N-heterocyclic carbene derivatives for the activation of sulfur fluorides

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For my family

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Abstract

The metal-free activation of the greenhouse gas SF_6 using electron-rich *N*-heterocyclic carbenes (NHCs) furnished 2,2-difluoroimidazolines or 2,2-difluoroimidazolidines and 2-thio derivatives of the NHC precursors. The NHCs can reduce SF_4 as well to give same products. A complete degradation of an another greenhouse gas SF_5CF_3 also gave 2,2-difluoro- and 2-thio-derivatives along with the 2-fluoro-2-trifluoromethyl- derivative of the NHC precursors.

The 1,3-dimesityl-2,2-difluoroimidazolidine [SIMes$(F)_2$] was taken as an exemplary substrate to be applied in deoxyfluorination reactions and acyl fluorination of aldehydes *via* aldehydic C(sp^2)–H bond activation. Additionally, the activation of SF_6 and the fluorination of 1-octanol into 1-fluorooctane can be coupled in a one-pot process. Furthermore, trifluoromethylation of Me_3SiCl and arenes was observed with the 1,3-dimesityl-2-fluoro-2-trifluoromethylimidazolidine [SIMes$(F)(CF_3)$].

SIMes$(F)_2$ was also used for the fluorination of complex [(SIMes)$AlMe_3$] to synthesize the NHC stabilized Al(III) fluoride [(SIMes)Al$(F)(Me)_2$]. Various alternative reaction routes have been developed to synthesize the NHC stabilized Al(III) fluorides [(SIMes)Al$(F)(Me)_2$] and [(SIMes)Al$(F)_3$] through the fluorination of [(SIMes)$AlMe_3$] with SF_4, SF_6 and Me_3SnF. The complex [(SIMes)Al$(F)_3$] was successfully employed for a F/Cl exchange reaction by treating it with Me_3SiCl to yield [(SIMes)Al$(Cl)_3$] and Me_3SiF.

Kurzzusammenfassung

Die metallfreie Aktivierung des Treibhasgases SF_6 unter Verwendung von elektronenreichen *N*-heterocyclischen Carbenen (NHCs) resultierte in der Bildung des jeweiligen 2,2-Difluorimidazolins und Imidazolin-2-thions bzw. 2,2-Difluorimidazolidins und Imidazolidin-2-thions. Die Reduktion der NHCs mit SF_4 liefert dieselben Produkte. Im Abbau von SF_5CF_3 mit NHCs werden ebenfalls die zuvor genannten Produkte erhalten, wobei zusätzlich das entsprechende 2-Fluor-2-trifluormethylderivat gebildet wird.

Exemplarisch wurde 1,3-Dimesityl-2,2-difluorimidazolidin [SIMes$(F)_2$] als Fluorierungsreagenz von Aldehyden unter Bildung von Acylfluoriden sowie als Deoxyfluorierungsreagenz eingesetzt. In einem *one-pot*-Prozess kann zudem die Aktivierung von SF_6 mit der Deoxyfluorierung von 1-Oktanol zu 1-Fluoroktan kombiniert werden. Des Weiteren konnte 1,3-Dimesityl-2-fluor-2-trifluormethylimidazolidin [SIMes$(F)(CF_3)$] zur Trifluormethylierung von Me_3SiCl und Arenen eingesetzt werden.

Der Einsatz von SIMes$(F)_2$ ermöglicht die Darstellung von des NHC-stabilisierten Al(III)-Fluorids [(SIMes)Al$(F)(Me)_2$] durch Monofluorierung von [(SIMes)$AlMe_3$]. Durch Variation des Fluorierungsmittels (SF_4, SF_6, Me_3SnF) kann ein höherer Fluorierungsgrad erreicht und [(SIMes)Al$(F)_3$] synthetisiert werden. Dieser Al-Komplex konnte durch Halogenaustausch mit Me_3SiCl in [(SIMes)Al$(Cl)_3$] überführt werden.

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1. General Introduction

1.1. Role of fluorine in everyday life

Fluorine is a highly advantageous element because it has found its way into almost every branch of chemistry and opened up new paths for scientific progress. The element fluorine plays a key role in pharmaceutical, agrochemical and material science research. [1][2][3] The interest in fluorinated compounds is based essentially on the extraordinary electronic and chemical properties of the fluorine atom.[1a-c, 4] The replacement of hydrogen atoms by fluorine atoms often results in drastically changed physical, chemical and biological properties compared to the non-fluorinated parent compound in organic molecules.[5]

Fluorine has highest electronegativity of 4.0 on the Pauling scale among all elements in the periodic table.[5] Due to the high electronegativity of the fluorine atom, element – fluorine bonds show considerable ionic bond character, which results in a low polarizability and a short bond. These features often give element – fluorine bonds considerable thermodynamic and kinetic stability.[1b, 4e, 5-6] Thus, fluorine forms the strongest known σ bond to carbon among all elements.[5] The introduction of fluorine atoms in bioactive organic molecules can increase the lipophilicity and metabolic stability of drugs due to the considerable C – F bond energy and polarity.[1d, 1e, 3] Thayer in 2006 reported that nearly 20 % of pharmaceuticals are estimated to contain fluorine atom.[1c] Some representative examples of fluorinated pharmaceuticals are Lipitor® (atorvastatin), a cholesterol-lowering drug; fluorouracil, a chemotherapy drug; norfloxacin, a broad-spectrum antibiotic; risperidone, an antipsychotic drug (**Figure 1**).[1d, 1e, 3] Another important feature of the fluorine atom is its small atomic radius (1.4 Å) which induces low coefficient of friction and high hydrophobicity in highly fluorinated systems.[1b, 4c-e, 5]. Therefore, the highly fluorinated systems are useful in making surface coatings such as Teflon® (polytetrafluoroethylene) or water-repellent fabrics like Gore-Tex® (**Figure 1**).[1b] Perfluorinated and partially fluorinated molecules have diverse application in the form of coolants, fire extinguishing agents, dyes, anesthetics and plant protection agents.[4f, 7]

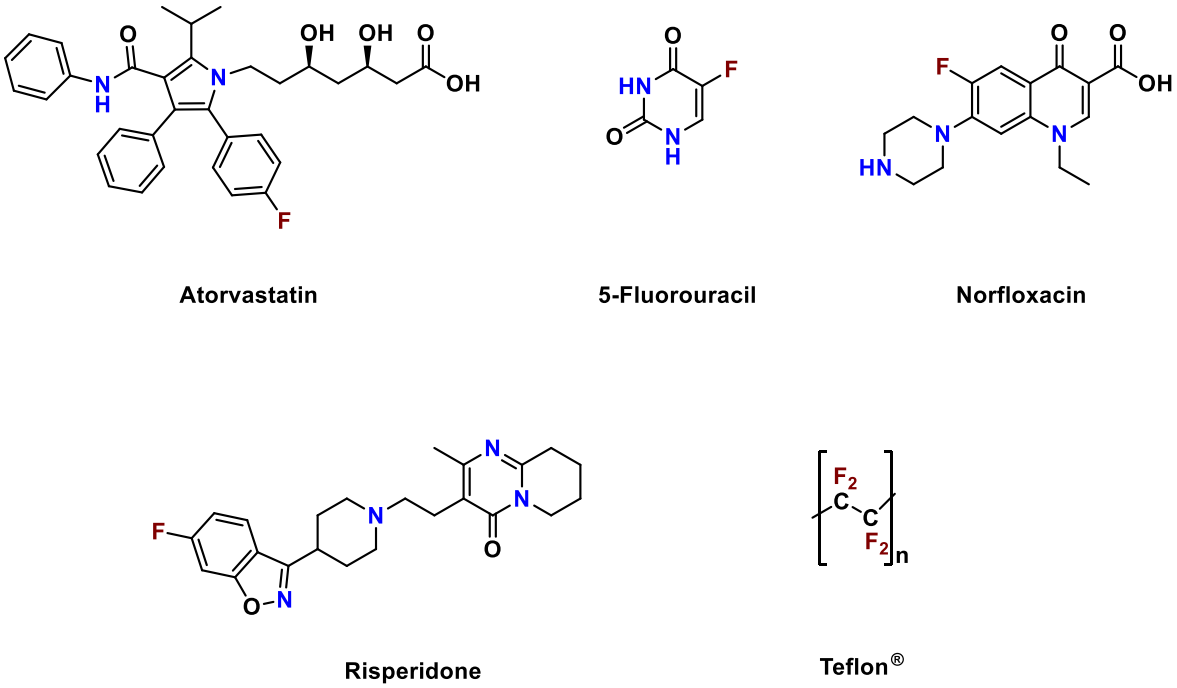


Figure 1. Examples of fluorinated pharmaceuticals and polymers.[1b, 1d, 1e, 3]

It is clear from the examples mentioned that the incorporation of fluorine into compounds indeed plays a pivot role in everyday life. However, although fluorine is the 13th most common element in the earth's crust, majority of naturally occurring fluorine is found in the form of fluorspar (CaF_2) and cryolite Na_3AlF_6. The fluorinated natural products are the least common organohalides on the earth, thus, development of new methods for the introduction of fluorine atom into organic or inorganic molecules is of enormous academic and industrial interest.[1a-g, 8][9][3]

1.2. Synthesis strategies of fluorination

Two general pathways for the preparation of fluorinated compounds are shown in **Figure 2**. The **Figure 2** depicts that the synthesis strategy of fluorination depends on the desired degree of fluorination of the target molecules. If a perfluorinated compound is used as the starting material, highly fluorinated organic molecules can be obtained through C−F bond activation.[6a, 8, 10] Low fluorinated molecules can be prepared by direct fluorination of organic molecules with electrophilic or nucleophilic fluorinating agents (**Figure 2**).[4f, 11]

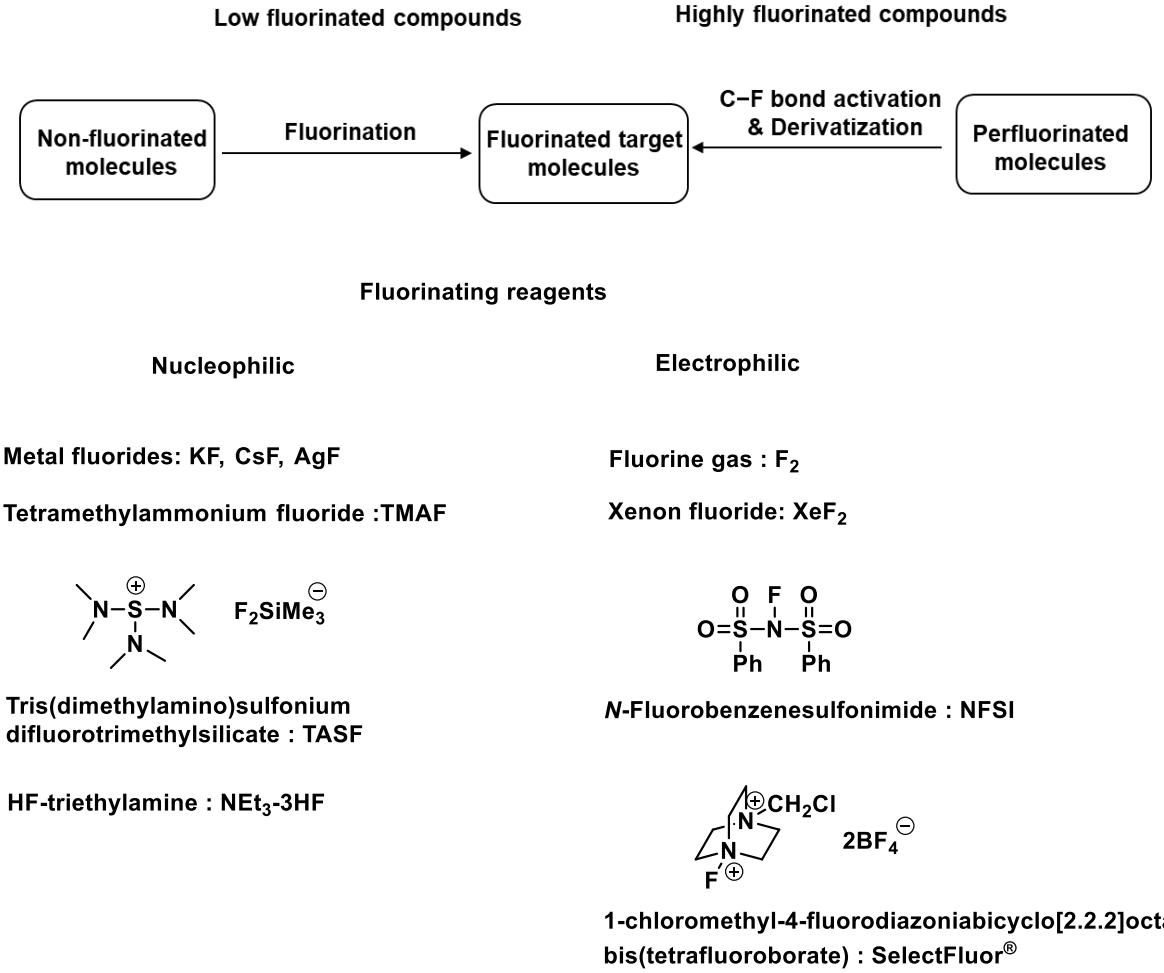


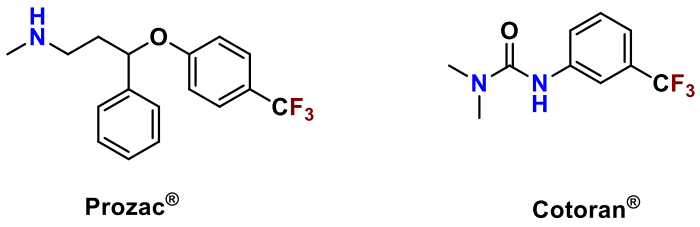
Figure 2. Synthetic strategies of fluorination with nucleophilic or electrophilic fluorinating reagents or *via* C−F bond activation.[4f, 6a, 10]

1.2.1 Deoxyfluorination

Despite the number of fluorinating reagents discussed above, incorporation of fluorine is not easy, often due to the high reactivity and poor selectivity of these reagents. An alternative synthesis strategy has emerged to incorporate the C–F bond in organic molecules through deoxyfluorination reaction.[12] Deoxyfluorination reagents are broadly categorized as lower sulfur fluorides derived reagents such as sulfur tetrafluoride (SF_4), *N,N*-diethylaminosulfurtrifluoride (DAST) or Deoxo-fluor® and imidazole derived reagents such as 2,2-difluoro-1,3-dimethylimidazolidine (DFI), PhenoFluor™ or AlkylFluor™.[13]

1.2.2. Trifluoromethylation

The introduction of trifluoromethyl group (CF_3) in organic molecules could significantly improve their molecular properties such as lipophilicity, metabolic stability and permeability.[1b, 1e, 11b, 14] Therefore, organic compounds bearing CF_3 groups are widely used in pharmaceuticals and agrochemicals. For example, the antidepressant fluoxetine (Prozac®) and the urea herbicide fluometuron (Cotoran®) contain the CF_3 group (**Figure 3**).[1]



Prozac® Cotoran®

Figure 3. Examples of CF_3 group containing pharmaceuticals (Prozac®) and herbicide (Cotoran®)[1]

The benefits of trifluoromethyl group (CF_3) in biologically active molecules has promoted the development of novel methods to construct C–CF_3 bonds. The CF_3 group can be introduced into various organic structures via nucleophilic, electrophilic and radical trifluoromethylation.[14c, 15] For the nucleophilic trifluoromethylation in organic molecules, Ruppert-Prakash reagent with a fluoride anion catalyst is the most commonly

used compound (**Figure 4)**.[15a-c, 15f, 15i, 16] The electrophilic trifluoromethylation is commonly achieved with trifluoromethylchalcogen salts (Umemoto's reagents) or iodonium salts (Togni's reagents) accompanied by an electron transferring catalyst (**Figure 4**).[13l, 15g-i, 17]

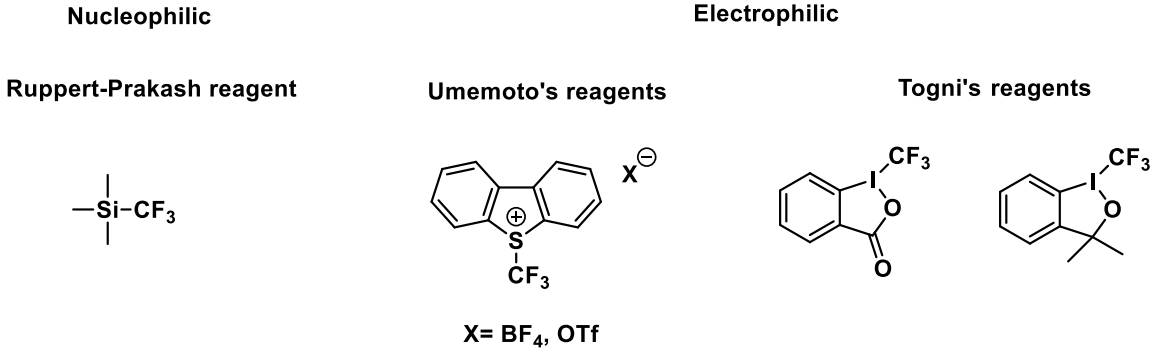


Figure 4. Examples of nucleophilic and electrophilic trifluoromethylation reagents.[15f, 15g, 15i]

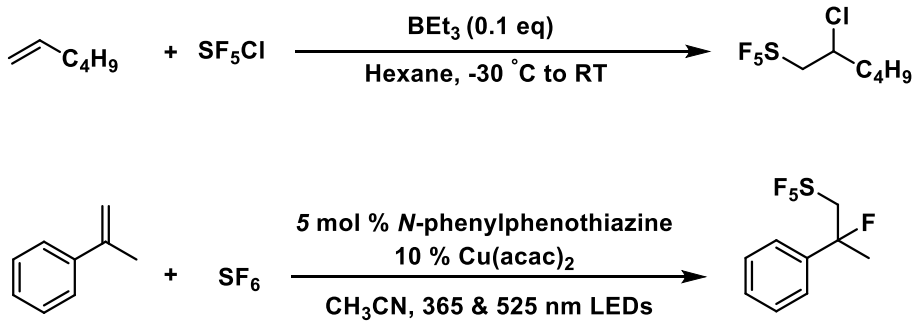
1.2.3. Pentafluorosulfanylation

In addition to organic compounds with carbon–fluorine bond, organic molecules with sulfur–fluorine bond have been in the focus of research for many years.[18] The combination of a "soft" sulfur and a "hard" fluorine atom as well as the ability of the sulfur atom to adopt the oxidation state up to + VI leads to a very wide list of substances containing sulfur–fluorine bond.[18-19] In particular, the organic molecules having a pentafluorosulfanyl group (SF_5 group), are becoming increasingly important as pharmaceuticals, pesticides, fungicides, liquid crystals and high-energy materials.[20][1b, 21]

The enormous interest in organic pentafluorosulfanyl compounds lies primarily in the unique properties of the SF_5 group. The introduction of SF_5 substituents in organic molecules can change the molecular properties of a compound by causing high electronegativity, increased lipophilicity, thermal stability and large steric bulk.[22] In organic compounds, the SF_5 group is usually considered to be chemically and hydrolytically stable.[22d] Based on these properties, the SF_5 group often considered as a

"better" alternative to the trifluoromethyl group (CF_3 group) in organic compounds. The electron withdrawing effects of SF_5 and CF_3 are observed comparable in magnitude. The electronegativity of the SF_5 and CF_3 group has been measured as 3.65 and 3.36 respectively.[22a-d]

The SF_5 group containing compounds can be synthesized from direct fluorination of thiols or sulfides with fluorine (F_2), metal fluorides (AgF_2, CoF_3) or HF.[22d, 23] An alternative milder and more efficient method in contrast to direct fluorination is the reaction of SF_5X (X= F, Br, Cl, CF_3) reagents with organic substrates (**Scheme 1**).[21, 22d, 22e, 24] The SF_6 and SF_5CF_3 are known as strong greenhouse gases having enormous global warming potential. [25] The examples shown in the **Scheme 1** make it clear that by developing methods for the effective and selective conversion of SF_5 group containing compounds into less harmful substances, not only provides an effective approach to eliminate the existing stock of greenhouse gases, but also provides an access to the compounds used in pharmaceuticals and agrochemicals.[26][1b, 21, 27]



Scheme 1. Pentafluorosulfanylation of organic molecules using SF_5Cl and SF_6.[24c, 24f, 24h]

2. Background Literature

2.1. Sulfur Hexafluoride (SF_6)

2.1.1. Properties and Usage

Sulfur hexafluoride (SF_6) was first synthesized by Lebeau and Moissan in 1900 *via* a highly exothermic reaction ($\Delta_f H^0$ = -1220 kJ mol^{-1}) where elemental sulfur was treated with elemental fluorine.[28][29] It is an inert, colorless, odorless, non-combustible and non-toxic gas.[30] Due to its extremely chemical inertness and other outstanding physical properties such as high density and high dielectric constant, SF_6 is used for many industrial applications, especially as an insulation gas in electrical equipment and electron trapping agent for high voltage power applications.[25a, 30-31]

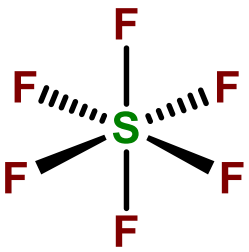


Figure 5. Representation of a SF_6 molecule in octahedral symmetry.

SF_6 is the model compound for octahedral symmetry (point group *Oh*) (**Figure 5**).[19, 32] For a long time it was assumed that the d orbitals of the sulfur atom are involved in the formation of S–F bonds , forming sp^3d^2 hybrid orbitals.[19] However, numerous theoretical studies has shown that the 3d orbitals, because of their high orbital energies make a very small contribution to the bonding in SF_6.[33] The molecular orbital (MO) theory suggests that SF_6 molecule has four bonding orbitals and two non-bonding orbitals, each occupied with two electrons. One bonding orbital has a_{ig} character and rest of the three bonding orbitals has t_{1u} character.[34]

The bond dissociation energy of the first S−F bond in SF_6 was calculated to be $D^0_{298\ K}$ = 387±13 kJ mol^{-1}.[35] The arrangement of six fluorine atoms around sulfur and formation of strong S−F bonds provide a steric hinderance for reactivity, especially for the attack of a nucleophile and hence S_N2-type reactions are not observed commonly.[33] A comparison of the first Ionization energy of SF_6 (E_i = 15.5 eV) with that of argon (E_i = 15.7 eV) shows that the SF_6 molecule has a noble gas character in regard to the ionization, which is further decisive for its stability.[1b, 36]

2.1.2. Greenhouse effect of SF_6

SF_6 has very low solubility in water and is also a radioactively-active gas with high fugacity and therefore, is a potent greenhouse gas.[25a, 25b] The atmospheric lifetime and global warming potentials (GWP) for SF_6 are reported by World Meteorological Organization (WMO) as 3200 year and 22,450 relative to carbon dioxide (CO_2), respectively.[37] Due to its extensive use in electrical industries, the atmospheric emission of SF_6 is increased from less than 1 ppt in 1975 to more than 8 ppt in 2008.[25a, 25b, 30] The demand of SF_6 in electrical industries is predicted as 4500–5500 ton per annual year by 2020 which is 5 times more than what was needed two decades ago.[38] Increase in the demand of SF_6 would lead to the increased concentration of SF_6 in atmosphere and hence this would make more environmental hazards.[39] Therefore, Kyoto protocol was signed in 1997 which listed SF_6 as one of the six greenhouse gases that should be restricted for use.[40] The European Union has also made an EU regulation (No 517/2014) to reduce the emission of fluorinated greenhouse gases.[41]

Besides the restricted use of the SF_6, it is also important to find ways for its degradation or removal. Over the years, various physical and chemical methods have been reported for the decomposition of SF_6. Also, investigations were carried out to substitute the SF_6 gas in electrical applications with other inert gases. In the following section different methods for the decomposition of SF_6 gas are discussed in details.

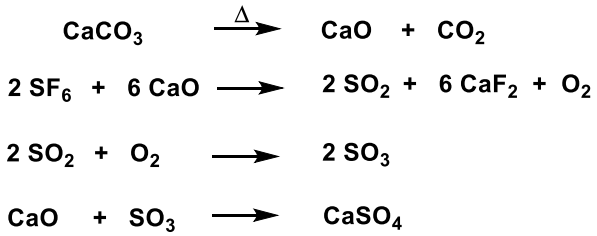
2.2. Approaches for the removal of SF_6

2.2.1. Replacement of SF_6 with other inert gases for its industrial use

To reduce the use of SF_6, a hybrid mix of SF_6 with N_2 was investigated for its application in electrical equipment. The dielectric strength of this mixed gas (SF_6/N_2) was found to be 85 %–90 % of pure SF_6. Since use of such hybrid mix can reduce the use of SF_6 to certain extent therefore electrical properties of the mixture of SF_6 with inexpensive inert gases such as He, CF_4, N_2O, CO_2 were also determined.[42] Due to their comparable electrical performance and almost negligible global warming potential and very low atmospheric lifetime as compared to SF_6; CF_3I and hybrid mix of CF_3I in inert gases has gained interest as a substitute for SF_6.[38, 43] CF_3OOCF_3 is a dielectric gas having non-ozone depleting nature and low global warming potential, can also provide a substitute for the SF_6 in electrical equipment.[44] Use of CF_3I or CF_3OOCF_3 in electrical industries is yet very limited due to the lack in adequate research; thus more investigation and development is required in this field.

2.2.2. Thermal decomposition

SF_6 can be thermally decomposed at elevated temperature (more than 1100 °C) in industrial waste treatment furnaces. In this process SF_6 reacts with $CaCO_3$ (calcite) to produce naturally occurring materials CaF_2 (fluorspar) and $CaSO_4$ (gypsum) (**Scheme 2**). Excess amount of $CaCO_3$ is added in the reaction mixture to ensure the complete reaction with HF or SO_2, which can be produced from thermal decomposition of SF_6.[45]



Scheme 2. General reaction mechanism for the thermal decomposition of SF_6.[45b]

2.2.3. Nonthermal plasma decomposition

Partially or fully ionized gas consisting of various particles, such as electrons, ions, atoms, and molecules is called as Plasma. In thermal plasma almost all its components are at thermal equilibrium while in nonthermal plasmas (NTPs) the electrons have a higher temperature than ionic, and neutral species. These highly energetic electrons then collide with a parent molecule and produces various active species such as ions, excited atoms, and free radicals in multiple step physical and chemical processes.[46] These particles can perform oxidative or reductive decomposition of gaseous pollutants such as SO_2[47], NO_x[48], HFCs[49] and SF_6[29, 50]. Common methods for producing NTPs, include, microwave plasma[51], dielectric barrier discharge[52] and radio frequency plasma[53]. During nonthermal plasma dissociation of SF_6, lower sulfur fluorides are formed, which in presence water vapor or oxygen produce SOF_4, HF, SOF_2, S_2F_{10}, SOF_{10}, $S_2O_2F_{10}$.[25a, 54] Final products obtained from the degradation of the SF_6 with this method are toxic and corrosive in nature.

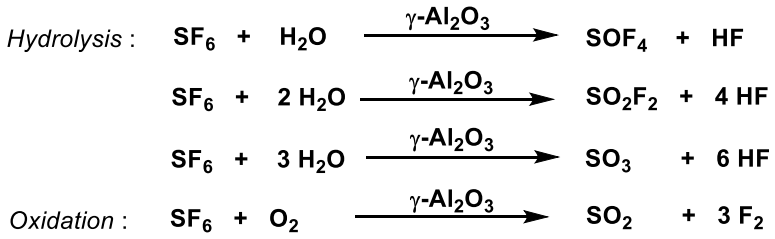
2.2.4. Photo-reductive decomposition

The photochemical degradation of SF_6 is a relatively new approach. For the photoreduction of the SF_6, chemically active species are produced from the photolysis of some reductive agents such as olefins or acetone, which then react with SF_6 to decompose it. It has been reported that photodissociation of SF_6 would not take place for wavelength more than 160 nm.[55] Since commonly used UV lamps emit light more than 160 nm therefore agents like styrene, propene and acetone are used, which get dissociated above 160 nm to produce reactive species such as CH_3, CH_2, H, C_6H_5 radicals. These reactive

species then react with fluorine atoms in the SF_6 to decompose it.[56] Although this method has advantage of consuming less power and toxic products such as SOF_2, SOF_4, SO_2F_2 are not produced, however, formation of by products such as hydrofluorocarbons (HFCs), HF and SiF_4 can't be avoided.

2.2.5. Catalytic hydrolysis and oxidation

The hydrolysis and oxidation of SF_6 consumes less amount of energy than thermal or photo-reductive decomposition of SF_6. Park *et al*. reported that γ-alumina or a $AlPO_4$/γ-alumina based catalyst can be efficiently used for the catalytic hydrolysis or oxidation of SF_6.[57] Zhang *et al*. reported on the efficient removal of SF_6 by reacting it with various metal oxides and silicates present in the electroplating sludge.[58] In the catalytic degradation process of hydrolysis and oxidation of SF_6, hazardous metal fluorides and SOF_4, SO_2F_2, SO_2, SO_3, HF, and F_2 are formed (**Scheme 3**).



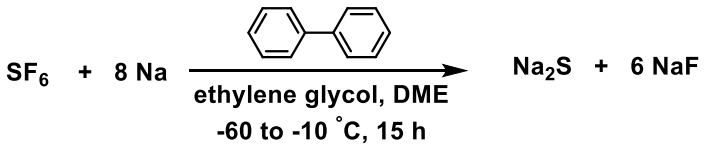
Scheme 3. Reaction pathway for the hydrolysis and oxidation of SF_6.[45b]

2.2.6. Chemical reduction

Case and Nyman reported that SF_6 when reacted with $AlCl_3$ at high temperature (180-200 °C) results in the formation of AlF_3 and sulfur chlorides with a very low conversion (15 %) of SF_6 (**Scheme 4**).[59]

Scheme 4. Reaction of SF_6 with $AlCl_3$ at high temperature.[59-60]

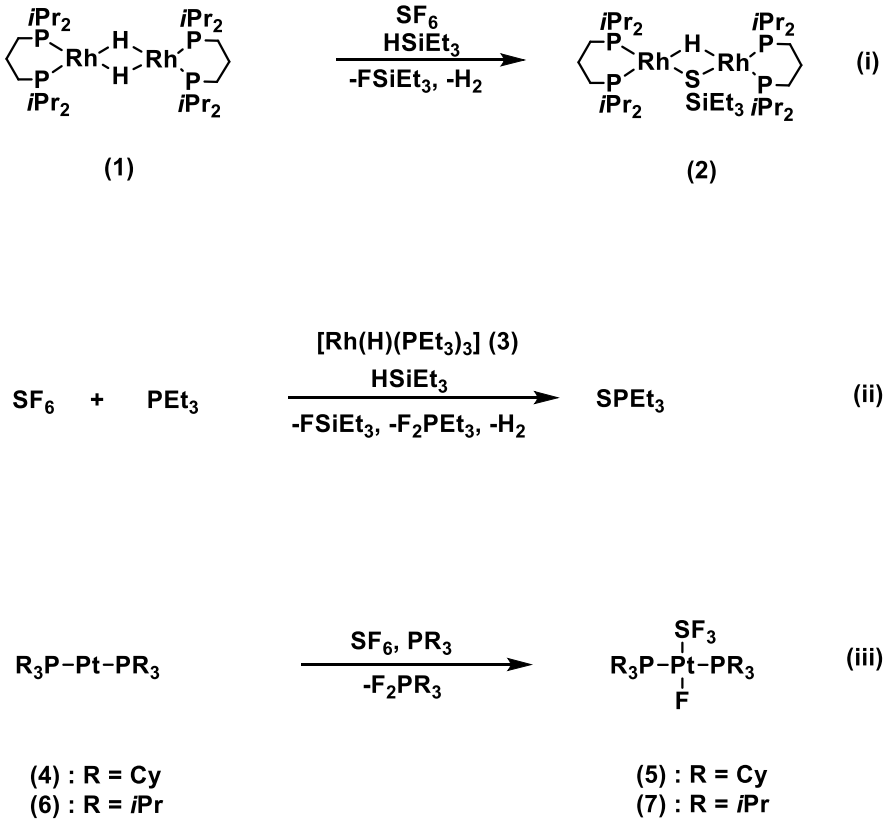
Alkali (Li-Cs), alkaline (Sr, Ba) and rare (Eu, Yb) earth metals are reported to transform SF_6 into sulfides and corresponding metal fluorides when dissolved in liquid ammonia via electron transfer mechanism.[61] Demitras *et al*. reported that SF_6 can be activated with sodium (Na) metal dissolved in diphenyl-ethylene glycol, dimethyl ether (DME) solution between -64 °C and -10 °C (**Scheme 5**).[61b]



Scheme 5. Reduction of SF_6 with sodium.[60, 61b]

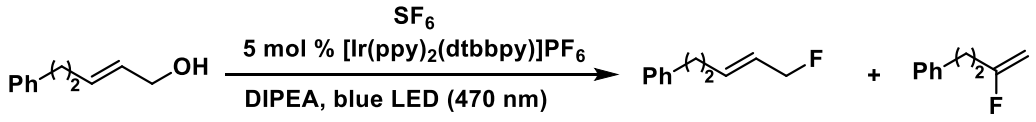
Activation of SF_6 at transition metal complexes has been studied extensively in the past 15 years. Ernst *et al*. and Limberg *et al.* described the activation of SF_6 at low-valent Ti, V, Cr, Zr, Fe and at reduced Ni (I) complexes respectively, to obtain organometallic fluoride or poly fluoride complexes. The fate of sulfur is described only for the reactions of SF_6 with [Ti(1,3-*t*Bu$_2$C$_5$H$_3$)(6,6-dmch)(PMe$_3$)](6,6-dmch = 6,6-dimethylcyclohexa-dienyl), [Cr(C$_5$Me$_5$)$_2$] and $K_2[(L^{tBu}Ni)_2(\mu_1\text{-}\eta^1\text{:}\eta^1\text{-}N_2)]$ (L^{tBu} = [HC(C*t*BuNC$_6$H$_3$(*i*Pr)$_2$)$_2$]$^-$ to yield SPMe$_3$, $[\{Cr(C_5Me_5)(\mu\text{-}F)\}_3(\mu_3\text{-}S)]^+[Cr(C_5Me_5)(F)_3]^-$ and $[(L^{tBu}Ni^{II})_2(\mu\text{-}S)]$ respectively.[62]

Braun *et al*. reported on the degradation of SF_6 at the binuclear rhodium complex [{Rh(μ-H)(dippp)}$_2$] (**1**; dippp =1,3-bis(diisopropylphosphanyl)propane) in presence of $HSiEt_3$ to give exclusively the thiolato-bridged complex [Rh_2(μ-H)(μ-$SSiEt_3$)(dippp)$_2$] (**2**), $FSiEt_3$ and H_2 [**Scheme 6, (i**)].[63] For a more efficient degradation of SF_6 in homogeneous phase, complex [Rh(H)(PEt_3)$_3$] (**3**) was employed catalytically in the presence of PEt_3 and silane, which yielded F_2PEt_3, $SPEt_3$, fluorosilanes and H_2 as a result of the degradation [**Scheme 6, (ii)**].[64] Additionally, a selective activation of SF_6 with the complexes [Pt(PCy_3)$_2$] (**4**) or [Pt(P*i*Pr$_3$)$_2$] (**6**) was shown to generate the SF_3 complexes *trans*-[Pt(F)(SF_3)(PCy_3)$_2$] (**5**) or *trans*-[Pt(F)(SF_3)(P*i*Pr$_3$)$_2$] (**6**) respectively which were further employed in deoxyfluorination reactions [**Scheme 6, (iii)**].[65]



Scheme 6. Degradation of SF_6 at; (i) complex [{Rh(μ-H)(dippp)}$_2$](**1**), (ii) with catalyst [Rh(H)(PEt$_3$)$_3$](**3**) and (iii) complexes [Pt(PR$_3$)$_2$] (**4**, **6**).[63-65]

The last approach for the degradation of SF_6 involving metals is a photoredox catalytic activation of the SF_6. Jamison *et al.* reported on the activation of the SF_6 in homogeneous phase using [Ru(bpy)$_3$(PF$_6$)$_2$] (bpy = 2,2' bipyridine) and [Ir(ppy)$_2$(dtbbpy)PF$_6$] (ppy = 2-phenylpyridine; dtbbpy = 4,4'- di-*tert*-butyl-2,2' bipyridine) as photocatalysts in the presence of diisopropylethyl amine (DIPEA) as a stoichiometric reductant and irradiation with blue LED (470 nm).[66] The active species generated form the photochemical activation of the SF_6, were utilized for the deoxyfluorination of allylic alcohols to give the corresponding allylic fluorides (**Scheme 7**). A mechanism was suggested for the deoxyfluorination of alcohol, which involves the activation of alcohol *via* O–S bond formation resulting in a R-O-SF_x intermediate. Subsequently C–O bond cleavage would formally result in the formation of an ion pair comprising $[OSF_x]^-$ anion which delivers fluorine for the fluorination.[66]



Scheme 7. Deoxyfluorination of an allylic alcohol *via* activation of the SF_6 at a photoredox-catalyst $[Ir(ppy)_2(dtbbpy)PF_6]$.[66]

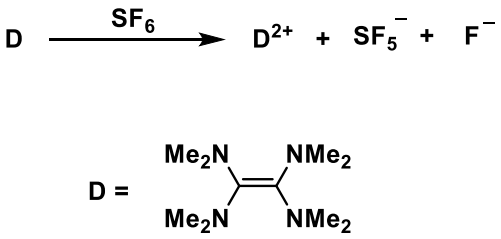
2.2.7. Metal-free activation of SF_6

The first metal-free reduction of SF_6 was reported in 1964 by Padma and Murthy where SF_6 was treated with hydrogen iodide (HI) at room temperature. The reduction of SF_6 with HI produced HF, hydrogen sulfide (H_2S) and iodine (I_2) as end products (**Scheme 8**).[67]

Scheme 8. Reduction of SF_6 with HI.[67]

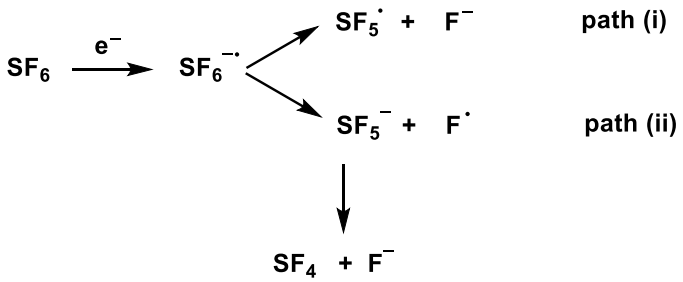
In a patent in 2004, Röschenthaler and Kirsch *et al*. covered the activation of SF_6 using an organic reducing reagent, tetrakis(dimethylamino)ethylene. It was described that under UV light, an organic donor can reduce the SF_6 to give a salt containing $[SF_5]^-$, $[F]^-$and divalent cationic organic donor molecule $[D^{2+}]$ (**Scheme 9**).[68] These studies were further extended by Rueping *et al*. where 2,2'-bipyridyl or 4,4' bipyridyl based organic electron donors are shown to reduce the SF_6 at room temperature without involving UV light.[69] A mixture of $[SF_5]^-$, $[F]^-$ and $[D^{2+}]$ was obtained *via* single electron transfer to the SF_6 from an organic donor. The redox potentials of different organic electron donors were calculated and it was

concluded that in order to activate the SF_6, an electron donor needs to have a redox potential of about $E_{1/2} = -0.8$ V *vs*. SCE. The mixture of $[SF_5]^-$, $[F]^-$ and $[D^{2+}]$ produces SF_4 when dissolved in the solvents and hence was employed for the fluorination of alcohols and carbonyl compounds.[69-70]



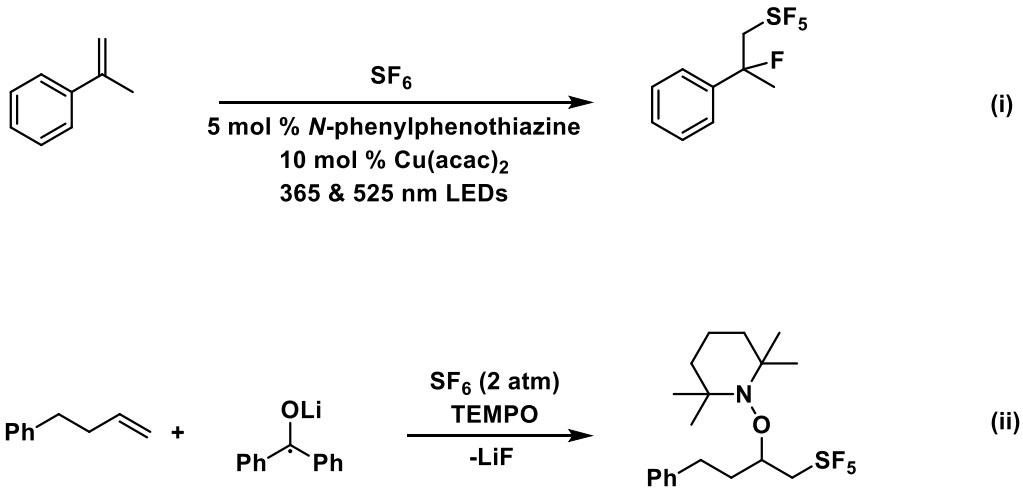
Scheme 9. Metal free activation of SF_6 with organic electron donors.[71]

An initial single electron transfer from the electron rich substrate to the SF_6 presumably generates a SF_6 radical anion ($SF_6^{\bullet -}$).[72] The SF_6 radical anion can dissociate into two possible ways as depicted in the **Scheme 10**. Path (i) generates a relatively stable SF_5 radical ($SF_5^{\bullet}$) and stable fluoride ion (F^-) and path (ii) generates highly unstable fluorine radical ($F^{\bullet}$) and unstable SF_5 anion (SF_5^-) which can further dissociate to give SF_4 and F^-.[73] The electron excess energy associated with the reducing electron determines which pathway will be followed for the dissociation of SF_6 radical anion.[24g, 74] Kline *et al.* and Chen *et al.* reported that path (i) is followed for an electron energy higher than 2.2 eV.[62a, 72, 75] The SF_6 is reported to get activated with Na metal dissolved in liq. ammonia or diphenyl-ethylene glycol, DME solution. The sodium metal has reducing potential of -2.7 V, therefore a photoredox catalyst or an electron donor having reduction potential similar to that of Na should be able reduce the SF_6 into fluorides.[61b, 61c]



Scheme 10. Possible pathways for the activation of the SF_6 *via* an initial electron transfer.[24g]

Wagenknecht *et al*. demonstrated the activation of SF_6 using *N*-phenylphenothiazines as a strong reducing photoredox catalyst having an excited state potential of $E_{1/2}^{*} = -2.1$ V *vs*. SCE [**Scheme 11, (i)**].[76] A SF_5 radical ($SF_5^{\bullet}$) was generated favorably from the photochemical activation of SF_6 by following the path (**i**) in **Scheme 10**. The SF_5 radical was then successfully transferred to photochemically activated styrene at room temperature to yield SF_5 substituted organic products.[24f, 24g] The copper salt [$Cu(acac)_2$] was used to obtain good yields by stabilizing the $SF_5^{\bullet}$. In a similar manner, Beier *et al*. also reported on the activation of SF_6 *via* single electron transfer from TEMPOLi, generated from a reaction of TEMPO {(2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl} with lithium benzophenone ketyl. A SF_6 radical anion produced from the electron transfer, decomposes into lithium fluoride and a SF_5 radical. The latter was transferred to terminal alkenes to access SF_5-subsituted organyls in very small amounts (2 %) [**Scheme 11, (ii)**].[77]



Scheme 11. Activation of the SF_6 *via* electron transfer mechanism using; (i) *N*-phenylphenothiazines as photoredox catalyst, (ii) TEMPOLi.[24g, 66, 77]

In 2018, Dielman *et al*. reported on the activation of SF_6 with super-basic imidazolin-2-imine or pyridin-4-imine substituted phosphines. A complete degradation of SF_6 into nonvolatile well-defined solid mixture of phosphine sulfides and difluorophosphoranes or formation of SF_5^- salt was observed. Mechanistically, a nucleophilic attack of the basic phosphines at fluorine atom in SF_6 *via* S_N2 type reaction was proposed.[78]

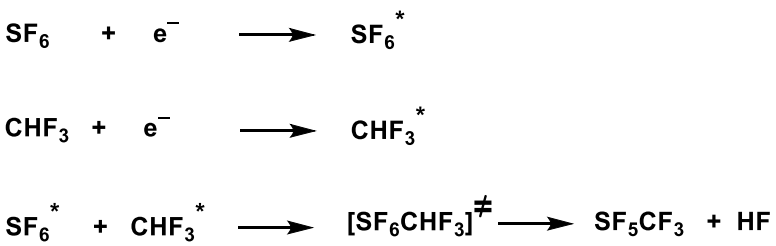
The activation of SF_6 provides synthetic routes for the fluorination of organic substrates *via* deoxyfluorination and for synthesizing SF_5- substituted organyl compounds. The SF_5 group possess high electronegativity, lipophilicity and is thermally and chemically stable therefore can be recommended as an alternative to the CF_3 group in organic compounds, especially in drugs. Similar to the SF_6, trifluoromethyl sulfur pentafluoride (SF_5CF_3) has also been reported as a greenhouse gas and its activation might also provide a way to access the SF_5-substituted organic derivatives.[25c] In contrast to the SF_6, reports on the activation of SF_5CF_3 are very limited.

2.3. Trifluoromethyl sulfur pentafluoride (SF_5CF_3)

2.3.1. Origin and properties of SF_5CF_3

The SF_5CF_3 is a colorless, odorless, and non-flammable gas at normal atmospheric conditions. Like SF_6, it is potentially used as refrigerant, tracer gas and electrical insulating gas due to its electrical characteristic and chemical & thermal stability. SF_5CF_3 is relatively polar than SF_6 and hence has a greater affinity for organic matter as compared to the SF_6.[79]

The presence of trifluoromethyl sulfur pentafluoride (SF_5CF_3) in the earth's atmosphere was first detected and described by Sturges *et al*.[80] Due to a parallel trend in increase in the concentration of SF_6 and SF_5CF_3 in the atmosphere over past 30 years, it was suggested that the formation of SF_5CF_3 is associated with the production of the SF_6 . It was speculated that SF_5CF_3 is mainly produced *via* recombination of SF_5 and CF_3 free radicals which are produced as breakdown products of SF_6 and fluoropolymers respectively in high-voltage equipment.[25c] Huang *et al.* reported a reaction between SF_6 and fluorocarbons such as CHF_3 and CH_2F_2 under electric discharge, to investigate the relation between SF_6 and SF_5CF_3 production. (**Scheme 12**).[81] Santoro *et al*. suggested that SF_5CF_3 can be produced as a by-product in an electrochemical fluorination for the production of perfluorooctanyl sulphonate (PFOS) and other fluorosurfactants.[82] SF_5CF_3 can also be prepared independently from a reaction of carbon disulfide or methyl mercaptan with cobalt trifluoride at 200-250 °C by an electrochemical process.[83]



Scheme 12. Suggested pathway for the formation of SF_5CF_3.[81]

The structure of SF_5CF_3 in gas phase has been established using microwave spectroscopy, electron diffraction method and infrared & Raman spectroscopy.[84] Based on the infrared and Raman spectroscopy, the SF_5CF_3 was reported to have C_{4v} symmetry. In contradiction, according to the theoretical calculations made by Schaefer *et al*., the SF_5CF_3 molecule should have C_s symmetry in its ground state.[85] **Figure 6** is depicting a simple representation of SF_5CF_3 molecule having C_s symmetry around S−C bond.

R. P. Tuckett has explained the structural properties of the SF_5CF_3 based on the theoretical calculations made by P. J. Knowles.[86] The S−C bond length in SF_5CF_3 was calculated as 0.187 nm and the FSF and FCF bond angles were calculated approximately 90° and 109.3° respectively. These values were found in agreement with the microwave and electron diffraction studies of the SF_5CF_3 molecule.

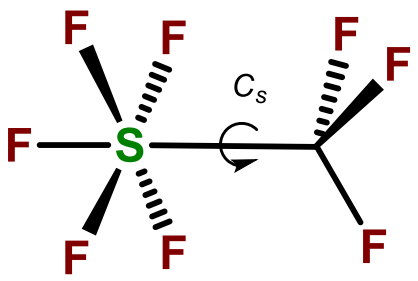


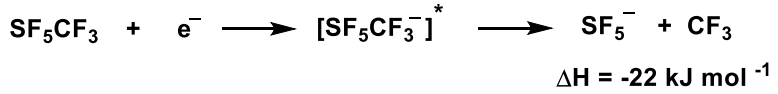
Figure 6. Representation of the SF_5CF_3 molecule with C_s point of symmetry along the S−C bond.[84b, 85]

2.3.2. Global warming potential of the SF_5CF_3

Sturges *et al*. has identified the SF_5CF_3 as a potential greenhouse gas present in the stratosphere because infrared absorption measurements of the SF_5CF_3 showed that it has a strong radiative forcing per molecule (0.57 W m^{-2} ppb^{-1}).[80] Although SF_5CF_3 is present in the atmosphere in low concentrations of about 0.12 ppt, it has a tendency to increase at a rate of about 6% per year.[25c] A report from the "World Meteorological Organization" about global ozone research and monitoring, mentioned that abundance of SF_5CF_3 in the air trapped in polar snow has risen from near zero in the 1960s to about 0.12 ppt in 1999, and is growing at rate of 0.008 ppt per year.[87] Since SF_5CF_3 can't be degraded by reactions with hydroxyl radicals present in the earth's lower atmosphere, the lifetime of SF_5CF_3 in the atmosphere was estimated through dissociative electron attachment experiments as 800 ± 150 years.[88] The global warming potential (GWP) of SF_5CF_3 was estimated to be 18000 times more than carbon dioxide (CO_2).[88-89] To avoid the undesirable accumulation of this potent greenhouse gas in the atmosphere, it is important to control the source(s) of emission of SF_5CF_3 and methods to degrade this gas are needed to be taken into consideration.

2.3.3. Reduction or chemical transformation of SF_5CF_3

The stability of SF_5CF_3 in the stratosphere has led to the research interest towards exploring the ways for its atmospheric degradation. Kennedy *et al.* reported on the decomposition of potent greenhouse gas SF_5CF_3 by fast dissociative electron attachment method.[90] When electrons with a kinetic energy of at least 1.7 eV were attached to the SF_5CF_3, formation of only SF_5^- was observed according to the reaction showed in the **Scheme 13**. The CF_3^- was not observed even when electrons with kinetic energy higher than 1.7 eV were applied due to the exothermic dissociative attachment reaction for the formation of SF_5^- (ΔH = -22 kJ mol^{-1}) and endothermic dissociative attachment reaction for the formation of CF_3^- (ΔH = 162 kJ mol^{-1}). (ΔH corresponds to the enthalpy of the reaction for zero kinetic energy electrons.)[90]

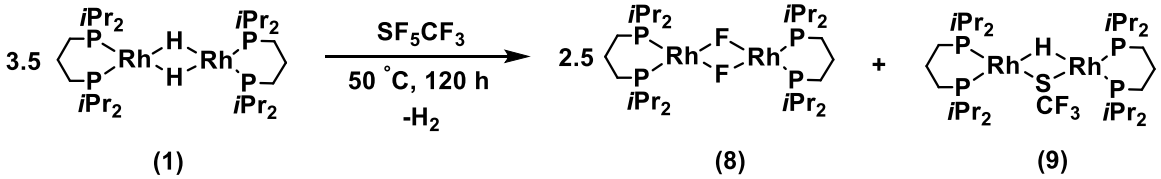


Scheme 13. Decomposition of the SF_5CF_3 by a fast dissociative electron attachment method.[90]

Zhang *et al*. showed the decomposition reactions of the SF_5CF_3 gas using a Dielectric Barrier Discharge (DBD) reactor in the presence of additive gases (Ar, N_2 or O_2) at high voltage (3000 V). The decomposition efficiency of the SF_5CF_3 was found higher than that of SF_6. SO_2F_2, SOF_2, SF_5SF_5, CF_3CF_3, COF_2 , CF_4 and SiF_4 were formed as main products from the decomposition of SF_5CF_3.[52b] Other channels to degrade the SF_5CF_3 gas in the atmosphere involves attachment of the positive ions (H_2O^+, N_2O^+, O^+, CO^+, CO_2^+, N_2^+) and the negative ions (O_2^-, O^-, OH^-, F^-) present in the ionosphere.[91] Photo-initiated (Lyman-α solar radiation) reactions in the mesosphere also provide an atmospheric sink for the SF_5CF_3 gas.[55a, 92] Similar to the SF_6, photo-reductive decomposition of the SF_5CF_3 gas with propene has been reported by Hou *et al*. giving hydrofluorocarbons, CH_4 and SiF_4 as end products.[56b]

The SF_5CF_3 gas was found thermally stable when heated at 500 °C in a closed system. However its decomposition was observed when reacted with perfluoropropylene (C_3F_6) at temperatures of 425 °C and 518 °C in a nickel-packed reactor, producing fluorocarbons products and SF_4.[24d]

Owing to its inertness, chemical activation or reduction of SF_5CF_3, is very challenging. No hydrolysis was achieved for SF_5CF_3 when treated with 6*N* sodium hydroxide (NaOH) for several months at room temperature.[83] The reduction of SF_5CF_3 in the presence of rhodium hydrido species reported by Braun *et al*., is the only example found in the literature for the chemical transformation of the SF_5CF_3 in homogeneous reaction system under mild reaction conditions. The S−C and S−F bond activation was achieved when SF_5CF_3 was treated with the complex **1** ([{Rh(μ-H)(dippp)}$_2$], 3.5 equivalents) for 120 h at 50 °C, yielding the fluorido complex **8** [{Rh(μ-F)(dippp)}$_2$] and hydrido thiolato complex **9** [Rh_2(μ-H)(μ-SCF_3)(dippp)$_2$ in a ratio of 2.5:1 respectively, along with the formation of H_2 (**Scheme 14**).[63]



Scheme 14. Activation of the SF_5CF_3 with rhodium hydrido complex **1**.[63]

As discussed in the *Section 2.2*, SF_4 is often produced as a by-product from the reduction or activation of the SF_6 *via* physical methods of degradation or chemical transformations. Electrical decomposition of the SF_5CF_3 or thermal decomposition of S_2F_{10} also produces SF_4.[83, 93] Investigations on the reactivity of the SF_4 provide an insight into the mechanisms possibly involved in the complete degradation of the SF_6 and SF_5CF_3. Therefore, in the next section reactivity of the SF_4 is discussed in detail.

2.4. Sulphur tetrafluoride (SF_4)

2.4.1. Properties and structure of SF_4

In contrast to the SF_6, SF_4 is a highly reactive and toxic gas at room temperature.[13d, 94] It should be noted that there is no significant difference in the bond dissociation energies D^0 for the cleavage of the respective first S–F bond in SF_6 (387 ± 13 kJ mol^{-1}) and SF_4 (354 ± 13 kJ mol^{-1}).[35] The enormous chemical stability of SF_6 is based primarily on kinetic factors. SF_4 is extremely reactive with moisture and produces toxic and corrosive products such as HF, thionyl fluoride (SOF_2) and sulfur dioxide (SO_2).[95] Sulfur tetrafluoride can be prepared by suspending powdered sulfur in trichlorofluoromethane ($CFCl_3$) at −78 °C with elemental fluorine in N_2.[96][97] Tullock *et al*. reported a more convenient synthesis of SF_4 from the reaction of sulfur chlorides with metal fluorides, such as NaF, KF, CsF, BaF and CuF_2 (**Scheme 15**).[13a]

Scheme 15. Reaction of sulfur dichloride with NaF to synthesize the SF_4.[13a]

By taking the lone pair into account, bonding and geometry in SF_4 is expected to be trigonal bipyramidal. But the crystal structure of SF_4 showed that equatorial bonds have the length of a normal $S–F_{eq}$ bond (1.545 Å), while the axial $S–F_{ax}$ bond lengths were found longer (1.646 Å); also, the equatorial angle was found to be 101° (**Figure 7**).[98] This distorted geometry is observed due to the presence of lone pair in the SF_4 [99] Thus the structure of SF_4 was established as C_{2v}, having molecular see-saw geometry. The solid state structure of the SF_4 was found to be in good accordance with its gas phase structure studied with Raman and IR spectroscopy, electron diffraction and microwave spectroscopy.[99-100] Based on the ^{19}F NMR spectroscopy, a berry pseudo rotation can be observed for the SF_4, induced by the rapid exchange between the axial and equatorial fluorine atoms.[101]

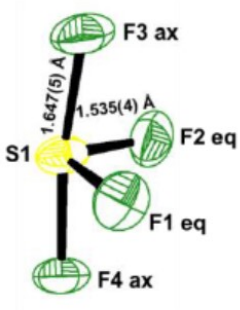
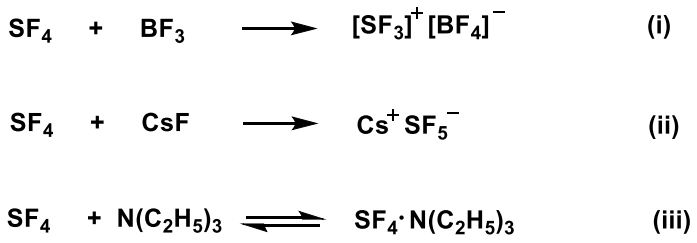


Figure 7. Structure of SF_4 in the solid state as elucidated by Gerken *et al*.[102]

2.4.2. SF_4 reactivity

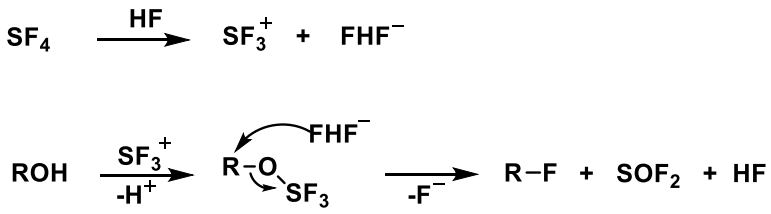
The presence of unpaired electrons and empty σ^* (SF) antibonding orbitals make SF_4 both, a weak Lewis base and a weak Lewis acid.[103] Several examples of reaction of the SF_4 with Lewis acids such as BF_3, PF_5, AsF_5 and SbF_5 have been reported to produce trifluorosulfonium (SF_3^+) salts.[104] SF_4 can act as a Lewis acid by accepting fluoride from strong fluoride ion donor molecules to form SF_5^- salts.[105] Adducts of SF_4 with nitrogen and oxygen based bases have also been reported (**Scheme 16**).[106]



Scheme 16. Reactivity of the SF_4; (i) as Lewis acid, (ii) & (iii) as Lewis base.[104-106]

SF_4 can be used as a deoxyfluorinating reagent for alcohols and carbonyl compounds to obtain fluorinated building blocks.[13a-f] Catalytic or sometimes stoichiometric amounts of HF are required to activate the SF_4 to perform the fluorination reaction. The mechanism

of the deoxyfluorination of alcohols with SF_4 has been proposed based on the reaction products (**Scheme 17**).[13d][107] The trifluorosulfonium ion (SF_3^+) generated from the reaction of SF_4 with HF reacts with the alcohol to give an oxygen-sulfur bonded intermediate. Depending on the structure of the substrate, a fluoride ion can replace the leaving group in the intermediate via a S_N1 or a S_N2 pathway to give the corresponding alkyl fluoride. Thionyl fluoride and HF are obtained as byproducts.[108]



Scheme 17. Possible mechanism for the deoxyfluorination of the alcohols with SF_4.[108]

Due to the toxic and corrosive nature of SF_4, its usage is not widespread in the laboratories. Several SF_4 derived reagents such as, *N,N*-diethylaminosulfur trifluoride (DAST), Deoxy-fluor®, Fluolead™ have been synthesized and used for the fluorination (**Figure 8**). These reagents have advantage over SF_4 for being relatively stable and often selective in reactivity.[13g-l] However, drawbacks associated with these reagents are their thermal instability and extremely violent reaction with water to generate HF.[109]

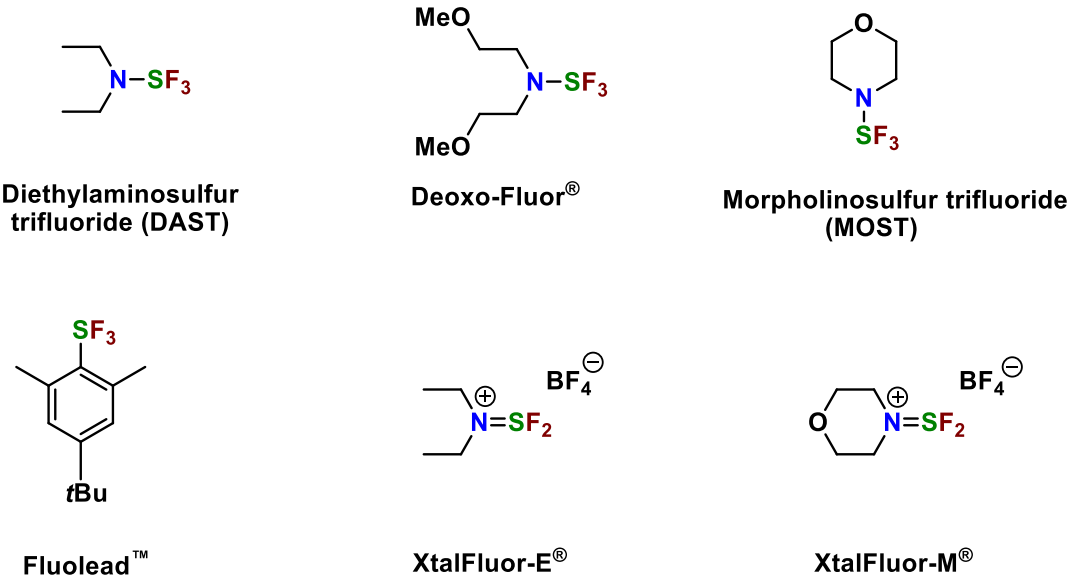


Figure 8. SF_4 derived fluorinating reagents.[18]

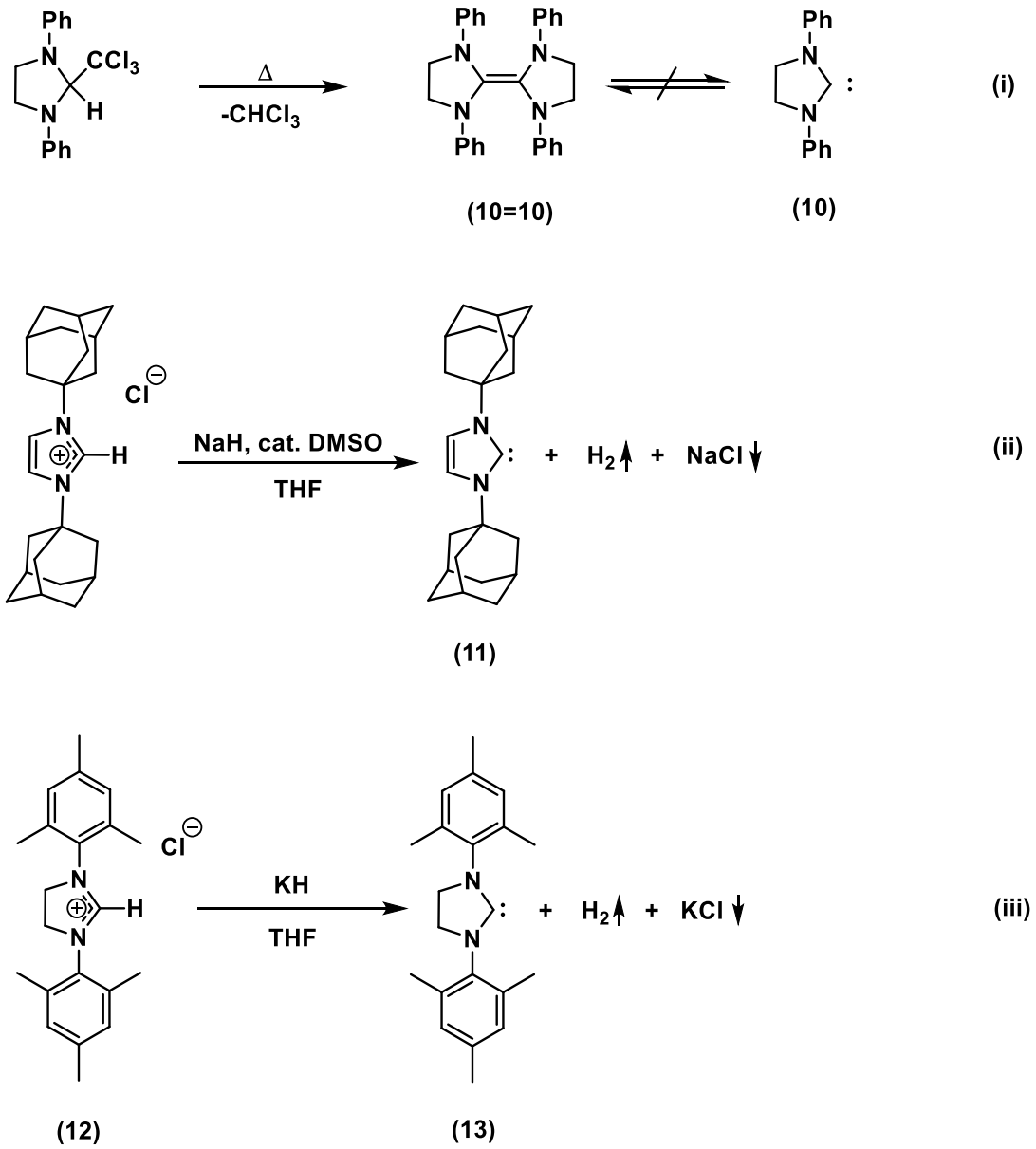
Besides the SF_4 derived deoxyfluorinating reagents; several imidazole derived reagents are available for fluorinating the alcohols or phenols and carbonyl compounds. 2,2-difluoro-1,3-dimethylimidazolidine (DFI) was synthesized and isolated by Nagata *et al.* in 2002 as the first thermally stable imidazole derived deoxyfluorinating reagent.[110] A few years later, Ritter *et al.* synthesized another deoxyfluorinating reagent, PhenoFluor™ comprising a bulkier NHC.[13p] Further details on the imidazole derived deoxyfluorinating reagents are discussed later in the *Chapter 4* .

The classical *N*-heterocyclic carbenes (NHCs) are reported to have an electron donating tendency comparable to the super basic phosphines having imidazoline-2-imines or benzimidazolin-2-imines as substituents.[111] The latter have been implemented by Dielmann *et al.* towards successful activation of the SF_6.[78] Thus, it can be presumed that NHCs could also activate the SF_6 to possibly generate a difluoro-imidazole derivative. In the next section; stability, basic properties and versatile applications of *N*-heterocyclic carbenes (NHCs) are discussed.

2.5. *N*-heterocyclic carbenes (NHCs): Stability and reactivity

Wanzlick *et al*. started investigations on isolating free NHCs in 1960, but their attempts remained unsuccessful, observing only dimerization of imidazolidin-2-ylidenes to give entetraamines (**10=10**) (10 = 1,3-diphenyl-2-imidazolidin-2-ylidene).[112] The first stable diaminocarbene (1,3-diadamantylimidazolin-2-ylidene, **11**) was synthesized and isolated by Arduengo *et al.* in 1991.[113] Furthermore, Arduengo *et al*. used bulkier *N,N'*-substituted imidazolinium salts (1,3-dimesitylimidazolinium chloride, **12**) to successfully obtain a saturated NHC (1,3-dimesitylimidazolidin-2-ylidene, SIMes, **13**) as they calculated that bulky mesityl groups provide enough steric hinderance towards the dimerization of singlet carbene centers along a non-least-motion pathway (**Scheme 18**).[114]

Even the non-bulky methyl group substituted, 1,3-dimethylimidazolin-2-ylidene can be isolated *via* an electronic stabilization of the carbene center through the unsaturated backbone.[115] In contrast, saturated 1,3-dimethylimidazolidin-2-ylidene could not be isolated due to its dimerization. This explains that kinetic stabilization of NHCs *via* steric protection is an important factor more for saturated NHCs as compared to its unsaturated analogue.[116]



Scheme 18. (i) Wanzlick's olefin; (ii) Arduengo's first stable NHC; (iii) Arduengo's isolated saturated NHC.[112-114]

The stability of NHCs can further be explained in terms of multiplicity of the carbenes. Singlet carbenes owns a filled σ orbital and an empty p orbital, which makes it ambiphilic in nature. Triplet carbenes have two unpaired electrons in two degenerated p orbitals which makes it biradical in nature. For a large energy difference (>1.5 eV) between σ and p_{Π} orbitals in carbenes, the singlet ground state is observed.[117] Sterically demanding, electron withdrawing and two π- electrons donor substituents in the backbone of carbenes increase the σ - p_{Π} energy gap and hence stabilize the singlet ground state in carbenes.[117-118] (**Figure 9**) The singlet and triplet gap for saturated imidazolidin-2-ylidenes and unsaturated imidazolin-2-ylidenes was calculated as 69 kcal mol^{-1} and 85 kcal mol^{-1} respectively.[119] The bigger energy gap in the unsaturated analogue can be attributed to aromaticity of the imidazolin-2-ylidenes. The smaller singlet-triplet gap in the saturated imidazolidin-2-ylidenes leads to the formation of entetraamines via dimerization in the absence of kinetic or steric stabilization and explains why 1,3-dimethylimidazolidin-2-ylidene couldn't be isolated as free NHC.[120]

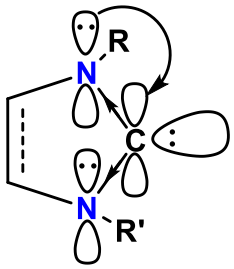
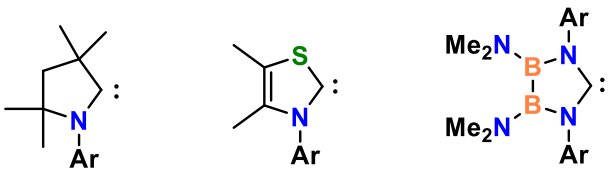


Figure 9. Stabilization of the singlet ground state in NHCs *via* electronic (+M) and inductive (-I) effects.

Imidazole based NHCs bearing only one nitrogen substituent, such as cyclic (alkyl) (amino) carbenes (CAACs, **14**)[121], thiazolin-2-ylidene (**15**)[122] and having boron atoms in the backbone in NHCs (**16**)[123] are also accessible (**Figure 10**).[124]



(14) (15) (16)

Figure 10. Five membered NHCs having variable substitutions.

Several stable NHCs are isolated since the isolation of first Arduengo's free carbene (**11**). A large number of complexes bearing NHC ligands, has been reported. NHC stabilized complexes with transitional metals[125], f-block elements[126] and adducts with main group elements[127] are well known due to the ambiphilic nature of the NHCs. Metal bound complexes and adducts of NHCs are discussed later in detail in *Chapter 5* of this thesis. NHC bearing transition metal complexes show remarkable catalytic activities in reactions which include C–C cross coupling[125b, 128] and olefin metathesis[129]. NHCs are reported to be used as organocatalysts, where nucleophilic NHCs attack aldehydes to form the Breslow intermediate (**17**)[130][131] which leads to many organic transformations via condensation, transesterification or umpolung reactions.[129c, 132] In recent years, NHCs mediated metal – free activation of the robust C–F bond in various aryl fluorides and fluorinated olefins has gained extensive interest (**Figure 11**).[133]

Kuhn *et al*. were first to report on the C–F bond activation through a reaction involving the nucleophilic aromatic substitution of pentafluoropyridine by 1,3-dimethyl-4,5-dimethylimidazolin-2-ylidine (**18**) or 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidine (**19**) [**Scheme 19, (i)**].[134] This approach was later extended by Lee *et al*. where double C–F bond activation was observed when two equivalent of octafluorotoluene were treated with a bulkier NHC; 1,3-di-(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr, **20**). An imidazolium salt was obtained with perfluoro substituents at : i) the former carbene carbon atom, and ii) the backbone of the carbene [**Scheme 19, (ii)**].[135]

.

A variety of NHC fluoroalkene compounds were obtained by Baker *et al*. when 1,3-di-(2,6-diisopropylphenyl)imidazolidin-2-ylidene (SIPr, **21**) or SIMes (**13**) was treated with fluorinated alkenes [**Scheme 19, (iii)**].[136] Furthermore, an oxidative addition of the C–F bond to more nucleophilic carbene CAAC (1-dipp-3,3-diethyl-5,5-dimethyl-2-pyrrolidinylidene, **22**) (dipp = 2,6-diisopropylphenyl) was observed for the activation of the fluoroarenes and pentafluoropyridine [**Scheme 19, (iv)**].[133d, 137]

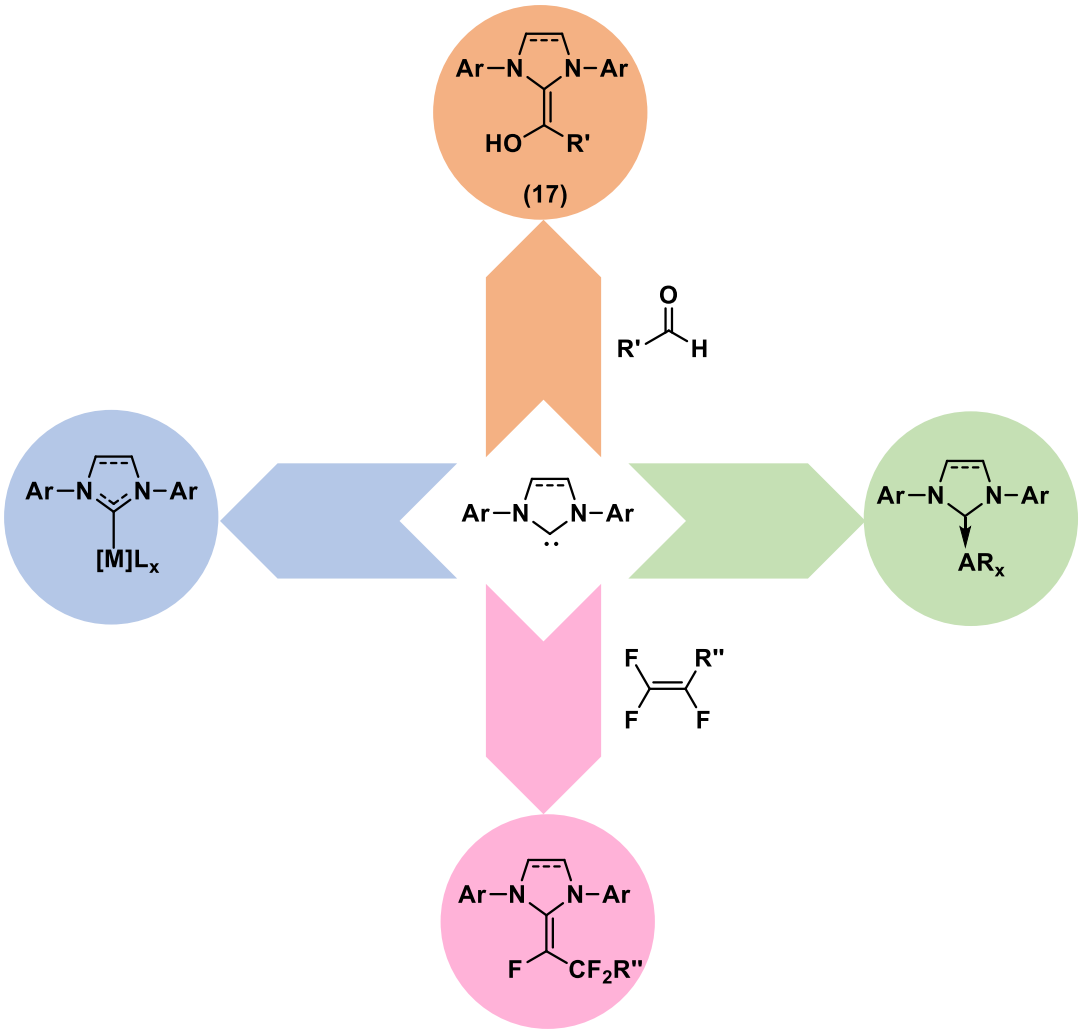
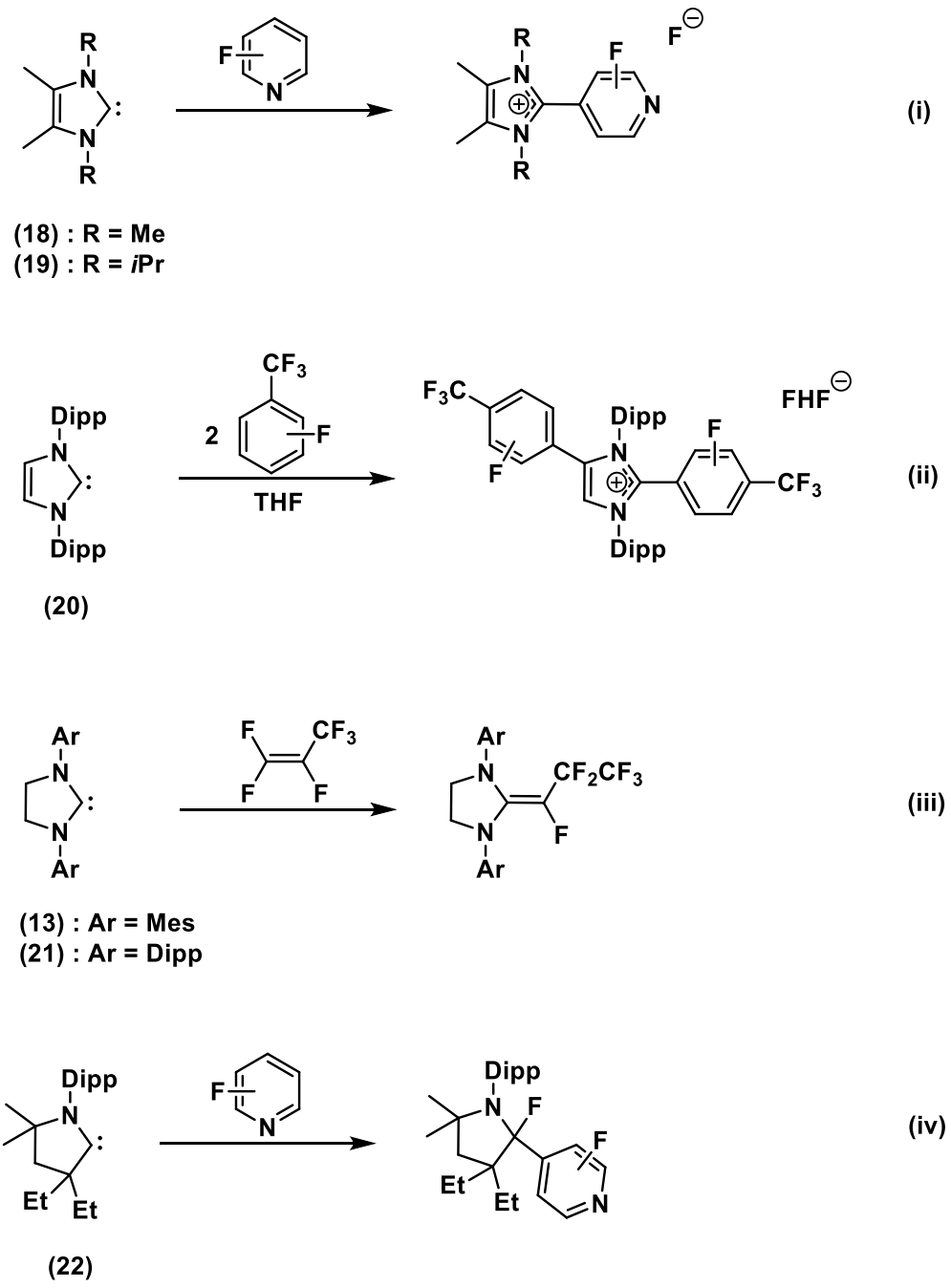


Figure 11. Wide range of applications of *N*-heterocyclic carbenes (NHCs).



Scheme 19. Examples of C–F bond activation by NHCs; Mes= mesityl, Dipp = 2,6-diisopropylphenyl.[133d, 134-137]

3. Research Objective

The chemical reduction of the SF_6 and SF_5CF_3 is described in the *Chapter 2* and it can be concluded that metal-free activation of SF_6 and SF_5CF_3 has not yet been studied extensively to develop new fluorinating reagents. However Rueping *et al*. showed the application of SF_5^-/F^- ion pair obtained from the SF_6 activation, towards the fluorination of organic substrates; but it can be presumed that it is rather SF_4 responsible for such reactivity.[69] Wagenknecht and Beier reported on the generation of SF_5-substituted organyl compounds from the activation of the SF_6.

NHCs are capable of activating C− F bonds in the fluorinated olefinic or aromatic substrates therefore it can be expected from them to activate S−F bond in SF_6 , SF_4 and SF_5CF_3 as well since the bond dissociation energy for S−F bond (343.5 ± 6.7 kJ mol^{-1}) is smaller than C−F bond (513.8 ± 10.0 kJ mol^{-1})[138]. From previous literature studies it can be extracted that a strong electron donor or a strong reducing agent having a redox potential similar to that of Na i.e. -2.7 V is needed to activate the SF_6. In this thesis, the redox potential of various NHCs is calculated to estimate their reducing power for the activation.

These findings were set as an inspiration to carry out investigations towards the S−F bond activation in SF_6, SF_4 and SF_5CF_3 with NHCs. The greenhouse gases SF_6 and SF_5CF_3 are attempted to be transformed into well-defined products and used as cheap and safe starting materials to develop new fluorinating reagents for synthesizing organic fluorine building blocks and organometal fluorides (**Figure 12**). The end products obtained from the activation of SF_6, SF_4 and SF_5CF_3, are tested for the fluorination of organic substrates such as alcohols, acids and aldehydes as well as for the synthesis of organoaluminium fluorides.

The synthesis of molecular AlF_3 complexes bearing neutral ligands has been reported only rarely. In this thesis, different synthetic routes for the synthesis of NHC stabilized aluminium (III) fluorides are investigated by using SF_6, SF_4 and Me_3SnF as fluorinating agents. Furthermore, reactivity of the NHC stabilized aluminium (III) fluorides are tested towards the halogen exchange reactions.

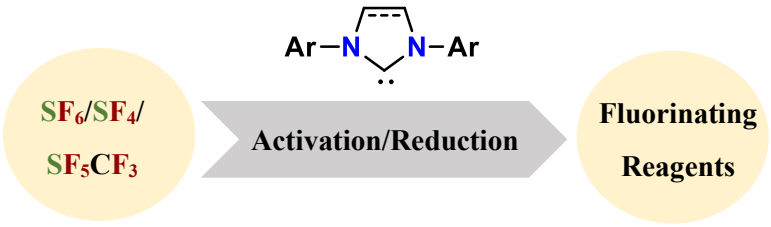


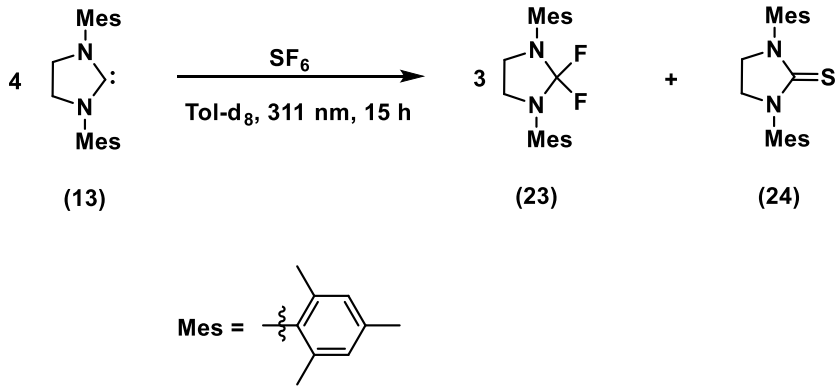
Figure 12. Development of new fluorinating reagents *via* NHC mediated activation of the greenhouse gases.

4. Results and Discussion

4.1. Reduction of sulfur hexafluoride with NHCs

4.1.1. Photochemical activation of SF_6 with *N*-heterocyclic carbenes (NHCs)

Activation of SF_6 was initiated by condensing of SF_6 (0.10 mmol) into a solution of SIMes (**13**, 0.05 mmol) at room temperature. The reaction was monitored with the help of ^{19}F NMR spectroscopy. No activation of SF_6 was observed at room temperature. When the reaction mixture containing was heated for 24 h at 80 °C, activation of SF_6 took place to give 1,3-dimesityl-2,2-difluoroimidazolidine ($SIMes(F)_2$, **23**) and 1,3-dimesitylimidazolidine-2-sulfide (**24**) as end products, which were identified with ^{19}F NMR, ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR spectroscopy and LIFDI mass spectrometry (**Scheme 20**). A signal in the ^{19}F NMR spectrum was observed at δ = -55.6 ppm, which is in accordance with the data of difluoroimidazolidine reported by Ritter *et al.*(**Figure 13**). [13o] LIFDI mass spectrometry gave molecular ion peaks at *m/z* 344.3 and *m/z* 339.3, which fit to the calculated molecular masses of difluoroimidazolidine (**23**) and imidazolidine sulfide (**24**) respectively. The yield for **23** was estimated to be only 10 % when calculated with ^{19}F NMR spectroscopy using 1,2 difluorobenzene as external standard and assuming that three equivalents of **23** were formed. Since no considerable activation of the SF_6 was observed with SIMes at 80 °C, the reaction mixture was put under UV light radiation at 311 nm. After 15 h of irradiation, the mixture of compounds **23** and **24** was obtained in a ratio of 3 : 1 with a yield of 82 % estimated for **23** by the ^{19}F NMR spectrum.



Scheme 20. Photochemical activation of the SF_6 with SIMes.

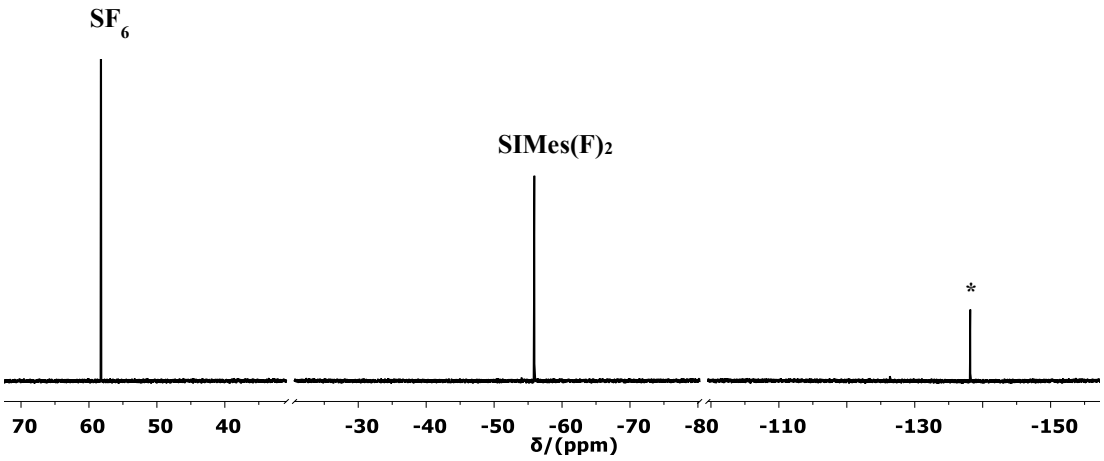


Figure 13. ^{19}F NMR (282.4 MHz, Tol-d_8) spectrum for the activation of SF_6 with SIMes. * = 1,2 difluorobenzene (external standard).

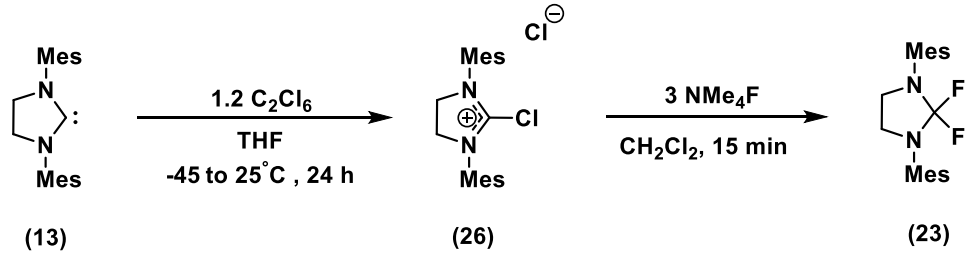
Sterically and electronically different NHCs such as IPr (**20**), SIPr (**21**) and 1,3-dimesitylimidazolin-2-ylidene (IMes, **25**) were also tested for the activation of SF_6 using UV light at 311 nm for 15 h. The ^{19}F NMR resonances and yields of the 2,2-difluoro-derivatives of these NHCs are listed in the **Table 1**. The ^{19}F NMR resonances obtained for the difluoro-imidazolidin or difluoro-imidazolin derivatives of SIPr, IMes and IPr were found in good agreement of the reported literature.[13o, 13p, 139]

Table 1. ^{19}F NMR data and yields of the 2,2-difluoro- derivatives of different NHCs obtained from the activation of the SF_6.[13o, 13p, 139]

NHC(F)$_2$	**^{19}F NMR (δ) ppm**	**Yield**
SIMes(F)$_2$	-55.8	82 %
SIPr(F)$_2$	-55.7	75 %
IMes(F)$_2$	-34.3	62 %
IPr(F)$_2$	-33.9	15 %

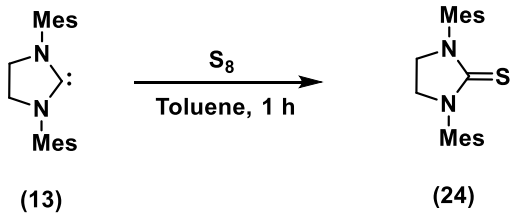
4.1.2. Independent synthesis of the products obtained from the activation of SF_6 with SIMes

At first, 1,3-dimesityl-2-chloroimidazolinium chloride (**26**) was synthesized from a reaction between SIMes (**13,** 1 equivalent) and C_2Cl_6 (1,1,1,2,2,2-hexachloroethane, 1.2 equivalents) and characterized with LIFDI mass spectrometry.[13p] The molecular ion peaks obtained for the 1,3-dimesityl-2-chloroimidazolinium ion showed an isotopic pattern at *m/z* 341.1 (100 %), 343.1(32 %) and 344.1(22.7 %). This data matched well with the molecular mass and isotopic pattern calculated for the 1,3-dimesityl-2-chloroimidazolinium ion. $SIMes(F)_2$ (**23**) was obtained by treating the **26** (1 equivalent) with tetramethylammonium fluoride (NMe_4F, 3 equivalents). **23** was characterized by ^1H NMR, $^{13}C\{^1H\}$ NMR, ^{19}F NMR spectroscopy and LIFDI mass spectrometry (**Scheme 21**). LIFDI mass spectrometry gave a molecular ion peak at *m/z* 344.3, which fits to the calculated molecular mass of $SIMes(F)_2$. In the ^{19}F NMR spectrum a signal was observed at δ = -55.8 ppm, which fits to the signal attributed for the $SIMes(F)_2$ in the reaction of SF_6 activation with SIMes.



Scheme 21. Synthetic route for the formation of the 1,3-dimesityl-2,2-difluoroimidazolidine ($SIMes(F)_2$, **23**).[13o, 13p, 139]

The 1,3-dimesitylimidazolidine-2-sulfide (**24**) was also obtained as one of the end product from the reduction of SF_6 with SIMes. The thiourea derivative (**24**) was synthesized independently by treating sulfur with SIMes as depicted in the **Scheme 22**. The characterizations of the product were made by ^{1}H , $^{13}C\{^{1}H\}$ NMR spectroscopy and LIFDI mass spectrometry. LIFDI mass spectrometry gave a molecular ion peaks at *m/z* 339.3, which is consistent with the calculated molecular mass of **24**. The signal obtained in the $^{13}C\{^{1}H\}$ NMR spectrum at δ = 184.92 ppm is reported characteristic for the C=S unit in **24**.[140] Thiourea derivatives of other NHCs (SIPr, IMes, IPr) were also prepared by following the reaction shown in the **Scheme 22**.[140-141]

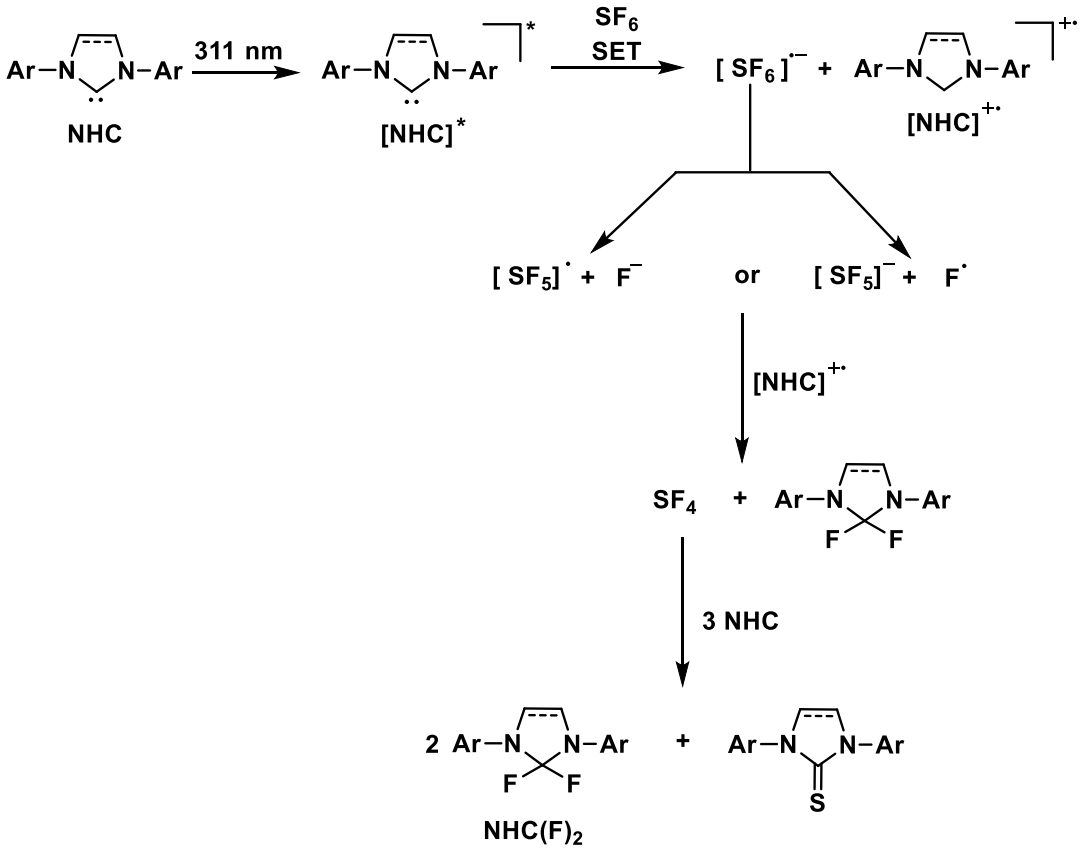


(13) (24)

Scheme 22. Synthetic route for the formation of the 1,3-dimesitylimidazolidine-2-sulfide (**24**).

4.1.3. Mechanistic proposal for the activation of SF_6 with NHCs

A possible mechanism for the activation of SF_6 can be proposed from the excited state of NHCs *via* single electron transfer (SET) pathway (**Scheme 23)**.

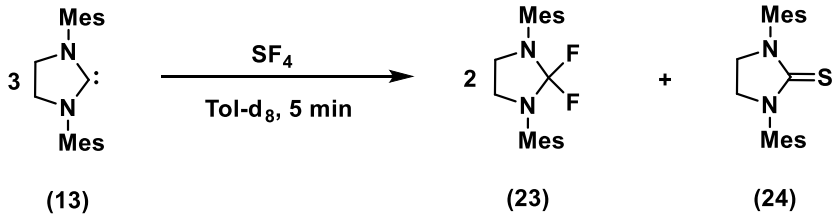


Scheme 23. Proposed pathways for the reduction of SF_6 with NHC.

The excited state of carbene (NHC^*) can transfer a single electron to the SF_6 to generate the radical anion $SF_6^{\bullet-}$ and the NHC radical cation $NHC^{\bullet+}$. The SF_6 radical anion is known to be unstable in solution and therefore continues to fragment into a SF_5 radical ($SF_5^{\bullet}$) and a fluoride anion F^- or into a SF_5^- anion and a fluoride radical $F^{\bullet}$.[24g, 69, 74] Since no sulfur containing intermediate was detected or trapped during the progress of the reaction, therefore it is uncertain that which route was favored for the fragmentation of the $SF_6^{\bullet-}$ radical anion.

If SF_5^- and $F^{\bullet}$ are generated from the fragmentation of $SF_6^{\bullet-}$, the $NHC^{\bullet+}$ could recombine with $F^{\bullet}$ to yield NHC–F^+ and SF_5^- . The SF_5^- can readily decompose into SF_4 and a fluoride anion which could combine with NHC–F^+ to ultimately give $NHC(F)_2$.[98, 104e] Alternatively, if $SF_5^{\bullet}$ and F^- are generated from the fragmentation of $SF_6^{\bullet-}$, it is conceivable that $SF_5^{\bullet}$ can decompose to generate SF_4 and a fluoride radical. The $NHC^{\bullet+}$ can recombine with F^- and $F^{\bullet}$ to generate $(NHC)F_2$ and SF_4 can further react with NHC to yield $NHC(F)_2$ and 2-thio carbene. The electron excess energy associated with the reducing electron determines which pathway will be favored for the dissociation of $SF_6^{\bullet-}$.[24g, 74] Kline *et al.* and Chen *et al.* reported that $SF_5^{\bullet}$ and F^- are generated from the fragmentation of $SF_6^{\bullet-}$, for an electron energy higher than 2.2 eV.[62a, 72, 75] Note that, for non-photolytic activation of the SF_6, Dielmann *et al*. proposed a nucleophilic attack of imidazolin-2-ylidenaminophosphines (IAPs) at SF_6 to give SF_5^- and a fluorophosphonium salt.[78]

An independent reaction was carried out between SF_4 (0.10 mmol) and SIMes (0.05 mmol) to confirm the assumption that SF_4 is a reactive intermediate which can further readily react with NHC to furnish the $SIMes(F)_2$ (**23**) and 2-thio carbene (**24**) (**Scheme 24**).



(13) (23) (24)

Scheme 24. Reduction of SF_4 with SIMes (**13**).

4.1.4. Redox potential of NHCs

Through the attempts made for the activation of SF_6 with NHCs it has been observed that irradiation of the reaction mixture is needed to accomplish the activation. It is conceivable that electron transfer mechanism is involved in the reduction of SF_6 from the excited state of NHCs. To understand the difference in the reactivity among different NHCs for the activation of SF_6, when irradiated at 311 nm, their reducing efficiency was determined by estimating the redox potential in the excited state by using the following formula.[142]

$$\mathbf{E\ (D^{+}/D^{*}) \approx E\ (D^{+}/D) - E_{0-0}}$$

for an oxidative electron transfer reaction ($D^{*} + A \longrightarrow D^{+} + A^{-}$)

where E (D^{+}/D^{*}) = potential of the excited-state couples

E (D^{+}/D) = potentials of the ground-state couples measured using cyclic voltammetry.

E_{0-0} = one-electron potential corresponding to the 0–0 excited-state energy measured as midpoint from maxima of UV-visible (UV-vis) and emission spectra.

A solution of the carbene (1mM) in THF was taken under an argon atmosphere to perform cyclic voltammetry, UV-visible and emission spectroscopic studies. SIMes is taken here as an example to depict the cyclic voltammogram, absorption and emission spectra.

4.1.4.1. Cyclic voltammetry

The voltammogram obtained for the SIMes is shown in the **Figure 14**. An oxidation peak potential (E_p^{ox}) of 1.024 V *vs.* Fc^0/Fc^+ was estimated from the cyclic voltammogram. The oxidation potential can be re-calculated as E_p^{ox} = 1.584 V *vs*. SCE by taking the redox potential of the Fc^0/Fc^+ couple *vs.* SCE as 0.56 V in THF.[143]

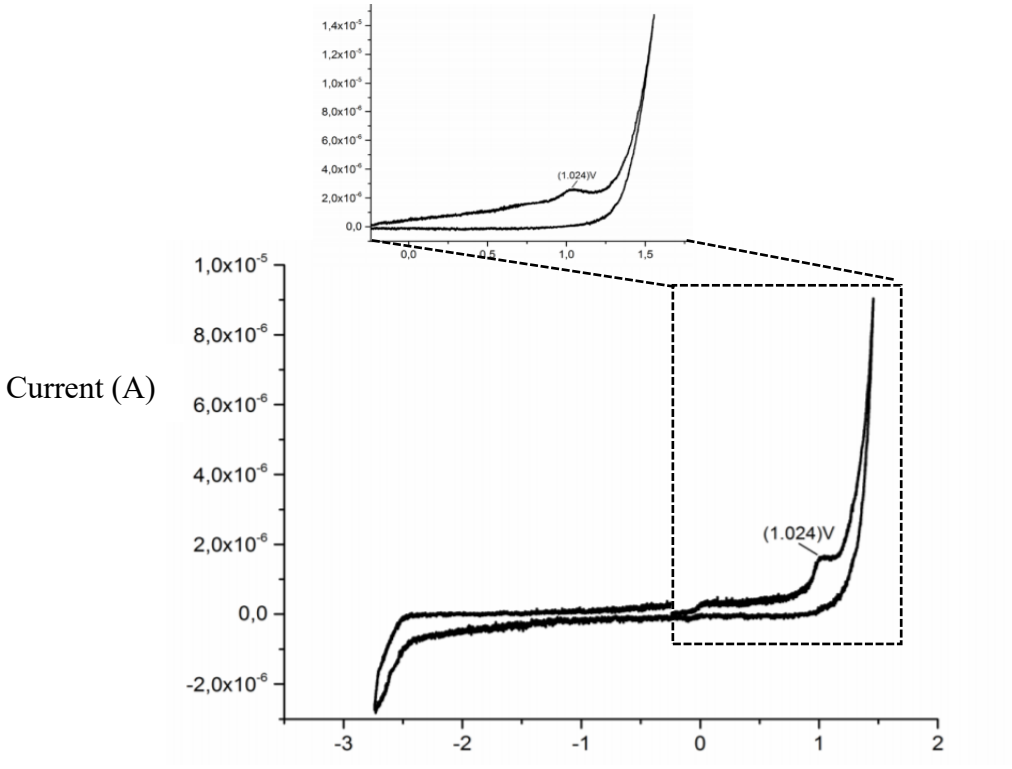


Figure 14. Cyclic voltammogram obtained for a solution of SIMes (1mM) in THF, measured with a scan rate of 200 mV/s. E_p^{ox} = 1.024 V *vs*. Fc^0/Fc^+ and E_p^{ox} = 1.584 V *vs*. SCE.

The cyclic voltammogram obtained for the SIMes is typical for an irreversible reaction (**Figure 15**).[144] Similar voltammograms were observed for the other investigated NHCs (see **appendix**).

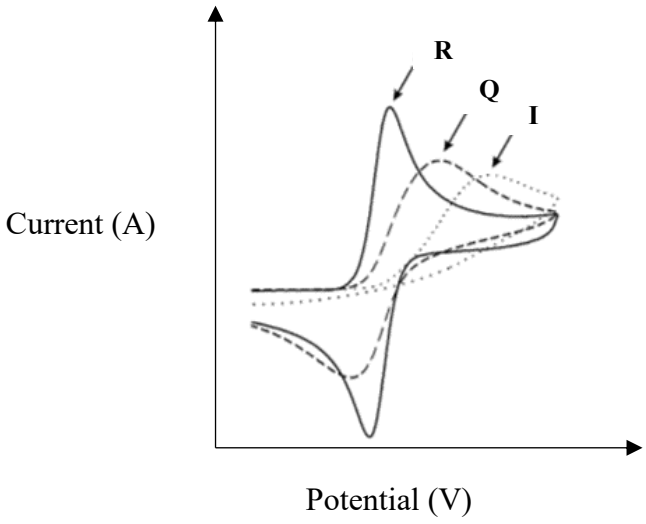


Figure 15. Typical cyclic voltammograms for **R** = reversible ; **Q** = quasi-reversible; **I** = irreversible reactions.[144]

4.1.4.2. UV-visible spectroscopy

The **Figure 16** shows a UV-vis spectrum obtained for the SIMes showing two absorbance maxima at 220 nm and 247 nm. Absorbance maximum at 220 nm or 221 nm was observed for every carbene investigated (see **appendix**) and therefore can be attributed to the aromatic substituents at the N-atoms.[145] The maximum at 247 nm can be attributed to the absorption from the inner imidazolyl unit.

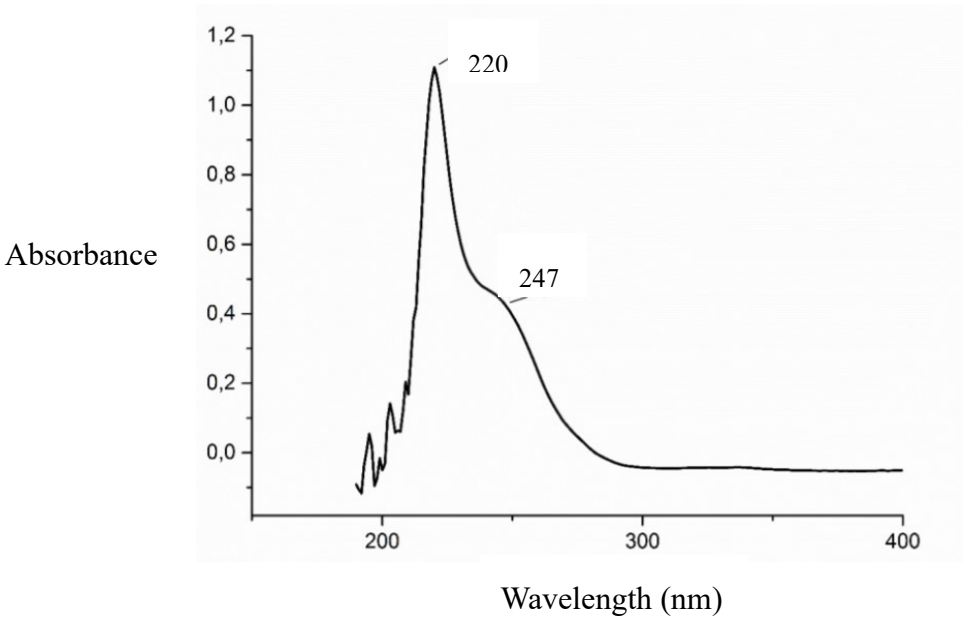


Figure 16. UV-vis spectrum obtained for a solution of SIMes (1mM) in THF showing absorbance maxima at 220 nm and 247 nm.

4.1.4.3. Emission spectroscopy

The emission spectrum for SIMes is shown in the **Figure 17**. The excitation wavelength for different NHCs was estimated from the absorbance maxima obtained from scanning them at a fixed emission wavelength of 350 nm. The excitation wavelength for SIMes was chosen at 298 nm and for rest of the investigated NHCs excitation wavelength was chosen at 318 nm (see **appendix**). On being excited at a wavelength of 298 nm, SIMes showed an emission maxima at 327 nm.

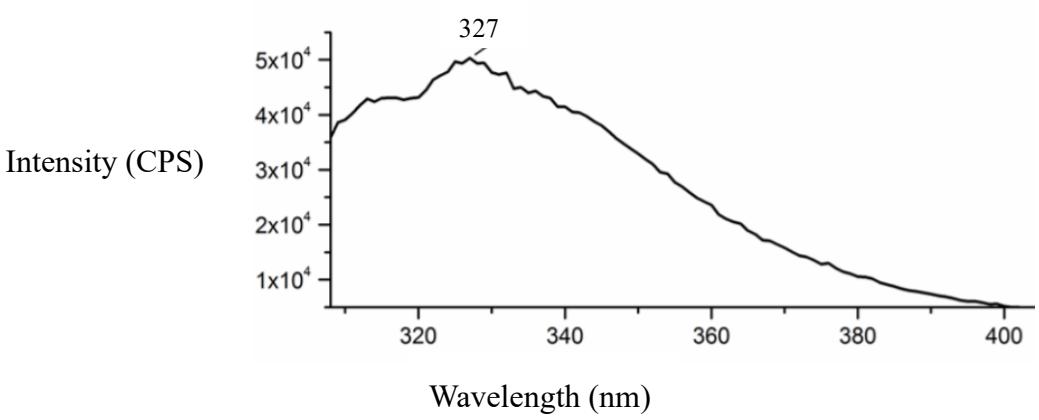


Figure 17. Emission spectrum obtained for a solution of SIMes (1mM) in THF when excited at 298 nm, slit width = 5.00 nm. Emission maximum is obtained at 327 nm, slit width = 2.00 nm.

4.1.4.4. Calculation of the excited state potential of NHCs

For simplicity, the oxidation potential (E_p^{ox} *vs*. SCE) estimated from cyclic voltammetry was used as E (D^+/D) and E_{0-0} was estimated from the maximum in the emission spectrum (see above). Excited state oxidation potentials E (D^+/D^*) for NHCs were calculated from the following formula and are listed in the **Table 2**.

$$\mathbf{E\ (D^+/D^*) \approx E\ (D^+/D) - E_{0-0}}$$

Table 2. Estimation of the excited state oxidation potential of NHCs.

NHC	Emiss. Max (nm)	E_{0-0} (V)	E_p^{ox} (V) *vs.* SCE	E (D^+/D^*) (V) *vs.* SCE
SIMes	327	3.792	1.584	-2.208
SIPr	349	3.553	1.613	-1.940
IMes	349	3.553	1.622	-1.931
IPr	349	3.553	1.538	-2.015

SIMes can be considered as most reducing among all the measured NHCs because it has highest excited state oxidation potential of -2.2 V *vs*. SCE in the excited state (**Table 2**) and also produces the difluoro-imidazolidine derivative SIMes$(F)_2$ in maximum yield (80%) from the activation of SF_6 when compared to the other NHCs (**Table 1)**. Although IPr has the second highest reducing potential, but it gave lowest yield (15%) for difluoro-imidazoline derivative due to the formation of side products from the activation of SF_6. The excited state oxidation potential obtained for SIPr and IMes are found in accordance to the yield obtained for their respective difluoro-derivatives.

4.2. Reduction of SF_5CF_3 with SIMes

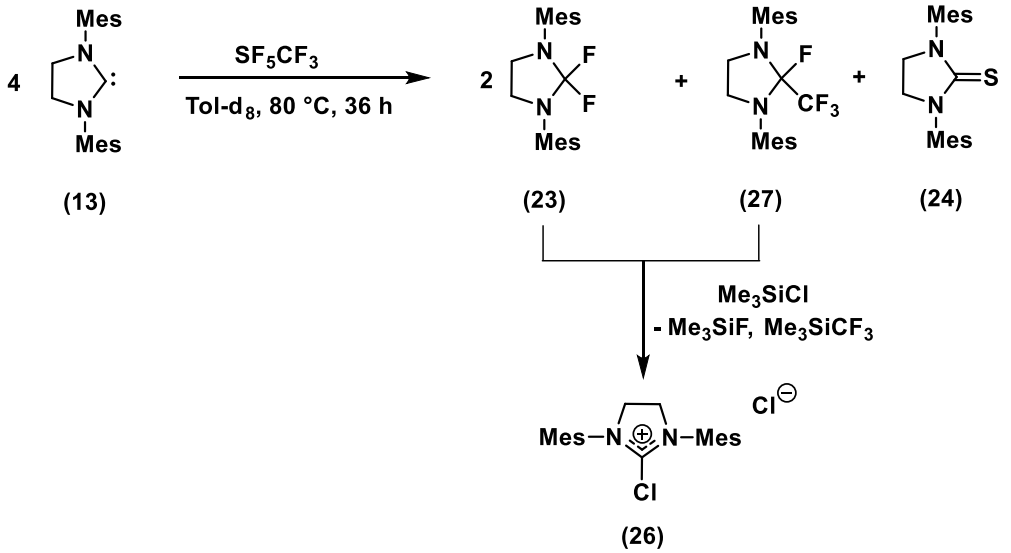
Owing to its chemical and thermal stability, harsh physical methods such as fast electron attachment or dielectric-barrier discharge (DBD) are usually employed to degrade or eliminate the potential greenhouse gas SF_5CF_3 from the atmosphere.[52b, 90] These methods usually results in the formation of toxic end products or other greenhouse gases. The activation of the SF_5CF_3 in homogeneous reaction system has been reported with the rhodium hydrido complex [{Rh(μ-H)(dippp)}$_2$] (**1**).[63] Although several examples of organometallic transformation of SF_5 substituted aromatic or heteroaromatic compounds have been reported the S–F or S–C bond in these cases remained unaffected.[23b, 24c, 146] Similar to the SF_6; activation of SF_5CF_3 was carried out with SIMes to achieve its complete degradation and transformation into fluorinating reagents under mild reaction conditions without involving metals.

4.2.1. Activation of SF_5CF_3 with SIMes

Treatment of SF_5CF_3 (0.10 mmol) with 4 equivalents of SIMes (**13**, 0.05 mmol) at 80 °C for 36 h yielded the 1,3-dimesityl-2,2-difluoroimidazolidine (SIMes(F)$_2$, **23**) and 1,3-dimesityl-2-fluoro-2-trifluoromethylimidazolidine [(SIMes(F)(CF_3)] (**27**) as well as 1,3-dimesitylimidazolidine-2-sulfide (**24**) in a ratio of 2:1:1 (**Scheme 25**). Due to similarity in the solubility of the end products obtained from the reduction of SF_5CF_3, it was difficult to separate them from the reaction mixture. **Figure 18** is depicting a ^{19}F NMR spectrum where a signal at δ = -55.6 ppm was attributed to the SIMes(F)$_2$ (**23**). A doublet at δ = -76.4 ppm and a quartet at δ = -82.9 ppm with a coupling constant of $^3J_{FF}$ = 4.9 Hz were assigned to the compound **27**. The presence of **27** was also confirmed through LIFDI mass spectrometry, revealing a molecular ion peak at *m*/*z* 394.2, which fits with the calculated ion molecular mass of **27**. The SF_5CF_3 can be reduced with SIMes at room temperature also, but with only 15 % conversion of SIMes after 12 h of reaction.

Treatment of the product mixture obtained after the activation of SF_5CF_3 with trimethyl chlorosilane (Me_3SiCl) led to the generation of Me_3SiF, Me_3SiCF_3 as well as 1,3-dimesityl-2-chloroimidazolinium chloride (**26**) (**Scheme 25**). The Me_3SiF and Me_3SiCF_3 were identified in the ^{19}F NMR spectrum at δ = -157.9 ppm and -67.3 ppm respectively.[15c, 147] Me_3SiCF_3 is commonly known as Ruppert-Prakash reagent.[15a, 15c, 148] The reactivity pattern of the product mixture obtained from the reduction of SF_5CF_3

with SIMes confirms the identity of **27** and indicates its principle applicability as a source for a CF_3^- building block.



Scheme 25. Activation of SF_5CF_3 with SIMes.

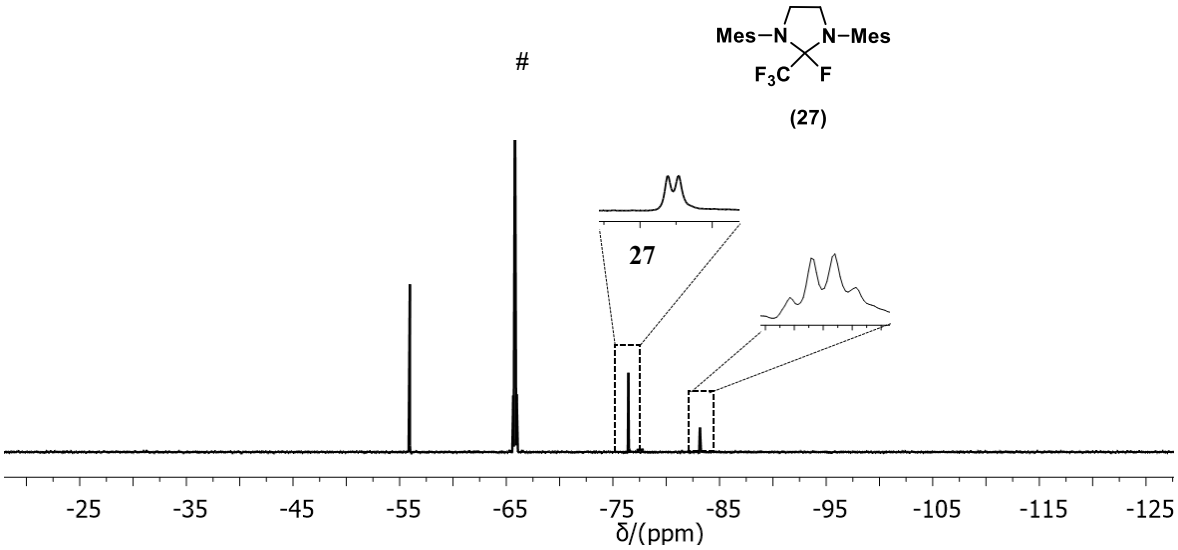
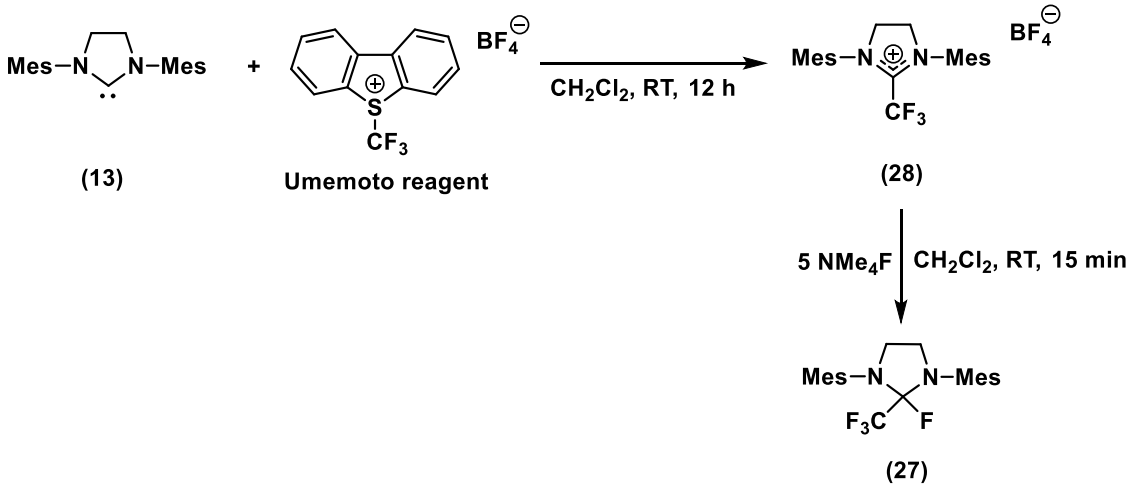


Figure 18. ^{19}F NMR (282.4 MHz, Tol-d_8) spectrum for the activation of SF_5CF_3 with SIMes. **23** = $SIMes(F)_2$, **27** = [(SIMes(F)(CF_3)], # = SF_5CF_3

4.2.2. Independent synthesis of 1,3-dimesityl-2-fluoro-2-trifluoromethylimidazolidine [SIMes(F)(CF_3)] (27)

An independent synthesis of [(SIMes(F)(CF_3)] **(27)** was carried out by treating SIMes (**13,** 1 equivalent) with Umemoto reagent (1 equivalent) to obtain the 1,3-dimesityl-2-trifluoromethylimidazolinium tetrafluoroboarate salt **(28)** through an electrophilic trifluoromethylation (**Scheme 26**). In the ^{19}F NMR spectrum of **28**, two signals at δ = -65.2 ppm and δ = -152.6 ppm were observed for the CF_3 group and BF_4^- ion. LIFDI mass spectrometry gave a molecular ion peak at *m/z* 376.4, which is consistent with the calculated molecular mass of the 1,3-dimesityl-2-trifluoromethylimidazolinium ion. The addition of NMe_4F (5 equivalents) to **28** at room temperature yielded the desired compound **27** in 10 mins, showing two signals in the ^{19}F NMR spectrum at δ = -76.3 and δ = -82.7 ppm in a ratio of 3:1 (**Figure 19**).



Scheme 26. Synthesis route for the formation of 1,3-dimesityl-2-fluoro-2-trifluoromethylimidazolidine [(SIMes(F)(CF_3)] **(27)**.

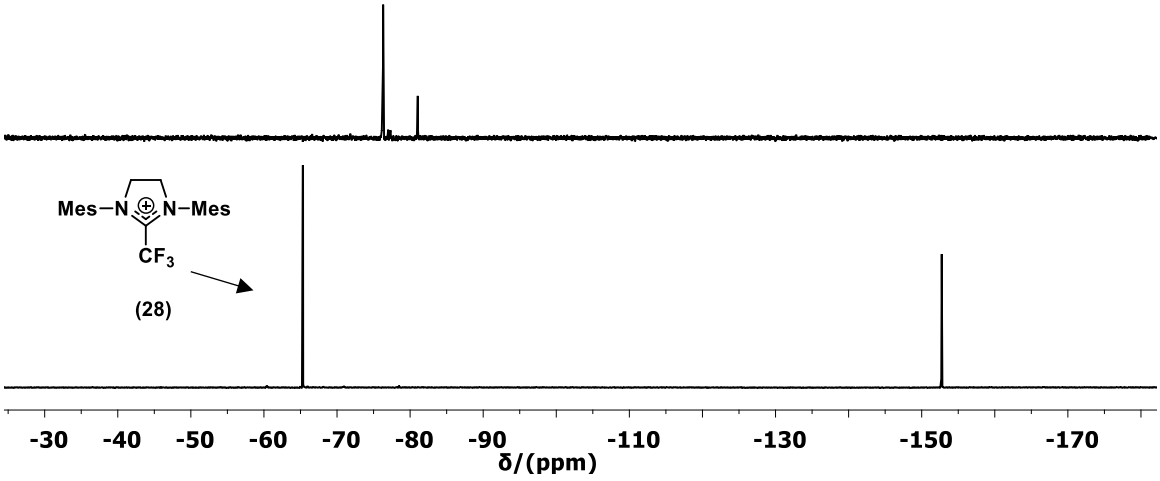


Figure 19. ^{19}F NMR {282.4 MHz, (a) CD_2Cl_2 (b) C_6D_6} spectra showing (a) 1,3-dimesityl-2-trifluoromethylimidazolinium tetrafluoroboarate **(28)** (b) [(SIMes(F)(CF_3)] **(27)** after adding NMe_4F to **28.**

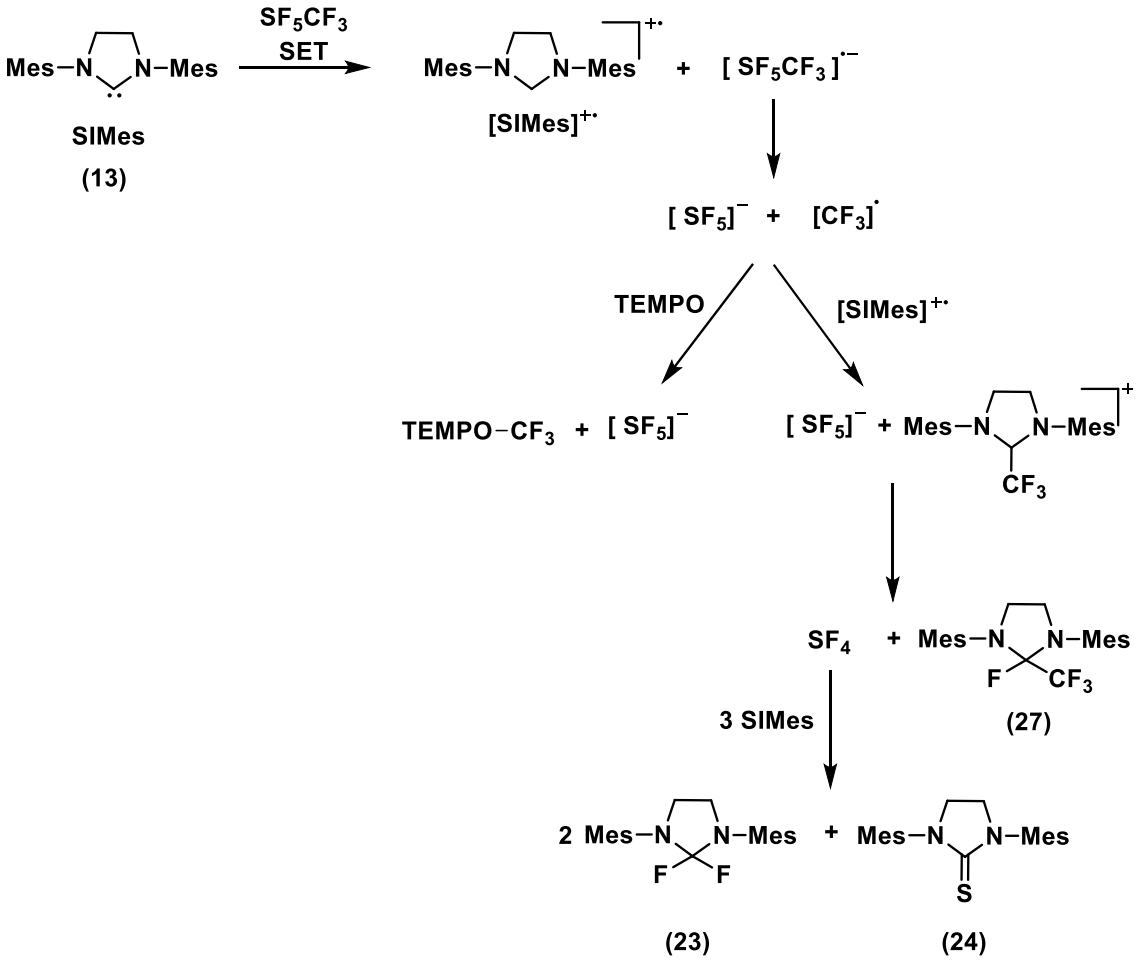
4.2.3. Comparison among NHCs for the reduction of SF_5CF_3

For comparison , other electronically and sterically different NHCs (**SIPr, IMes, IPr**) were reacted with SF_5CF_3 at 80 °C for 36 h. The yield of respective 2,2-difluoroimidazolidine or 2,2-difluoro-imidazoline derivatives was calculated as 38 % for SIMes, 12 % for SIPr, 20 % for IMes and 8 % for IPr from ^{19}F NMR spectra using 1,2 difluorobenzene as external standard and assuming that two equivalents of the 2,2-difluoro- derivative of NHCs were formed. Similar to the [SIMes(F)(CF_3)] (**27**), signals in the ^{19}F NMR spectrum at δ = -76.5 ppm and -87.2 ppm can be attributed to the [SIPr(F)(CF_3)], when SIPr was used for the activation of SF_5CF_3. 2-fluoro-2-trifluoromethyl- derivative of the IMes and IPr were formed in very small amount which makes their characterization very difficult in the NMR spectra. However, signals which are present in the ^{19}F NMR spectrum besides the IMes$(F)_2$ and IPr$(F)_2$ derivatives, can be assigned to the 2-fluoro-2-trifluoromethyl- derivative of these NHCs. Based on the yield of the 2,2-difluoro- derivatives, SIMes has shown the best reactivity towards the activation of SF_5CF_3 when compared with other NHCs.

4.2.4. Mechanistic proposal for the activation of SF_5CF_3 with SIMes

It is noteworthy that in contrast to SF_6, SF_5CF_3 can be activated by NHCs from its ground state. Mechanistically, the activation of the SF_5CF_3 with SIMes is proposed to occur *via* single electron transfer pathway. SIMes can transfer a single electron to SF_5CF_3 to generate a radical anion $SF_5CF_3^{\bullet -}$ and a radical cation $SIMes^{\bullet +}$. Note that Kennedy *et al.* has reported on the decomposition of the SF_5CF_3 by fast dissociative electron attachment method where the CF_3^- was not observed even when electrons with kinetic energy higher than 1.7 eV were applied due to the exothermic dissociative attachment reaction for the formation of SF_5^- (ΔH = -22 kJ mol $^{-1}$) and endothermic dissociative attachment reaction for the formation of CF_3^- (ΔH = 162 kJ mol $^{-1}$) (**Scheme 13**).[90] Therefore, it is conceivable that the radical anion $SF_5CF_3^{\bullet -}$ continues to fragment into a SF_5^- anion and a trifluoromethyl radical $CF_3^{\bullet}$. The $CF_3^{\bullet}$ can recombine with $SIMes^{\bullet +}$ to give a SIMes-CF_3^+ cation. SF_5^- is reported to be a very reactive intermediate hence it couldn't be isolated and readily decomposes to give SF_4 and a 2-fluoro-2-trifluoromethyl NHC derivative [NHC(F)(CF_3)].[69, 78, 98, 104e] It has been established in the *Section 4.1.3* that SIMes can readily activate the SF_4 when treated at room temperature to give 2,2-difluoroimidazolidine (SIMes$(F)_2$, **23**) and 2-thioimidazolidine (**24**) (**Scheme 24**).[149]

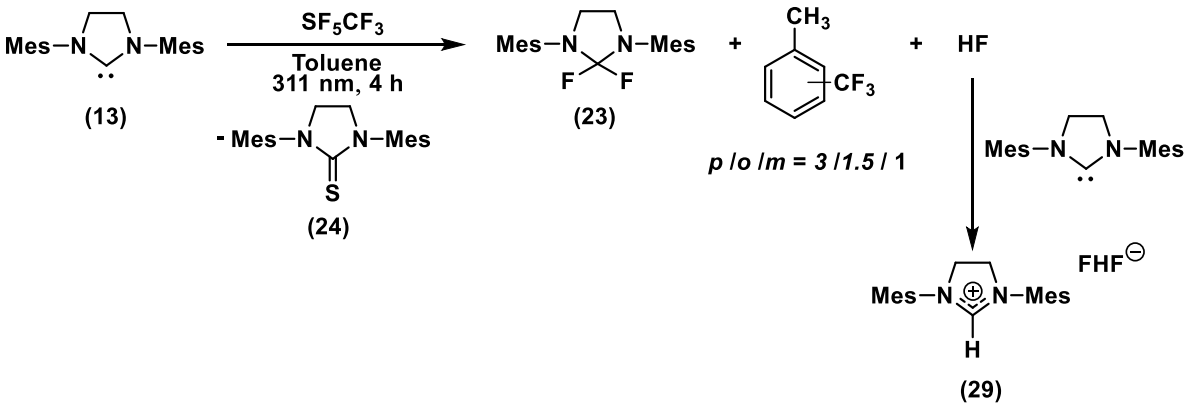
The formation of a trifluoromethyl radical was proved by adding a radical trapping agent TEMPO into the reaction mixture containing SIMes and SF_5CF_3. The $CF_3^{\bullet}$ which was generated from the activation of the SF_5CF_3, reacted with TEMPO to give an TEMPO-CF_3 adduct. A signal in ^{19}F NMR spectrum at δ = -55.3 ppm and molecular ion peak in GC-MS at *m/z* 225.2, were found consistent with the data reported for the identification of the TEMPO-CF_3 adduct.[150] The SF_5^- present in the reaction mixture decomposes into SF_4 and subsequently yielded SIMes$(F)_2$ (**23**) and **24** (**Scheme 27**).



Scheme 27. Proposed mechanism for the activation of SF_5CF_3 with SIMes.

4.2.5. Photochemical activation of SF_5CF_3 with SIMes

SIMes (**13**) was treated photochemically with SF_5CF_3 to enhance the activation and electron transfer, as observed for the activation SF_6. After 4 h of UV treatment (311 nm) in toluene SIMes$(F)_2$ (**23**), the *p*-, *o*-, *m*- isomers of methylbenzotrifluoride in a ratio of 3:1.5:1 and **24** were furnished, as identified by ^{19}F NMR and ^{1}H NMR spectroscopy (**Scheme 28**) (**Figure 20**).[151] Additionally, signals at δ = 10.7 ppm and δ = 14.5 ppm in the ^{1}H NMR spectrum and a weak signal at δ = -149.7 ppm in the ^{19}F NMR spectrum, could be assigned to the 1,3-dimesityl-2-imidazolinium bifluoride salt (**29**). **29** has been reported to be usually formed from an attack of HF to the free NHCs.[151b]



Scheme 28. Photochemical activation of the SF_5CF_3 with SIMes.

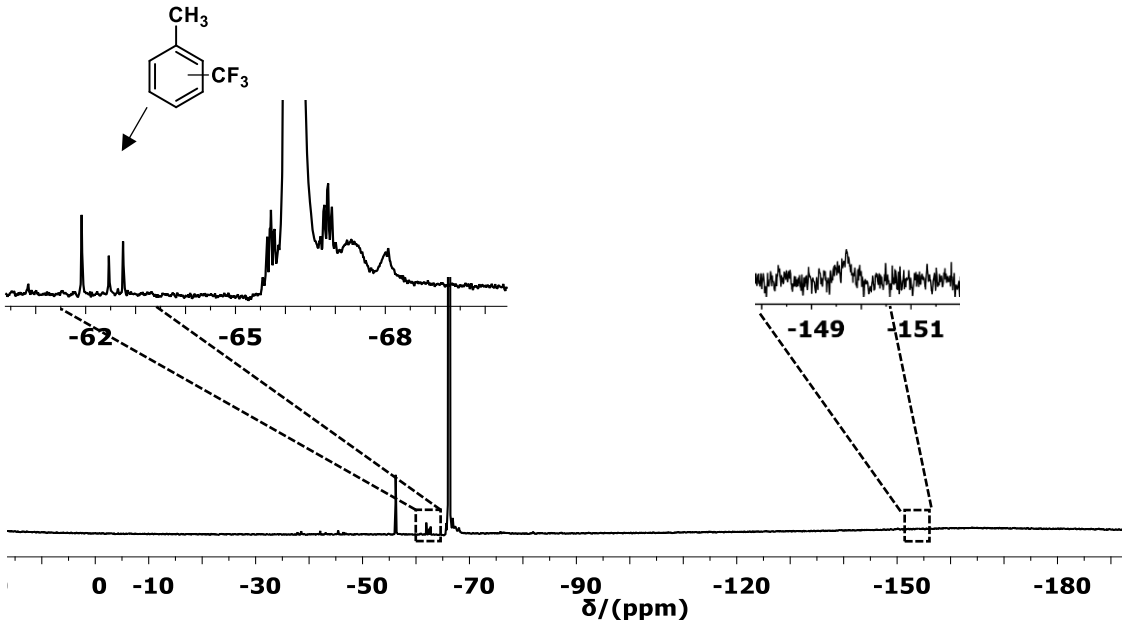
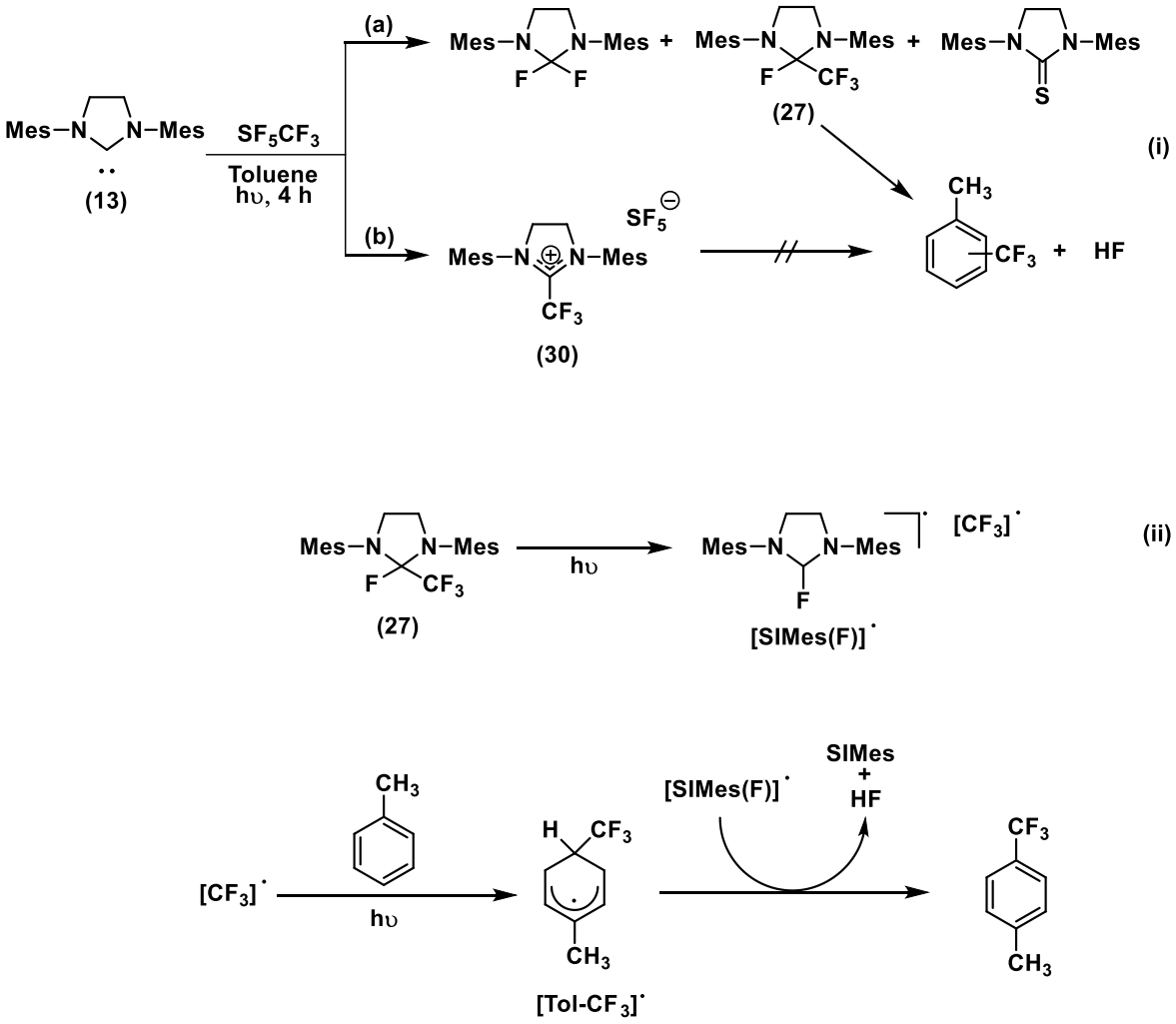


Figure 20. ^{19}F NMR (282.4 MHz, C_6D_6 capillary) spectrum for the activation of SF_5CF_3 with SIMes at 311 nm. **23** = $SIMes(F)_2$, **29** = 1,3-dimesityl-2-imidazolinium bifluoride, # = SF_5CF_3

4.2.6. Possible pathways of CF_3 group transfer to arenes

There are two possible pathways for transferring the CF_3 group *via* photochemical activation of SF_5CF_3 in the presence of NHC (**Scheme 29**). Path (a) involves the [(SIMes(F)(CF_3)] (**27**) formed from the reduction of SF_5CF_3, responsible for the CF_3 transfer to toluene. Path (b) involves an intermediate **30** generated from the initial electron transfer from the SIMes to SF_5CF_3 [**Scheme 29, (i)**], responsible for the CF_3 transfer. Transfer through path (b) can be discarded based on an attempted reaction of 1,3-dimesityl-2-trifluoromethylimidazolidium tetrafluoroboarate (**28**) with toluene. **28** is an analogous compound of the intermediate **30**. Trifluoromethylation of arene was not obtained when **28** was photochemically treated with toluene even in the presence of excess of SIMes. To confirm the occurrence of CF_3 transfer through path (a), the product mixture obtained from the thermal activation of SF_5CF_3 with SIMes was taken and put under UV (311 nm) for 2h. Successful trifluoromethylation took place to generate the isomers of methylbenzotrifluoride as identified through ^{19}F NMR spectroscopy. CF_3 group transfer was not achieved when the product mixture was irradiated in the presence

of TEMPO, indicating the trifluoromethylation of arenes *via* a radical pathway in a similar manner reported by Togni *et al*.[15i, 17b] [(SIMes(F)(CF_3)] (**27**) when treated with UV light, possibly generates the radicals $[CF_3]^{\bullet}$ and $[SIMes(F)]^{\bullet}$. $[CF_3]^{\bullet}$ can attack the toluene yielding an intermediate radical $[Tol\text{-}CF_3]^{\bullet}$, which subsequently gets deprotonated in the presence of $[SIMes(F)]^{\bullet}$ radical and generates methylbenzotrifluoride [**Scheme 29, (ii)**].



Scheme 29. (i) Possible pathways for the trifluoromethylation of toluene; (ii) proposed pathway for the trifluoromethylation of toluene with [(SIMes(F)(CF_3)] (**27**).

Overall, a complete reduction of SF_5CF_3 was achieved thermally and photochemically through S–F and S–C bond activation with SIMes, generating $SIMes(F)_2$, 1,3-dimesityl-2-fluoro-2-trifluoromethylimidazolidine [$(SIMes(F)(CF_3)$] (**27**) and 1,3-dimesitylimidazolidine-2-sulfide (**24**). The compound **27** can be utilized as CF_3^- or $CF_3^{\bullet}$ transfer reagent. The reactivity of $SIMes(F)_2$ has been also investigated as fluorinating reagent and discussed in the following chapters.

4.3. Fluorination with 2,2-difluoroimidazolidin SIMes(F)$_2$

4.3.1. Deoxyfluorination

Due to the abundance of compounds containing alcohols and carbonyl groups, deoxyfluorination is an efficient means for introducing fluorine atoms into organic molecules. It has been described in the *Section 2.4.2* that deoxyfluorination can be successfully achieved by using SF_4 and SF_4 derived reagents.[13a-l] Due to difficulties associated with handling toxic SF_4 derived reagents; the development of new deoxyfluorination reagents has gained interest in recent years. In 2002, Nagata *et al*. reported a thermally stable deoxyfluorination reagent, 2,2-difluoro-1,3-dimethylimidazolidine (DFI) (**Figure 21**). The DFI was applied to oxygen-containing functional groups such as alcohols, acids, carbonyl compounds to transform them into the corresponding fluorides.[110] Ritter *et al*. also synthesized the reagent 1,3-di(2,6-diisopropylphenyl)-2,2-difluoroimidazoline (PhenoFluor™) for fluorinating phenols and alcohols. Since PhenoFluor™ tends to undergo hydrolysis upon storage, less moisture sensitive variants of PhenoFluor™ such as PhenoFluorMix and AlkylFluor were developed later (**Figure 21**).[13o, 13p]

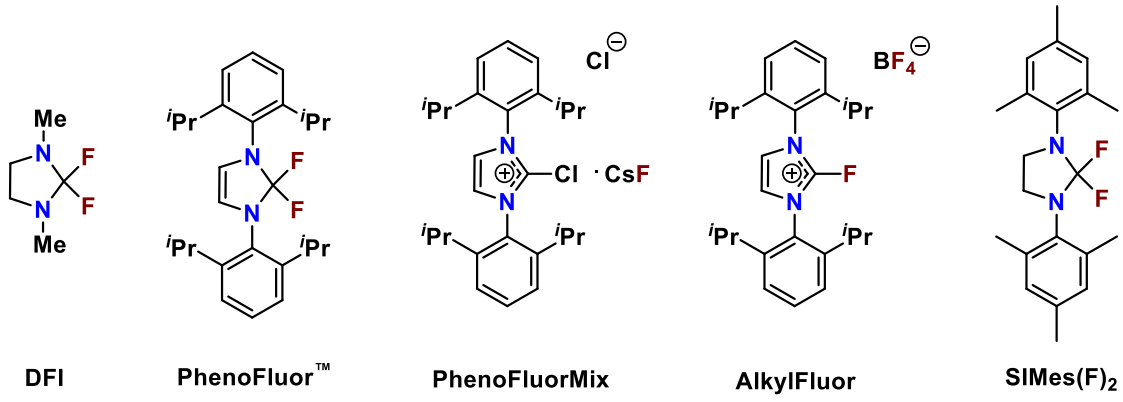
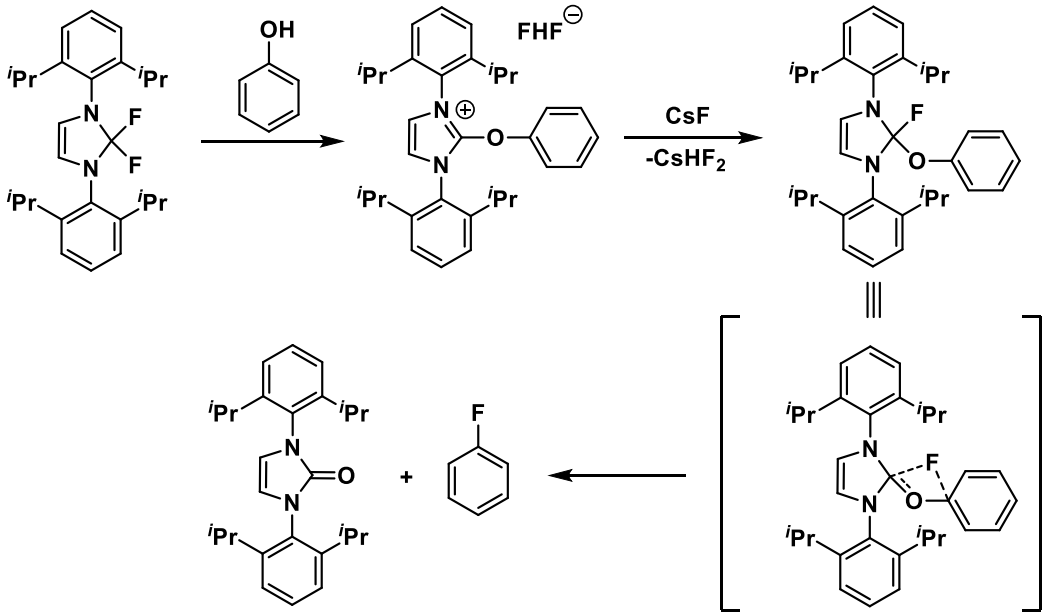


Figure 21. Deoxyfluorination reagents having imidazolidine or imidazoline framework.

Ritter *el al*. proposed a concerted nucleophilic aromatic substitution (CS_NAr) mechanism for the deoxyfluorination of phenols by PhenoFluor™ in the presence of CsF to yield aryl fluorides and the urea derivative of the imidazoline. (**Scheme 30**)[13p]



Scheme 30. Proposed concerted nucleophilic aromatic substitution (CS_NAr) mechanism for the deoxyfluorination of phenols.[13p]

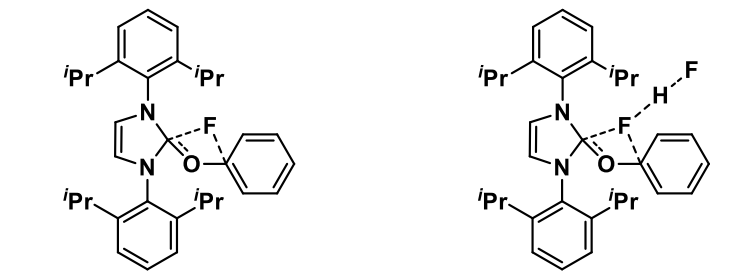
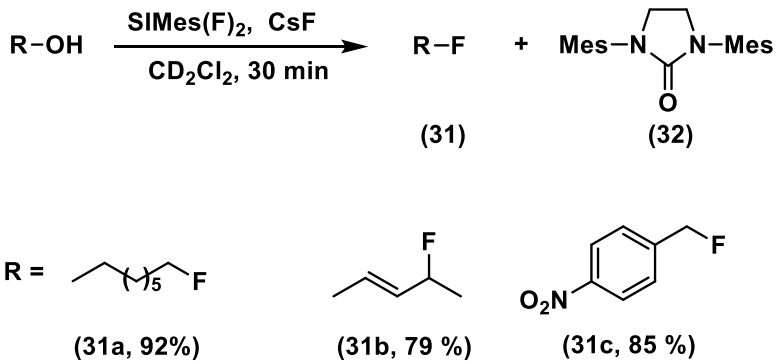


Figure 22. Transition state structure for F^- or FHF^-attack at the arene.[13o]

4.3.2. Deoxyfluorination of alcohols with SIMes(F)$_2$

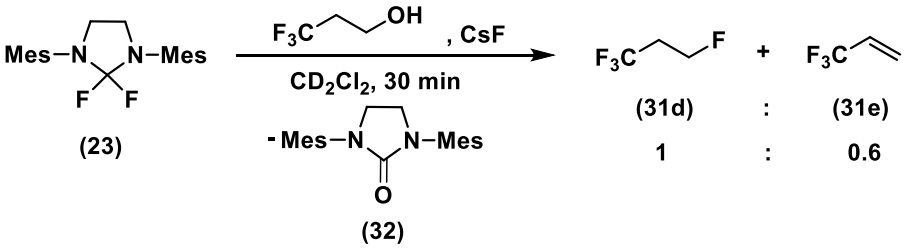
1,3 dimesityl-2,2-difluoroimidazolidine (SIMes(F)$_2$, **23**) was obtained as one of the end products from the reduction of SF_6 with SIMes and has a structural framework similar to the DFI and PhenoFluor™ (**Figure 21**). **23** can be synthesized also independently by fluorination of 1,3-dimesityl-2-chloroimidazolinium chloride with NMe_4F (**Scheme 21**). The reactivity of SIMes(F)$_2$ was tested towards the deoxyfluorination of alcohols and acids.

Electronically different alcohols were treated with SIMes(F)$_2$ (**23**) at room temperature in the presence of CsF. The treatment of SIMes(F)$_2$ with octanol, allylic and benzylic alcohol yielded 1-fluorooctane (**31a**, 92 %), 4-fluoropent-2-ene (**31b**, 79 %) and 4-nitrobenzylfluoride (**31c**, 85 %) respectively, *via* deoxyfluorination within 30 min at room temperature (**Scheme 31**). The urea derivative of SIMes (1,3-dimesitylimidazolidine-2-one, **32**) was also observed.[152] All products were identified with the help of ^1H and ^{19}F NMR spectroscopy and quantified using 1,2 difluorobenzene (0.2 M in C_6D_6) as an external standard.[153]



Scheme 31. Deoxyfluorination of alcohols with SIMes(F)$_2$.

In case of 1,1,1-trifluoropropanol a slightly different reactivity was observed. When treated with SIMes(F)$_2$, a mixture of tetrafluoropropane (**31d**) and trifluoropropene (**31e**) was obtained in the ratio of 1: 0.6. (**Scheme 32**) When the reaction mixture was followed for 3 h by ^{19}F NMR spectroscopy, the ratio changed to 1: 0.9, which indicates that the deoxyfluorination was followed by a dehydrofluorination.[154] Note that it is not very common to see the formation of trifluoropropene by dehydrofluorination in a homogeneous reaction system.[155]



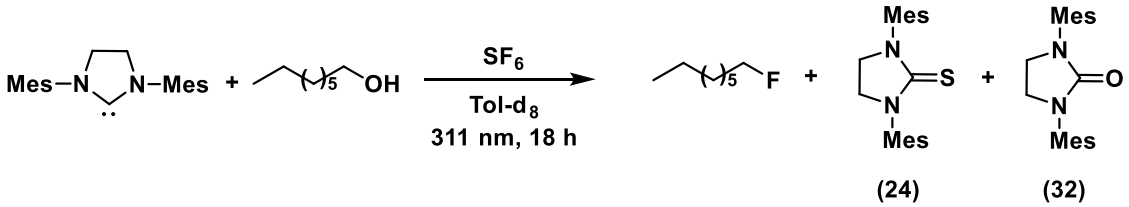
Scheme 32. Deoxyfluorination of 1,1,1-trifluoropropanol with SIMes(F)$_2$ (**23**).

4.3.3. Role of CsF

When 1-octanol was treated with SIMes(F)$_2$ (**23**) without CsF, the formation of 1,3-dimesityl-2-alkoxyimidazolinium bifluoride was observed, as indicated by a signal at δ = -169.2 ppm in the ^{19}F NMR spectrum,[133b, 151b] and 1-fluorooctane was obtained in lower yield when compared to the deoxyfluorination reaction in the presence of CsF. Utility of the CsF in the deoxyfluorination was described by Ritter *et al*. by taking phenol as an example (**Figure 22**).[13o] The activation energy for the deoxyfluorination of phenol via attack of bifluoride (FHF^-) and fluoride (F^-) ion at the arene was calculated as 30 kcal mol^{-1} and 24 kcal mol^{-1} respectively. The experimental barrier for the deoxyfluorination of phenol was calculated as $\Delta G^{\ddagger}$(110 °C) = 23.4 ± 0.19 kcal mol^{-1} which is closer to the activation energy for deoxyfluorination of phenol in presence of F^- and hence yield for the fluorinated products was found to be better in the presence of CsF.[13o]

In contrast to the PhenoFluor™, when SIMes(F)$_2$ was used for the deoxyfluorination of phenol in presence of CsF, no fluorobenzene was observed. Only formation of 1,3-dimesityl-2-phenoxyimidazolinium bifluoride was observed even after heating the reaction mixture at 90 °C for 48 h.[110] This supports the assumption made by Ritter *et al*. for the need of an unsaturated backbone to stabilize bifluoride (FHF^-) via hydrogen bonding.[13o, 13p]

4.3.4. One-pot deoxyfluorination of alcohols with SF_6



Scheme 33. One-pot deoxyfluorination of 1-octanol.

Deoxyfluorination of alcohols can not only be achieved in a stepwise fashion by treating them with the mixture of $SIMes(F)_2$ (**23**) and **24** generated from the reduction of SF_6 but also be achieved in a one-pot manner (**Scheme 33**). The SF_6 (0.10 mmol) was added into a solution of SIMes (0.05 mmol) and 1-octanol (0.05 mmol) and the reaction mixture was put under irradiation using UV light at 311 nm (**Scheme 33**). Monitoring of the reaction with ^{19}F NMR spectrum shows that $SIMes(F)_2$ was formed initially, which subsequently reacts with 1-octanol to give 1-fluorooctane in 18 h (**Figure 23**). For one-pot deoxyfluorination, addition of CsF was not required to get a good yield of 1-fluorooctane and a signal for the bifluoride anion was not observed in the ^{19}F NMR spectrum. 1,3-dimesitylimidazolidine-2-sulfide (**24**) and 1,3-dimesitylimidazolidine-2-one (**32**) were also identified as end products after completion of the reaction.[140, 152a]

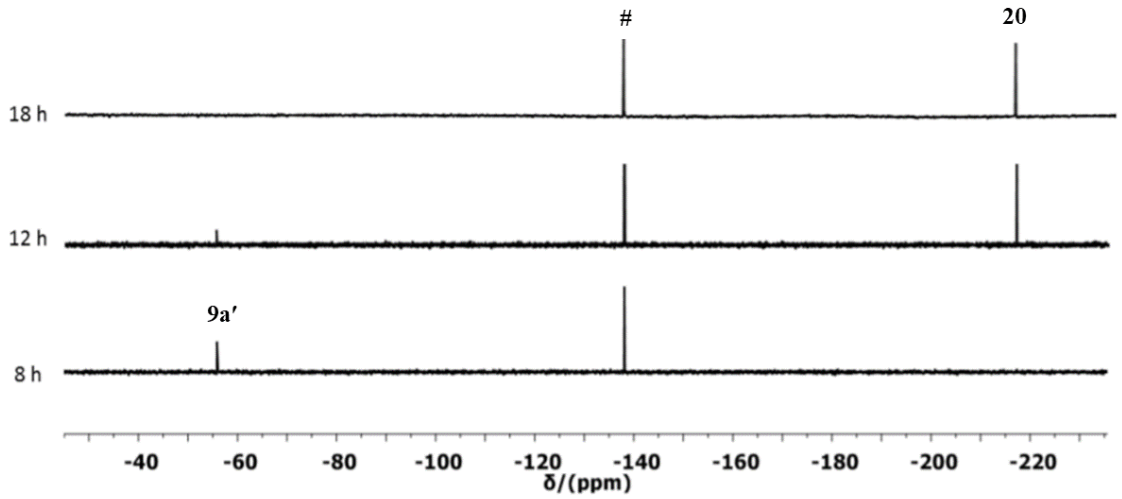
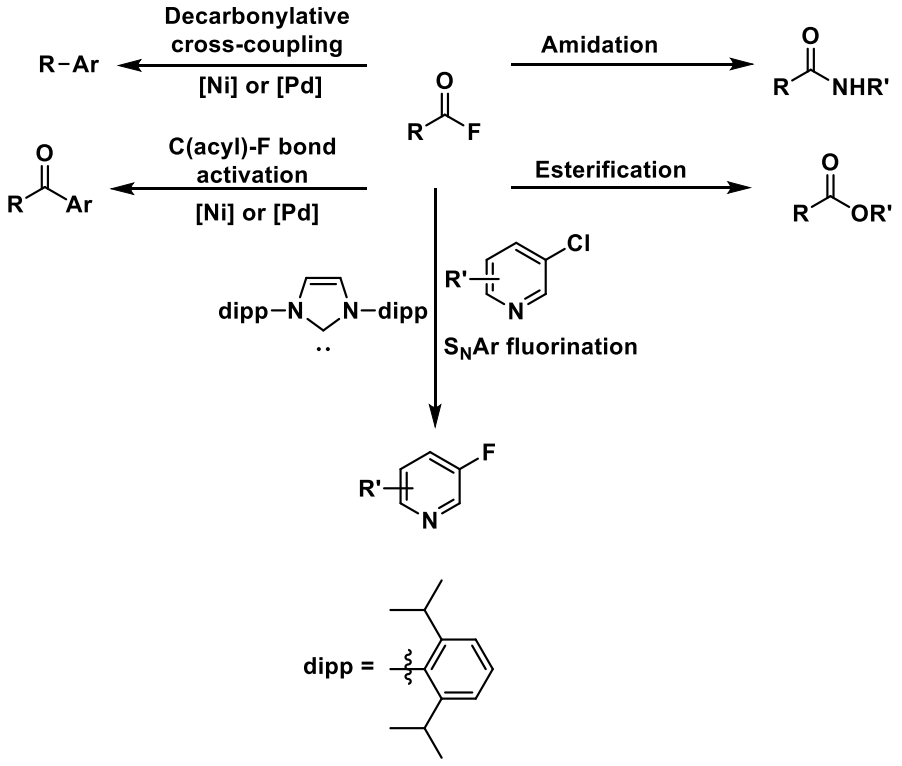


Figure 23. ^{19}F NMR (282.4 MHz, Tol-d_8) spectrum for the one-pot deoxyfluorination of 1-octanol *via* reduction of SF_6 with SIMes. ***** = 1,2 difluorobenzene (external standard).

4.4. Fluorination of aldehydes with 2,2-difluoroimidazolidin SIMes(F)$_2$ to access acyl fluorides

4.4.1 Properties and synthesis of acyl fluorides

Due to their superior stability and distinct reactivity, acyl fluorides are versatile intermediates in organic synthesis.[156] They are often prepared as fluorinating reagent in the total synthesis of biologically active enzymes and drugs.[157] Acyl fluorides have been successfully employed in esterification and amidation to synthesize peptides.[156, 157b, 157c, 158] Sanford *et al*. reported the use of acyl fluorides as anhydrous fluoride ion source for S_NAr fluorination reactions.[159] C−H bond formation and Suzuki – Miyaura coupling with arenes can also be achieved with acyl fluorides *via* metal catalyzed decarbonylation or defluorination.[160] **Scheme 34** is showing synthetic utility of the acyl fluorides.



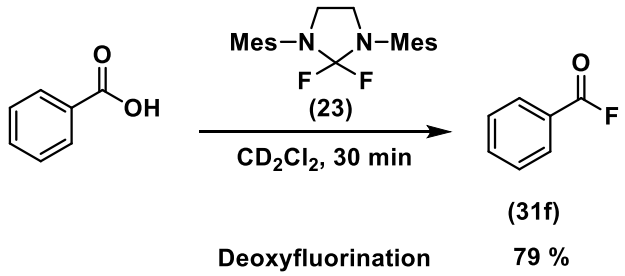
Scheme 34. Usage of acyl fluorides in organic synthesis.[161]

Acyl fluorides are variably reported to be synthesized from aldehydes using cesium fluoroxysulfate ($CsSO_4F$), uranium hexafluoride (UF_6), F_2 gas, *N*-fluorobenzenesulfonimide (NFSI) with photoactivated decatungstate or SelectFluor™.[162]

All these methods involve either harsh reaction conditions, lower yields or long time durations to achieve the fluorination of aldehydic C(sp^2)–H bond. Alternatively acyl fluorides can also be prepared from acids via deoxyfluorination or from acyl chlorides *via* halogen exchange reactions.[13g, 13j, 69, 149, 156, 161, 163]

4.4.2 Deoxyfluorination of benzoic acid with SIMes(F)$_2$

SIMes(F)$_2$ (**23**) is discussed in the last section to be successfully employed for the deoxyfluorination of alcohols. Benzoyl fluoride can be obtained in a similar way by treating benzoic acid with **23** at room temperature for 30 mins (**Scheme 35**). The formation of benzoyl fluoride (**31f,** 79 %) was identified by using NMR spectroscopy. The ^{19}F NMR spectrum shows a signal at δ = 17.7 ppm whereas the $^{13}C\{^1H\}$ NMR spectrum, reveals a signal for the benzoyl carbon at δ = 153.2 ppm. GC-MS, gives a molecular ion peak at *m/z* 124. These analytical data were found in accordance with the literature reported for the synthesis of benzoyl fluoride.[160c]

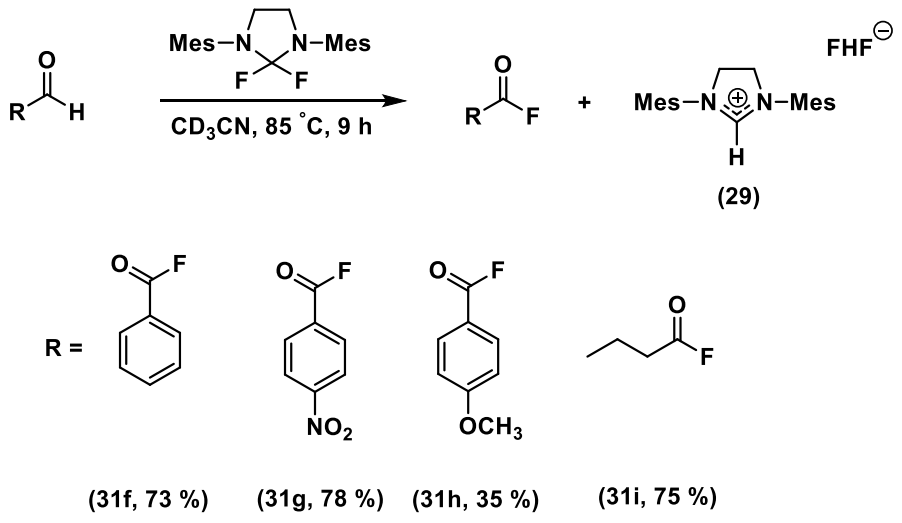


Scheme 35. Deoxyfluorination of the benzoic acid with SIMes(F)$_2$ (**23**).

4.4.3 Direct fluorination of aldehydes

A solution of $SIMes(F)_2$ in acetonitrile (**23,** 1 equivalent) on being treated with benzaldehyde (1.5 equivalent) at 85 °C for 9 h produced benzoyl fluoride (**31f,** 73 %) (**Scheme 36**). Formation of the benzoyl fluoride was identified by the ^{19}F NMR spectrum, showing a signal at δ = 17.7 ppm. The 1,3-dimesitylimidazolinium bifluoride (**29**) was also obtained along with the benzoyl fluoride.[151b] Yield of acyl fluoride **31f**, was estimated from the ^{19}F NMR spectrum by using 1,2 difluorobenzene (0.2 M in C_6D_6) as an external standard.

Various other substituted benzaldehydes and an aliphatic aldehyde were screened for the fluorination with $SIMes(F)_2$ at 85 °C for 9 h. (**Scheme 36**) Successful conversion of *p*-nitrobenzaldehyde, *p*-methoxybenzaldehyde and butyraldehyde into *p*-nitrobenzoylfluoride (**31g**, 78 %), *p*-methoxybenzoylfluoride (**31h**, 35 %) and butanoylfluoride (**31i**, 75 %) respectively was observed.[161, 163b, 164] Observed difference in the yield of acyl fluorides can be attributed to the difference in the electrophilicity of carbonyl center. A electrophilic carbonyl center led to the better yield of the corresponding acyl fluoride. No reaction was observed when acetophenone was treated with $SIMes(F)_2$.

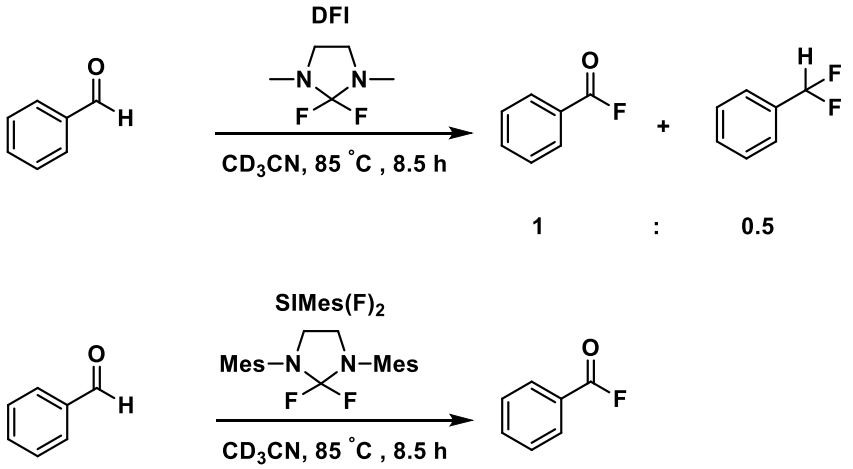


Scheme 36. Fluorination of various aldehydes with $SIMes(F)_2$ (**23**).

4.4.4 Comparison of the SIMes(F)$_2$ with DFI and PhenoFluor™ as fluorinating agents

To get more insights on the unusual reactivity of SIMes(F)$_2$ towards the fluorination of aldehydes, other NHC derived deoxyfluorinating reagents such as DFI and PhenoFluor™ were also treated with benzaldehyde. DFI was used from the commercial source. DFI is reported to produce difluoromethylbenzene when treated with benzaldehyde at 85 °C in acetonitrile for 8.5 h.[110, 165] The reaction sample containing DFI and benzaldehyde was heated at 85 °C and progress of the reaction was monitored with the ^{19}F NMR spectrum. A mixture of benzoyl fluoride and difluoromethylbenzene at δ = 17.7 and δ = -111.1 ($^2J_{FH}$ = 57.2 Hz) ppm, in a ratio of 1: 0.5 was observed after 8.5 h of heating (**Scheme 37**) (**Figure 24**). When the reaction mixture was continued to heat for 15 h, the ratio of the benzoyl fluoride and difluoromethylbenzene in the mixture changed to 0.5 : 1. PhenoFluor™ was synthesized by following a synthetic route adopted for the synthesis of SIMes(F)$_2$ (**23**) (**Scheme 21**). Fluorination of the benzaldehyde with PhenoFluor™ gave benzoyl fluoride with a yield of 65 %.

SIMes(F)$_2$ has the advantage over DFI as it selectively only gives benzoyl fluoride when treated with the benzaldehyde even after heating the reaction mixture for 15 h. Compared to the PhenoFluor™, a better yield for the benzoyl fluoride was observed when SIMes(F)$_2$ was used for the fluorination.



Scheme 37. Comparison between DFI and $SIMes(F)_2$ towards the fluorination of benzaldehyde at 85 °C.[110]

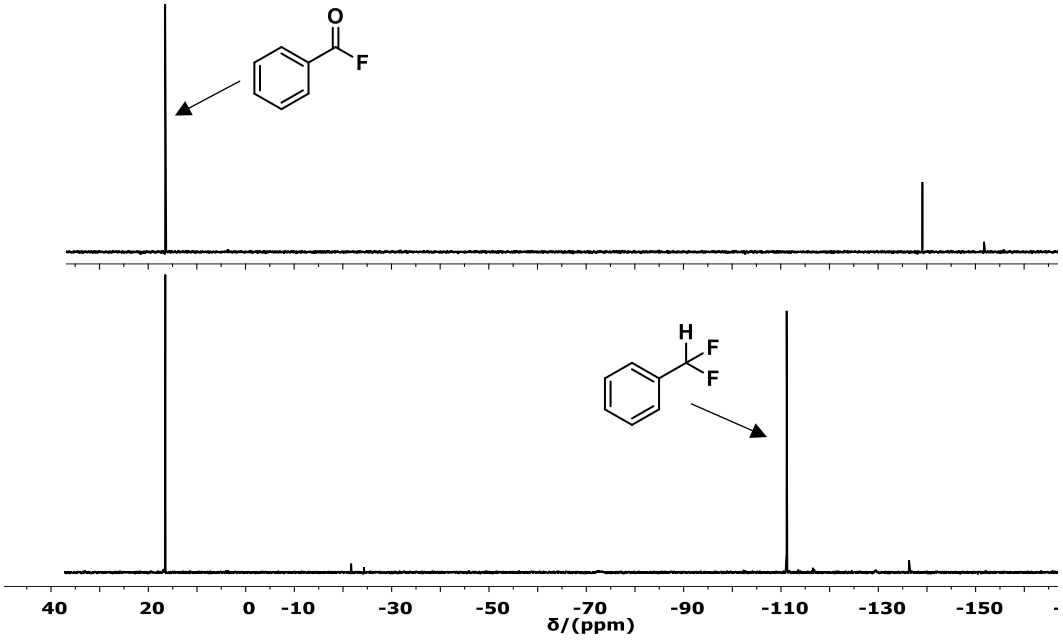


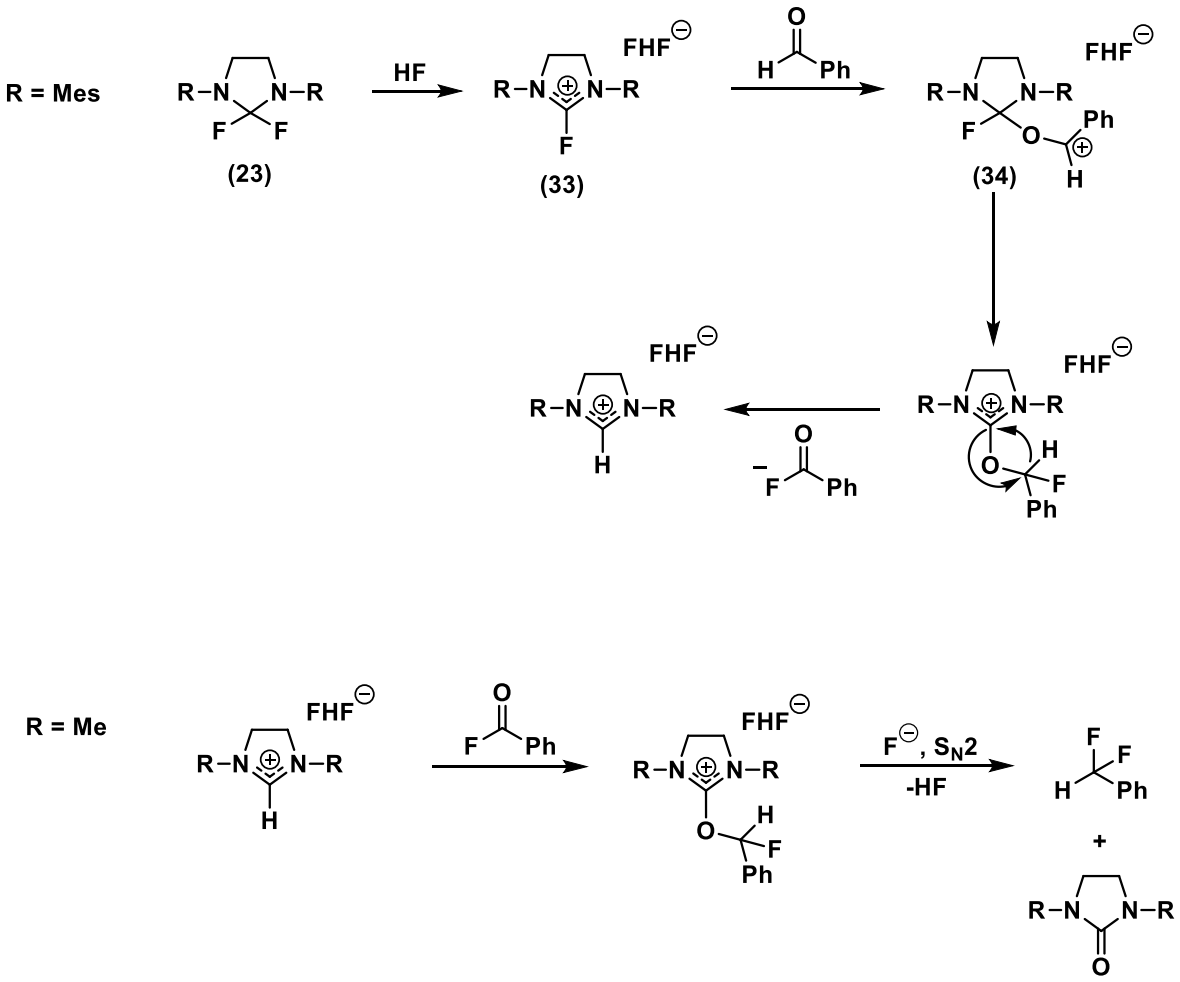
Figure 24. ^{19}F NMR (282.4 MHz, CD_3CN) spectra for the fluorination of benzaldehyde with (a) DFI and (b) $SIMes(F)_2$ at 85 °C after 8.5 h. * = 1,2 difluorobenzene (external standard).

4.4.5. Mechanistic proposal for the formation of acyl fluorides with SIMes(F)$_2$

Scheme 38 is showing a tentative mechanism for the formation of benzoyl fluorides with SIMes(F)$_2$ (**23**). Fluorination of the aldehyde can be postulated to be initiated from the reaction of adventitious HF present in the reaction system with SIMes(F)$_2$ yielding a 1,3-dimesityl-2-fluoroimidazolinium bifluoride salt (**33**). An nucleophilic attack of aldehyde to the salt **33** followed by fluoride migration can produce a uronium bifluoride salt (**34**). Subsequent rearrangement in the salt **34** can lead to the formation of benzoyl fluoride and the 1,3-dimesitylimidazolinium bifluoride salt (**29**). When fluorination of the benzaldeyde was performed with **23** in the presence of CsF, a smaller yield of benzoyl fluoride (15 %) was obtained which further supports the involvement of HF in the fluorination.

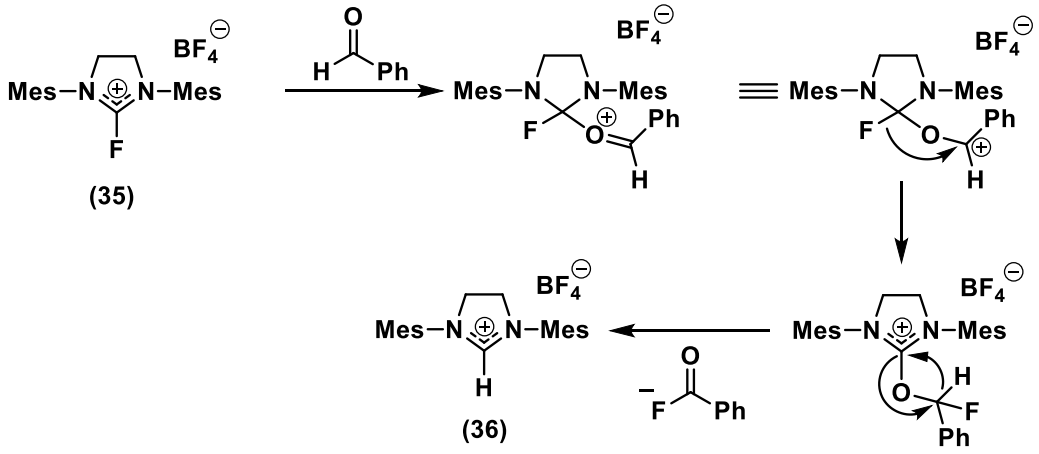
The presence of less bulky substituents in the DFI can facilitate the further attack of benzoyl fluoride at 1,3-dimesitylimidazolidinium bifluoride. A subsequent attack of the fluoride ion *via* S_N2 can yield difluoromethylbenzene and 1,3 dimethylimidazolidine-2-one.[110]

The difference in the reactivity of benzaldehyde, *p*-nitrobenzaldehyde, *p*-methoxybenzaldehyde and butyraldehyde towards the fluorination with SIMes(F)$_2$ can be explained on the basis of electrophilicity of carbonyl center in the intermediate salt **34** . More electrophilicity and less conjugation in the **34** will favor the acyl group fluorination.



Scheme 38. Proposed mechanism for the fluorination of aldehydes with $SIMes(F)_2$ (**23**).

To support the proposed mechanism, the 1,3-dimesityl-2-fluoroimidazolinium tetrafluoroborate salt (**35**) was prepared as an analogue of the 1,3-dimesityl-2-fluoroimidazolidinium bifluoride (**33**) by following the procedure reported for the synthesis of AlkylFluor.[13n] A reaction of the compound **26** with KF and KBF_4 yielded **33** (see experimental). Addition of the benzaldehyde to **35** yielded benzoyl fluoride which supports the formation and need of the 1,3-dimesityl-2-fluoroimidazolinium bifluoride salt (**33**) to achieve the fluorination of aldehydes (**Scheme 39**).



Scheme 39. Proposed mechanism for the fluorination of aldehydes with 1,3-dimesityl-2-fluoroimidazolinium tetrafluoroborate (**35**).

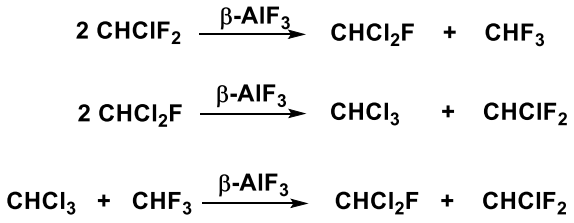
$SIMes(F)_2$ (**23**) can be successfully used for synthesizing organic building blocks as it has shown versatile reactivity for the deoxyfluorination of alcohols, acids and direct fluorination of aldehydes in a convenient manner without involving any harsh reaction conditions. In the following chapter usage of the $SIMes(F)_2$ (**23**) for synthesizing organoaluminium fluorides is investigated and elaborately described.

5. Synthesis of organoaluminum fluorides with 2,2-difluoroimidazolidin SIMes(F)$_2$

5.1. Introduction

5.1.1. Aluminium fluorides

Inorganic metal fluorides have commercial importance for catalyzing reactions involved in the production of fluoro-organic compounds. Antimony pentafluoride (SbF_5) is likely one of the first and most important fluorination catalysts for the large scale production of chlorofluorocarbons (CFCs) via halogen exchange reactions.[166][167][168] Various aluminum fluoride and fluorinated alumina phases have also been reported as active Lewis acid catalysts for the preparation of chlorofluorocarbons and hydrofluorocarbons and in cracking, isomerization or polymerization reactions.[169] The activity of these catalysts is attributed to the significant concentration of defects or distorted structures. Particularly for crystalline aluminium fluorides, two phases are well studied in the literature, α-AlF_3 and β-AlF_3. The β-AlF_3 phase displays activity for the chlorofluorocarbon (CFC) or hydrochlorofluorocarbon (HCFC) dismutation and halogen exchange as shown in the **Scheme 40**, whereas the thermodynamically more stable α-AlF_3 displays no catalytic activity, even after prolonged treatment with fluorocarbons at high temperatures, up to 600 °C.[169d, 170]

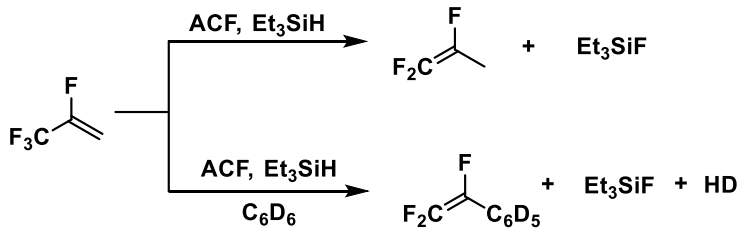


Scheme 40. β-AlF_3 catalyzed dismutation and halogen exchange reactions.[169d, 170]

The most common methods of synthesizing the aluminium fluorides involve the treatment of aluminium oxides or hydroxides with HF and/or NH_4F.[169a] These methods generate a mixture of aluminium fluoride hydrates, aluminium hydroxide fluorides and ammonium fluoroaluminates in either amorphous or crystalline state. The obtained products, when treated thermally, yield aluminium fluorides in different metastable phases or partially hydrolyzed aluminium fluorides. The metastable phases, upon heating at temperatures between 450 and 650 °C, undergo an irreversible phase change to α-AlF_3.[169a] Herron *et al*. reported a successful synthesis of AlF_3 that show different metastable phases (η, β, θ, κ) via thermal decomposition of the fluoroaluminates with ammonium, tetramethylammonium or pyridinium cations.[171] Case and Nyman reported on the the synthesis of AlF_3 *via* decomposition of the SF_6 at $AlCl_3$ at 180–200 °C for 24 h. This method produces sulfur chlorides along with the AlF_3.[59] The AlF_3 can also be produced from the fluorination of aluminium hydroxide [$Al(OH)_3$] by SF_4 at 20 °C.[172]

In past 15 years, there has been tremendous progress in the synthesis of nanoscopic aluminium fluorides.. Amorphous aluminium fluorides such as aluminium chlorofluoride (ACF, $AlCl_xF_{3-x}$, x = 0.05–0.3) and high-surface aluminium fluoride (*HS*-AlF_3) have shown a Lewis acidity comparable to that of SbF_5.[169d, 169e] Owing to their high Lewis acidity, ACF and *HS*-AlF_3 are known as good heterogeneous catalysts for C–H and C–F bond activation reactions at ambient temperature and pressure.[166, 169d] In the presence of silanes or germanes, ACF and *HS*-AlF_3 are useful compounds to perform dehydrohalogenation or hydrodehalogenation reactions of halogenated alkanes or olefins (**Scheme 41**).[173] Typically, Friedel-Crafts-type reactions are also observed besides hydrodehalogenation when ACF or *HS*-AlF_3 are used in the presence of silanes in C_6D_6 (**Scheme 41**).[154, 173c, 174] Microporous ACF is obtained by treating $AlCl_3$ with trichlorofluoromethane (CCl_3F) whereas mesoporous *HS*-AlF_3 is prepared by the

fluorination of aluminium isopropoxide [Al(O^{i}Pr)$_3$] with anhydrous HF followed by a post-fluorination step with dichlorodifluoromethane (CCl_2F_2) or chlorodifluoromethane ($CHClF_2$) at 240 °C in a flow reactor.[175][169d, 176]



Scheme 41. ACF catalyzed hydrodefluorination and Friedel-Crafts-type reaction in the presence of Et_3SiH in 2,3,3,3-tetrafluoropropene.[154]

$(AlF_3)_x$ is a non-volatile compound due to its very high melting point (1290 °C).[177] Being as well very insoluble, the use of the aluminium fluorides was limited to the heterogeneous reaction systems. In contrast, the development of soluble AlF_3 complexes could become an interesting alternative to overcome this limitation and thus has become a topic of research in the past years. Development of synthetic routes for organoaluminium fluorides has therefore lately emerged and are investigated for their reactivity in solutions.

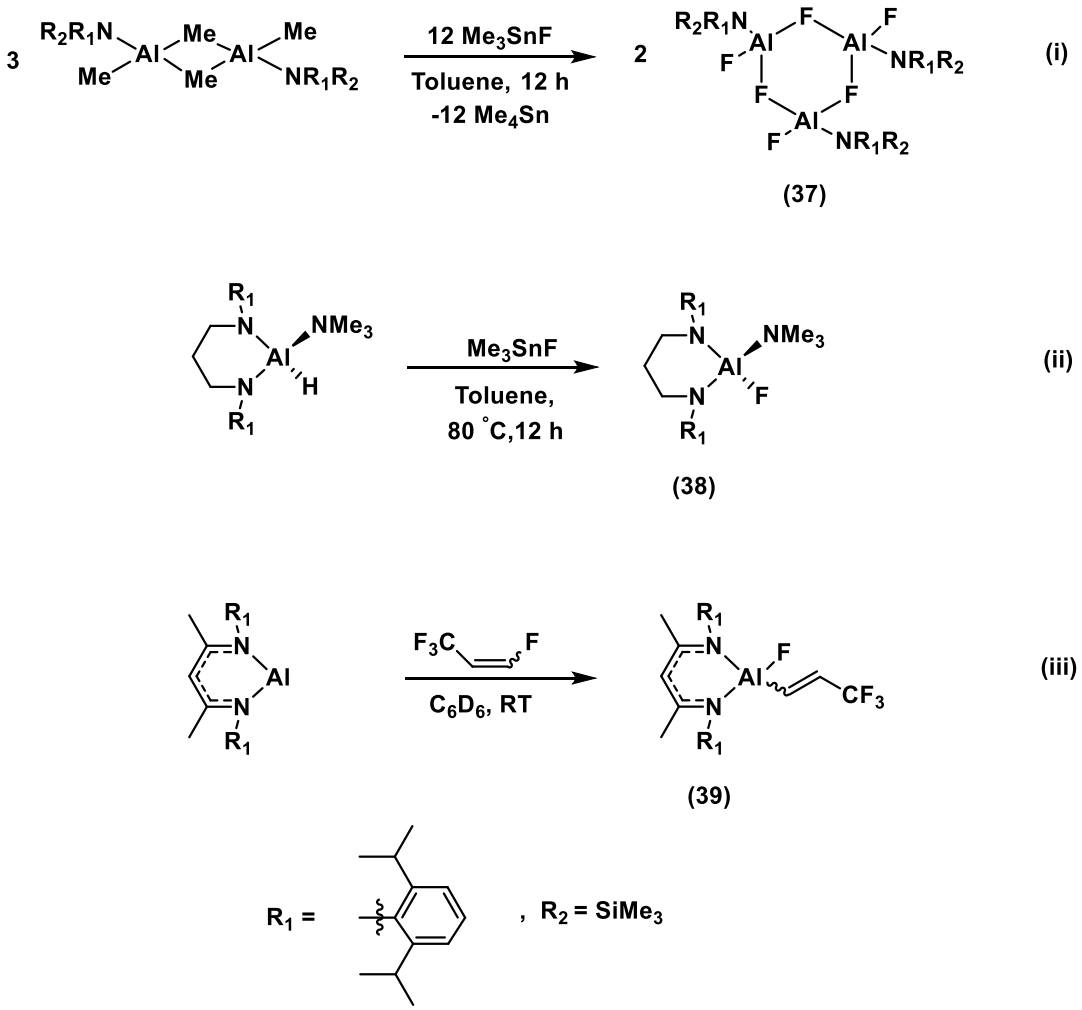
5.1.2. Organoaluminium fluorides

Organoaluminium fluorides can be synthesized by replacing one or two of the fluorine atoms in the AlF_3 by carbon, nitrogen, or oxygen atoms.[178] The presence of organyl groups in the organoaluminium fluorides makes them soluble in various organic solvents and lowers their melting point. Hence, they become accessible in the homogeneous reaction systems, and can show reactivity in solution. Organoaluminium fluorides such as dimethylaluminium fluoride $(Me_2AlF)_4$ were established as suitable precursors to access aluminium fluoride clusters.[179]

In 1957, Ziegler reported the synthesis of the first organoaluminium fluorides and their use as intermediates in the synthesis of trialkylalanes. Latter are used as catalysts in the oligopolymerization of olefins.[180][181][182] Roesky *et al*. have extensively described the synthesis, properties and applications of various organoaluminium fluorides in their reviews.[177-178, 183] The **Scheme 42, (i-ii)** depicts some examples of organoaluminium fluorides reported by Roesky *et al*. on the synthesis of organoaluminium fluorides such as aminoalane difluoride $[(2,6\text{-}i\text{Pr}_2C_6H_3)N(SiMe_3)Al(F)_2]$ (**37**) and diamidoaluminium fluoride $[(2,6\text{-}i\text{Pr}_2C_6H_3)N]_2(CH_2)_3AlF(NMe_3)$ (**38**) through fluorination of dimethyl alane or aluminium hydrides with trimethyltin fluoride (Me_3SnF).[184] Recently, Crimmin *et al*. reported on the synthesis of organoaluminium fluorides such as $[\{HC(CMeNAr)_2\}Al(F)_2]$ (Ar = 2,6-iPr$_2$C$_6$H$_3$) (**39**) *via* activation of the C–F bonds of fluoroalkenes by treating them with an Al(I) complex [**Scheme 42, (iii)**].[185]

5.1.2.1. Trimethyltin fluoride (Me_3SnF): A fluorinating reagent for synthesizing organoaluminium fluorides

In the solid state, Me_3SnF is reported to have a polymer-chain-like structure with bridging fluorine atoms and is insoluble in commonly used solvents.[186] Roesky *et al*. pioneered the use of Me_3SnF as a fluorinating reagent for synthesizing organometallic fluorides.[187] It has been reported that Me_3SnF can broadly be used in the synthesis of organoaluminium fluorides via chloride, hydride or methyl exchange reactions.[179, 184] Over the years, Me_3SnF has been used to prepare various inorganic and organometallic fluoride complexes of alkaline-earth metals, transition metals, lanthanide metals and main-group metals (**Scheme 42**).[178, 188]



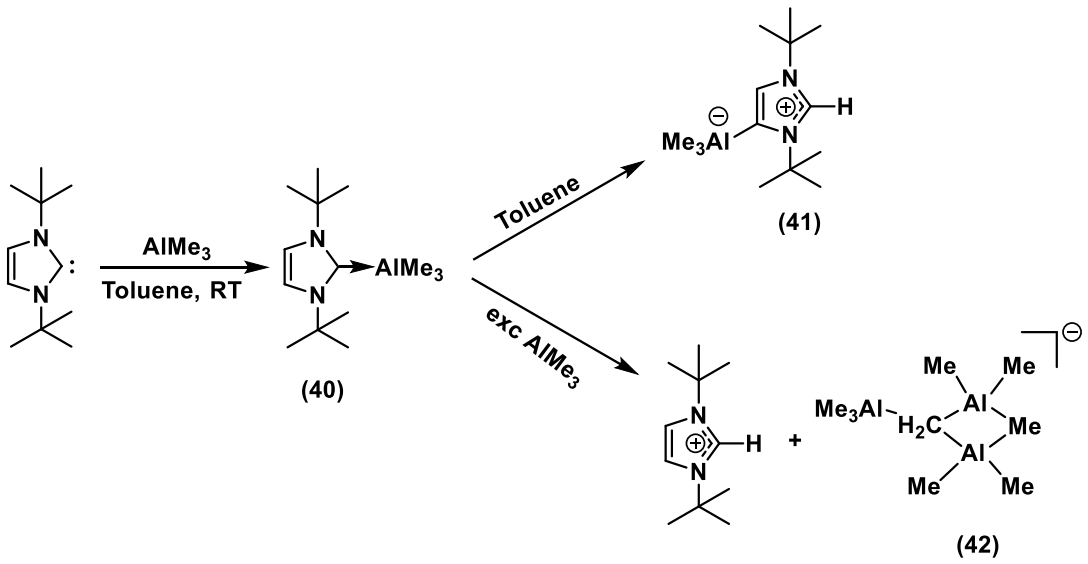
Scheme 42. Different approaches for the synthesis of organoaluminum fluorides *via* ; (i-ii) direct fluorination with Me_3SnF; (iii) C–F bond activation.[184-185]

5.1.2.2. AlF_3 complexes bearing neutral ligands

In *Chapter 2,* it has been mentioned that *N*-heterocyclic carbenes (NHCs) are widely used as ligands for stabilizing a wide range of metal complexes bearing unique and interesting properties. The availability of a sp^2 hybridized lone pair in the NHCs for donation into an empty orbital of metal centers makes NHCs suitable for synthesizing complexes of transition-metals and adducts with a large number of main-group elements.[125, 127] Transition metal complexes bearing NHCs ligands are widely used in homogeneous catalysis.[132c] Some examples of important organic transformations include Rh- and Pt-catalysed hydrosilylation, Pd-catalyzed cross-coupling reactions, Au-catalyzed double-bond activation, Ir- and Ru-catalyzed hydrogenation and Ru-catalyzed olefin metathesis.[189][190]

NHCs play an important role in the stabilization of highly unstable and reactive Lewis acidic group 13 molecular compounds in all of their possible oxidation states.[191] Several Lewis pairs comprising NHC-supported Al(III) complexes have been prepared for instance by the direct reaction of NHCs with AlX_3 (X= halide or alkyl/aryl).[192]

The stability of the (NHC)AlX_3 adducts depends on the sterics around the aluminum center. Dagorne *et al*. reported that when sterically bulky carbene 1,3-di-*tert*-butylimidazolin-2-ylidene (I*t*Bu) is treated with trimethyl aluminium ($AlMe_3$), the complex [(I*t*Bu)$AlMe_3$] (**40**) was obtained in the beginning which subsequently isomerized to the less sterically crowded "abnormal" NHC adduct [(I*t*Bu)$AlMe_3$] (**41**) in THF or toluene (**Scheme 43**). Also, in the presence of an excess of $AlMe_3$, complex **40** transforms into the trinuclear aluminate anion $Me_3Al(\mu^3\text{-}CH_2)(AlMe_2)_2(\mu^2\text{-}CH_3)^-$ (**42**) through the deprotonation of $AlMe_3$ (**Scheme 43**).[193] Sterically hindered Lewis acid/base pairs which are restricted toward the formation of usual Lewis acid/Lewis base adducts, are defined as "frustrated Lewis pairs" (FLPs).[194] The adduct **40** can be referred as a frustrated Lewis pair. The FLP combination between the sterically encumbered Lewis base I*t*Bu and the strong Lewis acid tris(pentafluoro)phenyl aluminium [$Al(C_6F_5)_3$] exhibits an interesting activity in polymerization reactions.[195] FLPs comprising NHC and tris(pentafluoro)phenyl borane [$B(C_6F_5)_3$] are widely used in the activation of small molecules such as hydrogen (H_2), carbon dioxide (CO_2), ammonia (NH_3) and alkynes.[195-196]



Scheme 43. Unusual reactivity of the sterically bulky adduct [(I*t*Bu)AlMe$_3$] (**40**).[193]

Among several synthesized NHC−aluminum(III) halide complexes, no report on the adducts of NHC and aluminum(III) fluoride could be found. The synthesis of molecular AlF_3 complexes bearing neutral ligands has been reported only rarely. In 1999, Kolis *et al.* reported the hydrothermal synthesis of aluminium fluoride amine complex [$AlF_3(NH_3)_2$] by treating aluminium nitride (AlN) and ammonium fluoride (NH_4F) in supercritical ammonia at 400 ˚C.[197] In a recent report, Reid *et al*. documented a 1,4,7-triazacyclononane(tacn)-stabilized AlF_3 complex solvated with water molecules, synthesized *via* fluorination of an analogous tacn-stabilized $AlCl_3$ complex with NMe_4F or KF.[198] Certainly, there is a lack of knowledge in the synthesis of organoaluminium fluorides bearing neutral ligands. In this chapter, the research is focused on finding different synthetic routes to synthesize NHC stabilized aluminium (III) fluorides. Furthermore, reactivity of NHC stabilized aluminium (III) fluorides has been investigated towards the halogen exchange reactions.

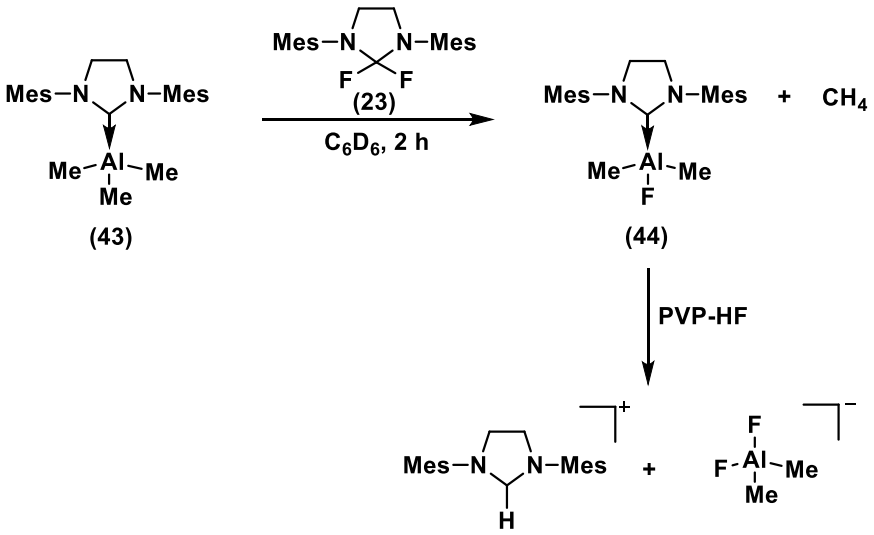
5.2. Results and Discussion

A two-step reaction was designed to obtain NHC stabilized aluminium (III) fluorides. The first step involved the synthesis of a SIMes-stabilized trimethyl aluminium (III) complex [(SIMes)$AlMe_3$] (**43**) by treating a solution of $AlMe_3$ with SIMes as reported by García *et al*.[192d] The second step involved the fluorination of [(SIMes)$AlMe_3$] either *via* direct fluorination with mild fluorinating reagents such as SIMes$(F)_2$ (**23**) and Me_3SnF or *via* activation of SF_4 and SF_6.[199]

5.2.1. Fluorination of [(SIMes)$AlMe_3$] with SIMes$(F)_2$

Addition of the complex [(SIMes)$AlMe_3$] (**43**) to SIMes$(F)_2$ (**23**) at room temperature generated a monofluorinated aluminium complex [(SIMes)Al(F)$(Me)_2$] (**44**) with a quite low conversion (**Scheme 44**). In the ^{19}F NMR spectrum, a broad signal was observed at δ = –169.9 ppm for the complex **44**. This ^{19}F NMR signal fits in the reported range of four-fold coordinated aluminium fluoride species such as for [{HC(CMeNAr)$_2$}Al$(F)_2$] (Ar = 2,6-$^{i}Pr_2C_6H_3$).[178, 185] For the methyl groups attached to the Al center in the complex **44**, a doublet at δ = –1.09 ppm with a coupling constant of $^3J_{HF}$ = 3.2 Hz was observed in the ^1H NMR spectrum (**Figure 25**). This coupling constant is in good agreement with the range of $^3J_{HF}$ values reported for other organofluoroaluminates.[200]

Along with the complex **44**, presence of methane was also observed in the ^1H NMR spectrum at δ = 0.16 ppm, which suggests that reaction mixture contains HF.[201] The latter might react with the complex **43** to give CH_4. When the reaction was carried out in the presence of CsF, the formation of aluminium fluoride was not observed, possibly because HF was trapped by CsF. Also when **23** was treated with a solution of $AlMe_3$, protonated SIMes and a mixture of fluoroaluminates were formed. These observations are indicative towards the role of HF in the fluorination of complex **43**. The generation of HF can be speculated from the reaction of SIMes$(F)_2$ (**23**) with adventitious water present in the reaction system. However, reaction of the complex **43** with a HF source such as poly[4-vinylpyridinium poly(hydrogen fluoride)] (PVP-HF) generated protonated SIMes and tetrafluoroaluminate $[AlF_4]^-$.[151b, 178] Treatment of the complex **44** with PVP-HF also produced protonated carbene and difluorodimethylaluminate $[AlMe_2F_2]^-$ (**Scheme 44**).[202]



Scheme 44. Fluorination of the complex [(SIMes)AlMe$_3$] (**43**) with SIMes(F)$_2$ (**23**).

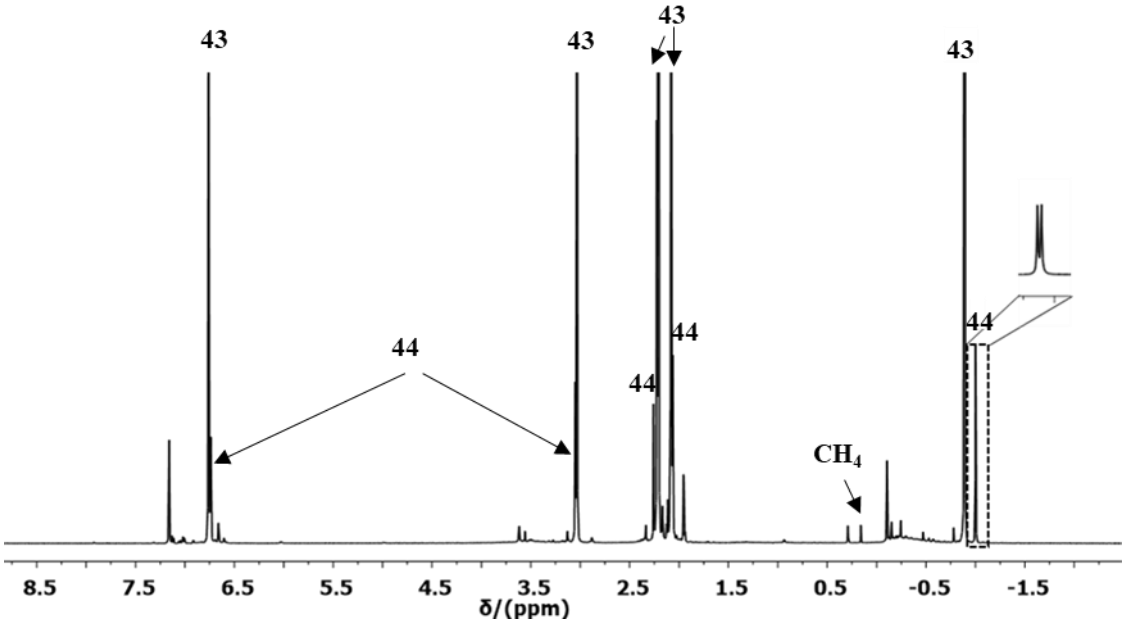


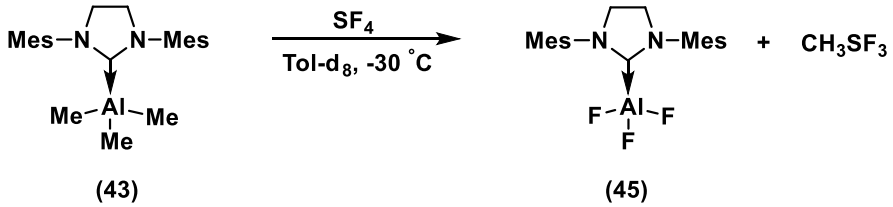
Figure 25. ^{1}H NMR (300.1 MHz, C_6D_6) spectrum of fluorination of the complex **43** with SIMes(F)$_2$ giving complex **44** at δ = –1.09 ppm. **43** = [(SIMes)AlMe$_3$], **44** = [(SIMes)Al(F)(Me)$_2$] .

A reliable reaction pathway for the synthesis of SIMes-stabilized aluminium (III) fluoride complexes could not be established by using SIMes(F)$_2$ for the fluorination of complex

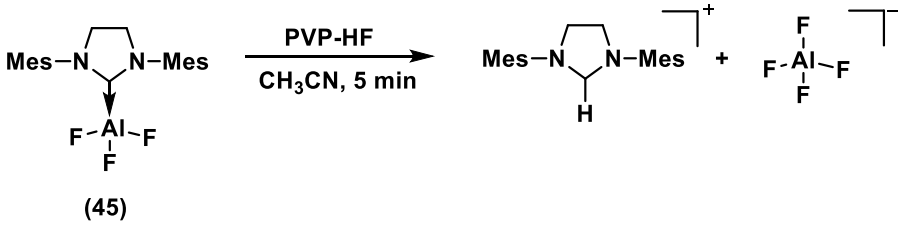
43. It has been discussed in the *Chapter 4* that SIMes(F)$_2$ is obtained as a product of the degradation of SF_4 and SF_6 with SIMes. Analogously, [(SIMes)AlMe$_3$] (**43**) was treated with SF_4 and SF_6 to investigate if it could also activate these gases to produce organoaluminium fluorides.

5.2.2. Fluorination of [(SIMes)AlMe$_3$] with SF_4

Studies were initiated by treating a solution of complex [(SIMes)AlMe$_3$] (**43,** 0.05 mmol) with SF_4 (0.10 mmol) in tol-d$_8$. In contrast to the formation of [(SIMes)Al(F)(Me)$_2$] as in the case of SIMes(F)$_2$ (**23**), the reaction of SF_4 with **43** produced the aluminium trifluorido complex [(SIMes)Al(F)$_3$] (**45**). The reaction was carried out at a low temperature (–70 °C) and warmed up until room temperature. A complete fluorination of **43** along with the generation of considerable amounts of CH_3SF_3 were observed at –30 °C when monitored by NMR spectroscopy **(Scheme 45)**. Since no methyl group attached to the aluminium center was identified in the ^{1}H NMR spectrum, the broad resonance at δ = –164.5 ppm in the ^{19}F NMR spectrum was attributed therefore to the fully fluorinated aluminium complex **45** (**Figure 26**). The ^{27}Al NMR spectrum showed a signal for the complex **45** at δ = 49.8 ppm which is consistent with the typical range for four-fold coordinated aluminium fluoride species.[178, 185] For CH_3SF_3, two signals at δ = –50.6 ppm and 60.9 ppm were observed in the ^{19}F NMR spectrum, which are in accordance to the literature.[203] When the reaction mixture of complex **45** and CH_3SF_3 was warmed up from -30 °C to room temperature, decomposition of the complex **45** was observed yielding protonated SIMes and tetrafluoroaluminate $[AlF_4]^-$.[178] This suggests the presence of HF in the reaction mixture, which could react with complex **45** to yield a salt of imidazolinium ion and $[AlF_4]^-$. Independent treatment of the complex the **45** with PVP-HF also gave the protonated SIMes and $[AlF_4]^-$ (**Scheme 46**).[151b]



Scheme 45. Formation of [(SIMes)Al(F)$_3$] (**45**) *via* reaction of **43** with SF_4.



Scheme 46. Addition of PVP-HF to the complex [(SIMes)Al(F)$_3$](**45**).

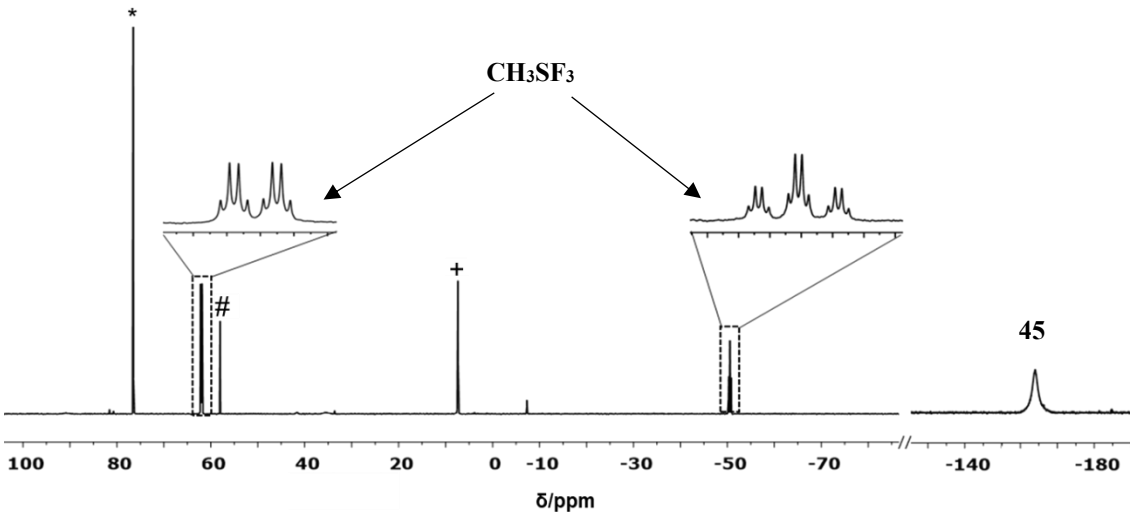


Figure 26. ^{19}F NMR (282.4 MHz, Tol-d$_8$, –30 °C) spectrum for the formation of complex **45** at δ = –164.5 ppm and CH_3SF_3 at δ = –50.6 ppm and 60.9 ppm. $^{*}SOF_2$ (impurity from SF_4), $^{\#}SF_6$, $^{+}CH_3SOF$.

5.2.3. Fluorination of [(SIMes)AlMe$_3$] with SF$_6$

Activation of the SF_6 with metals is discussed in details in the *Section 2.2.6*. Here, the reactivity of **43** towards SF_6 was investigated with the aim of obtaining SIMes-stabilized aluminium fluorides *via* S–F bond activation. Formation of the monofluorinated complex [(SIMes)Al(F)(Me)$_2$] (**44**) with a low yield (30 %) was observed upon treatment of the complex [(SIMes)AlMe$_3$] (**43,** 0.05 mmol) with SF_6 (0.10 mmol) at 70 °C for 15 h. The reaction mixture was heated for longer time to obtain better yields of **44**, but the reaction did not proceed further. Treatment of the complex **43** with SF_6 under UV radiation at 311 nm for 24 h produced [(SIMes)Al(F)(Me)$_2$] (**44**) and subsequently complex [(SIMes)Al(F)$_3$] (**45**) was formed. ^{1}H NMR spectroscopy indicated the evolution of methane (CH_4) in addition.

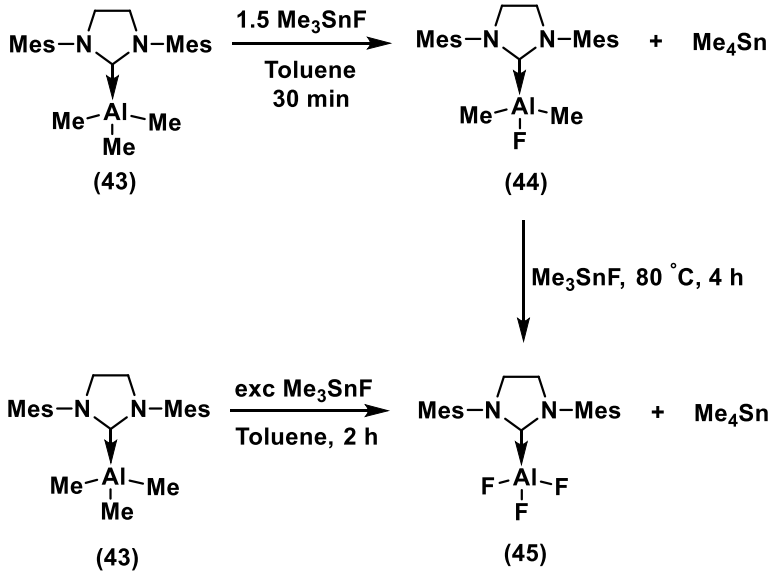
It can be speculated that the decomposition of the complex **43** took place when it was treated with SF_6 at 70 °C yielding free SIMes. The latter in turn could react with SF_6 at 70 °C within 48 h to give a SIMes(F)$_2$ (**23**) derivative in very low yield. Fluorination of the complex **43** might have taken place according to a pathway proposed in the *Section 5.2.1*.

5.2.4 Fluorination of [(SIMes)AlMe$_3$] (43) with Me$_3$SnF

Due to the involvement of HF in the above mentioned methods of fluorination, a more reliable synthetic route was employed to obtain the complexes **44** and **45** by using Me_3SnF as a fluorinating agent.

Treatment of the complex **43** with 1.5 equivalents of Me_3SnF led to the formation of the complex **44** with full conversion of complex **43**. A signal was obtained in the ^{27}Al NMR at δ = 81.9 ppm , which was assigned to the complex **44**. Tetramethyltin (Me_4Sn) was also observed in addition, identified in the ^{1}H NMR spectrum as a signal at δ = 0.05 ppm, in the ^{13}C{^{1}H} NMR spectrum at δ = –9.4 ppm and in the ^{119}Sn NMR spectrum at δ = 0.00 ppm.[204] Reaction of the complex **43** with 3 equivalents of Me_3SnF gave a mixture of complexes **44** and **45** in a ratio of 0.5:1 respectively after 2 h at room temperature. When this mixture was heated at 80 °C for 4 h, ^{1}H and ^{19}F NMR spectra reveal that the complex

44 got converted into the complex **45** (**Figure 27**). The reaction of the complex **43** with an excess of Me_3SnF for 2 h yielded complex **45**, as shown in the **Scheme 47.**



Scheme 47. Synthesis of the SIMes-stabilized aluminium (III) fluorides with Me_3SnF.

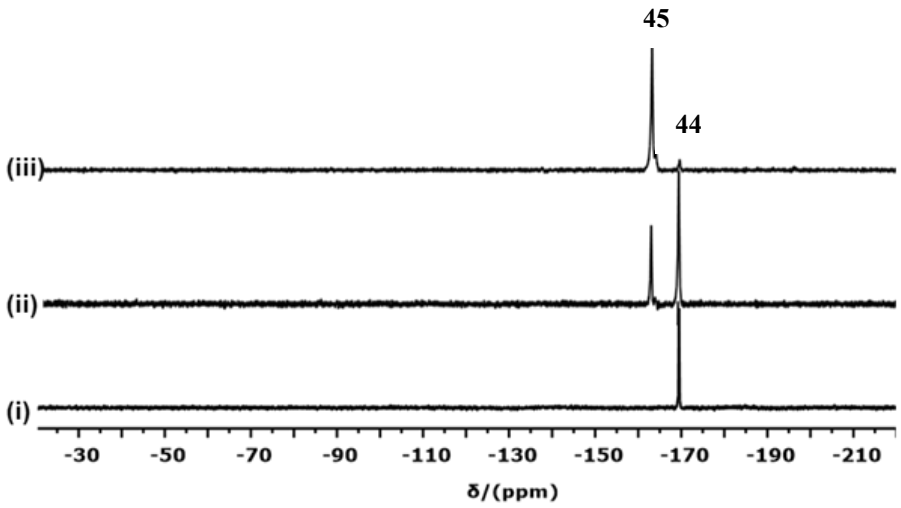
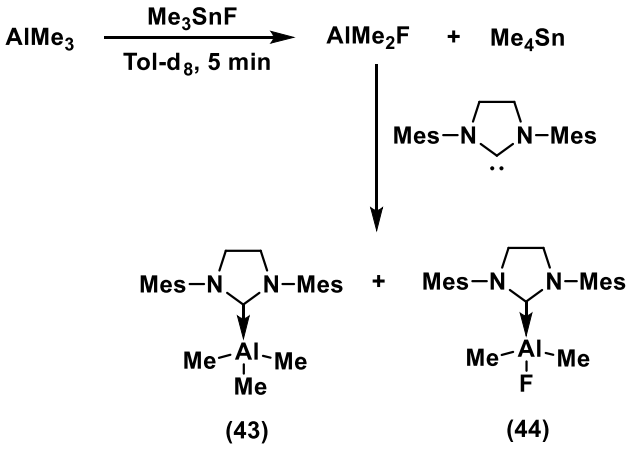


Figure 27. ^{19}F NMR (282.4 MHz, Tol-d_8) spectrum of the reaction of complex **43** with 3 equivalents of Me_3SnF (i) after 30 min, (ii) after 2 h, (iii) after heating the mixture of complex **44** at δ = –169.9 ppm and complex **45** at δ = –164.8 ppm at 80 °C for 4 h.

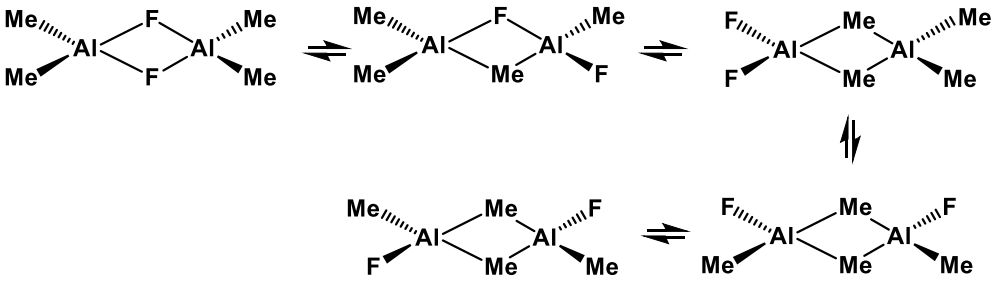
5.2.5 Alternative routes for the synthesis of NHC-stabilized aluminium (III) fluorides

In this section an alternative approach was investigated to synthesize the SIMes-bearing aluminium (III) fluorides. At first $AlMe_3$ was treated with various fluorinating reagents such as Me_3SnF, SF_4 and SF_6 to synthesize aluminium fluoride, followed by the addition of free carbene.

a) Me_3SnF: Treatment of a solution of $AlMe_3$ in toluene with Me_3SnF resulted in the formation of $AlMe_2F$, which is described in the literature to exist as a dynamic mixture of dimers (**Scheme 48 & 49**).[205] The ^{19}F NMR spectrum shows four signals at δ = –143.6 ppm, –145.8 ppm, –148.9 ppm and –150.8 ppm. These values were found to be in a good accordance with the data reported for the $AlMe_2F$ by Oliva *et al*.[206] The $^{1}H\{^{19}F\}$ NMR spectrum measured for the compound $AlMe_2F$ shows resonances at δ = –0.43 ppm, –0.55 ppm, –0.63 ppm and –0.69 ppm, but not with equal intensities, as reported.[205-206] It can be assumed that binuclear Al compounds containing only one fluorine atom (Al_2Me_5F) were also present and their corresponding NMR resonances might overlap with the reported signals of the dimers of $AlMe_2F$, therefore former couldn't be identified. When SIMes was added to this reaction mixture, formation of complexes **43** and **44** was observed (**Scheme 48**). These observations support the proposed structure of the complex **44**. There was no evidence for the formation of SIMes stabilized aluminium (III) bifluorido complex [(SIMes)Al(F)$_2$(Me)].

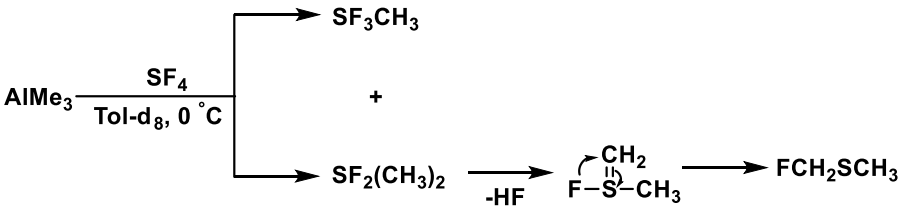


Scheme 48. An alternative route for the synthesis of the complex **44**.



Scheme 49. Dynamic equilibrium between different dimers of $AlMe_2F$.

b) SF_4: Treatment of a solution of $AlMe_3$ (0.05mmol) in toluene with SF_4 (0.10 mmol) at 0 °C yielded a mixture of SF_3CH_3 and FCH_2SCH_3 in solution. Furthermore, a white solid precipitated in the reaction mixture which presumably can be considered as AlF_3. The ^{19}F NMR spectrum reveals resonances for SF_3CH_3 which are in accordance to the signals observed in the case of fluorination of the complex **43** with SF_4 (see *Section 5.2.2*). FCH_2SCH_3 was identified in the ^{19}F NMR spectrum at δ = –188.1 ppm as a quartet of triplets having coupling constants $^2J_{FH}$ = 53.9 Hz and $^4J_{FH}$ = 2.4 Hz. In the ^1H NMR spectrum, FCH_2SCH_3 displays two doublets at δ = 4.83 ppm with a coupling constant of $^2J_{HF}$ =53.9 Hz and at δ = 1.69 ppm with a coupling constant of $^4J_{HF}$ = 2.4 Hz (**Figure 28**). The formation of FCH_2SCH_3 can be postulated as originating from the transfer of two methyl groups from $AlMe_3$ to SF_4 yielding $SF_2(CH_3)_2$ followed by a fast loss of HF to give CH_2=$SFCH_3$. Then the latter would undergo fluorine migration to give finally FCH_2SCH_3 (**Scheme 50**).



Scheme 50. Proposed reaction pathway for the reaction between $AlMe_3$ and SF_4.

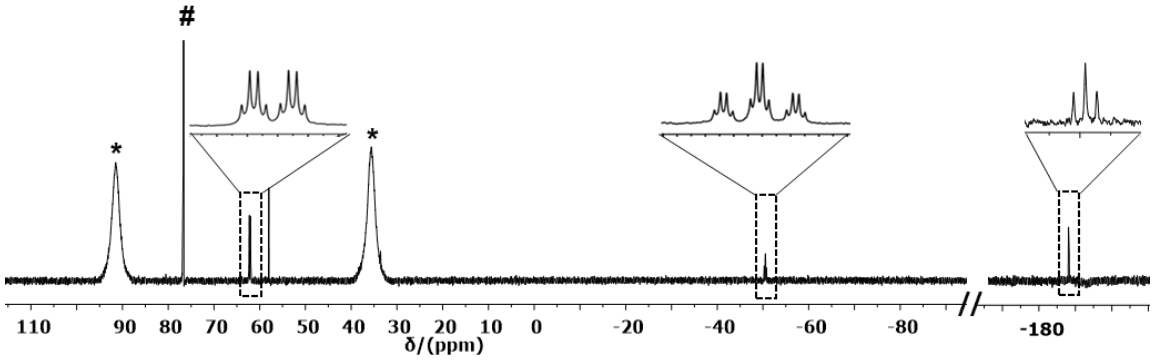
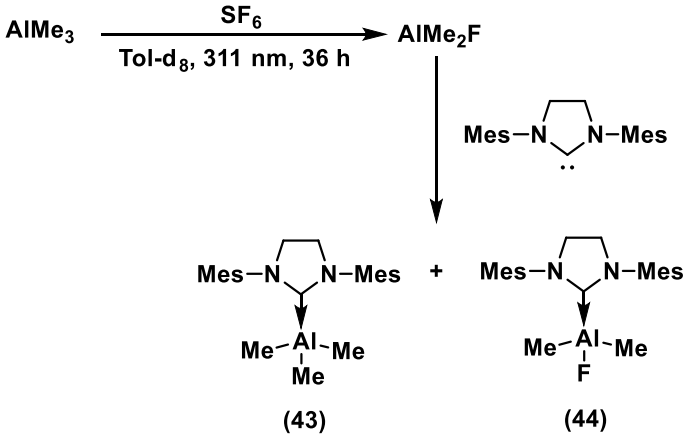


Figure 28. ^{19}F NMR (282.4 MHz, Tol-d_8, 0 °C) spectrum for the formation of CH_3SF_3 at δ = –50.6 ppm and 60.9 ppm and FCH_2SCH_3 at δ = –188.1 ppm. $^{*}SF_4$, $^{\#}SF_6$

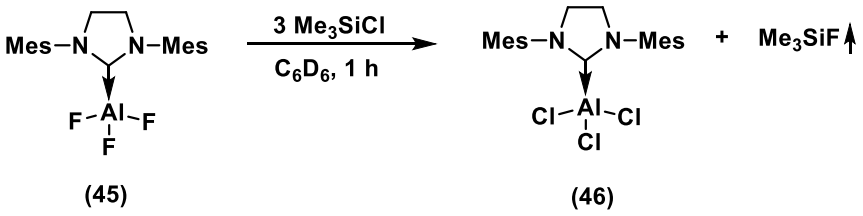
c) SF_6: It has been reported that $AlMe_3$ can activate SF_6 through laser powered homogeneous pyrolysis to generate $AlMe_2F$ vapors.[207] The activation of SF_6 was attempted in this thesis with a solution of $AlMe_3$. No activation was observed when a solution of $AlMe_3$ (0.05 mmol) and SF_6 (0.10 mmol) in toluene was heated at 70 °C. The formation of $AlMe_2F$ was observed when this solution was subjected to UV light at 311 nm for 36 h. Subsequent addition of the SIMes (0.05 mmol) to this reaction mixture at room temperature gave the mixture of complexes **43** and **44** (**Scheme 51**).



Scheme 51. Reaction between $AlMe_3$ and SF_6.

5.2.6. Reactivity of the NHC-stabilized aluminium (III) fluorides towards halogen exchange reactions

There are many examples reported where metal chloride complexes can be obtained from the reaction of metal fluoride complexes *via* F/Cl exchange reaction with chlorosilanes.[208] The reaction of complex [(SIMes)Al(F)$_3$] with trimethylchlorosilane (Me_3SiCl) indeed generated the chlorido complex [(SIMes)Al(Cl)$_3$] (**46**) along with trimethylfluorosilane (Me_3SiF) (**Scheme 52**). A signal at δ = 104.7 ppm in the ^{27}Al NMR spectrum was assigned to the complex **46**, since it coincides with the signal obtained for the complex [(SIMes)Al(Cl)$_3$] synthesized independently by following a reported procedure.[209] Me_3SiF showed signals at δ = –156.9 ppm in the ^{19}F{^{1}H} NMR and at δ = 30.3 ppm in the ^{29}Si NMR spectrum. The formation of SIMes stabilized aluminium trichloride complex **46** can be established as an indirect proof for the identity of the complex [(SIMes)Al(F)$_3$] (**45)**.

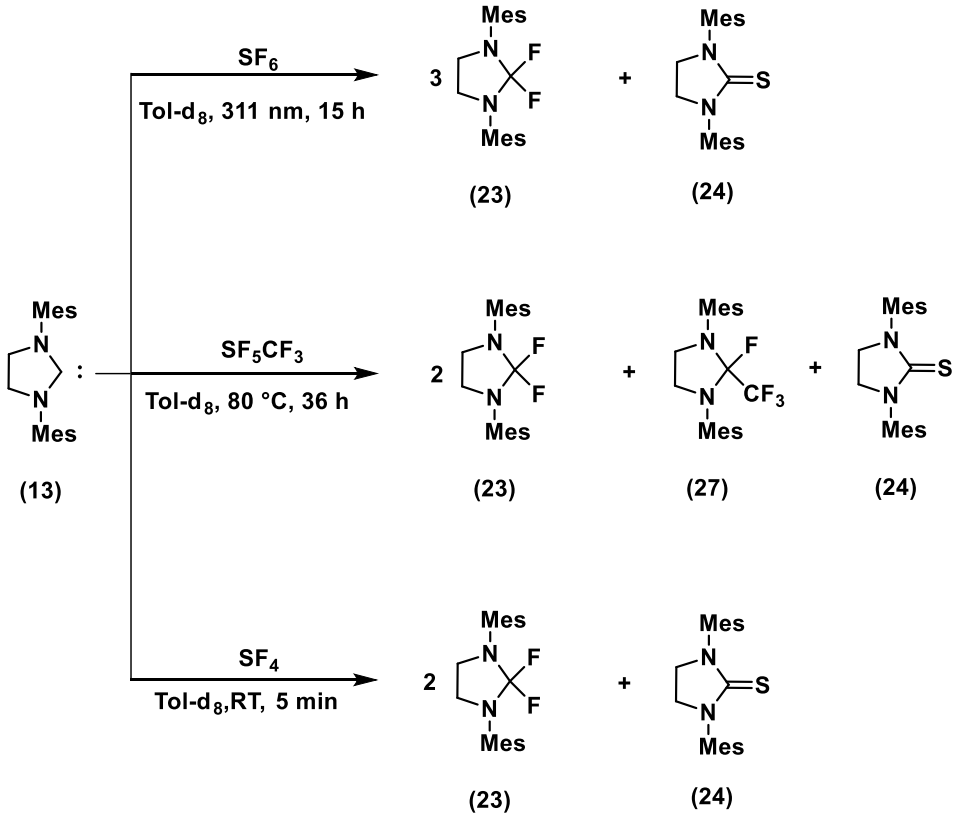


(45) (46)

Scheme 52. Conversion of the complex **45** into **46** *via* F/Cl exchange reaction.

6. Summary

The incorporation of fluorine into compounds plays a pivot role in everyday life. Thus, development of new methods for the introduction of fluorine atoms into organic or inorganic molecules is of enormous academic and industrial interest. This thesis deals with the development of new fluorinating reagents for synthesizing organic fluorine building blocks and organometal fluorides by activating or reducing the greenhouse gases SF_6 and SF_5CF_3 in a metal-free approach. A complete degradation of SF_6 and SF_5CF_3 into non-volatile, well-defined products was achieved through S−F and S−C bond activation reactions with *N*-heterocyclic carbenes (NHCs) (**Scheme 53**).

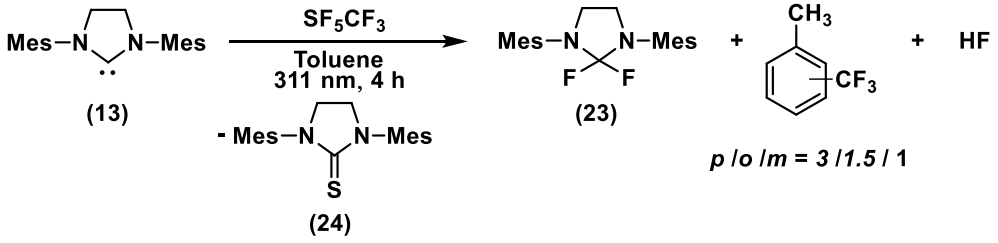


Scheme 53. Reduction of SF_6, SF_5CF_3 and SF_4 with SIMes.

Scheme 53 shows a successful reduction of the SF_6 into 1,3-dimesityl-2,2-difluoroimidazolidine ($SIMes(F)_2$, **23**) and 1,3-dimesitylimidazolidine-2-sulfide (**24**)

when treated with SIMes (**13**) under UV radiation at 311nm. Activation of SF_6 was achieved also with other sterically and electronically different NHCs such as SIPr, IMes and IPr. SIMes was found most reducing among all the NHCs as indicated by the estimated redox potential of -2.2 V *vs*. SCE in the excited state and a maximum yield of the difluoro-imidazole derivative obtained from the reaction with SF_6.

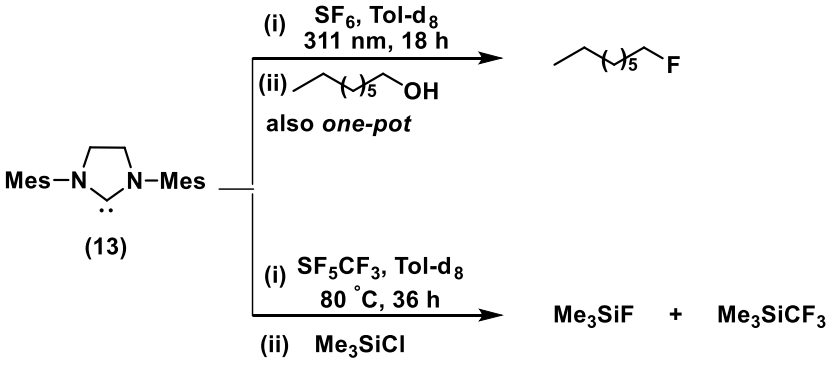
Activation of the SF_5CF_3 was achieved by treatment with SIMes at 80 °C, furnishing $SIMes(F)_2$, 1,3-dimesityl-2-fluoro-2- trifluoromethylimidazolidine [$SIMes(F)(CF_3)$] (**27**) and **24** (**Scheme 53**). Among other NHCs (SIMes, SIPr, IMes and IPr), the best reactivity was observed for SIMes. Reduction of SF_5CF_3 was attained from the ground state of the NHCs and irradiation was not required for the activation. Photochemical activation of SF_5CF_3 with SIMes (**13**) using UV radiation at 311 nm showed an unprecedented reactivity of trifluoromethylation of the solvent (toluene) in addition to the formation of $SIMes(F)_2$ (**23**) (**Scheme 54**). Irradiation (311 nm) of the product mixture obtained from the thermal activation of the SF_5CF_3 also showed -CF_3 group transfer to the arenes which suggest that [$(SIMes(F)(CF_3)]$ (**27**) is behaving as a trifluoromethylation reagent.



Scheme 54. Photochemical activation of SF_5CF_3 with SIMes.

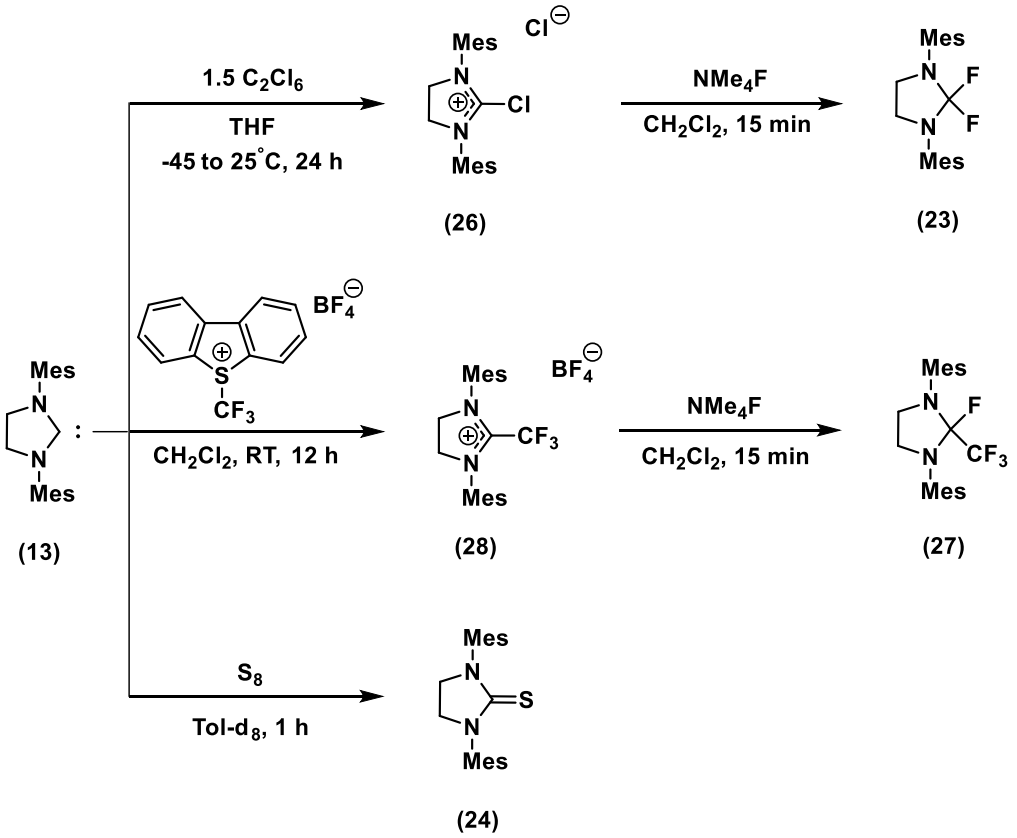
Mechanistically, the activation of SF_6 and SF_5CF_3 with NHCs is proposed to occur *via* single electron transfer pathways. Intermediates such as SF_5 anion (SF_5^-) or SF_5 radical ($SF_5^{\bullet}$) are proposed to be generated from the activation. It is well known that SF_5^- is a very reactive intermediate and readily decomposed to give SF_4. An independent reaction between SF_4 and SIMes yielded SIMes$(F)_2$ (**23**) and **24**, confirming the generation of SF_4 in the reaction sequence of the reduction of SF_6 and SF_5CF_3 (**Scheme 53**).

Treatment of the product mixture obtained from the activation of SF_6, with 1-octanol yielded 1-fluorooctane. Thus, fluorides can be shuttled from SF_6 to the 1-octanol by NHC mediation in an one-pot process (**Scheme 55**). Also, an addition of Me_3SiCl to the product mixture generated from the reaction between SIMes and SF_5CF_3, furnished Me_3SiF and Me_3SiCF_3 (**Scheme 55**). Me_3SiCF_3 is commonly known as the Ruppert-Prakash reagent. The reactivity pattern of the product mixture obtained from the reduction of SF_6 and SF_5CF_3 with SIMes also confirms the identity of **23** and **27** and indicates its principle applicability as a source for a deoxyfluorination reagent or for CF_3^- building block respectively.



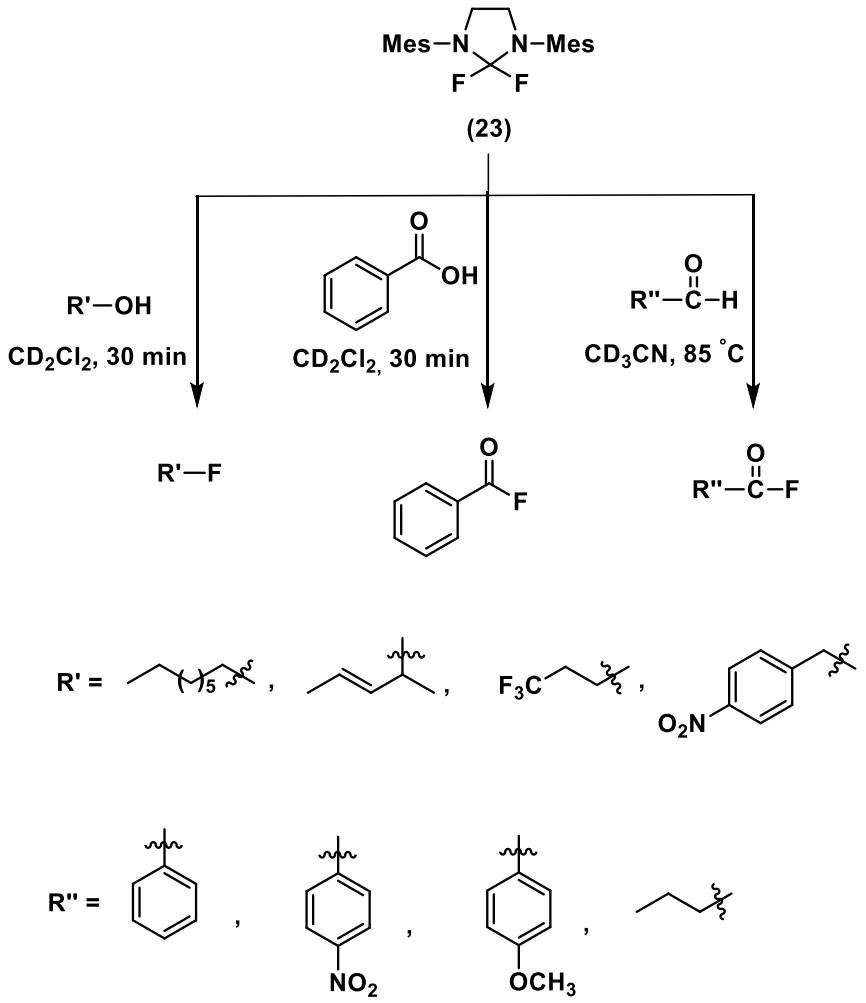
Scheme 55. Fluorination with the product mixture obtained from the activation of SF_6 and SF_5CF_3 with SIMes.

SIMes(F)$_2$ (**23**), **24** and [SIMes(F)(CF$_3$)] (**27**) were synthesized independently starting from the SIMes to prove their identity (**Scheme 56**).



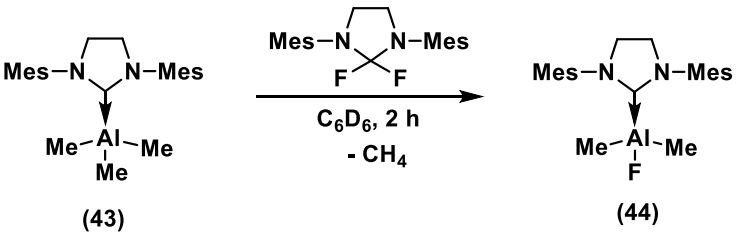
Scheme 56. Independent synthesis of compounds **23**, **24** and **27**.

The independently synthesized SIMes(F)$_2$ (**23**) was successfully implemented into the fluorination reactions. Various alcohols and benzoic acid were converted into their corresponding fluorinated products *via* deoxyfluorination reactions. Usually, the direct fluorination of aldehydes to acyl fluorides involves either harsh reaction conditions, lower yields or long time durations. Usage of the SIMes(F)$_2$ enabled the fluorination of aldehydes *via* aldehydic C(sp^2)–H bond activation to furnish acyl fluorides in a mild and convenient way (**Scheme 57**). SIMes(F)$_2$ shows versatile reactivity for the deoxyfluorination and acyl fluorination as it can tolerate various aliphatic, allylic and aromatic functional groups.



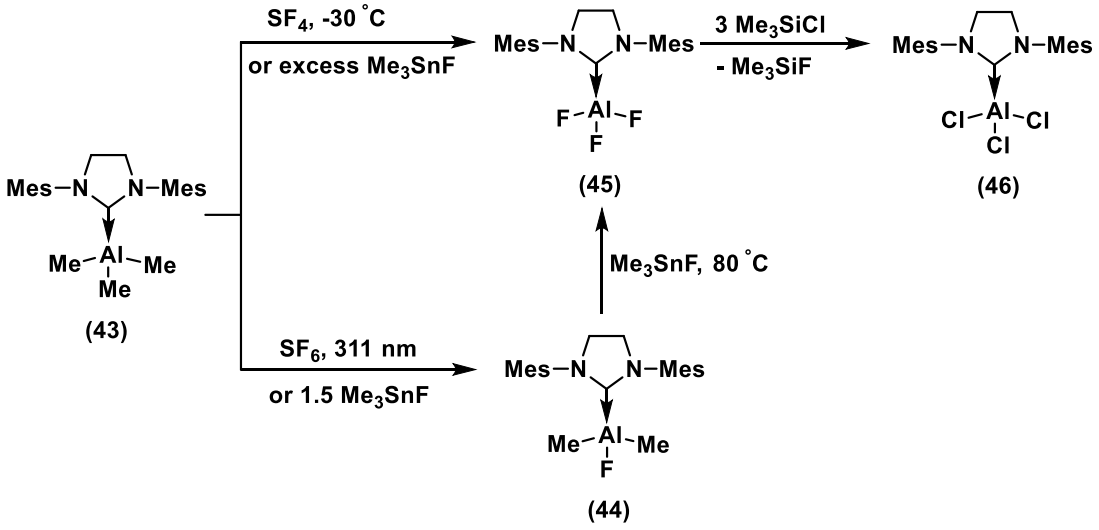
Scheme 57. Fluorination of alcohols, benzoic acid and aldehydes with $SIMes(F)_2$ (**23**).

Furthermore, $SIMes(F)_2$ (**23**) can be used as a fluoride source in the synthesis of the organoaluminium fluoride $[(SIMes)Al(F)(Me)_2]$ (**44**) (**Scheme 58**). This shows that **23** can not only be used for the synthesis of fluorinated organic building blocks, but also for the synthesis of metal fluorides in homogeneous reaction systems.



Scheme 58. Synthesis of the organoaluminium fluoride [(SIMes)Al(F)(Me)$_2$] (**44**).

SIMes(F)$_2$ is obtained as a product of the degradation of SF_4 and SF_6 with SIMes. However, [(SIMes)AlMe$_3$] (**43**) was also treated with SF_4 and SF_6 to synthesize organoaluminium fluorides. [(SIMes)Al(F)$_3$] (**45**) was obtained from a reaction of SF_4 with the complex **43** at -30 °C. The photochemical reaction between complex **43** and SF_6 yielded [(SIMes)Al(F)(Me)$_2$] (**44**). Synthesis of the complexes **44** and **45** through the activation of SF_4 and SF_6 involved the formation of HF which gradually leads to the decomposition of theses complexes. A more reliable synthetic route was used to obtain the complexes **44** and **45** by using Me_3SnF as a fluorinating agent. The addition of Me_3SnF to complex **44** and heating this reaction mixture at 80 °C for 4 h, converted the complex **44** into complex **45**. [(SIMes)Al(F)$_3$] (**45**) was successfully employed for the F/Cl exchange reaction by treating it with Me_3SiCl, affording the chlorido complex [(SIMes)Al(Cl)$_3$] (**46**) (**Scheme 59**).



Scheme 59. Fluorination of the [(SIMes)AlMe$_3$] (**43**) with SF_4, SF_6 and Me_3SnF.

Overall, a complete degradation of sulfur fluorides SF_6, SF_5CF_3 and SF_4 was achieved with *N*-heterocyclic carbenes (NHCs) to afford the fluorination and trifluoromethylation reagents; SIMes(F)$_2$ and [SIMes(F)(CF_3)]. The NHC stabilized Al(III) fluorides were synthesized by fluorinating the complex [(SIMes)AlMe$_3$] with the fluorinating agents SIMes(F)$_2$, SF_4, SF_6 or Me_3SnF.

7. Experimental

7.1. General working techniques

All of the compounds presented below were synthesized and handled with the exclusion of air and moisture. Unless otherwise described, all reactions were carried out in pre-heated, argon-filled glass apparatus using the standard *Schlenk* -technique or in an argon-filled glove box. All substances sensitive to air and hydrolysis were weighed or stored in an *MBraun Lab Master 130* glovebox under an argon atmosphere. Toluene, tetrahydrofuran (THF), hexane, C_6D_6 and toluene-d_8 (Tol-d_8) were dried using Solvona®. Dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), dichloromethane-d_2 (CD_2Cl_2), acetonitrile-d_3 (CD_3CN) were dried using calcium hydride. After drying, all solvents were distilled, degassed three times using "freeze-pump-thaw" and then stored under argon over molecular sieves (3 Å). All commercially bought solid compounds were dried overnight in vacuum prior to use. Commercially purchased liquid compounds or reagents were stored over molecular sieves (3 Å) for two nights prior to use. Trimethylaluminium (2M in Toluene) and trimethylchloro- silane were purchased from the Sigma-Aldrich and used without further drying or purification.

SF_6 was obtained as a gift from the Solvay Fluor GmbH, SF_4 and SF_5CF_3 were purchased from the abcr GmbH. Reactions with SF_6, SF_4 and SF_5CF_3 were carried out on a *Swagelok* stainless steel line under argon atmosphere. The mass of these gases were determined by condensing them into a dried and weighed Young-NMR tube.

The UV irradiation experiments were carried out in a photo multirays reactor (Helios Italquartz) equipped with ten light sources (each 15 W) with an emission maximum at 311 nm.

7.2. Instrumentation

7.2.1. Nuclear Magnetic Resonance (NMR) spectroscopy

Unless otherwise stated, the NMR spectra were recorded at room temperature on a *Bruker AV III 300* or *Bruker DPX 300* spectrometer. The chemical shifts in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were calibrated to the residual solvent signal of the deuterated solvents. The ^{1}H NMR spectra were referenced as C_6D_5H: δ = 7.16 ppm; toluene-d_7: δ = 6.97 ppm; $CHDCl_2$: δ = 5.32 ppm; CHD_2CN: δ = 1.94 ppm. The $^{13}C\{^{1}H\}$ NMR spectra were referenced as C_6D_6: δ = 128.06 ppm; toluene-d_8: δ = 20.43 ppm; CD_2Cl_2: δ = 53.84 ppm; CD_3CN: δ = 1.32 ppm The ^{19}F NMR spectra were referenced externally to $CFCl_3$ at δ = 0.0 ppm. ^{27}Al NMR spectra were referenced externally to $AlCl_3$ in D_2O at δ = 0.00 ppm. ^{29}Si NMR spectra were referenced externally to TMS at δ = 0.0 ppm. For quantification 1,2-difluorobenzene at δ = –138.1 ppm in the ^{19}F NMR spectra was used as an external standard. The acquisition, procession and evaluation of all spectra recorded was carried out with the TopSpin or MestreNova software.

7.2.2. Mass spectrometry

Gas chromatography- mass spectrometry: GC–MS measurements were conducted using an Agilent 6890N gas chromatograph with a capillary column (Agilent 19091S-433 Hewlett-Packard 5 MS: 30 m length, 0.25 mm inside diameter, 0.25 μm film thickness) and an Agilent 5973 Network mass selective detector. Helium (0.74 bar, 1.2 mL / min, 40 cm / s) was used as the carrier gas. The electron impact ionization was carried out with an ionization voltage of 70 eV.

Liquid Injection Field Desorption Ionization-Mass Spectrometry (LIFDI-MS): Mass spectra were recorded on a Micromass Q-Tof-2 instrument which was equipped with a Linden LIFDI source (Linden CMS GmbH).

7.2.3. Cyclic voltammetry

A potentiostat/galvanostat Reference 600 from Gamry Instruments was used for the voltammetry experiments. Cyclic Voltammograms (CVs) were measured in THF containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) and 1mM of the carbene under an argon atmosphere at room temperature. A conventional one-compartment three electrode cell was equipped with glassy carbon disk as working electrode, a platinum wire as counter electrode, and Ag/Ag^+ wire in (0.1 M TBAP + 0.01 M $AgNO_3$ in acetonitrile) used as a reference electrode. CVs were recorded at scan rates of 200 mV s^{-1}. All data were referenced to the $Fc^{0/}Fc^+$ couple at a redox potential $E_{1/2}$ = +0.242 V in THF.

7.2.4. Ultraviolet-visible spectroscopy

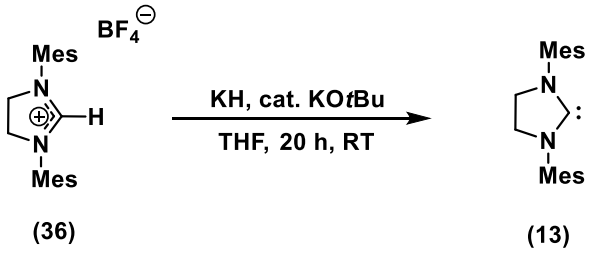
UV-vis spectra were recorded at room temperature under argon atmosphere by an Agilent 8453 diode array spectrometer connected with a cryostat from Unisoku Scientific Instruments, Japan using 10mm quartz cuvette.

7.2.5. Emission spectroscopy

Emission spectra were recorded with a FluoroMax-4P from Horiba Jobin Yvon in 10 mm quartz cuvettes at room temperature. The solution of the carbenes in THF (1mM) were scanned at a fixed emission wavelength of 350 nm and the excitation wavelength was chosen where maximum absorbance was observed for the different carbenes.

7.3. Procedures

7.3.1. Synthesis of 1,3-dimesitylimidazolin-2-ylidene (SIMes, 13)



(36) (13)

1,3-dimesitylimidazolidin-2-ylidene (SIMes, **13**) was synthesized by following the procedure mentioned in the literature.[210] To a suspension of 1,3-dimesityl-4,5-dihydroimidazolinium tetrafluoroborate (**36**, 394 mg, 1.0 mmol) in THF (6 mL) were added KH (80.2 mg, 2.0 mmol) and KO*t*Bu (21.1 mg, 0.2 mmol) . The resulting suspension was stirred at room temperature for 20 h. H_2 gas produced during the reaction was allowed to escape through a bubbler. The reaction mixture was then filtered, and the volatiles were removed *in vacuo*. The residue was re-dissolved in a mixture of toluene (1 mL) and hexane (5 mL), and the resulting solution was filtered. The filtrate was cooled to -80 °C for 2 nights. The crystalline solids were isolated by decanting the supernatant and dried in vacuum to afford the SIMes (400 mg, 65 % yield).

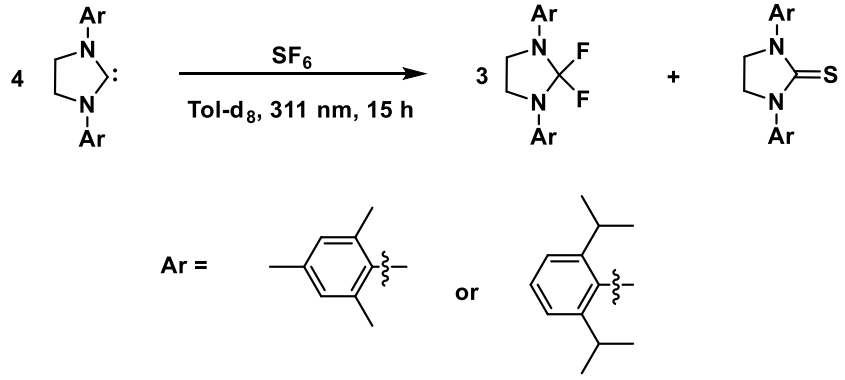
Analytical data for SIMes (13):

^{1}H NMR (500.1 MHz, C_6D_6): δ = 2.16 (s, 6H, *p*-CH_3), 2.30 (s, 12H, *o*-CH_3), 3.27 (s, 4H, NCH_2), 6.83 (s, 4H, *m*-Ar-H) ppm.

^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6): δ = 18.63 (*p*-CH_3), 21.38 (*o*-CH_3), 51.13 (NCH_2), 129.76 (*m*-Ar-C), 136.63 (*p*-Ar-C), 136.70 (*o*-Ar-C), 140.04 (*ipso*-Ar-C), 243.25 (NCN) ppm.

The other carbenes 1,3-di(2,6-di-i-propylphenyl)-imidazolidin-2-ylidene (SIPr), 1,3-dimesityl-imidazolin-2-ylidene (IMes) and 1,3-di(2,6-diisopropylphenyl)-imidazolin2-ylidene (IPr) were purchased from Sigma-Aldrich.

7.3.2. Photochemical activation of SF_6 with NHCs



A solution of carbene (0.05 mmol) in Tol-d_8 (0.5 mL) was prepared in a Young NMR tube. The solution was frozen to -180 °C and degassed *in vacuo* followed by a condensation of the SF_6 (0.10 mmol) into it. The reaction sample was brought to room temperature and irradiated with UV light at 311nm for 15 h. The color of the reaction solution changed from pale yellow to brown. In case of SIMes, full conversion of the carbene was observed after 15 h, whereas other carbenes took 20-24 h for the completion of the reaction. The product mixtures obtained after 15 h were characterized and quantified with NMR spectroscopy and LIFDI spectrometry. NMR yield of fluorinated compounds in the reaction mixture were calculated by using 1,2 difluorobenzene (0.2 M in C_6D_6) as an external standard and are based upon the assumption that three equivalents of 2,2-difluoroimidazolidine or 2,2-difluoroimidazoline and one equivalent of respective sulfide were formed (see **Table 3**). Formation of the 2-thio- derivatives of the NHCs was confirmed by synthesizing them independently (see *Section 7.3.7*). Unreacted SF_6 was identified in the ^{19}F NMR spectrum with a signal at $\delta = 58.7$ ppm.

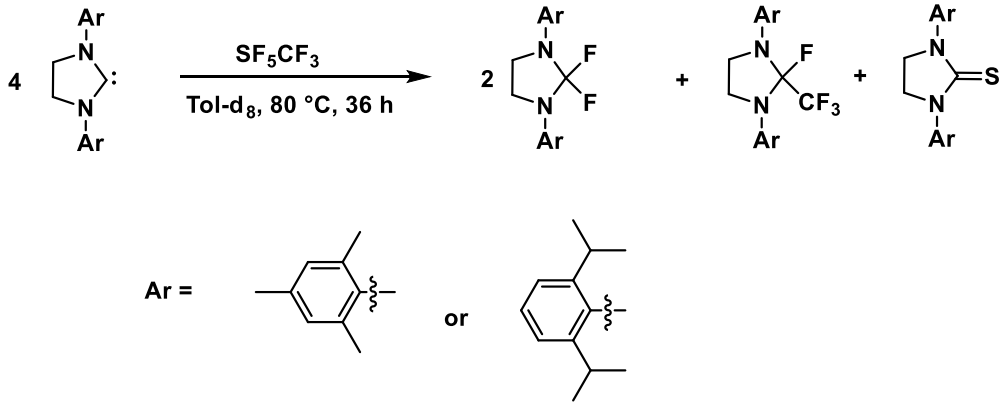
Table 3. ^{19}F NMR and $^{13}C\{^1H\}$ NMR data for the 2,2-difluoro- and 2-thio- derivatives of NHCs obtained from the activation of the SF_6. Yields of $NHC(F)_2$ were calculated by using 1,2 difluorobenzene (0.2 M in C_6D_6) as an external standard.

$NHC(F)_2$	^{19}F NMR (δ) ppm	$^{13}C\{^1H\}$ NMR (δ) ppm	Yield of $NHC(F)_2$
$SIMes(F)_2$	-55.8	181.51	82 %
$SIPr(F)_2$	-55.7	184.94	75 %
$IMes(F)_2$	-34.3	165.17	62 %
$IPr(F)_2$	-33.9	168.45	15 %

7.3.3. Reduction of SF_4 with SIMes

A solution of SIMes (0.015g, 0.05 mmol) in Tol-d_8 (0.3 mL) was prepared in a PFA tube. The solution was frozen to -180 °C and degassed *in vacuo* followed by condensation of the SF_4 (0.10 mmol) into it. The PFA tube was sealed, brought to room temperature and inserted into a NMR tube. A change in color from pale yellow to brown was observed as soon as the sample was brought to room temperature. The formation of 1,3-dimesityl -2,2-difluoroimidazolidin (SIMes$(F)_2$, **23**) and 1,3-dimesitylimidazolidine-2-sulfide (24) was obtained in 5 mins. Unreacted SF_4 was identified in the ^{19}F NMR spectrum with a signal at δ = 76.9 ppm.

7.3.4. Reduction of SF_5CF_3 with NHCs



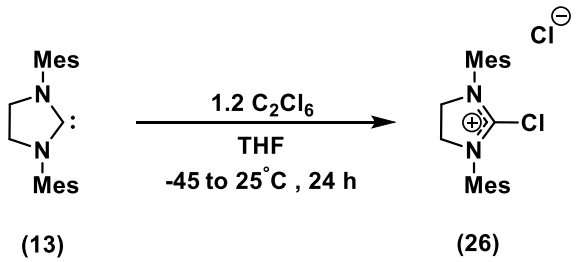
A solution of the carbene (0.05 mmol) in Tol-d_8 (0.5 mL) was prepared in a Young NMR tube. The solution was frozen to -180 °C and degassed *in vacuo* followed by condensation of the SF_5CF_3 (0.10 mmol) into it. The reaction sample was brought to the room temperature and heated at 80 °C for 36 h The color of the reaction solution changed from pale yellow to light brown. The product mixture obtained after 36 h was characterized and quantified with NMR spectroscopy. The NMR yield of 2,2-difluo- derivative of the NHCs in reaction mixture were calculated by using 1,2 difluorobenzene (0.2 M in C_6D_6) as an external standard and are based upon the assumption that two equivalents of 2,2-difluoroimidazolidine or 2,2-difluoroimidazoline were formed (see **Table 4**). Along with the 2,2- difluoro- derivatives, 2-fluoro-2-trifluoromethyl- derivative of NHC precursors were also formed. In case of the activation of SF_5CF_3 with SIMes, [SIMes(F)(CF_3)] (**27**) was identified in the reaction mixture at δ = -76.4 ppm and δ = -82.9 ppm. Similar to the [SIMes(F)(CF_3)], signals in the ^{19}F NMR spectrum at δ = -76.5 ppm and -87.2 ppm were attributed to the [SIPr(F)(CF_3)], when SIPr was used for the activation. 2-fluoro-2-

trifluoromethyl- derivative of the IMes and IPr were formed in very small amount which makes their characterization very difficult in the NMR spectra. However, signals which are present in the ^{19}F NMR spectrum besides the IMes$(F)_2$, and IPr$(F)_2$ derivatives, can be assigned to the 2-fluoro-2-trifluoromethyl- derivative of these NHCs. Formation of the 2-thio- derivatives of the NHCs was confirmed by comparing the NMR data obtained for these derivatives from their independent synthesis (see *Section 7.3.7*). Unreacted SF_5CF_3 was identified in the ^{19}F NMR spectrum with signals at δ = 62.4 (F), 37.4 (SF_4) and -65.9 (CF_3) ppm.

Table 4. ^{19}F NMR data and yields of 2,2-difluoro- derivatives of NHCs obtained from the activation of the SF_5CF_3.

NHC$(F)_2$	**^{19}F NMR (δ) ppm**	**Yield of NHC$(F)_2$**
SIMes$(F)_2$	-55.8	38 %
SIPr$(F)_2$	-55.7	12 %
IMes$(F)_2$	-34.3	20 %
IPr$(F)_2$	-33.9	08 %

7.3.5. Synthesis of the 1,3-dimesityl-2-chloroimidazolidinium chloride (26)



(13) (26)

1,1,1,2,2,2-hexachloroethane (142 mg, 0.6 mmol) was added to a solution of SIMes (153 mg, 0.5 mmol) in 1.0 mL of THF at -40 °C. The reaction mixture was then warmed to room temperature and stirred for 24 h. The reaction mixture was cooled to - 40 °C and filtered. The filter cake was washed with cold THF (-25 °C, 2 x 1 mL), toluene (1 x 3 mL) and dried *in vacuo* to afford 226 mg of compound **26** as a colorless solid (60 %).[13p]

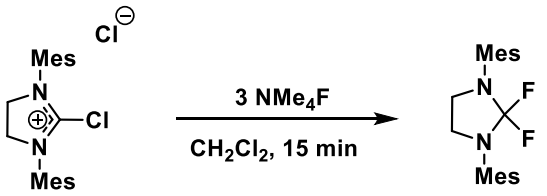
Analytical data for 26:

^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 2.33 (s, 6H, *p*-CH_3), 2.37 (s, 18H, *o*-CH_3), 4.95 (s, 4H, NCH_2), 7.05 (s, 4H, *m*-Ar-H) ppm

^{13}C{^{1}H} NMR (125.7 MHz, CD_2Cl_2): δ = 17.89 (*p*-CH_3), 21.25 (*o*-CH_3), 52.25 (NCH_2), 129.79 (Ar-C), 130.58 (Ar-C), 135.87 (Ar-C), 142.21 (Ar-C), 156.91 (NCN) ppm.

LIFDI-TOF-MS (CH_2Cl_2): Calculated (*m/z*) for [**26-Cl**]$^{+}$: 341.1 (100.0 %) , 343.1 (32.0 %), 344.1 (22.7 %); Experimental (*m/z*) for [**26-Cl**]$^{+}$: 341.1 (100 %), 343.1 (32.0 %), 344.1 (22.7 %).

7.3.6. Synthesis of the 1,3-dimesityl -2,2-difluoroimidazolidin (SIMes(F)$_2$, 23)



(26) (23)

Compound **26** and NMe_4F were dried *in vacuo* at 70 °C for 8 h prior to use. To a Schlenk tube containing **26** (200 mg, 0.53 mmol) and NMe_4F (262.8 mg, 3 mmol) was added CH_2Cl_2 (5 mL). The Schlenk tube was stirred for 15 min and the reaction mixture was then filtered and the volatiles were removed *in vacuo*. The residue was re-dissolved in toluene (3 mL) and the resulting solution was filtered to a PFA tube followed by the evaporation of solvent to afford 282 mg of a pale yellow solid compound **23** (82 %).

Analytical data for 23:

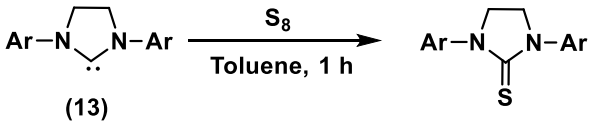
^{1}H NMR (300.1 MHz, C_6D_6): δ = 2.33 (s, 6H, *p*-CH_3), 2.37 (s, 18H, *o*-CH_3), 4.95 (s, 4H, NCH_2), 7.05 (s, 4H, *m*-Ar-H) ppm

^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6): δ = 18.07 (*p*-CH_3), 20.98 (*o*-CH_3), 49.08 (NCH_2), 128.92 (br, CF_2), 129.57 (Ar-C), 134.81 (Ar-C), 137.19 (Ar-C), 139.98 (Ar-C) ppm.

^{19}F NMR (282.4 MHz, C_6D_6): δ = -55.8 ppm

LIFDI-TOF-MS (Toluene): Calculated (*m/z*) for [**23**]$^+$: 344.2; Experimental (*m/z*) for [**23**]$^+$: 344.2.

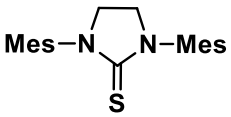
7.3.7. Synthesis of 2-thio carbenes



(13)

S_8 (0.020 g, 0.05 mmol) was added into a solution of carbene (0.05 mmol) in Tol-d_8 (0.5mL) in a NMR tube. After 1h the reaction mixture was separated from the excess of S_8 through filtration to afford 2-thio carbene.[140-141]

Analytical data for 1,3-dimesitylimidazolidine-2-sulfide:

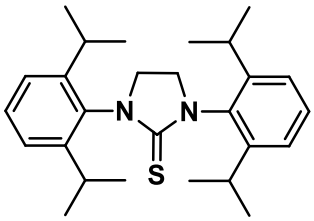


(24)

^{1}H NMR (300.1MHz, Tol-d_8): δ = 2.09 (s, 6H, *p*-CH_3), 2.24 (s, 12H, *o*-CH_3), 3.27 (s, 4H, NCH_2), 6.73 (s, 4H, *m*-Ar-H) ppm.

^{13}C{^{1}H} (125.7 MHz, Tol-d_8): δ = 17.94 (*p*-CH_3), 21.04 (*o*-CH_3), 47.36 (NCH_2), 129.57 (Ar-C), 135.66 (Ar-C), 136.94 (Ar-C), 137.61(Ar-C), 181.51 (C=S) ppm.

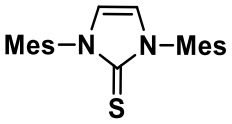
Analytical data for 1,3-di(2,6-diisopropylphenyl)-imidazolidine-2-sulfide:



^{1}H NMR (300.1MHz, Tol-d_8): δ = 1.32 (dd, 24H, *o*-CH(CH_3)$_2$), 3.11 (sept, 4H, *o*-CH(CH_3)$_2$), 3.47 (s, 4H, NCH_2), 7.05 (d, 4H, *m*-Ar-H), 7.17 (m, 2H, *p*-Ar-H), ppm.

^{13}C{^{1}H} (125.7 MHz, Tol-d_8): δ = 24.55 (*o*-CH_3), 24.77 (*o*-CH_3), 29.38 (*o*-CH), 50.29 (NCH_2), 124.40 (Ar-C), 129.31 (Ar-C), 135.69 (Ar-C), 147.80 (Ar-C), 184.94 (C=S) ppm.

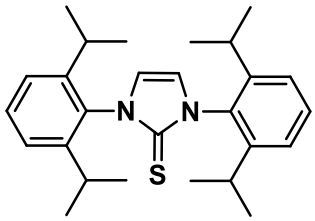
Analytical data for 1,3-dimesitylimidazoline-2-sulfide:



^{1}H NMR (300.1MHz, Tol-d_8): δ = 2.09-2.05 (m, 18H, CH_3), 5.91 (s, 2H, NCH) , 6.70 (s, 4H, *m*-Ar-H) ppm.

^{13}C{^{1}H} NMR (125.7 MHz, Tol-d_8): δ = 18.10 (*p*-CH_3), 21.07 (*o*-CH_3), 117.20 (NCH), 129.30 (Ar-C), 134.23 (Ar-C), 136.13 (Ar-C), 138.59 (Ar-C), 165.17 (C=S) ppm.

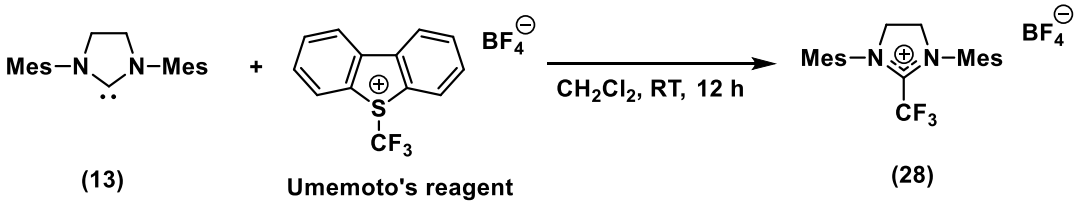
Analytical data for 1,3-di(2,6-diisopropylphenyl)-imidazoline-2-sulfide:



^{1}H NMR (300.1MHz, Tol-d_8): δ = 1.26 (dd, 24H, *o*-CH(CH_3)$_2$), 2.86 (sept, 4H, *o*-CH(CH_3)$_2$), 6.21 (s, 4H, NCH), 7.07 (d, 4H, *m*-Ar-H), 7.20 (m, 2H, *p*-Ar-H), ppm.

^{13}C{^{1}H} NMR (125.7 MHz, Tol-d_8): δ = 23.8 1(*o*-CH_3), 24.16 (*o*-CH_3), 29.24 (*o*-CH), 118.59 (NCH), 124.20 (Ar-C), 130.08 (Ar-C), 134.66 (Ar-C), 146.88 (Ar-C), 168.45 (C=S) ppm.

7.3.8. Synthesis of the 1,3-dimesityl-2-trifluoromethylimidazolinium tetrafluoroboarate salt (28)



(13) Umemoto's reagent (28)

In a Schlenk tube, SIMes (307 mg, 1 mmol) and the Umemoto's reagent (340.1 mg, 1mmol) were dissolved in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 12 h and the solvent was removed *in vacuo*. The residue was washed with toluene (2 x 5 mL) and dried *in vacuo* to give 350 mg of a pale yellow solid compound **28** (75 %).

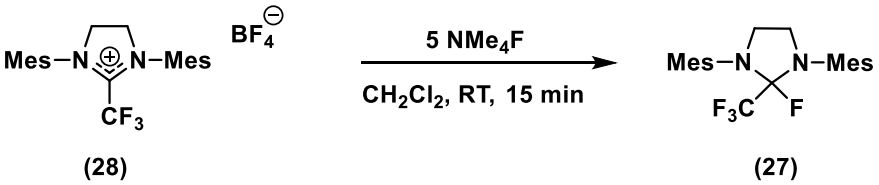
Analytical data for 28:

^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 2.33 (s, 6H, *p*-CH_3), 2.37 (s, 18H, *o*-CH_3), 4.95 (s, 4H, NCH_2), 7.05 (s, 4H, *m*-Ar-H) ppm

^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = = -65.2 (s, 3F, CF_3), -152.6 (s, 4F, BF_4) ppm.

LIFDI-TOF-MS (CD_2Cl_2): Calculated (*m/z*) for [**28-BF$_4$**]$^+$: 376.4; Experimental (*m/z*) for [**28-BF$_4$**]$^+$: 376.4.

7.3.9. Synthesis of the 1,3-dimesityl-2-fluoro-2-trifluoromethylimidazolidine [SIMes(F)(CF_3)] (27)



(28) (27)

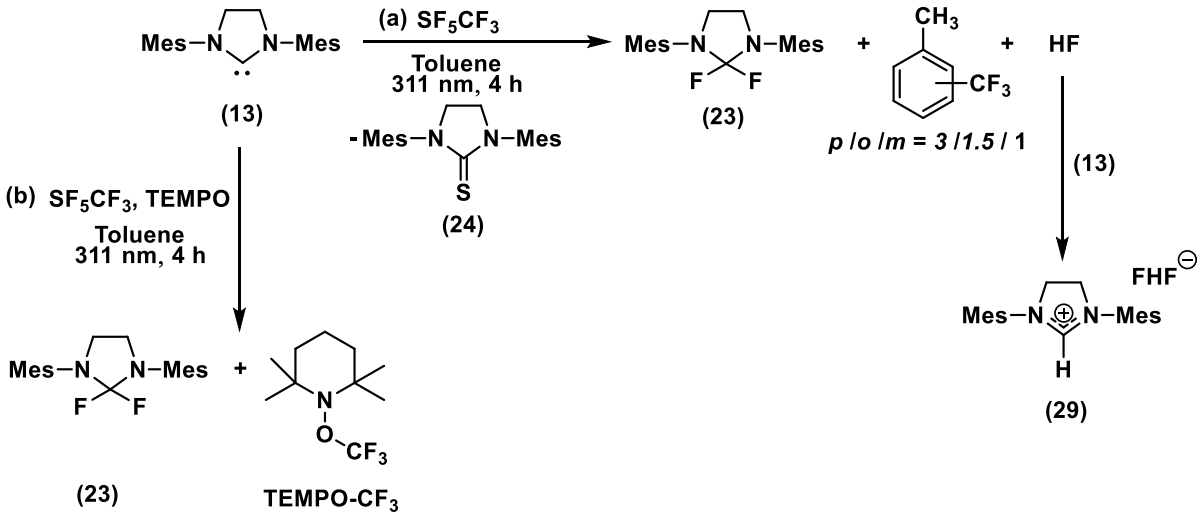
The compound **28** was dried overnight *in vacuo* at room temperature and NMe_4F was dried *in vacuo* at 70 °C for 8 h prior to use. To a Schlenk tube containing **28** (231.6 mg, 0.5 mmol) and NMe_4F (262.8 mg, 3 mmol) was added CH_2Cl_2 (2 mL). The reaction mixture was stirred for 15 min and the volatiles were removed *in vacuo*. The residue was re-dissolved in Tol-d_8 (0.5 mL) and the resulting solution was filtered to a PFA NMR tube to identify the compound **27** in solution.

Analytical data for 27:

^{1}H NMR (300.1 MHz, C_6D_6): δ = 2.33 (s, 6H, *p*-CH_3), 2.37 (s, 18H, *o*-CH_3), 4.95 (s, 4H, NCH_2), 7.05 (s, 4H, *m*-Ar-H) ppm

^{19}F NMR (282.4 MHz, C_6D_6): δ = -76.3 (d, 3F, $^3J_{CF}$ = 4.7 Hz, $HNCFCF_3$), -82.7 (q, 1F, $^3J_{CF}$ = 4.7 Hz, $NCFCF_3$) ppm.

7.3.10. Photochemical activation of SF_5CF_3 with SIMes



A solution of the SIMes (0.05 mmol) in toluene (0.05 mL) was prepared in a Young NMR tube. The solution was frozen to -180 °C and degassed *in vacuo* followed by condensation of the SF_5CF_3 (0.10 mmol) into it. The reaction sample was brought to the room temperature and irradiated at 311 nm for 4 h. The color of the reaction solution changed from pale yellow to light brown. A product mixture was obtained after 4 h containing the compounds **23**, **24** and *p*-, *o*-, *m*- isomers of the methylbenzotrifluoride in a ratio of 3:1.5:1. In the presence of TEMPO (0.10 mmol), only compound **23, 24** and the TEMPO-CF_3 adduct were observed.

Analytical data for methylbenzotrifluoride:[151a, 211]

^{1}H NMR (300.1 MHz, C_6D_6 capillary): δ = 2.42-2.48 (9H, *p*/*o*/*m* isomers-CH_3)

^{19}F NMR (282.4 MHz, C_6D_6 capillary): δ = -61.7 (s, *p*-CF_3), -62.4 (s, *m*-CF_3), -62.7 (s, *o*-CF_3) ppm.

GC-MS (Toluene): *m/z* = 160.0

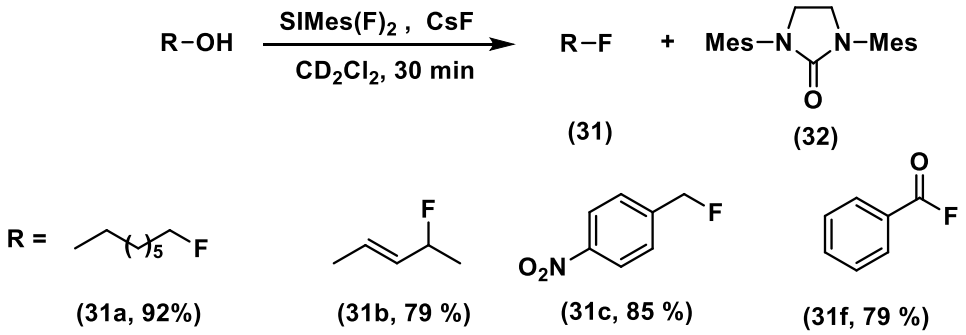
Analytical data for TEMPO-CF_3:[150]

^{19}F NMR (282.4 MHz, C_6D_6 capillary): δ = -55.3 (s)

GC-MS (Toluene): *m/z* = 225.2

Analytical data for 29: ^{1}H NMR (300.1 MHz, C_6D_6 capillary): δ = 2.27 (s, 6H, CH_3), 2.32 (s, 12H, CH_3), 4.63 (s, 4H, NCH_2), 6.87 (s, 4H, *m*-Ar-H), 10.7 (s, 1H, NCHN), 14.5 (br, 1H, FHF) ppm. **^{19}F NMR** (282.4 MHz, CD_3CN): δ = -149.7 (br) ppm.

7.3.11. Deoxyfluorination with SIMes(F)$_2$ (23)



A solution of **23** (0.05 mmol) in CD_2Cl_2 (0.5 mL) was prepared in a NMR tube. To this solution alcohol (0.025 mmol) or benzoic acid (0.025 mmol) and CsF (0.075 mmol) were added. The respective fluorinated product was observed within 30 mins at room temperature and characterized by ^{19}F NMR spectroscopy. The yields of the fluorinated compounds were calculated by using 1,2 difluorobenzene (0.2 M in C_6D_6) as an external standard. Fluorination of trifluoropropanol yielded a mixture of tetrafluoropropane (**31d**) and trifluoropropene (**31e**) in a ratio of 1: 0.6. Along with the fluorinated products, 1,3-dimesitylimidazolidin-2-one (**32**) was also identified in the ^{19}F NMR and $^{13}C\{^{1}H\}$ NMR spectra.

Analytical data for fluorinated products:[153, 173b]

31a: ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = -218.0 (tt, $^{2}J_{FH}$ = 47.3 Hz, $^{3}J_{FH}$ = 24.5 Hz) ppm.

31b: **^{19}F NMR** (282.4 MHz, CD_2Cl_2): δ = -162.3 (m) ppm

31c: ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = -215.4 (t, $^{2}J_{FH}$ = 44.8 Hz) ppm.

^{19}F NMR (282.4 MHz, CD_2Cl_2): **31d:** δ = -65.0 (m, 3F, $^4J_{FF}$ = 6.3 Hz), -221.8 (m, 1F, $^4J_{FF}$ = 6.3 Hz); **31e:** δ = -66.1 (d, $^3J_{FH}$ = 7.08 Hz) ppm.

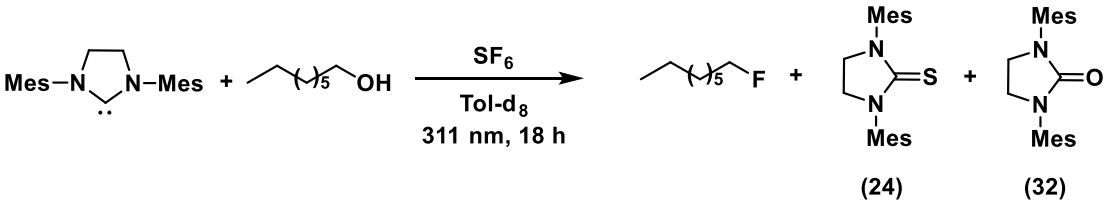
31f: ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = 17.7 (s) ppm.

Analytical data for 32:[152b]

^{1}H NMR (300.1MHz, CD_2Cl_2): δ = 2.25 (s, 6H, *p*-CH_3), 2.29 (s, 12H, *o*-CH_3), 3.78 (s, 4H, NCH_2), 6.89 (s, 4H, *m*-Ar-H) ppm.

^{13}C{^{1}H} (125.7 MHz, CD_2Cl_2): δ = 17.94 (*p*-CH_3), 20.99 (*o*-CH_3), 44.26 (NCH_2), 129.37 (Ar-C), 134.01 (Ar-C), 136.94 (Ar-C), 137.61(Ar-C), 164.21 (C=O) ppm.

7.3.12. One-pot fluorination of 1-octanol *via* activation of SF_6 with SIMes

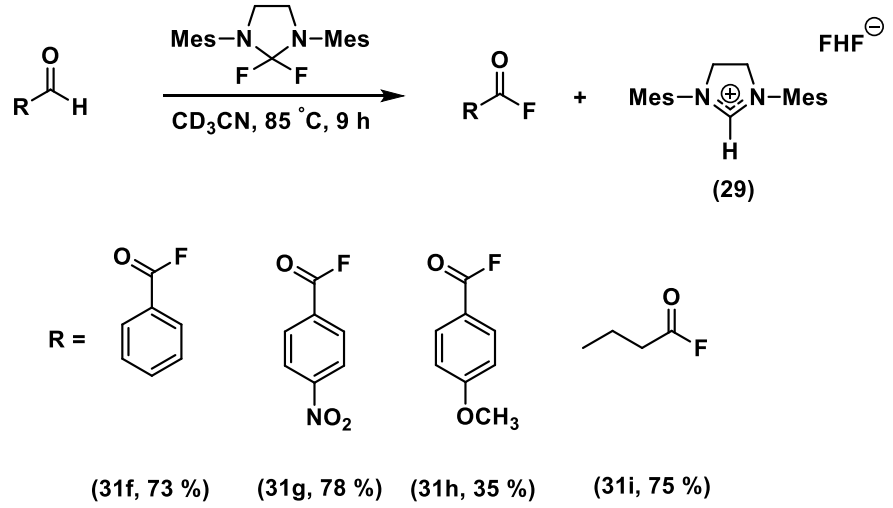


A solution of SIMes (0.015 g, 0.05 mmol) in Tol-d_8 (0.5 mL) was prepared in a Young NMR tube and 1-octanol (4µL, 0.025 mmol) was added into it. The reaction mixture solution was frozen at -180 °C and degassed *in vacuo*. SF_6 (0.10 mmol) was condensed on it and the reaction sample was brought to room temperature and irradiated with UV at 311 nm. The ^{19}F NMR spectrum showed a signal for $SIMes(F)_2$ (**23**) at δ = 55.8 ppm when reaction sample was measured after 8 h. After 18 h, the resonance for **23** disappeared and a signal for 1-fluorooctane at δ = -218.0 ppm was observed after 18 h. Compound **24** and **32** were identified in the mixture of end products with the help of LIFDI mass spectrometry.

LIFDI-TOF-MS (Tol-d_8): Calculated (*m/z*) for [**24**]$^+$: 338.1; Experimental (*m/z*) for [**24**]$^+$: 338.1.

LIFDI-TOF-MS (Tol-d_8): Calculated (*m/z*) for [**32**]$^+$: 322.2; Experimental (*m/z*) for [**32**]$^+$: 322.2.

7.3.13. Fluorination of aldehydes with SIMes(F)$_2$ (23)



A solution of **23** (0.05 mmol) in CD_3CN (0.5 mL) was prepared in a NMR tube. To this solution 0.075 mmol of aldehyde were added and reaction mixture was heated at 85 °C for 9 h. The respective fluorinated product was characterized by ^{19}F NMR spectroscopy. The yields of the fluorinated compounds were calculated by using 1,2 difluorobenzene (0.2 M in C_6D_6) as an external standard.

Analytical data for acyl fluorides:[160c, 161, 163b, 164]

31f: ^{19}F NMR (282.4 MHz, CD_3CN): δ = 17.5 ppm.

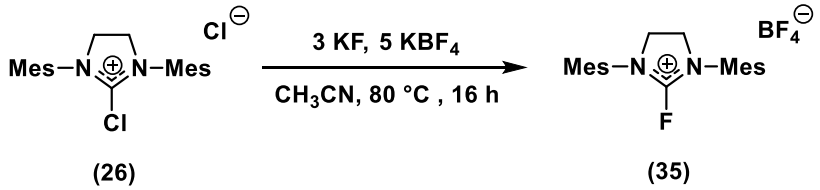
31g: ^{19}F NMR (282.4 MHz, CD_3CN): δ = 21.3 ppm.

31h: **^{19}F NMR** (282.4 MHz, CD_3CN): δ = 15.4 ppm

31i: ^{19}F NMR (282.4 MHz, CD_3CN): δ = 44.5 ppm.

Analytical data for 29: ^1H NMR (300.1 MHz, CD_3CN): δ = 2.27 (s, 6H, CH_3), 2.37 (s, 12H, CH_3), 4.63 (s, 4H, NCH_2), 6.90 (s, 4H, *m*-Ar-H), 9.8 (s, 1H, NCHN), 14.9 (br, 1H, FHF) ppm; **^{19}F NMR** (282.4 MHz, CD_3CN): δ = -145.7 (br) ppm.

7.3.14. Synthesis of 1,3 dimesityl-2-fluoroimidazolinium tetrafluoroboarate salt (35)



(26) (35)

Compound **26**, KF, and KBF_4 were dried *in vacuo* at 70 °C for 8 h prior to use. **26** (200 mg, 0.5 mmol), KF (1.5 mmol) and KBF_4 (5 equivalent) were suspended in dry acetonitrile (20 mL) in a Schlenk tube. The mixture was heated at 80 °C for 16 hours with vigorous stirring. The reaction mixture was cooled to room temperature and filtered. The filtrate was dried *in vacuo*, and the residue was dissolved in CH_2Cl_2 (15 mL) and filtered again. The filtrate was dried *in vacuo* to afford the compound **35** (164 mg, 80 %).

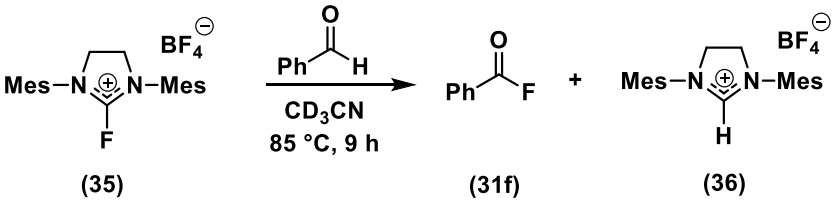
Analytical data for 35:

^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 2.24 (br, 18H, CH_3), 3.94 (s, 4H, NCH_2), 6.90 (s, 4H, *m*-Ar-H) ppm

^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = = -84.1 (s, NCFN), -152.7 (s, 4F, BF_4) ppm.

LIFDI-TOF-MS (CD_2Cl_2): Calculated (*m/z*) for [**35-BF$_4$**]$^+$: 326.4; Experimental (*m/z*) for [**35-BF$_4$**]$^+$: 326.4.

7.3.15. Fluorination of the benzaldehyde with 35

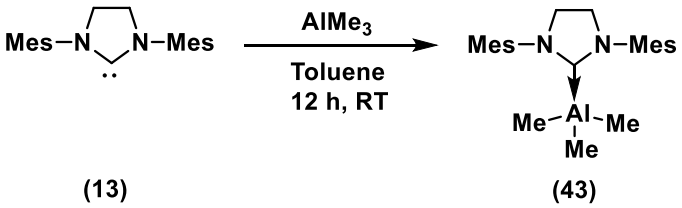


A solution of **35** (0.05 mmol) in CD_3CN (0.5 mL) was prepared in a NMR tube. To this solution 0.075 mmol of benzaldehyde were added and reaction mixture was heated at 85 °C for 9 h. The benzoyl fluoride (**31f**) was identified by ^{19}F NMR spectrum at δ = 17.5 ppm.

Analytical data for 36:[212]

^{1}H NMR (300.1 MHz, CD_3CN): δ = 2.27 (s, 6H, CH_3), 2.39 (s, 12H, CH_3), 4.62 (s, 4H, NCH_2), 6.90 (s, 4H, *m*-Ar-H), 8.91 (br, 1H, NCHN) ppm.

7.3.16. Synthesis of [(SIMes)AlMe3] (43)[192d]



(13) (43)

In a Schlenk tube, SIMes (**13**) (1.53 g, 5.0 mmol) was dissolved in toluene (15 mL) and $AlMe_3$ (5.0 mmol, 2M in toluene) was added. The solution was stirred for 12 h at room temperature and the volatiles were evaporated. The residue was washed with hexane to afford the complex **43** (87 %).

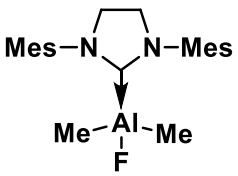
Analytical data for 43:

^{1}H NMR (300.1 MHz, C_6D_6): δ = 2.07 (s, 6H, *p*-CH_3), 2.20 (s, 12H, *o*-CH_3), 3.01 (s, 4H, CH_2), 6.76 (s, 4H, *m*-Ar-H), -0.87 (s, 9H, $AlCH_3$) ppm.

^{27}Al NMR (130.3 MHz, C_6D_6): δ = 159.1 ppm.

LIFDI-TOF-MS (Toluene): Calculated (*m/z*) for [**43**]$^+$: 379.28. Experimental (*m/z*) for [**43**]$^+$: 379.27, [**43-CH3**]$^+$: 364.26, [**43-2CH3**]$^+$: 349.24.

7.3.17. Synthesis of [(SIMes)Al(F)(Me)$_2$] (44)



(44)

Method A: Fluorination with SF_6

A solution of [(SIMes)AlMe$_3$] (**43**) (37.8 mg, 0.05 mmol) was prepared in Tol-d$_8$ (0.3 mL) in a PFA tube. The solution was frozen to -180 °C and degassed *in vacuo* followed by a condensation of SF_6 (0.10 mmol) into it. The PFA tube was sealed and warmed up to room temperature. The sealed PFA tube was inserted into a NMR tube and the reaction mixture was heated at 70 °C for 48 h to obtain the complex **44**. The yield after 48 h was found to be 30 % when calculated by using 1,2 difluorobenzene (0.2 M in C_6D_6) as an external standard.

Method B: Fluorination with Me_3SnF

In a Schlenk tube, complex [(SIMes)AlMe$_3$] (**43**) (37.8 mg, 0.1 mmol) and Me_3SnF (18.6 mg, 0.1 mmol) were dissolved in toluene (5 mL). The solution was stirred for 30 min at room temperature and filtered. The filtrate was then evaporated *in vacuo* to obtain the complex **44** (62 %).

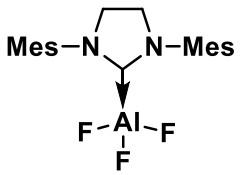
Analytical data for 44:

^{1}H NMR (300.1 MHz, C_6D_6): δ = –1.16 (d, 6H, $^3J_{HF}$ = 3.07 Hz, AlCH$_3$), 2.06 (s, 6H, *p*-CH$_3$), 2.22 (s, 12H, *o*-CH$_3$), 3.04 (s, 4H, CH$_2$), 6.59 (s, 4H, *m*-Ar-H) ppm.

^{19}F NMR (282.4 MHz, C_6D_6): δ = –169.9 (br, AlF) ppm.

^{27}Al NMR (130.3 MHz, C_6D_6): δ = 81.9 ppm.

7.3.18. Synthesis of [(SIMes)Al(F)$_3$] (45)



(45)

Method A : Fluorination with SF_4

A solution of [(SIMes)Al(Me)$_3$] (**43**) (37.8 mg, 0.05 mmol) was prepared in Tol-d$_8$ (0.3 mL) in a PFA tube. The solution was frozen to -180 °C and degassed *in vacuo* followed by condensation of the SF_4 (0.10 mmol) into it. The PFA tube was sealed and inserted into a NMR tube. Formation of the complex **45** and CH_3SF_3 was obtained at –30 °C.

Method B: Fluorination with Me_3SnF

In a Schlenk tube, complex [(SIMes)Al(Me)$_3$] (**43**) (37.8 mg, 0.1 mmol) was dissolved in toluene (5 mL) and an excess of Me_3SnF (6 equivalents) was added. The solution was stirred for 2 h at room temperature followed by filtration. The filtrate was evaporated *in vacuo* to obtain the complex **45** (68 %).

Analytical data for 45:

^{1}H NMR (300.1 MHz, C_6D_6): δ = 2.01 (s, 6H, *p*-CH_3), 2.22 (s, 12H, *o*-CH_3), 4.24 (s, 4H, CH_2), 6.60 (s, 4H, *m*-Ar-H) ppm.

^{19}F NMR (282.4 MHz, C_6D_6): δ = –164.5 (br, AlF) ppm.

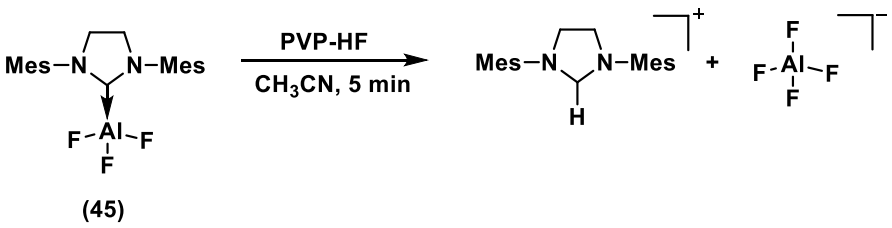
^{27}Al NMR (130.3 MHz, C_6D_6): δ = 49.8 ppm.

Analytical data for CH_3SF_3:[203]

^{1}H NMR (300.1 MHz, Tol-d$_8$, -30 °C) : δ = 4.96 (br, CH_3SF_3) ppm.

^{19}F NMR (282.4 MHz, Tol-d$_8$, -30 °C) : δ = –50.6 (tq, 1F, $^2J_{FF}$ =73 Hz, $^3J_{HF}$ =15.3 Hz, CH_3SF_3), 62.1 (dq, 2F, $^2J_{FF}$ =73 Hz, $^3J_{HF}$ = 15.3 Hz, CH_3SF_3) ppm.

7.3.19. Addition of HF to the complex [(SIMes)Al(F)$_3$] (45)



(45)

In a NMR tube, complex **45** (0.025 mmol) was prepared by following *Method B* and dissolved in acetonitrile (0.5 mL) followed by an addition of PVP-HF (0.05 mmol). The solvent was evaporated and the residue was re-dissolved in CD_2Cl_2. ^{1}H , ^{19}F NMR and ^{27}Al NMR spectra shows the formation of a salt containing protonated SIMes and $[AlF_4]^-$.

Analytical data for the 1,3-dimesitylimidazolinium cation:

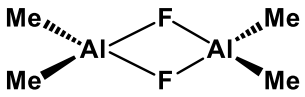
^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 2.32 (s, 6H, *p*-CH_3), 2.38 (s, 12H, *o*-CH_3), 4.43 (s, 4H, CH_2), 6.99 (s, 4H, *m*-Ar-H), 10.11 (s, NCHN) ppm.

Analytical data for $[AlF_4]^-$:

^{19}F NMR (282.4 MHz, CD_2Cl_2): δ = –197.9 (br, AlF) ppm.

^{27}Al NMR (130.3 MHz, CD_2Cl_2): δ = 46.9 (quint) ppm.

7.3.20. Formation of $AlMe_2F$



Method A : Fluorination with SF_6

A solution of $AlMe_3$ (2 M in toluene, 0.05 mmol) was prepared in Tol-d_8 (0.5 mL) in a Young NMR tube. The solution was frozen to -180 °C and degassed *in vacuo* followed by condensation of the SF_6 (0.10 mmol) into it. The reaction sample was irradiated with UV at 311 nm for 36 h to obtain the $AlMe_2F$.

Method B : Fluorination with Me_3SnF

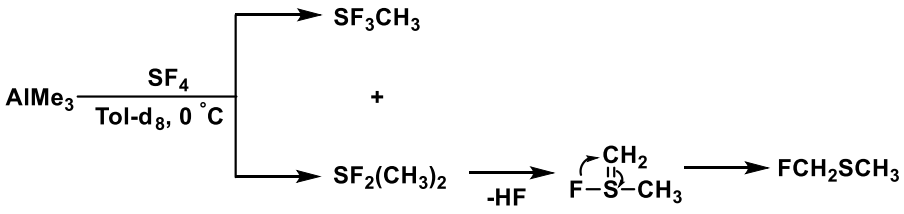
In a NMR tube, Me_3SnF (0.10 mmol) was suspended into Tol-d_8 (0.5 mL). $AlMe_3$ (2 M in toluene, 0.10 mmol) was added to the suspension. Formation of a mixture of $AlMe_2F$ dimers was observed within 5 min at room temperature.

Analytical data for $AlMe_2F$:

$^1H\{^{19}F\}$ NMR (300.1 MHz, Tol-d_8) : δ = –0.43, –0.55, –0.63, –0.69 ppm

^{19}F NMR (282.4 MHz, Tol-d_8) : δ = –143.6, –145.8, –148.9, –150.8 ppm.

7.3.21. Reaction of $AlMe_3$ with SF_4



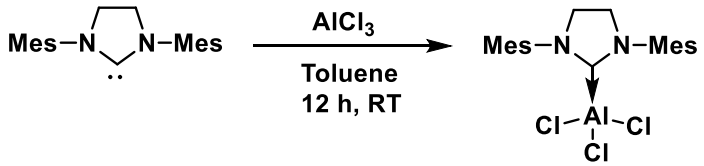
A solution of $AlMe_3$ (2 M in toluene, 0.05 mmol) was prepared in Tol-d_8 (0.53mL) in a PFA tube. The solution was frozen to -180 °C and degassed *in vacuo* followed by condensation of the SF_4 (0.10 mmol) into it. The PFA tube was sealed and inserted into a NMR tube. At 0 °C a mixture of SF_3CH_3 and FCH_2SCH_3 was identified in the solution. A white solid precipitated in the reaction mixture which presumably can be considered as AlF_3. The ^{19}F NMR spectrum reveals resonances for SF_3CH_3 which are in accordance to the signals observed in the case of fluorination of the complex **43** with SF_4 (see *Section 7.3.18*).

Analytical data for FCH_2SCH_3:

^1H NMR (300.1 MHz, Tol-d_8): δ = 1.69 (d, 3H, $^4J_{HF}$ = 2.4 Hz, SCH_3), 4.83 (d, 2H, $^2J_{HF}$ =53.9 Hz, CH_2F) ppm.

^{19}F NMR (282.4 MHz, Tol-d_8): δ = –188.1 (qt, $^2J_{FH}$ = 53.9 Hz, $^4J_{FH}$ = 2.4 Hz) ppm.

7.3.22. Synthesis of [(SIMes)Al(Cl)$_3$] (46)[209]



(13) (46)

In a Schlenk tube, SIMes (**13**) (307 mg, 1.0 mmol) was dissolved in toluene (5 mL) and $AlCl_3$ (132 mg, 1.0 mmol) was added. The solution was stirred for 12 h at room temperature and the volatiles were evaporated. The residue was washed with hexane to afford the complex **46** (53 %).

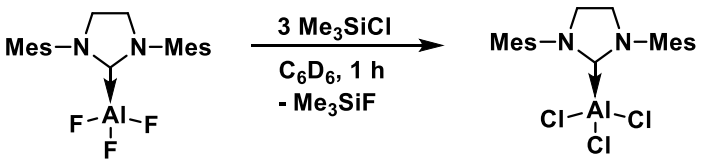
Analytical data for 46:

^{1}H NMR (500.1 MHz, C_6D_6): δ = 2.01 (s, 6H, *p*-CH_3), 2.21 (s, 12H, *o*-CH_3), 4.25 (s, 4H, CH_2), 6.56 (s, 4H, *m*-Ar-H) ppm.

^{27}Al NMR (130.3 MHz, C_6D_6): δ = 104.7 ppm.

LIFDI-TOF-MS (Toluene): Calculated (*m/z*) for [**46**]$^+$: 439.1; Experimental (*m/z*) for [**46**]$^+$: 439.1.

7.3.23. Addition of Me_3SiCl to the complex [(SIMes)Al(F)$_3$] (45)



(45) (46)

In a PFA NMR tube complex [(SIMes)Al(F)$_3$] (**45**) (39.2 mg, 0.10 mmol) was dissolved in C_6D_6 (0.3 mL) and Me_3SiCl (0.3 mmol) was added to it at room temperature. Formation of the complex [(SIMes)Al(Cl)$_3$] (**46**) and Me_3SiF was observed after 1 h. Signals at δ = –156.9 ppm in the $^{19}F\{^1H\}$ NMR and at δ = 30.3 ppm in the ^{29}Si NMR spectrum were assigned to the Me_3SiF. The ^1H NMR and ^{27}Al NMR spectra recorded for the complex **46** were found consistent with the data obtained from its independent synthesis (see *Section 7.3.22*).

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9. Appendix

9.1. Abbreviations

σ	Sigma
Å	Angstrom; 10^{-10} meters
°C	degree Celsius
RT	Room temperature
h	Hour
min	minute
UV	Ultra-violet
nm	Nanometer
BEt_3	Triethylborane
LED	Light emitting diode
CH_3CN	Acetonitrile
$\Delta_f H^0$	Standard enthalpy of formation
oh	Octahedral
K	Kelvin
kJ	kilo Joule
mol	Mole
Na	Sodium
SCE	Saturated calomel electrode

eV	Electronvolt
vs.	versus
W	Watt
ppb	Parts per billion
ppt	Parts per trillion
CF_3COOCF_3	Bis(trifluoromethyl)peroxide
V	Volt
Me	Methyl
*i*Pr	*iso*-Propyl
*t*Bu	*tert*-Butoxide
Ph	Phenyl
Cat.	Catalyst
Mes	Mesityl
Dipp	Diisopropylphenyl
SIMes	1,3-dimesityl-imidazolidin-2-ylidene
SIPr	1,3-di(2,6-di-i-propylphenyl)-imidazolidin-2-ylidene
IMes	1,3-dimesityl-imidazolin-2-ylidene
IPr	1,3-di(2,6-diisopropylphenyl)-imidazolin2-ylidene
DMSO	Dimethyl sulfoxide
THF	Tetrahydrofuran
kcal	Kilocalorie (1 kcal = 4,184 kJ)
KO*t*Bu	Potassium *tert*-butoxide
mV	Millivolt
A	Ampere

mM	Millimolar
CPS	Counts per second
PVP	Polyvinylpyrrolidone
PFA	Perfluoroalkoxy alkanes
TOF	Time of flight
Hz	Hertz
MHz	Megahertz
s	Singlet
d	Doublet
t	Triplet
q	Quintet
m	Multiplet
br	Broad signal
J	Coupling constant
δ	Chemical shift

9.2. Cyclic voltammograms of NHCs

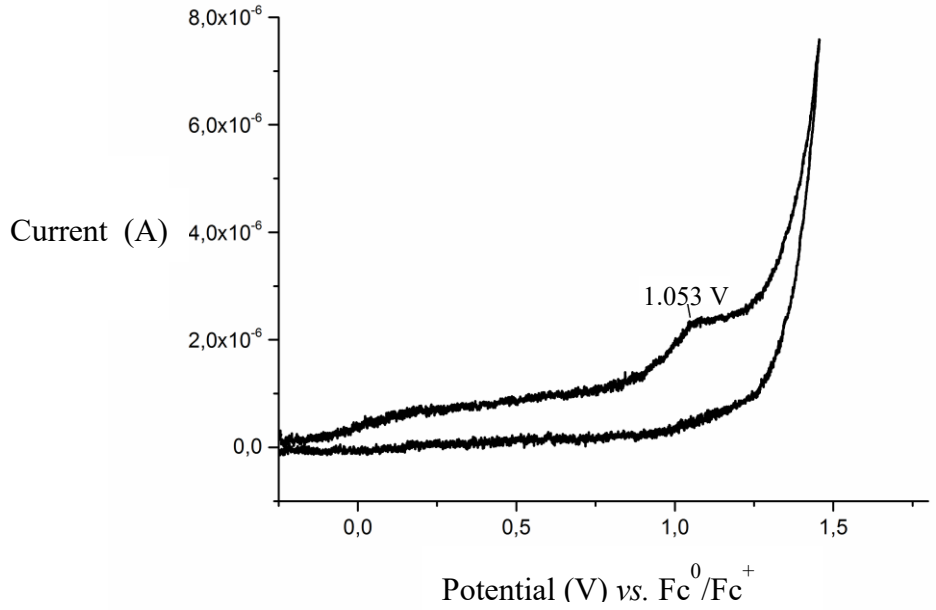

Figure 29. Cyclic voltammogram obtained for a solution of SIPr (1mM) in THF, measured with a scan rate of 200 mV/s. E_p^{ox} = 1.053 V *vs*. Fc^0/Fc^+ and E_p^{ox} = 1.613 V *vs*. SCE.

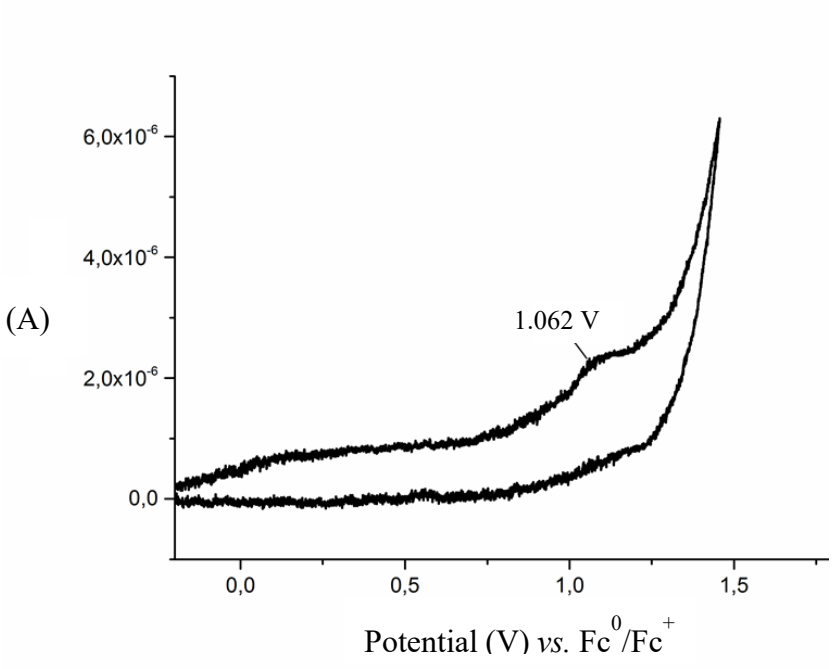

Figure 30. Cyclic voltammogram obtained for a solution of IMes (1mM) in THF, measured with a scan rate of 200 mV/s. E_p^{ox} = 1.062 V *vs*. Fc^0/Fc^+ and E_p^{ox} = 1.622 V *vs*. SCE.

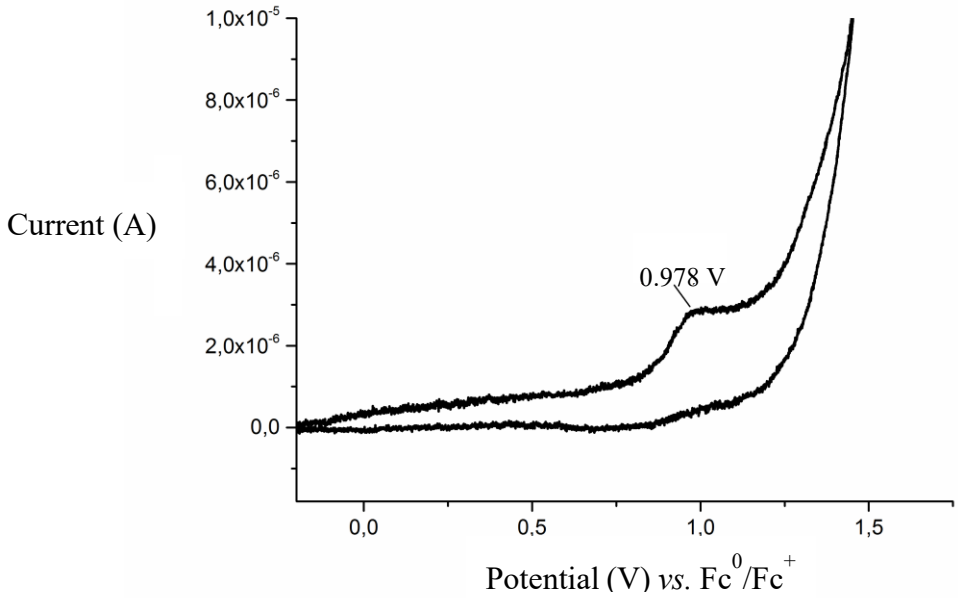

Figure 31. Cyclic voltammogram obtained for a solution of IPr (1mM) in THF, measured with a scan rate of 200 mV/s. E_p^{ox} = 0.978 V *vs*. Fc^0/Fc^+ and E_p^{ox} = 1.538 V *vs*. SCE.

9.3. UV-vis spectra of NHCs

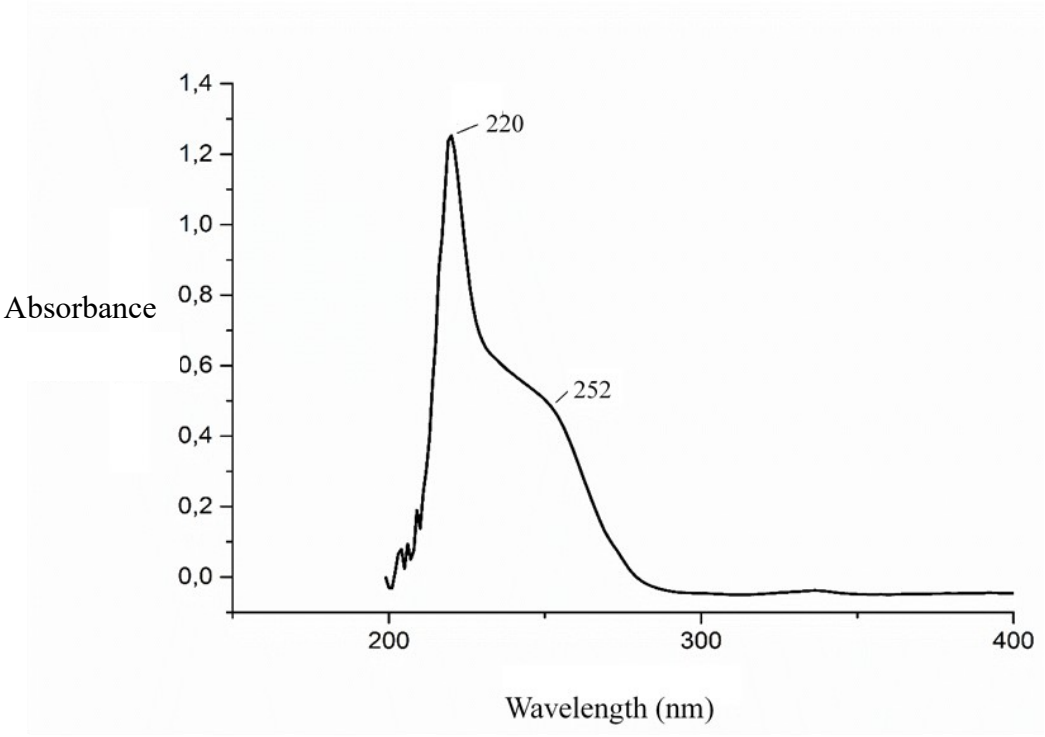

Figure 32. UV-vis spectrum obtained for a solution of SIPr (1mM) in THF showing absorbance maxima at 220 nm and 252 nm.

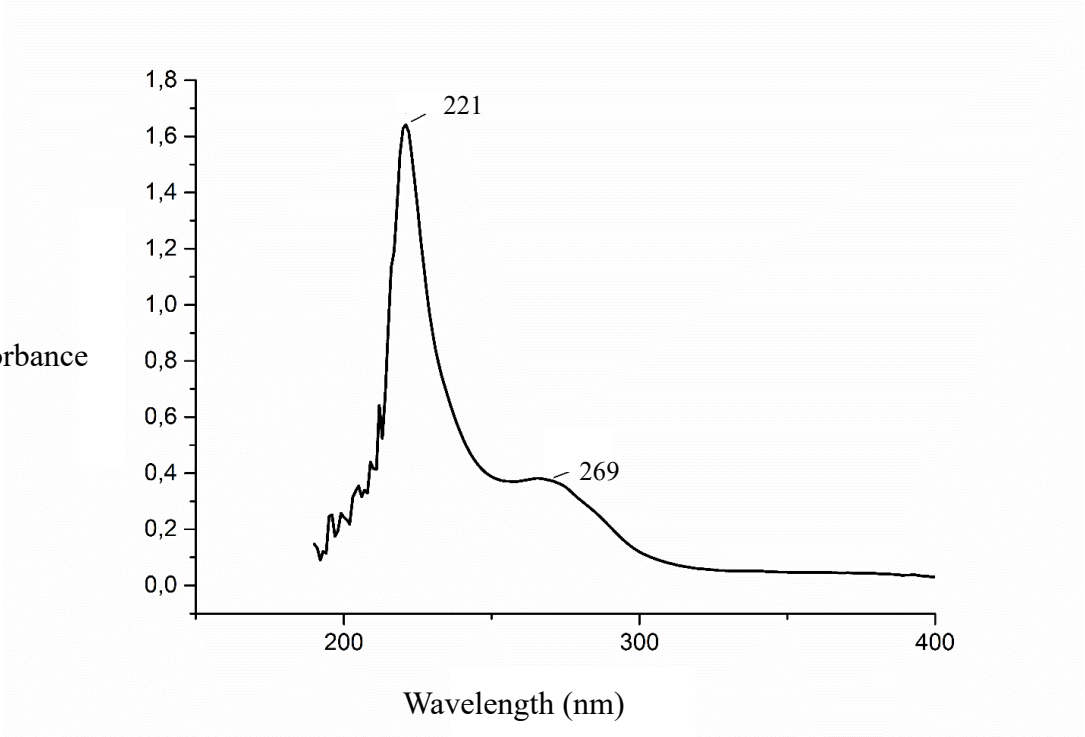

Figure 33. UV-vis spectrum obtained for a solution of IMes (1mM) in THF showing absorbance maxima at 221 nm and 269 nm.

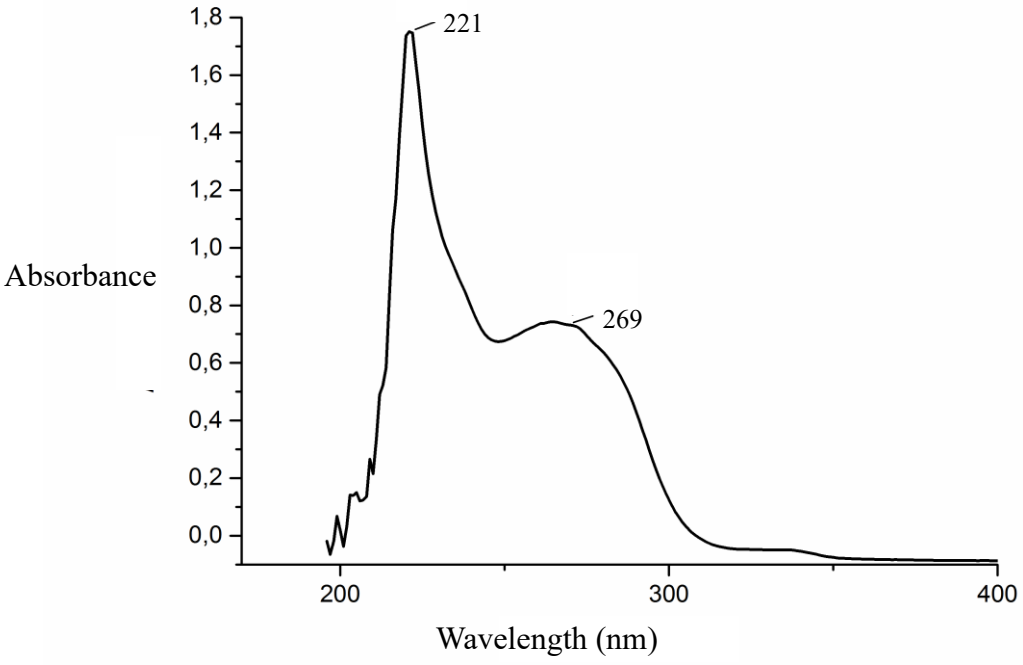

Figure 34. UV-vis spectrum obtained for a solution of IPr (1mM) in THF showing absorbance maxima at 221 nm and 269 nm.

9.4. Emission spectra of NHCs

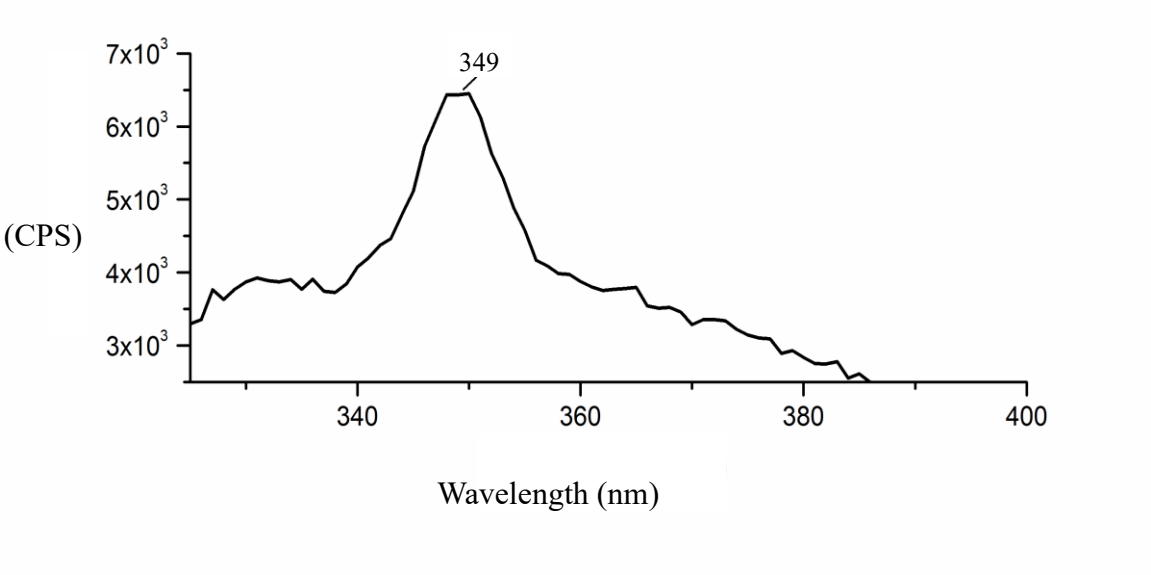

Figure 35. Emission spectrum obtained for a solution of SIPr (1mM) in THF when excited at 318 nm, slit width = 5.00 nm. Emission maximum is obtained at 349 nm, slit width = 2.00 nm.

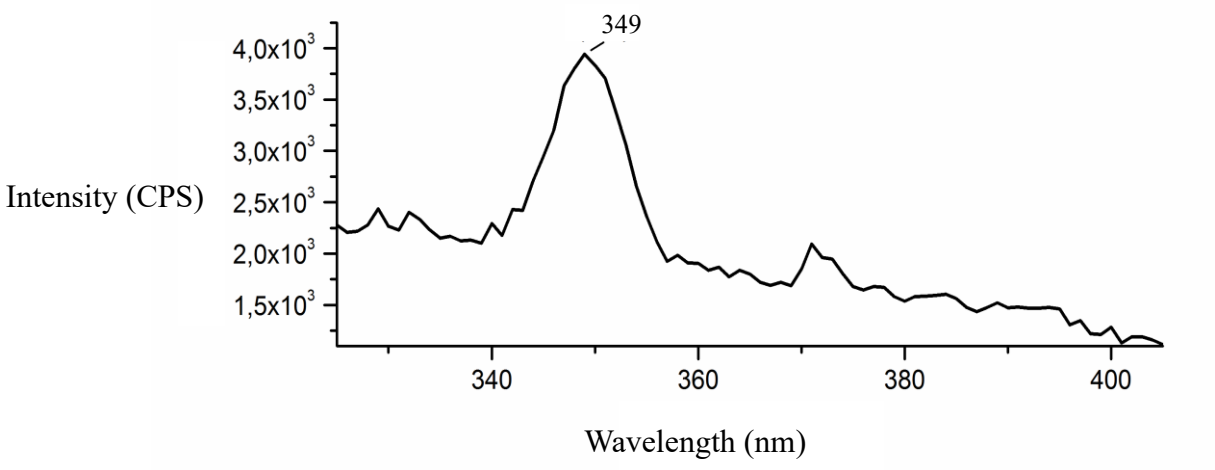

Figure 36. Emission spectrum obtained for a solution of IMes (1mM) in THF when excited at 318 nm, slit width = 5.00 nm. Emission maximum is obtained at 349 nm, slit width = 2.00 nm.

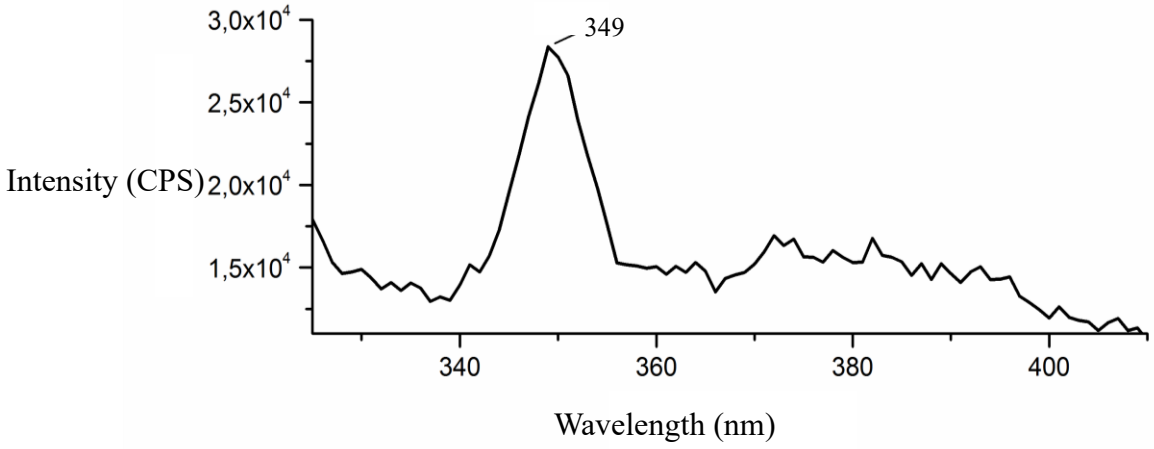

Figure 37. Emission spectrum obtained for a solution of IPr (1mM) in THF when excited at 318 nm, slit width = 5.00 nm. Emission maximum is obtained at 349 nm, slit width = 2.00 nm.

9.5. Selbstständigkeitserklärung

Ich erkläre, dass ich die Dissertation selbstständig und nur unter Verwendung der von mir gemäß § 7 Abs. 3 der Promotionsordnung der Mathematisch-Naturwissenschaftlichen Fakultät, veröffentlicht im Amtlichen Mitteilungsblatt der Humboldt-Universität zu Berlin Nr. 42/2018 am 11.07.2018, angegebenen Hilfsmittel angefertigt habe.

Berlin, den 24.03.2020

…….

Pooja Tomar