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# Preparation of NHC stabilized Al(III)fluorides: Fluorination of [(SIMes)AlMe$_3$] with SF$_4$ or Me$_3$SnF

Pooja Tomar[a], Thomas Braun*,[a], and Erhard Kemnitz*,[a]

**Abstract:** Various reaction routes have been developed to synthesize the *N*-heterocyclic carbene (NHC) stabilized Al(III) fluorides [(SIMes)Al(F)$_3$] (**2**) and [(SIMes)Al(F)Me$_2$] (**3**) through fluorination of [(SIMes)AlMe$_3$] (**1**) (SIMes: 1,3-bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene) with fluorinating agents such as SF$_4$, SF$_6$ and Me$_3$SnF. The reactivity of **2** was investigated towards a F/Cl exchange reaction by treating it with Me$_3$SiCl.

## Introduction

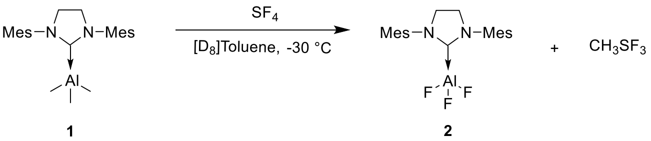
Aluminium trifluorides and derivatives have been used as heterogeneous Lewis acid catalysts to produce chlorofluorocarbons and hydrofluorocarbons.[1] β-AlF$_3$ was shown to catalyze intermolecular Cl/F exchange reaction, for instance to convert the greenhouse gas trifluoromethane CHF$_3$) into CHCl$_3$.[2] Nanoscopic, amorphous aluminium fluorides such as high-surface aluminium fluoride (*HS*-AlF$_3$) and aluminum chlorofluoride (ACF, AlCl$_x$F$_{3-x}$, x=0.05-0.3) are known to exhibit a Lewis acidity comparable to that of SbF$_5$.[1b] In the presence of silanes or germanes they are useful compounds to mediate hydrodefluorination or dehydrofluorination reactions of fluorinated alkanes.[3] Nanoscopic aluminium fluorides can be synthesized by treating alumina or AlCl$_3$ with chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), or with HF sources. Case and Nyman also documented in 1962 the decomposition of SF$_6$ at AlCl$_3$ at 180 – 200 °C to give within 24 h AlF$_3$ along with sulfur chlorides.[4] SF$_4$ was also used as fluorinating agent to obtain AlF$_3$ by reaction with aluminium hydroxide [Al(OH)$_3$] at 20°C .[5]

There are rare examples reported for the synthesis of molecular AlF$_3$ complexes bearing neutral ligands. Notably, Reid *et al.* documented a 1,4,7-triazacyclononane (tacn) stabilized AlF$_3$ complex solvated with water molecules.[6] Kolis and coworkers described the hydrothermal synthesis of AlF$_3$(NH$_3$)$_2$ by treating AlN and NH$_4$F at 400°C in supercritical ammonia.[7] In 1957 Ziegler reported on the generation of the first organoaluminium fluorides.[8] The organyl groups make the compounds soluble in various organic solvents, and hence, reactivity in solution can be investigated. The properties of organoaluminium fluorides and their applications have been covered very extensively in reviews by Roesky.[9] Organoaluminium fluorides such as dimethylaluminium fluoride (Me$_2$AlF)$_4$ were established to access aluminum fluoride clusters by Roesky and coworkers.[10] Kemnitz *et al.* also showed that reactions of Al(O*i*Pr)$_3$ with HF in pyridine as a solvent yield polynuclear aluminum alkoxide fluoride compounds.[11] In a recent report Crimmin and coworkers reported on the activation of C−F bonds of fluoroalkenes by treating them with an Al(I) complex to give organoaluminium fluorides such as [{HC(CMeNAr)$_2$}Al(F)$_2$] (Ar = 2,6-iPr$_2$C$_6$H$_3$).[12]

*N*-heterocyclic carbenes NHCs are widely used as ligands for stabilizing a wide range of group 13 compounds resulting in complexes bearing unique and interesting properties.[13] Lewis pairs with Al-based Lewis acids have been prepared for instance by treatment of AlMe$_3$ with aromatic NHCs.[14] Here we present, the development of reaction routes to access NHC stabilized aluminium fluorides by fluorination of [(SIMes)AlMe$_3$] (**1**) (SIMes: 1,3-bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene). Suitable fluorinating agents are SF$_4$, SF$_6$ and Me$_3$SnF.

## Results and Discussion

Treatment of complex **1** with SF$_4$ in toluene yielded the aluminium trifluorido complex [(SIMes)Al(F)$_3$] (**2**). The reaction was monitored by NMR spectroscopy and at -30 °C a complete fluorination as well as the generation of considerable amount of CH$_3$SF$_3$ were observed (Scheme 1). In the $^{19}$F NMR spectrum a broad resonance at δ = -164.5 ppm was found for **2** (Figure1). This resonance is consistent with data for four-fold coordinated aluminium fluorides such as the complex [{HC(CMeNAr)$_2$}Al(F)$_2$] (Ar=2,6-iPr$_2$C$_6$H$_3$).[12] A signal at δ = 49.8 ppm in the $^{27}$Al NMR spectrum appears also in a typical range for fourfold coordinated aluminium halide species.[15] The $^{19}$F NMR spectrum shows two signals for CH$_3$SF$_3$ at δ = -50.6 ppm and 60.9 ppm, which are in accordance to the literature.[16]



**Scheme 1.** Formation of SIMes aluminium(III)fluoride **2**.

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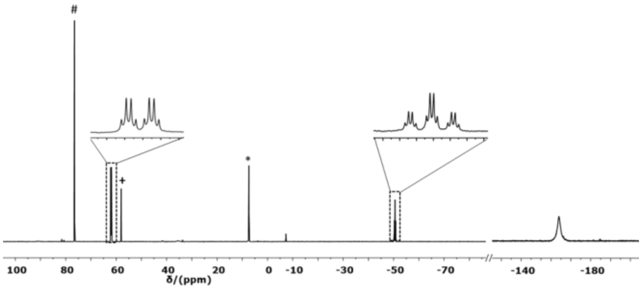
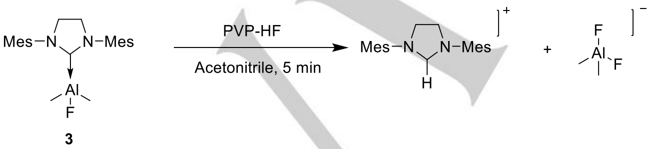


**Figure 1.** $^{19}F$ NMR (282.4MHz, [D$_8$]Toluene, -30 °C ) spectrum showing the formation of complex **2** and $CH_3SF_3$. $^{\#}SOF_2$ (impurity from $SF_4$), $^{+}SF_6$, $^{*}CH_3SOF$

The reactivity of **1** towards $SF_6$ has also been investigated. In general $SF_6$ activation has been considered to be challenging, but several interesting procedures were developed in the past years.[17] When the aluminium complex [(SIMes)AlMe$_3$] (**1**) was treated with $SF_6$ and the reaction mixture was heated at 70°C for 15 h , monofluorination at aluminium took place to give a complex in low yield (30 %), the data of which are consistent with [(SIMes)Al(F)Me$_2$] (**3**). The reaction did not proceed further, even after prolonged reaction times. When complex **1** and $SF_6$ were treated together at 311 nm under UV light for 24 h, the formation of **3** and subsequently of the aluminium trifluoride complex **2** was observed. In the $^{19}F$ NMR spectrum of **3** a broad signal was found at δ = -169.9 ppm. The $^{1}H$ NMR reveals a doublet at δ = -1.09 ppm with a coupling constant of $^{3}J_{H\text{-}F}$ = 3.2 Hz for the methyl groups attached to the Al center. The coupling constant is in the expected range of $^{3}J_{H\text{-}F}$ values reported for organofluoroaluminates.[18]

Along with complex **3** the evolution of methane was also observed as indicated by $^{1}H$ NMR spectroscopy. This suggests the presence of HF in the reaction mixture, which might react with **1** to yield $CH_4$. When the activation of $SF_6$ was performed in the presence of CsF, no reaction was observed, presumably due to trapping of HF by the base, which further supports a fluorination of **1** by HF. However, treatment of complex **3** with PVP · HF as an HF source gave the protonated SIMes and $[AlF_2Me_2]^-$[19], ,whereas a reaction of **1** with PVP · HF also generates the protonated carbene and $[AlF_4]^-$ (Scheme 2). The same products were formed when the reaction mixture of **1** and **3** were kept for 2 days at room temperature.



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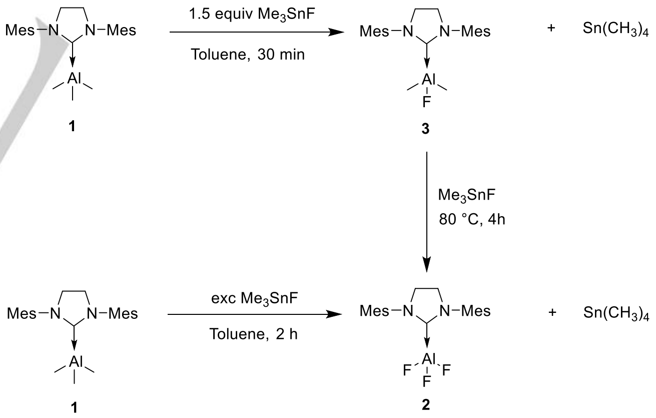
**Scheme 2.** Addition of HF to complex **3**.

Note that it was reported in the literature that SIMes and $SF_6$ can react at 80 °C within 48 h to give a 2,2-difluoroimidazolidine derivative in very low yield.[17d] The reaction can be promoted by photolysis. 2,2-Difluoroimidazolidine $C_3H_4N_2(Mes)_2F_2$ is water sensitive and can react to furnish HF and the corresponding urea derivative. Therefore, it can be speculated that when complex **1** was treated with $SF_6$ at 70 °C some decomposition occurs to yield SIMes, which then activates $SF_6$ to produce 2,2-difluoroimidazolidine and the respective 2-thiocarbene. The former reacts with adventitious water to yield HF which fluorinates **1**. Note, that on adding complex **1** to the 2,2-difluoroimidazolidine the generation of complex **3** was observed with very low conversion.

To develop a more reliable synthesis of the fluorido compounds **2** and **3**, $Me_3SnF$ was employed as fluorination agent. Note that $Me_3SnF$ has been widely used as fluorinating agent for fluorination of transition and main group chlorides.[9, 20] $Me_3SnF$ was also reported to convert dimethyl alane or aluminium hydrides into aluminium fluorides as shown for the synthesis of aminoalane difluoride [(2,6-*i*Pr$_2$C$_6$H$_3$)N(SiMe$_3$)Al(F)$_2$] and diamidoaluminium fluoride [(2,6-*i*Pr$_2$C$_6$H$_3$)N]$_2$(CH$_2$)$_3$AlF(NMe$_3$).[21] Reaction of complex **1** with 1.5 equivalents of $Me_3SnF$ led to the generation of **3** with full conversion of complex **1**. Tetramethyltin was also formed and identified in $^{1}H$ NMR spectrum by a signal at δ = 0.05 ppm, in $^{13}C$ NMR spectrum at δ = -9.4 ppm and in $^{119}Sn$ NMR spectrum at δ = 0.00 ppm.[22] When three equivalents of $Me_3SnF$ were added to complex **1** a mixture of complexes **2** and **3** was observed after 2h (ratio: 0.5 : 1). Monitoring the reaction by NMR spectroscopy revealed that **3** converted into **2** when heated at 80 °C for 4 h. However, treatment of complex **1** with an excess of $Me_3SnF$ for 2h gave complex **2** after heating, as evidenced by the resonance at -164.8 ppm in the $^{19}F$ NMR spectrum (Scheme 3, Figure 2).



**Scheme 3.** Fluorination of complex **1** with $Me_3SnF$.

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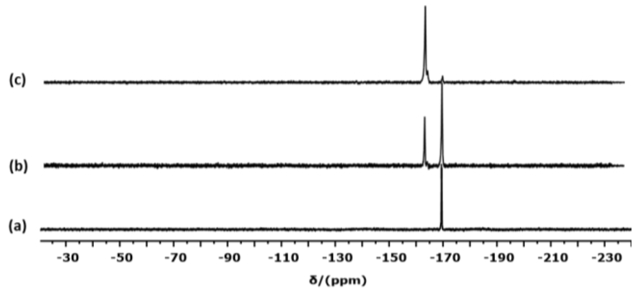
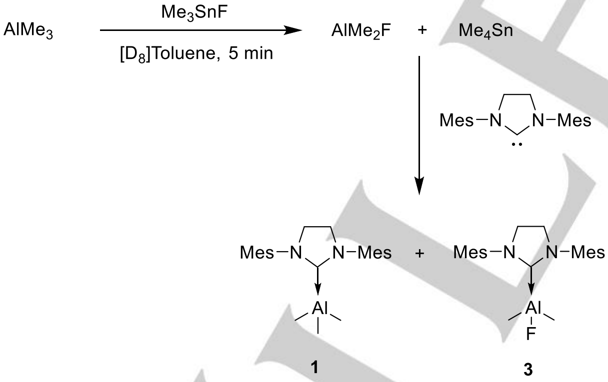


**Figure 2.** $^{19}F$ NMR spectra of the reaction of **1** with $Me_3SnF$ (3 equiv); (a) after 30 mins, (b) after 2 h, (c) after heating the mixture of complex **2** (-164.8 ppm) and complex **3** (-169.9 ppm) at 80 °C for 4 h.

For comparison, $AlMe_3$ was also treated with $Me_3SnF$ and the generation of $AlMe_2F$ was observed (Scheme 4). The latter exists as a dynamic mixture of dimers, as described in the literature.[23] The measured $^1H\{^{19}F\}$ NMR spectrum shows resonances at δ = -0.43 ppm, -0.55 ppm, -0.63 ppm and -0.69 ppm, but not with equal intensities as described in the literature.[24] It can be speculated that binuclear Al compounds bearing only one fluorine atom $Al_2Me_5F$ were also present. However, the $^{19}F$ NMR spectrum reveals four resonances at δ = -143.6 ppm, -145.8 ppm, -148.9 ppm and -150.8 ppm. These values are in accordance with data reported by Oliva et al.[25] Upon addition of SIMes to the reaction mixture the generation of complexes **1** and **3** was observed (Scheme 4), which supports the proposed structure of complex **3**. There is no hint for the generation of $[(SIMes)Al(F)_2Me]$.



**Scheme 4.** Formation of complex **3** using $Me_3SnF$ as fluorinating reagent.

It has been shown that metal fluorido complexes can be converted into chlorido complexes using chlorosilanes.[26] Indeed, when $Me_3SiCl$ was added to the SIMes stabilized aluminum(III)fluorido complex $[(SIMes)Al(F)_3]$ (**2**) the chlorido complex $[(SIMes)Al(Cl)_3]$ (**4**) was obtained along with $Me_3SiF$ (Scheme 5). This conversion further confirms the identity of complex **2**. A signal at δ = 104.7 ppm was found in the $^{27}Al$ NMR spectrum, which is consistent with data for **4**, synthesized independently.[27] Signals for $Me_3SiF$ were observed at δ = -156.9 ppm in $^{19}F\{^1H\}$ NMR spectrum and at δ = 30.3 ppm in $^{29}Si$ NMR spectrum.[28]

**Scheme 5.** Transformation of **2** into **4** with $Me_3SiCl$.

## Conclusions

Herein we have explored different synthetic routes to access NHC stabilized aluminium(III)fluorido complexes. $[(SIMes)Al(F)_3]$ (**2**) was formed when $[(SIMes)AlMe_3]$ (**1**) was treated with $SF_4$, whereas a reaction with $SF_6$ yielded $[(SIMes)Al(F)Me_2]$ (**3**). $Me_3SnF$ was also employed for fluorination of complex **1** to develop an alternative more reliable way to synthesize **2** and **3**. Complex **1** can be converted into the respective chlorido complex **4** via F/Cl exchange reaction by reaction with $Me_3SiCl$.

## Experimental Section

### Instruments and Methods

All reactions were carried out in a glove box under argon atmosphere or using standard Schlenk techniques under inert conditions. The reaction with $SF_4$ was performed on a stainless steel vacuum line. Solvents were distilled using conventional methods and degassed prior to use. Other reagents were bought either from Sigma-Aldrich or abcr. The NMR spectra were recorded at 25°C, if not stated otherwise, on a Bruker DPX 300, a Bruker Avance III 300, or a Bruker Avance II 500 spectrometer. The $^1H$ NMR spectra were referenced to residual $[D_7]$Toluene at δ = 7.09 ppm or $C_6D_5H$ at δ = 7.16. The $^{19}F$ NMR spectra were referenced to external $CFCl_3$ at δ = 0.0 ppm. The $^{29}Si$ NMR spectrum was referenced externally to TMS at δ = 0.0 ppm. $^{27}Al\{^1H\}$ NMR spectra were referenced externally to $AlCl_3$ in $D_2O$ at δ = 0.00 ppm. 1,2-Difluorobenzene at δ = -138.1 ppm in the $^{19}F$ NMR spectrum was used as an external standard for quantification

1,3-Bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene (SIMes) was synthesized by following the procedure described in the literature.[29] The NHC stabilized aluminium complex **1** was synthesised by treating saturated imidazolidine mesityl carbene (SIMes: 1,3-bis(2,4,6-trimethylphenyl)-imidazolidin-2-ylidene) with $AlMe_3$ (2M in Toluene) as reported.[14] Trimethyltin fluoride ($Me_3SnF$) was synthesized by treating trimethyltin chloride ($Me_3SnCl$) with potassium fluoride (KF) in a water/ethanol mixture.[30]

**Caution!** $SF_4$ is a toxic and corrosive gas which easily hydrolyses to give HF and exposure to these chemicals can cause serious injuries.

**Formation of complex [(SIMes)Al(F)$_3$] (2)**

*Method A: Fluorination with SF$_4$:*

In a PFA tube complex [(SIMes)Al(Me)$_3$] (**1**) (37.8 mg , 0.10 mmol) was dissolved in [D$_8$]Toluene (0.3 mL). The solution was degassed by freeze-thaw cycles followed by condensation of SF$_4$ (1 equivalent) into it. The PFA tube was sealed and inserted into a NMR tube. The reaction mixture was then brought to -30 °C and analysed by NMR spectroscopy.

*Method B: Fluorination with Me$_3$SnF:*

In a Schlenk tube complex [(SIMes)Al(Me)$_3$] (**1**) (37.8 mg , 0.10 mmol) was dissolved in toluene (5 mL) and an excess of Me$_3$SnF (6 equivalents) was added it. The solution was stirred for 2 h at room temperature followed by filtration. The filtrate was evaporated in vacuo to obtain complex **2**. Yield: 68%

Spectroscopic data for complex **2**: $^1$H NMR (300.1 MHz, C$_6$D$_6$): $\delta$ = 6.60 (s, 4H, *m*-ArH), 4.24 (s, 4H, CH$_2$), 2.22 (s, 12H, *o*-CH$_3$), 2.01 (s, 6H, *p*-CH$_3$) ppm; $^{19}$F NMR (282.4 MHz, C$_6$D$_6$): $\delta$ = -164.5 (bs, AlF) ppm; $^{27}$Al NMR (130.3 MHz, C$_6$D$_6$): 49.8 ppm.

Spectroscopic data for CH$_3$SF$_3$:[16] $^1$H NMR (300.1 MHz, [D$_8$]Toluene, -30 °C): 4.96 (bs, CH$_3$SF$_3$) ppm; $^{19}$F NMR (282.4 MHz, [D$_8$]Toluene): $\delta$ = 62.1 (dq, 2F, $^2J_{FF}$ = 73 Hz, $^3J_{HF}$ = 15.3 Hz, CH$_3$SF$_3$), -50.6 (1F, tq, $^2J_{FF}$ = 73 Hz, $^3J_{HF}$ = 15.3 Hz, CH$_3$SF$_3$) ppm.

**Formation of complex [(SIMes)Al(F)Me$_2$] (3)**

*Method A: Fluorination with SF$_6$:*

In a PFA tube complex [(SIMes)Al(Me)$_3$] (**1**) (37.8 mg , 0.10 mmol) was dissolved in [D$_8$]Toluene (0.3 mL). The solution was degassed by freeze-thaw cycles followed by condensation of SF$_6$ (1 equivalent) into it. The PFA tube was sealed and inserted into a NMR tube. The reaction mixture was warmed up to room temperature and heated at 70 °C for 48 h to obtain complex **3**. Yield after 48 h was found to be 30% when calculated by using a capillary with 1,2 difluorobenzene (0.2 M in C$_6$D$_6$) as an external standard.

*Method B: Fluorination with Me$_3$SnF:*

In a Schlenk tube complex [(SIMes)Al(Me)$_3$] (**1**) (37.8 mg , 0.10 mmol ) and Me$_3$SnF (18.6 mg, 0.10 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 complex **3**. Yield : 62%

Spectroscopic data for complex **3**: $^1$H NMR (300.1 MHz, C$_6$D$_6$): $\delta$ = 6.59 ( s, 4H, *m*-ArH), 3.04 (s, 4H, CH$_2$), 2.22 (s, 12H, *o*-CH$_3$), 2.06 (s, 6H, *p*-CH$_3$), -1.16 (d, 6H, $^3J_{HF}$ = 3.07 Hz, AlCH$_3$) ppm; $^{19}$F NMR (282.4 MHz, C$_6$D$_6$ ): $\delta$ = -169.9 (bs, AlF) ppm.

**Reactivity ofcomplex 2 towards Me$_3$SiCl.**

In a PFA tube complex [(SIMes)Al(F)$_3$] (**2**) (39.2 mg , 0.10 mmol) was dissolved in C$_6$D$_6$ (0.3 mL) and Me$_3$SiCl (3 equivalents) was added at room temperature. Formation of complex [(SIMes)Al(Cl)$_3$] (**4**) and trifluoromethyl silane (Me$_3$SiF) was observed after 1 h. The analytical data for complex **4** are in accordance with those in the literature.[27]

## Acknowledgments

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## Conflicts of interest

There are no conflicts to declare.

**Keywords:** *N*-heterocyclic carbenes • aluminium fluorides • sulfur fluorides • tin fluorides

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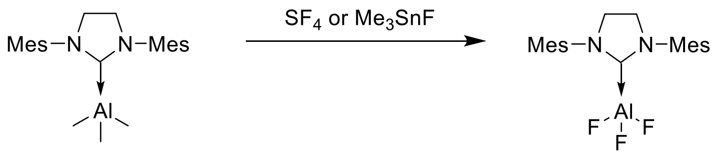
## Entry for the Table of Contents



Efficient routes to access NHC stabilized Al(III)fluorides are reported. The conversions include reactions of $SF_4$ or $Me_3SnF$ at [(SIMes)$AlMe_3$]. The generation of the Al(III) fluoride [(SIMes)Al$(F)_3$] was observed.

**Fluorination at Aluminium**

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***Page No. – Page No.***

**Title: Preparation of NHC stabilized Al(III)fluorides: Fluorination of [(SIMes)$AlMe_3$] with $SF_4$ or $Me_3SnF$**