacetophenone (Ar = 2,6-iPr$_2$C$_6$H$_3$).

δ 102.7 ppm, accompanied by two ^{207}Pb satellites (δ 106.4 and 99.0 ppm). The low temperature ^{207}Pb NMR spectrum shows a doublet at δ 787.4 ppm with a coupling constant of $^{1}J_{(19F-207Pb)}$ = 2792 Hz. When the measurements were performed at room temperature, the satellite signals and coupling constants of the ^{19}F and ^{207}Pb NMR spectra were not observed, reflecting the kinetically labile nature of the Pb–F bond at room temperature. The reactive nature of the Pb–F bond was further confirmed when **4** was treated with trifluoroacetophenone to yield a homoleptic Pb(II) compound (**34**) along with the formation of insoluble PbF_2 (Scheme 12).[20] The solid-state structure of **34** shows a spirocyclic structure where the two six-membered C_3ONPb rings are interconnected by the common Pb atom.

Activation of C–F bonds using compounds with a low valent silicon atom

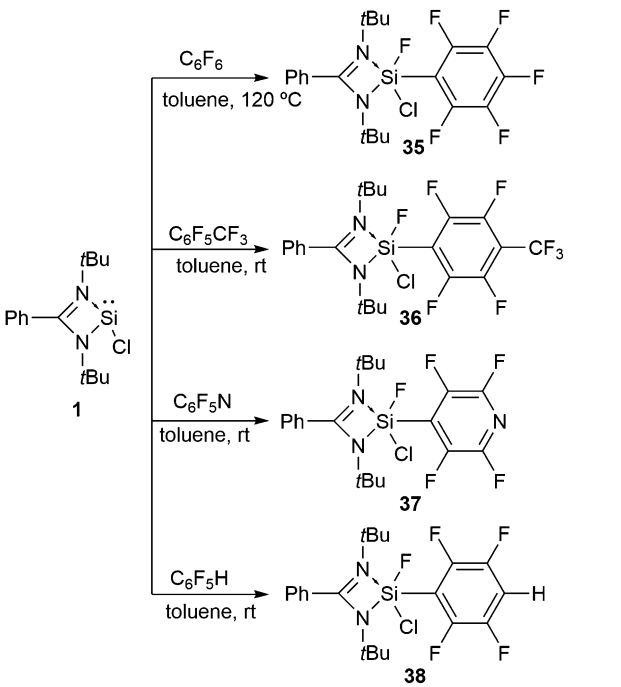
The activation of C–F bonds in fluorinated hydrocarbons is of fundamental interest from the standpoint of the potential application of organofluorine compounds in synthetic organic chemistry, pharmacy and agrochemistry,[41] as well as the ever-increasing environmental concerns related to fluorinated compounds.[42] Fluorinated hydrocarbons are not only contributing to global warming but cause the depletion of the ozone layer.[42] As a result, there is a need to develop new synthetic strategies for the activation of C–F bonds. Owing to the strength and the resulting high activation barrier of the C–F bonds in fluorocarbons, a strong Lewis acid with high fluoride affinity is sought-after for C–F bond activation. Recent years have witnessed the C–F bond activation using compounds with low-valent main group elements.[43–45] For example, the groups of Kuhn, Bertrand, Turner, Lee, Baker, Chaplin, Radius, and many others have demonstrated the activation of aromatic C–F bonds using various carbenes.[43] Studer and co-workers have described C–F bond activation in perfluoroarenes using aryl and alkyl isonitriles under UV irradiation.[44] The groups of Mikami, Nikonov, and Stephan have independently reported the respective use of boryl lithium, Al(I) compound and phosphonium cations for C–F bond activation.[45]

Compounds with low valent silicon atoms are especially appealing for C−F bond activation because they can integrate both Lewis acidity and fluoride affinity. The propensity of compounds with low valent silicon atom towards oxidative addition reactions can be tapped for cleaving inert bonds such as C–F bonds. Although never accredited, it was the groups of Timms and Margrave who noted that the reaction of hexafluorobenzene and *in situ* generated SiF_2 gave pentafluorophenyltrifluorosilane ($C_6F_5SiF_3$) as the major product arising from the oxidative addition of one of the C–F bonds at the Si(II) center (Scheme 1, eqn (g)). They were also able to trace the formation of $C_6F_4(SiF_3)_2$ as minor products in an o : m : p ratio of ~1 : 9 : 6. This was perhaps the first example of C–F bond activation using a compound with a low valent silicon atom.

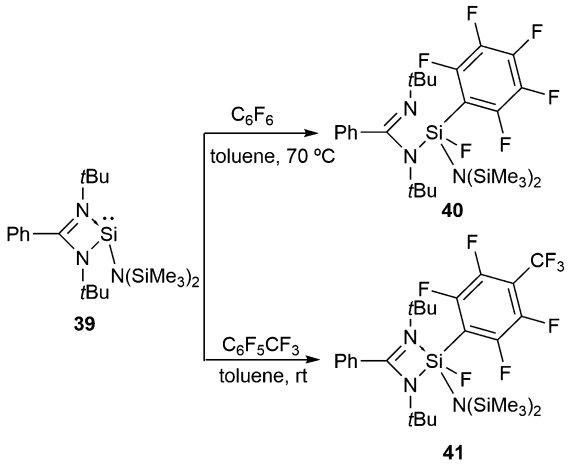
We embarked our investigation upon the reaction of **1** with C_6F_6, which led to the oxidative addition of the Si(II) center with the simultaneous cleavage of one of the C–F bonds in C_6F_6 (Scheme 13).[46] Similar activation of the aromatic C–F bond was achieved with $C_6F_5CF_3$ and C_6F_5N.[46] The resonances of the Si–F moiety present in **35**, **36**, and **37** arise at δ −63.4, −63.7, and −64.4 ppm in their respective ^{19}F NMR spectra. The ^{29}Si NMR spectra of **35**, **36**, and **37** show doublets (δ −91.9, −97.2, and −97.9 ppm) with a coupling constant of $^{1}J_{(29Si-19F)}$ 282.9, 283.6, and 282.7 Hz, respectively.

The introduction of C–H bonds into the fluorinated substrate often slows down the reactions and generates competition between the C–F and C–H oxidative addition reactions. For example, the Johnson group described the reaction of $Ni(PEt_3)_2$ with C_6F_5H, where the C–H activated species was formed as the kinetic product, while C–F oxidative addition led to the thermodynamic product.[47] The reaction of **1** with partially fluorinated benzene, C_6F_5H, yielded exclusively the product of C–F oxidative addition, **38** (Scheme 13). The formation of the Si–F bond in the product is assumed to drive the C–F bond activation.[46]

The reactions of the analogous silylene, $LSiN(SiMe_3)_2$ (L = $PhC(NtBu)_2$) (**39**), with hexafluorobenzene and octafluorotoluene follow an analogous oxidative addition pathway (Scheme 14) leading to **40** and **41**.[48] In the ^{19}F NMR spectra



Scheme 13 The activation of an aromatic C–F bond using chlorosilylene **1**.

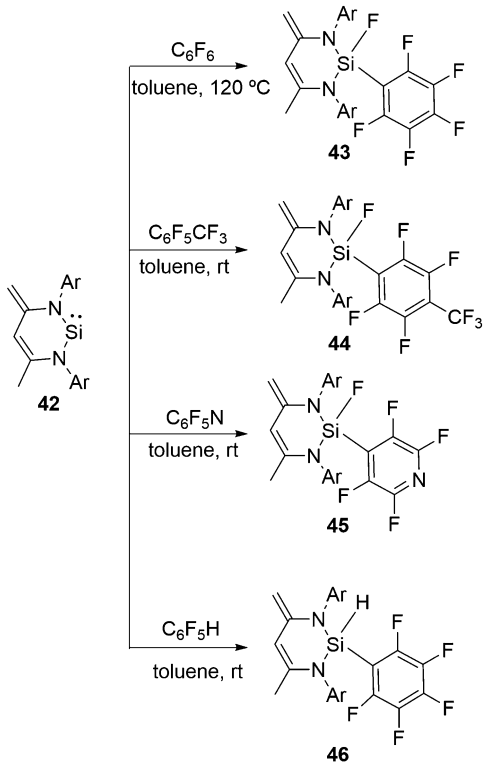


Scheme 14 $PhC(NtBu)_2SiN(SiMe_3)_2$ mediated aromatic C–F bond activation.

of **40** and **41**, the Si–F resonances appear at δ −89.09 and −85.09 ppm, respectively. The ^{29}Si NMR spectrum displays doublets at δ −62.17 ppm for **40** and −71.28 ppm for **41** with a coupling constant of $^{1}J_{(29Si-19F)}$ 243.19 and 245.02 Hz, respectively.

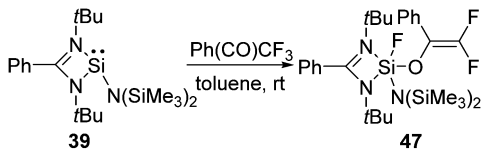
Of particular importance is the preference for the activation of the C–F bond *para* to the CF_3 moiety in octafluorotoluene. In a subsequent paper, Koley and co-workers computationally demonstrated that the activation energy barrier for the *para* C–F bond is lower than the *ortho* and *meta* C–F bonds by 5.2 kcal mol^{-1} and 8.0 kcal mol^{-1}, respectively.[49] Moreover, the overall distortion energy for the *para* C–F bond activation (25.4 kcal mol^{-1}) was found to be significantly smaller than those for the *ortho* (56.6 kcal mol^{-1}) and *meta* (63.8 kcal mol^{-1}) C–F bonds. The fact that the activation of the C–F bond in hexafluorobenzene occurs at elevated temperature while in octafluorotoluene its takes place at room temperature can be ascribed to the diminishing strength of the C–F bond upon increasing the fluorination and thereby lowering the energy barriers for the C–F bond activation in the more fluorinated substrates.

Apart from functionalized three coordinate silylenes, such as **1** and **39**, typical N-heterocyclic silylene, $CH[\{(C{=}CH_2)(CMe)(2,6\text{-}iPr_2C_6H_3N)_2\}]Si$ (**42**), was also reported for the activation of the aromatic C–F bonds.[46] All these aforementioned reactions with fluorinated substrates were investigated with **42** (Scheme 15). The oxidative addition of the C–F bond at the Si(II) atom takes place in the reactions with hexafluorobenzene, octafluorotoluene and pentafluoropyridine leading to the formation of **43–45**, respectively. However, the reaction of **42** with C_6F_5H exclusively led to the C–H activated product **46** instead of the C–F activated product observed in the case of **38**. No activation of the C–F bond was observed even at low temperature. These differences are likely to be due to the lower coordination number of the Si(II) atom in **42** than that in **1**. Usually, silicon hydrides with a high coordinate silicon atom are less stable than those of the corresponding fluoride analogues, which could be the underlying rationality for the preferred formation of low coordinate silicon with hydrides and not with fluorides.

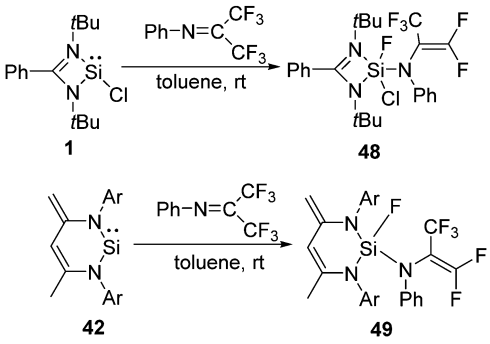


Scheme 15 N-Heterocyclic silylene mediated aromatic C–F bond activation (Ar = 2,6-$iPr_2C_6H_3$).

The selective activation of the aliphatic C(sp^3)–F bonds, such as the functionalization of the trifluoromethyl group, was not known for a long time.[50] Recently, we have shown that silylene **39** selectively activates one of the C–F bonds in 1,1,1 trifluoro acetophenone leading to a difluorinated alkene (**47**) featuring both the Si–O and Si–F bond (Scheme 16).[48] The DFT calculations revealed that the reaction goes through an Si–O bond formation with an energy barrier (ΔG) of 16.2 kcal mol^{-1}. Subsequently, the reaction proceeded through a five-membered transition state with a corresponding energy barrier of 6.8 kcal mol^{-1}, where a Si–F bond and C=C bond are formed. The final product, **47**, is very thermodynamically stable (−41.7 kcal mol^{-1}), which, along with the low barriers obtained, indicates that this reaction is both kinetically and thermodynamically viable at room temperature. Insertion of a Si(II) atom into the CF_3 group of hexafluoroacetimine was also reported. The reactions of **1** and **42** with $PhN{=}C(CF_3)_2$ led to the facile C–F activation of one of the CF_3 substituents and the formation of difluorinated alkenes, such as **48** and **49** (Scheme 17).[51] Such selective activation of one of the C–F bonds



Scheme 16 Activation of the C–F bond in trifluoro acetophenone by **39**.



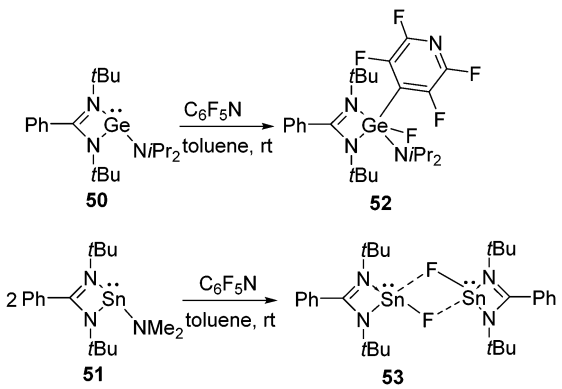
Scheme 17 Activation of the C–F bond in $PhC{=}N(CF_3)_2$ by **1** and **42**.

rather than complete defluorination of the CF_3 group by compounds with low valent silicon atoms was not known beforehand.

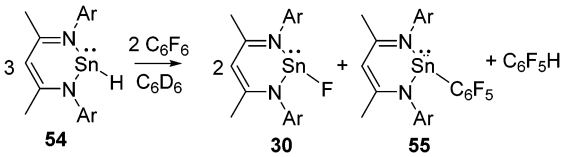
Activation of C–F bonds using compounds with low valent germanium and tin atoms

In addition to silylenes, germylenes and stannylenes have also been found to activate aromatic C–F bonds. In an early example, we showed that both $\{PhC(NtBu)_2\}GeNiPr_2$(**50**) and $\{PhC(NtBu)_2\}$-$SnNMe_2$ (**51**) can activate the C–F bond in pentafluoropyridine, however, divergent behavior was observed regarding their reactivities.[52] Like in the cases of silylenes, the C–F bond of pentafluoropyridine underwent an oxidative addition reaction at the Ge(II) atom leading to the formation of **52**. However, no oxidative addition product was formed with **51** and instead the substitution of the NMe_2 group by the fluoride ion occurred at the Sn(II) atom resulting in **53** (Scheme 18). Single crystal X-ray diffraction studies on **53** revealed that it exists as a dimer in which the two molecules are connected by weak intermolecular Sn···F bonds.

In a subsequent theoretical paper, Koley and co-workers explained the dichotomous reactivity pattern of germylene **50** and stannylene **51** towards pentafluoropyridine.[49] In **50**, the electron density is located on the Ge atom and due to the presence of the $NiPr_2$ substituent on Ge, the transition state for



Scheme 18 Activation of C–F bond of C_6F_5N by germylene and stannylene.



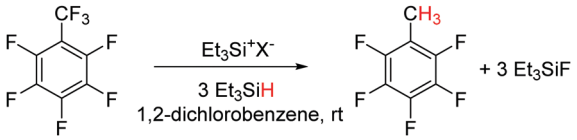
Scheme 19 Activation of C–F bond of C_6F_6 by stannylene hydride.

the oxidative addition pathway was found to be more favored than the metathesis pathway by 32.1 kcal mol^{-1}. However, they predicted that substitution on the Ge atom plays a part in determining which product will be formed. For example, they calculated that the replacement of the $NiPr_2$ substituent with an NMe_2 group may lead to a competition between the oxidative addition and metathesis pathways as the electronic and steric environments support both the transition states. An experimental verification of this prediction is deemed desirable and may open up a new avenue for C–F bond activation using functionalized germylenes. However, in case of **51**, the HOMO–LUMO energy gap increases due to the larger s–p gap. Therefore, the metathesis reaction was found to be more favored over the oxidative addition reaction by 13.3 kcal mol^{-1}. The same group also demonstrated the lower HOMO–LUMO energy gap is required for *para* C–F bond activation than the corresponding *ortho* or *meta* C–F bond activations and thereby explained the penchant for the *para* C–F bond activation of pentafluoropyridine.

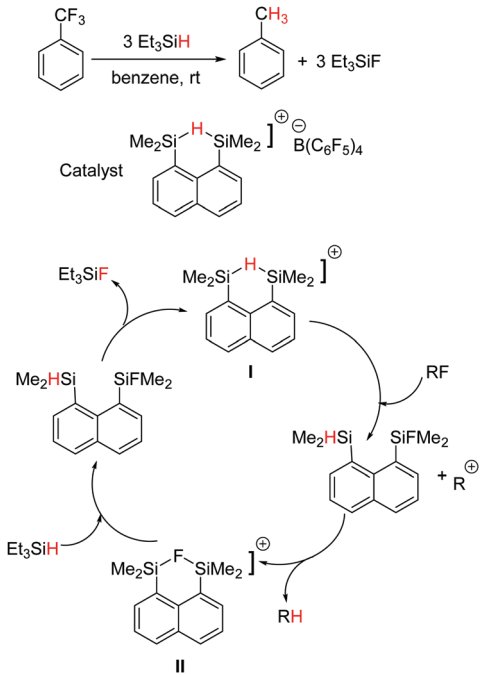
Tin(II) hydride **54** was also found to activate the C–F bond of C_6F_6 under ambient conditions and resulted in tin(II) fluoride **30** along with the tin(II) pentafluorophenyl compound, **55**, and C_6F_5H (Scheme 19).[53] A closer look at this reaction revealed that stoichiometric hydrodefluorination of C_6F_6 to C_6F_5H takes place during the reaction. The reaction is likely to occur *via* the metathesis between hydride and fluoride as well as hydride and the pentafluorophenyl substituent. The formation of **55** during the reaction was indicated by the ^{119}Sn NMR resonance at δ −176.4 ppm, which is significantly high-field shifted with respect to that of **54** (δ −4.5 ppm, $^1J_{Sn-H}$ = 64 Hz)[54] and **30** (δ −371.5 ppm, $^1J_{Sn-F}$ = 3100 Hz). To unequivocally prove the formation of **55** during the reaction, **28** was reacted with C_6F_5Li, which exclusively led to **55** and the resulting NMR spectra were compared.

Silylium ion in the hydrodefluorination reaction

Hydrodefluorination is a reaction in which a C–F bond is replaced by a C–H bond. The removal of fluorines from fluorocarbons compounds and replacement with hydrogen is an important goal, in order to convert them into more biodegradable compounds. Usually, transition metal catalysts are used for this conversion.[55] Ozerov and co-workers showed that a silylium–borane catalyst, $Et_3Si^+[B(C_6F_5)_4]^-$, can catalyze the selective hydrodefluorination of $C_6F_5CF_3$ to $C_6F_5CH_3$, although with a poor turn over number (TON = 19).[56] By varying the



Scheme 20 Silylium ion catalyzed hydrodefluorination.



Scheme 21 Silylium ion catalysed hydrodefluorination of trifluorotoluene and the tentative catalytic cycle.

counter-anion with a carborane catalyst, $Et_3Si^+[CHB_{11}H_5Cl_6]^-$, the TON of the same reaction was found to increase up to 2700 (Scheme 20).[57] The mechanism has been assumed to proceed *via* a silylium ion-mediated fluoride abstraction from the substrate with subsequent hydride transfer from the organosilane to the intermediate carbenium ion. The driving force for the overall reaction is the formation of Si–F and C–H bonds that counterbalance the cleavage of the C–F and Si–H bonds by 45.4 kcal mol^{-1}, thereby enabling the metathesis.

Parallel to Ozerov's findings, Müller and co-workers reported the hydrodefluorination of trifluorotoluene to give toluene using a hydride-bridged disilyl cation as the catalyst (Scheme 21).[58] The specialty of this case is that the cation combines the silicon electrophile as well as the hydride source. Both hydride (**I**) and fluoride (**II**) bridged silylium cations were observed as intermediates, structurally characterized and found to be interconvertible in the reaction with alkylfluorides or silanes. The tentative catalytic cycle is shown in Scheme 21, however, the cycle operates with a moderate TON.

Conclusions

While the basis of silicon(II) difluoride chemistry dates back into the 1970s, most progress in this area has been made during the last few years. The first stable silicon(II) difluoride (**14**) was made accessible using cyclic alkyl amino carbene (cAAC) ligand. The synthesis of the first compound containing an SiF_3 radical (**15**) has also been recently accomplished. The lion's share of the credit must go to the cAAC ligand due to its high lying HOMO and low lying LUMO, which not only donates electron density to the Si(II) center but unlike NHC, can accept electron density from the Si–F bonds. Structural analysis of these complexes in tandem with DFT calculations has significantly enhanced the understanding of their electronic properties. The reactivities of both **14** and **15** have yet to be reported but promise rich further chemistry. And of course, the success of cAAC and the failure of NHC (so far!!) for stabilizing the SiF_2 moiety will encourage synthetic chemists to make newer neutral ligands with tunable electronic properties. The chemistry of silicon(II) fluorides can be best described in Churchill's words "*...it is not even the beginning of the end...*". The game is on!

Of equal importance are the recent achievements in the activation of C–F bonds using compounds with low valent silicon atoms. Progress in the use of silylenes to activate both alkyl and aryl C–F bonds was also detailed. The formation of a strong Si–F bond is likely to be the driving impetus of these reactions. In addition to the commonly observed stoichiometric C–F bond activation, silylium ion catalyzed hydrodefluorination has been discovered with remarkable turn over numbers, which was previously considered the exclusive domain of transition metal complexes. Apart from the hydrodefluorination reactions, silylium cations have been recently employed in the Friedel Crafts reactions of fluoroarenes[59] and C–C coupling reactions,[60] which have not been discussed in this feature article. As a consequence, the focus in silicon fluorine chemistry will likely tilt from fundamental to application-oriented research in the near future. As part of a natural progression, the heavier congeners of silylenes, such as germylenes and stannylenes, have also been reported for C–F bond activation but their examples are still very scant. Nevertheless, we hold great hopes for studying these riveting molecules in the future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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