Facile and systematic access to the least-coordinating WCA [(R'O)₃Al–F–Al(R'O)₃]⁻ and its more Lewis-basic brother [F–Al(R'O)₃]⁻ (R' = C(CF₃)₃)

Useful starting materials with the anions [F–Al(R'O)₃]⁻ and [(R'O)₃Al–F–Al(R'O)₃]⁻ (R' = C(CF₃)₃) can be obtained by reaction of Me₃Si–F–Al(R'O)₃ with the respective [PF₆]⁻ salts in high purity and yield. [(R'O)₃Al–F–Al(R'O)₃]⁻ is probably one of the least coordinating anions known. Due to this weak coordination, unexpected reactivities of its silver salt have been observed. By contrast, the strongly bound (Al-)F atom of [F–Al(R'O)₃]⁻ is coordinating and may act as a hemi-labile ligand. [F–Al(R'O)₃]⁻ can be transformed into the fluoride bridged anion by addition of Me₃Si–F–Al(R'O)₃.
Facile and systematic access to the least-coordinating WCA [(R^F)O]_3Al−F−Al(OR^F)_3]− and its more Lewis-basic brother [F−Al(OR^F)_3]− (R^F = C(CF_3)_3)

By reaction of the Lewis acid Me_3Si−F−Al(OR^F)_3 with a series of [PF_6]− salts, gaseous PF_6 and Me_3Si−F are liberated and salts of the anion [F−Al(OR^F)_3]− ([f−al]−; R^F = C(CF_3)_3) can be obtained. By addition of another equivalent of Me_3Si−F−Al(OR^F)_3 to [f−al]−, gaseous Me_3Si−F is released and salts of the least coordinating anion [(R^F)O]_3Al−F−Al(OR^F)_3]− ([al−f−al]−) are formed. Both procedures work for a series of synthetically useful cations including Ag^+*, [NO]^+, [Ph_3C]^+ and in very clean reactions with 5 g batch sizes giving excellent yields typically exceeding 90%. In addition, the synthesis of Me_3Si−F−Al(OR^F)_3 has been optimized and scaled up to 85 g batches in an one-pot procedure. These anions could previously only be obtained by difficult to control decomposition reactions of [Al(OR^F)_4]− or by halide abstraction reactions with Me_3Si−F−Al(OR^F)_3, generating relatively large countercations that are unsuited for further use as universal starting materials. Especially [al−f−al]− is of interest for the stabilization of reactive cations, since it is even weaker coordinating than [Al(OR^F)_4]− and more stable against strong electrophiles. This bridged anion can be seen as an adduct of [f−al]− and Al(OR^F)_3. Thus, it is similarly Lewis acidic as BF_3 and eventually reacts with nucleophiles (Nu) from the reaction environment to yield Nu−Al(OR^F)_3 and [f−al]−. This prevents working with [al−f−al]− salts in ethereal or other donor solvents. By contrast, the [f−al]− anion is no longer Lewis acidic and may therefore be used for reactions involving stronger nucleophiles than the [al−f−al]− anion can withstand. Subsequently it may be transformed into the [al−f−al]− salt by simple addition of one equivalent of Me_3Si−F−Al(OR^F)_3.

Introduction

For many years our group has been interested in the stabilization of reactive cations with the weakly coordinating anion [Al(OR^F)_4]− (WCA, R^F = C(CF_3)_3). With this anion shown in Scheme 1, a large variety of reactive cations being electrophilic like [CX_3]^+, RZn^+ (R = Me, Et), [Sn(Cp)]^+, [P_2X_5]^+ (X = Cl, Br, I) and [P_x]^+, oxidizing like [NO]^+, [NO_2]^+ or [AgX_2]_n^−-complexes, or very weakly bound to a central atom like the huge number of [M(L)_n]^+ complexes with M = Cu, Ag, Au and L = CO, C_2H_2, C_2H_4, P_x, S_n, S_12, Se_n, Se_12 or Se_19 could be stabilized.1−3 One of the biggest advantages of this [Al(OR^F)_4]− anion is its facile and fast synthesis in high yields.4 Other commonly used WCAs are [B(C_6F_5)_4]^−, perhalogenated carborane anions [R−CB_{11}X_{12}]_− (X = F, Cl, Br) and the teflates [E(OTeF_5)]_− (E = B, Al, Sb, As, Bi, Nb; x = 4, 6).5,6 However, the synthesis of these anions either require handling of explosive LiC_6F_5,5 elaborated syntheses in small scales,6 or handling of the toxic and hydrolysis sensitive HOTeF_5.5,6,11 Yet, especially the carborane anions are chemically more stable against fierce electrophiles than [Al(OR^F)_4]−, e.g. against small sililyum ions.12 As shown in eqn (1a), [Al(OR^F)_4]− decomposes in the presence of small sililyum ions [R_xSi]^+ above

[Image of chemical structures]

Scheme 1 Overview to the anions presented in this paper and their abbreviations.
More general, very small and very potent electrophiles, like “[PCl3]−” or “[SiCl4]−” induce [Al(ORF)4]− decomposition, very often under formation of [[R2O]3Al−F−Al(ORF)3]− ([al−f−al]−, eqn (1b)), which is even less coordinating than [Al(ORF)4]−.15 For more than a decade, access to a starting material with this anion was only accessible by decomposition of Ag[Al(ORF)4]. However, this synthesis proved to be delicate to reproduce, requires the two-step synthesis of Ag[Al(ORF)4], and is combined with loss of Ag+ and ORF moieties. The bridging motif of [al−f−al]− may be seen in analogy to related bridged anions known to the literature, e.g. as in [(C6F5)3B−CN−B[(C6F5)3]]−, [(C6F5)3B−NH2−B[(C6F5)3]]− and [(C6F5)3E−F−E[(C6F5)3]]− (E = B, Al, Ga).18

In some cases, where decomposition of [Al(ORF)4]− occurred, formation of [al−f−al]− could not be observed. Instead the formal [F−Al(ORF)3]− anion ([f−al−]) was obtained, often as part of a neutral compound, like in Me3Si−F−Al(ORF)3, or Cp*Be−F−Al(ORF)3.19 Therefore, both were rationalized as being ion-like compounds that behave intermediate between being covalently bound or separated ions. Nevertheless also compounds, where [f−al]− and the cation are separated, were isolated.20

Me3Si−F−Al(ORF)3 has already shown its usefulness for silylation reactions.15−21 The polymerization of isobutene,13 halide abstraction reactions,21 and abstraction of [Cp]−.3 It is available in an one pot synthesis that was optimized here to 85 g scale. Upon investigation of its reactivity, formation of [al−f−al]− and [f−al]− could often be observed and proved to be easily controllable.21 Therefore we investigated here, if it is possible to use Me3Si−F−Al(ORF)3, to synthesize both anions with cations that would make them good starting materials for further chemistry.

Results and discussion

Large-scale optimized synthesis of Me3Si−F−Al(ORF)3

In order to establish optimized routes to the anions [al−f−al]− and [f−al]−, we needed access to larger amounts of Me3Si−F−Al(ORF)3. Therefore, we optimized this synthesis and performed an upscaled from 40 g (ref. 13) up to 85 g. Although we believe that further upscaiping is possible, we do not recommend it. The vigorous stirring of the reaction solution is crucial and becomes complicated in larger scales, when using a Dewar vessel for the cooling bath. Additionally, since 25 g of Me3SiF cost 364 € (ABCR), we elaborated a synthesis starting from Me3SiCl and [NH2]3[SiF6] on the basis of ref. 22, yielding Me3SiF in high purities at very low cost (see ES† for details).

In order to maximize the yield and purity of Me3Si−F−Al(ORF)3, it is highly important to dry all glassware with a gas burner in vacuo until the flame turns orange. When opening the reaction vessel containing the AlEt3, the argon flow must be carefully controlled. If the argon flow is too high, the AlEt3 may start to smoke due to swirling of ambient air. Additionally, the HORF has to be dried to a water content of less than 1 ppm, which can be achieved by stirring with P2O5 for two weeks. It is also highly advisable to use as large of a stir bar as possible, since vigorous stirring is crucial for this synthesis and during the reaction, the viscosity of the reaction solution increases.

The Me3Si−F−Al(ORF)3 used for all syntheses in this paper was prepared according to the following optimized procedure: AlEt3 (15.0 mL, 109 mmol, 93% purity) was dissolved in heptane (120 mL) and cooled to −40 °C. Under vigorous stirring, the first two equivalents of HORF (30.0 mL, 215 mmol, 2.0 eq.) were added dropwise to the reaction mixture, while keeping the cooling bath between −40 and −20 °C. During the addition of HORF, gas evolution (C2H4) was observed, the viscosity of the solution increased and small amounts of precipitate formed. After complete addition of the first HORF portion (typically within 1 hour), Me3SiF (12.5 g, 136 mmol, 1.2 eq.) was condensed onto the reaction mixture at −40 °C. The solution was stirred for 10 min, and then the third equivalent of HORF (20.0 mL, 143 mmol, 1.3 eq.) was added within 5 min. The cooling bath was removed and the reaction mixture was allowed to reach rt, which led to dissolution of the precipitate. After 30 min, more HORF (5.0 mL, 36 mmol, 0.3 eq.) was added and the solution was stirred overnight. From the clear solution, slowly a white powder crystallized. For product isolation, simply the solvent was removed in vacuo yielding a white crystalline powder (85.4 g, 103 mmol, 94%). Note: one needs the excess of the fluorinated alcohol, as this is very volatile (b.p. = +45 °C) and the continuous stream of evolving ethane removes the excess alcohol through the bubbler.

The quality of the Me3Si−F−Al(ORF)3 can be verified by different methods: if the obtained powder seems to be moist, but cannot be completely dried, there are probably residual Al−Et groups present in the product. In this case, more HORF should be added. Another qualitative test for the purity of the product is by dissolving it in 1,2-difluorobenzene (o-DFB). A solution of pure Me3Si−F−Al(ORF)3 is nearly colorless, while impurities (mainly residual Al−Cl groups stemming from the AlEt3) induce a light yellow color. These impurities usually enrich at the top of the crystallized product and stick to the glass of the reaction vessel. These crystals are yellow colored and isolable. Therefore they should not be scratched out of the reaction vessel. Purification of the white powder can be achieved either by sublimation at 60 °C in dynamic vacuum (10−3 mbar) or by washing with warm CH2Cl2, let it cool and then filter it. Additionally, NMR spectra of the product should be taken in both, o-DFB and CH2Cl2. Me3Si−F−Al(ORF)3 is only poorly soluble in CH2Cl2, but not its impurities. Therefore, if a NMR spectrum in CH2Cl2 shows only negligible amounts of impurities, the product can be considered pure. In o-DFB Me3Si−F−Al(ORF)3 is highly soluble and here the signal intensity is increased compared to the impurities. Therefore, NMR spectra in CH2Cl2 may show a purity of only 60%, while the real purity is >90%, as can be seen from NMR spectra in o-DFB. Pure
Me$_3$Si–F–Al(OR$_3$)$_3$ can be stored in a glove box for at least a year without decomposition.

**Synthesis of [f-al] − and [al–f–al] − salts**

In a general procedure [Cat][f-al]$^-$ and [Cat][al–f–al]$^-$ (Cat = Li, K, Ag, NO, Ph$_3$C) can be obtained by reaction of 1 and 2 equiv. Me$_3$Si–F–Al(OR$_3$)$_3$, respectively, with [Cat][PF$_6$] at rt or 60 °C, depending on the solubility of the [PF$_6$]$^-$ salt (eqn (2)). The calculated rather exergonic reaction energies are included with eqn (2) and are given in kJ mol$^{-1}$ (BP86-D3(BJ)/def-SV(P)).

The preferred reaction conditions for all investigated compounds are listed in Table 1. The formation of the respective anion is controlled by the stoichiometry of Me$_3$Si–F–Al(OR$_3$)$_3$, used (1 : 1 or 2 : 1) – the very Pearson hard Li$^+$ case presents the only exception and stops at the [f-al]$^-$ stage. The reactions performed at rt are usually finished within a few minutes and are accompanied by a vigorous evolution of PF$_5$ after addition of the solvent. In the following, we briefly describe the reactions for each cation separately.

**Lithium salts.** Due to the poor solubility of Li[PF$_6$] in o-DFB even at 60 °C, a donor has to be added. We chose Cl$_2$CCN as a weak donor in order to obtain a lithium cation with a Lewis acidity as high as possible. From this reaction the compound [Li(NCCH$_3$)$_2$][f-al]$^-$. As the only exception from eqn (2), the [f–al]$^-$. anion could not be obtained in combination with a lithium cation. This is probably due to strong coordination of Li$^+$ to [f–al]$^-$ (see molecular structures later) preventing the reaction to proceed towards [al–f–al]$^-$. Stronger donors, like MeCN or THF, lower the Lewis acidity of Li$^+$ and might therefore allow for the formation of [al–f–al]$^-$. due to a higher degree of dissociation of [Li(solv)$_n$][f-al]. However, strong donors are also able to coordinate to the Al(OR$_3$)$_3$ moiety of Me$_3$Si–F–Al(OR$_3$)$_3$, which may completely prohibit formation of the desired anions. Dimethylcarbonate (DMC) was also found to be suitable for the synthesis of [Li(DMC)$_2$][f-al]$^-$. In this case Me$_3$Si–F–Al(OR$_3$)$_3$ first reacts with DMC to form DMC–Al(OR$_3$)$_3$ before the anion is formed (see ESI for details).

**Potassium salts.** K[PF$_6$] is also only poorly soluble in o-DFB at rt. Nonetheless, heating the reaction solution to 60 °C increases the solubility enough to allow for the reaction with Me$_3$Si–F–Al(OR$_3$)$_3$, and formation of K[al–f–al] within 2 h.

The synthesis of K[f-al] proved to be more problematic. Compared to Me$_3$Si–F–Al(OR$_3$)$_3$, only little K[PF$_6$] is in solution, and thus only K[al–f–al] is formed at the beginning of the reaction. The [f–al]$^-$. anion is therefore mainly formed by reaction of [PF$_6$]$^-$ and [al–f–al]$^-$. which is hindered by coulombic repulsion. After heating the reaction mixture to 60 °C for 9 h with an excess of finely ground K[PF$_6$] (2 eq.) the reaction mixture still contained 4% K[al–f–al]. Additionally, NMR spectra show signals of K[OR]$^-$ (6%) and [F$_3$-Al(OR$_3$)$_3$]$^-$. (12%). Therefore we do not recommend to synthesize K[f-al] for the use as starting material, as it can only be obtained with significant amounts of impurities by this route. The K[f-al] obtained this way (~80% purity), however, is sufficiently pure for IR and Raman spectroscopy.

**Silver salts.** Ag[PF$_6$] is also only poorly soluble in CH$_2$Cl$_2$, SO$_2$ and o-DFB at rt. Nonetheless, the formation of [Ag(L)$_2$][f-al]$^-$ and [Ag(L)$_3$][al–f–al]$^-$ proceeds within a few minutes, probably due to the high solubility of the products. The pure crystalline products can be obtained by crystalization of the concentrated solutions with n-pentane and a sufficiently pure product can be obtained by simply removing the solvent in vacuo. When Ag[f-al] is crystalized from o-DFB at rt, the cation is coordinated by three o-DFB molecules. Interestingly, when Ag[al–f–al] is crystalized from o-DFB at rt, the Ag$^+$ is coordinated by only two o-DFB molecules, while at ~30 °C it is coordinated by three o-DFB molecules (Fig. 3e and f). This suggests that the third o-DFB molecule is only weakly bound.

The reaction in SO$_2$ has to be performed at ~20 °C in order to prevent loss of the solvent, while at the same time the evolving

<table>
<thead>
<tr>
<th>Cation</th>
<th>Solvent</th>
<th>Reaction time</th>
<th>Temperature</th>
<th>Yield</th>
<th>Cation (bulk)</th>
<th>Cation (single crystal)</th>
<th>CCDC number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^{a}$</td>
<td>o-DFB/Cl$_2$CCN</td>
<td>4 h</td>
<td>60 °C</td>
<td>— (84%)</td>
<td>—</td>
<td>[Li(NCCH$_3$)$_2$]$^-$</td>
<td>1845808</td>
</tr>
<tr>
<td>Li$^{a}$</td>
<td>DMC ([MeO$_2$]CO)</td>
<td>2 h</td>
<td>70 °C</td>
<td>— (86%)</td>
<td>[Li(DMC)$_2$]$^-$</td>
<td>[Li(DMC)$_3$]$^-$</td>
<td>1845810</td>
</tr>
<tr>
<td>K$^{b}$</td>
<td>o-DFB</td>
<td>2 h</td>
<td>60 °C</td>
<td>90%$^{b}$</td>
<td>K$^+$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>CH$_2$Cl$_2$</td>
<td>1 h</td>
<td>rt</td>
<td>97% (98%)</td>
<td>[Ag(CH$_2$Cl)$_2$]$^+$</td>
<td>[Ag(CH$_2$Cl)$_3$]$^+$</td>
<td>—</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>SO$_2$</td>
<td>2 h</td>
<td>−20−0 °C</td>
<td>95% (98%)</td>
<td>Ag$^+$</td>
<td>[Ag(o-DFB)$_3$]$^+$</td>
<td>[Ag(o-DFB)$_2$]$^+$</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>o-DFB</td>
<td>30 min</td>
<td>rt</td>
<td>96% (70%)</td>
<td>Ag$^+$</td>
<td>[Ag(o-DFB)$_3$]$^+$, [Ag(o-DFB)$_2$]$^+$</td>
<td>[Ag(o-DFB)$_2$]$^+$</td>
</tr>
<tr>
<td>NO$^{-}$</td>
<td>SO$_2$</td>
<td>1 h</td>
<td>−35−0 °C</td>
<td>88% (90%)</td>
<td>NO$^-$</td>
<td>[NO]$^-$</td>
<td>18458114</td>
</tr>
<tr>
<td>[Ph$_3$C]$^-$.</td>
<td>o-DFB</td>
<td>1 h</td>
<td>rt</td>
<td>88% (95%)</td>
<td>[Ph$_3$C]$^-$.</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$^{a}$ Only the [f-al]$^-$ anion is obtained. $^{b}$ K[f-al] can only be obtained with significant amounts of impurities, therefore no yield is given.

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**Table 1** Reaction conditions for the synthesis of [Cat][f-al]$^-$ and [Cat][al–f–al]$^-$ . When using 1 equiv. of Me$_3$Si–F–Al(OR$_3$)$_3$, the [f–al]$^-$. anion is obtained. [al–f–al]$^-$ is obtained by using 2 equiv. of Me$_3$Si–F–Al(OR$_3$)$_3$. The values in parentheses correspond to [Cat][f-al]$^-$.
PF₅ is allowed to evaporate from the solution. The turbid reaction solution is then stirred at −20 °C until the gas evolution has completely stopped. Subsequently, the reaction solution is allowed to reach 0 °C, followed by removal of the solvent. The solvent free product is obtained as an off-white powder.

**Nitrosonium salts.** Due to the poor solubility of [NO][PF₅] in CH₂Cl₂ at rt, SO₂ has to be used as solvent. Here, the reaction is possible.

Al atoms. As a result, the ¹³¹Al resonance for the C(CF₃)₃ groups at 800 cm⁻¹ for the region between 900 and 500 cm⁻¹, and 75.6 ppm in the ²⁷Al NMR spectrum a sharp doublet at 41 ppm with 5J(F–F) = 1.5–2 Hz due to coupling to the Al-bound fluorine atom. In the ²⁷Al NMR spectrum a sharp doublet at 41 ppm with 5J(F–F) = 1.5–2 Hz due to coupling to the Al-bound fluorine atom. In the ²⁷Al NMR spectrum a sharp doublet at 41 ppm with 5J(F–F) = 1.5–2 Hz due to coupling to the Al-bound fluorine atom. In the ²⁷Al NMR spectrum a sharp doublet at 41 ppm with 5J(F–F) = 1.5–2 Hz due to coupling to the Al-bound fluorine atom. In the ²⁷Al NMR spectrum a sharp doublet at 41 ppm with 5J(F–F) = 1.5–2 Hz due to coupling to the Al-bound fluorine atom. In the ²⁷Al NMR spectrum a sharp doublet at 41 ppm with 5J(F–F) = 1.5–2 Hz due to coupling to the Al-bound fluorine atom.

**Trityl salts.** When a few drops of o-DFB or CH₂Cl₂ are added to a mixture of [Ph₃C][PF₅] and Me₂Si–F–Al(OR₃)₃, immediately a fierce evolution of PF₅ takes place and is finished in less than a minute. Nevertheless, the reaction solution should be stirred for another 30 min in order to allow for a complete conversion. After removal of the solvent in vacuo, the product is obtained as a yellow powder.

**Spectroscopic differentiation of the anions**

Both anions can be differentiated by standard spectroscopic methods (IR, Raman, NMR). However, in all cases spectra of [f–al]⁻ and [al–f–al]⁻ are very similar and therefore we highlight key differences in the following.

**Differentiation by NMR-spectroscopy.** Fig. 1 shows the characteristic NMR signals of [al–f–al]⁻ and [f–al]⁻ in direct comparison. For [f–al]⁻ the ¹⁹F NMR spectrum shows a broad signal for the bridging fluorine atom at −184.5 ppm and a resonance for the C(CF₃)₃ groups at −75.5 ppm with a small doublet splitting of 0.5 Hz due to the ⁵J(F–F) coupling to the bridging fluorine atom. In the ²⁷Al NMR spectrum, only a very broad resonance at about 37 ppm (Δm₁/₂ = 1200 Hz) is obtained. This broadness of the signal is caused by a fast relaxation of the Al atom. As a result, the ¹³¹Al–F coupling is not resolved neither in the ²⁷Al nor in the ¹⁹F NMR spectra. The presence of this coupling can be deduced from the broadening of the signal of the bridging fluorine atom in the ¹⁹F NMR spectrum. In the ¹⁹F (²⁷Al) NMR spectrum this signal is sharp, which unambiguously proves that the broadening of this signal results from the ¹⁹F–¹³¹Al coupling (see ESIF for details – investigations on the Al(OR₃)₃ exchange reactions).

By contrast, for [f–al]⁻ the Al–F signal in the ¹⁹F NMR spectrum generates a sextet, due to coupling to the aluminum atom. This signal is usually found between −185 and −200 ppm, but may also be found at −145 ppm in case of the [NO]⁺ and [SeCl₄]⁺ salts. The signal of the alkoxyl groups is visible at −75.6 ppm with ⁵J(F–F) = 1.5–2 Hz due to coupling to the Al-bound fluorine atom. In the ²⁷Al NMR spectrum a sharp doublet at 41 ppm with ⁵J(Al–F) = 40 Hz is observable due to an increased relaxation time of the Al atom compared to [al–f–al]⁻.

**Differentiation by IR- and Raman-spectroscopy.** Parts of the IR and Raman spectra of different [Al(OR₃)₃]⁻, [al–f–al]⁻ and [f–al]⁻ salts are shown in Fig. 2 and are discussed in reference to Ag[Al(OR₃)₄]⁺. It should be noted that it is not possible to obtain a Raman spectrum of [Ag(CH₂Cl₂)][Al(OR₃)₃], prepared from Li [Al(OR₃)₄] and AgF in CH₂Cl₂ due to decomposition. When this metathesis reaction is performed in SO₂, instead of CH₂Cl₂, donor-free Ag[Al(OR₃)₄] suitable for Raman spectroscopy can be obtained.

The main differences between these anions can be found in the region between 900 and 500 cm⁻¹ (Fig. 2a). In the IR spectra additional bands at 636 (vₐₛ(Al–F–Al)) and 862 cm⁻¹ are visible for [al–f–al]⁻, and at 762 (v(Al–F)) and 808 cm⁻¹ for [f–al]⁻, when compared to [Al(OR₃)₄]⁺. The Raman spectra of these anions also show new bands at 636 and 723 cm⁻¹, respectively. One of the most characteristic differences between the three discussed anions in the Raman spectra is the frequency of the vibrational bands at ~750 and ~800 cm⁻¹ and their intensities. These bands are approximately equally intense for [Al(OR₃)₄]⁺. When looking at [al–f–al]⁻ and [f–al]⁻, the vibrational band at ~750 cm⁻¹ is about twice as intense as the band at ~800 cm⁻¹.

Especially for [f–al]⁻, the coordination of the cation to the (Al–F) atom may have an impact on the vibrational bands in the vibrational spectra. Therefore, we compared the IR and Raman spectra of Ag[f–al]⁻, K[f–al]⁻ and [NO][f–al] (Fig. 2b). Among these cations, [NO]⁺ is considered to be the least and Ag⁺ (donor-free) to be the strongest coordinating. Most of the vibrational bands in these compounds are identical. Only the molecular vibrations containing partial Al–F contributions (~810, ~760 and ~730 cm⁻¹) are influenced by the coordination to the cation. These bands appear at higher wave numbers, the weaker coordinating the cation is. For [NO][f–al]⁻ and K[f–al]⁻ these bands are blueshifted by up to 12 cm⁻¹ compared to Ag[f–al]⁻. Although a comparison of these compounds with the analogous [Ph₃C]⁻ and [Li(Li)]⁻ salts would be interesting, it proved to be rather complicated, since these bands overlap with the ones of the anion.

**Molecular structures of [f–al]⁻ and [al–f–al]⁻ salts**

Although our commonly used [Al(OR₃)₃]⁻ anion usually does not show significant coordination, very small cations, like Li⁺ and [Ag(Li)]⁺ are able to be coordinated by its oxygen atoms. As can be seen from Fig. 3, [f–al]⁻ usually coordinates to the cation with the (Al–F) atom. In case of the dimeric [Li(NCCl₃)]⁻ [f–al]⁻ the Al–F atom is coordinated to two Li atoms and also
the alkoxy moieties are involved in the coordination, forming a nearly planar Al–O–Li–F plane. This coordination leads to an elongation of the Al–F and Al–O coordinated bonds compared to [Li(DMC)]_3[Li–al] (Table 2). A similar coordination of the oxygen atoms of [al–f–al]− to a cation is highly unlikely for sterical reasons and was not observed in the compounds presented in this work. However, the [ZnEt]^+ cation is small enough to coordinate to these alkoxy groups. Here, both Zn–O distances are nearly equal (209.8 pm on average), while in [ZnEt][Al(OR)^3] they differ by ~5 pm (211.2 and 205.8 pm on average). The non-existing difference between the Zn–O distances in [ZnEt][al–f–al] not only is evidence for the weaker coordination of [al–f–al]− compared to [Al(OR)^3]−, but also for the inferior accessibility of the oxygen atoms.

**Some aspects for single crystal X-ray diffraction refinements**

For [Al(OR)^3]− compounds, the structure determination by single crystal X-ray diffraction frequently tends to be problematic. Due to the very weak interactions of the perfluorinated residues with the cation, but also with each other, these residues are able to rotate around the C–O and the Al–O bonds. As a result, the OC(CF^3)^3 moieties in this anion are often heavily disordered and/or feature rather large anisotropic displacement ellipsoids. This is one of the reasons, why we introduced the DSR program code, nowadays included with OLEX2 (ref. 24) and ShelXL,^25 to facilitate the description of these often very complicated disorders. These problems are typically less pronounced in salts containing [al–f–al]−. This is due to the further shortened Al–O bonds (169.7 pm vs. 172.5 pm on average)^6,16 that force the six OC(CF^3)^3 groups to be distributed over the rather small Al–F–Al core and increase the steric strain. For these reasons, the OC(CF^3)^3 groups are not able to rotate as freely as in [Al(OR)^3]− and are usually locked in one or two orientations. Therefore in many cases there is much less disorder and also smaller displacement ellipsoids were observed for [al–f–al]− structures compared to [Al(OR)^3]−. Nevertheless, there are also cases, where the entire anion is disordered around the bridging fluorine atom (see ESI of ref. 21).

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**Fig. 2** IR (top) and Raman (bottom) spectra in the region between 900 and 500 cm−1 and frequencies of characteristic bands in cm−1 of (a) Ag[Al(OR)^3] (black), Ag[al–f–al] (blue) and Ag[al–f–al] (red); (b) Ag[al–f–al] (red), K[al–f–al] (black) and [NO][al–f–al] (blue).

**Fig. 3** Overview of molecular structures of some starting materials presented in this work. Disorder was omitted in all cases, for the sake of clarity. (a) DMC–Al(OR)^3; (b) [Li(DMC)]_3[Li–al]; (c) [Li(NCCCl^3)]_2[Li–al]; (d) |Ag(o–DFB)|_3[Li–al]; (e) [Ag(o–DFB)]_3[al–f–al]; (f) [NO][al–f–al].
Inter alia

Anion Cation  
[f-al]−  [Li(NCCl3)]=  171.2(2)  169.9(5)/177.4(4)  167.4(2)  171.9(2)  185.7(7)/206.0(9)  220(1)
[f-al]−  [Li(DMC)]=  167.8(1)  168.7(1)  172.7(1)  174.1(3)  184.1(5)  242.0(1)
[f-al]=  [Ag(o-DFB)]=  176.1(2)  176.7(2)  169.3(2)  170.2(3)  348.1(1)  273.0(3)
[al-f-al]=  [Ag(o-DFB)]=  [NO]−  176.7(2)  170.2(3)  169.3(2)  273.0(3)

a Li–F(1).  b Li–O.  c Li–F(2).  d Ag–F.  e H–F.  f N–F.

Attempts to exchange Cat^[PF6]= for Cat^[BF4]=

[PF6]= salts are usually more expensive than the analogous [BF4]= salts (the price per mole of Ag[PF6] is more than 3 times as high as that of Ag[BF4]). Therefore, we tried to use [Cat][BF4] for the synthesis of [f-al]− and [al–f–al]=. NMR spectra of the reaction solution taken in C6H5F/acetone-d6 showed several signals for the OR− and Al−F moieties in the 19F NMR spectrum. This suggests a ligand scrambling reaction and formation of [AlF(ORF)4]= (x = 1–3) and their F-bridged analogues. From the 11B NMR spectrum only formation of BF(ORF)2 was visible. Since this solution contained lots of precipitate, another sample was prepared in C6H5F/acetic-acetone-d6 in order to dissolve this precipitate. Here NMR spectra showed mainly the formation of BF2(ORF) features a tricoordinated boron species. The formation of [AlF(ORF)4]= occurs due to the Lewis basicity of acetone and will be discussed later. These NMR spectra suggested a complex mixture of different boron and aluminum containing species. Inter alia, [Ag(PhF)] [F2B(ORF)=] (see ES† for details) crystallized from one of the mixtures. Interestingly, in this structure the Ag+ is coordinated to the oxygen atoms of the anion, since the more Lewis basic (B−)F atoms form hydrogen bonds with the coordinated solvent molecules.

Due to the lower Lewis acidity of the evolving BF3 compared to PF5, the ligand scrambling reaction would rather be expected when using [PF6]= salts for these reactions (FIA = 346 vs. 380 kJ mol−1; the CIA, HIA and MIA are also higher for PF5). The same trend holds, when comparing the calculated [OR]= ion affinities of BF3 (208 kJ mol−1) and PF5 (239 kJ mol−1) at BP86-D3(BJ)/def-SV(P) level. Therefore, a kinetic reason for this ligand scrambling has to be considered. The reacting reaction intermediate very likely involves Al−O(R5)=−B/P and Al−F−B/P bridging. In case of PF5, this transition state is energetically less accessible due to its increased size and decreased tendency to undergo bridging.

Additionally, the stabilities of the theoretical reaction products, i.e. BF2(OR)= and PF2(OR)=, also should be considered, but this is rather a secondary effect. BF2(OR)= features a tricoordinated, planar boron atom, which is able to undergo π back bonding with the lone pairs of the alkoxo moiety. This back bonding is stronger than that of fluoride and leads to a considerable stabilization of this molecule. The BF2(OR)= is able to undergo a second ligand scrambling to form the observed BF(OR)=. In PF2(OR)= this π back bonding is not present, presumably resulting in less favorable thermodynamics in matters of the discussed ligand scrambling reaction. Therefore, the isolation of [f-al]− and [al–f–al]= is best possible when using [PF6]= salts, although the Lewis acidities of PF5 and BF3 would suggest otherwise.

Improved WCA performance of [al–f–al]=

When considering the calculated electrostatic potentials of [Al(OR)=]−, [al–f–al]= and [f–al]= (Fig. 4) it can be concluded that [al–f–al]= should be the least coordinating of these anions and about as coordinating as [(C6F5)Al−F–Al(C6F5)=]. This is mainly due to the delocalization of the negative charge over 55 fluorne atoms, but also because the negative charge is partially localized at the bridging fluorine atom with an NPA charge of −0.67 vs. −0.34 for the terminal F atoms, similar to [f–al]= (NPA charge = −0.69 vs. −0.35; BP86/def-SV(P)). This makes [al–f–al]= more stable towards F− and [RFO]= abraction than [Al(OR)=]− (see later).16,28,29

The reactions of Ag[Al(OR)=] with halosilanes R3SiX (R = Me, tBu; PH; X = Cl, Br, I) in CH2Cl2 were already described.13,14 At rt these reactions yield R3Si–F–Al[OR]=, while at −50 °C the
halide bridged bis-silylium ions [R₃Si–X–SiR₃]⁺ were obtained. When we tried to reproduce these reactions with Ag[al–f–al] we noticed several curiosities. First of all, while Ag[Al(OR)₃] is highly soluble in CH₂Cl₂ at low temperatures, Ag[al–f–al] is only poorly soluble in cold CH₂Cl₂, although a higher solubility would have been expected with the weaker interactions between cation and anion. Secondly, when Me₃SiCl, Ph₃SiCl or Bu₃SiBr were added to the reaction solution, no silver halide formed. NMR spectra also revealed almost quantitative retention of the anion and the halosilane. The ²⁵Si NMR chemical shifts of the silanes, however, were slightly shifted to lower field (0.5–2 ppm), probably due to coordination to the silver cation. From the reaction with Bu₃SiBr single crystals could be obtained and were identified as [Ag(Bu₃SiBr)₂(CH₂Cl₂)][al–f–al] (Fig. 5). It is possible that related products may form with Me₃SiCl and Ph₃SiCl.

Although the formation of this cation is in agreement with the findings of Reed et al. that silylum ions are able to dissolve AgBr,⁹ at the same time it is contradictory to the reactions of Ag[Al(OR)₃]Cl where halide abstraction from halosilanes was observed.¹⁵,¹⁶ This leads to the conclusion that [Al(OR)₃]⁻ cannot be innocent in these reactions as similar halide abstractions are observed with Ag[ClO₄]⁻. Only when Me₃SiBr was added to Ag[al–f–al] in toluene/1,2,3-C₆H₃F₃ in a 1 : 1 stoichiometry, the formation of AgCl could be observed. NMR spectra of this solution predominantly showed decomposition of the anion and formation of Me₃Si–F–Al(OR)₃ next to other unidentified products.

Judged from these reactions and their solution NMR spectra, we propose that upon reaction of Ag[WCA] and halosilanes, R₃SiX, always the according silver complexes [Ag(X–SiR₃)(solvent)]⁻ are formed (eqn (3a)). These complexes contain an activated silicon and are strong silylating reagents. They react with nucleophiles (Nu) under formation of Nu–SiR₃ and AgX. It appears, that for anions like [ClO₄]⁻ or even [Al(OR)₃]⁻ this nucleophile can also be the anion (!), which subsequently may decompose (eqn (3b)). However, apparently the nucleophilicity of the [al–f–al]⁻ WCA is too low, to induce AgX separation. In addition, the silylation strengths of the [Ag(X–SiR₃)(solvent)]⁻ cation increases, when going from X = Cl to I, mainly due to weakening of the Si–X bond.

Further, the lacking formation of AgX by reaction of Ag[al–f–al] with R₃SiX (X = Cl, Br) can be seen as first experimental proof for the less coordinating nature of [al–f–al]⁻ with respect to [Al(OR)₃]⁻ or other WCAs that react with halosilanes under separation of AgX.

Another evidence for the weaker coordination and increased stability of [al–f–al]⁻ compared to [Al(OR)₃]⁻ is the intermediate synthesis of silylum ions by reaction of [Ph₃C][WCA] with Me₃SiH in CH₂Cl₂. In case of [WCA]⁻ = [Al(OR)₃]⁻ only Me₃Si–F–Al(OR)₃ is formed at rt within 30 min. In contrast to this, in case of [WCA]⁻ = [al–f–al]⁻ the solvent is attacked under formation of Me₃SiCl. In the NMR spectra of the latter reaction, the anion is mostly intact but decomposes within two days at room temperature. We were not able to identify the according cation, but judged by the formation of Me₃SiCl, it might be a chlorinated carboxylation resulting from the solvent CH₂Cl₂. Exchanging the CH₂Cl₂ for o-DFB, we were not able to isolate silylum ions at rt by this route when using Me₃SiH or iPr₃SiH. Again, we mainly observed formation of R₃Si–F–Al(OR)₃ and other decomposition products, similar to the reaction of Ag[al–f–al] with Me₃SiCl.

**Fig. 5** Molecular structure of Ag[Bu₃SiBr]₂(CH₂Cl₂)₁[al–f–al] at 100 K with thermal ellipsoids at 50% probability level. The C(CH₃)₃ moieties are shown in wireframe. Scheme: Ag (light gray), Br (brown), Si (yellow), Cl (green), Al (pink), O (red), F (light green), C (grey), H (white). Selected distances (Å) and bond angles (°): Si–Br₁ 231.87(7), Si₂–Br₂ 231.86(8), Ag–Br₁ 265.68(5), Ag–Br₂ 268.33(5), Ag–Cl₁ 262.22(8), Ag–Cl₂ 276.00(1), Al₁–F₁ 176.6(1), Al₂–F₁ 176.9(1), Al₁–F₁–Al₂ 159.51(8).
noted, that the calculated reactions are only the first step in the decomposition of CH₂Cl₂, [Al(ORF)₃]⁻ and [al-f-al]⁻ and are not the final reaction products. As a result, [al-f-al]⁻ is not stable against small silylum ions at rt, although these calculations suggest so.

The Lewis acidity of [al-f-al]⁻: implications for solvent compatibility

The increased stability of [al-f-al]⁻ against electrophiles compared to [Al(ORF)₃]⁻ seems to make it the anion of choice for the synthesis of reactive cations. However, this increased stability comes for a price: it’s clearly noticeable Lewis acidity. Thus, when investigating the NMR spectra of K⁺[al-f-al], we learned that as soon as we added Et₂O to the NMR sample in order to completely dissolve the K[al-f-al], the NMR signals of the anion disappeared, and only the signals of Et₂O and [al-f-al] remained. The fluoride bridged anion [al-f-al]⁻ can thus be seen as an adduct of [f-al]⁻ and the Lewis superacid Al(ORF)₃. Obviously, a large part of the Lewis acidity is retained in the final product leading to the cleavage of the anion in presence of Lewis bases (Scheme 2).

Using the Fluoride Ion Affinity (FIA) as a measure, the Lewis acidity of [al-f-al]⁻ is with a FIA-value of 329 kJ mol⁻¹ in the region of BF₃ (346 kJ mol⁻¹). This limits the choice of solvents: in basic solvents such as Et₂O and MeCN the equilibrium shown in Scheme 2 is on the side of LB-Al(ORF)₃ and [f-al]⁻. In SO₂, PhF, o-DFB, CH₂Cl₂, and CHCl₃ the fluoride bridged anion [al-f-al]⁻ was found to be completely intact by NMR spectroscopy. However, since SO₂-Al(ORF)₃ and Ph-F-Al(ORF)₃, are known to be relatively stable, an equilibrium between [al-f-al]⁻ and LB-Al(ORF)₃/[f-al]⁻ [here LB = SO₂, PhF] may be possible. For SO₂ this equilibrium was calculated to be on the side of [al-f-al]⁻ by \( \Delta G'_{\text{soh}} = -66 \text{ kJ mol}^{-1} \) using the COSMO model (\( \varepsilon = 16.3 \)) at BP86-D3(BJ)/def-SVP(P) level. This is in agreement with our experimental data, since we were able to synthesize [al-f-al]⁻ salts free of [f-al]⁻ in SO₂. Theoretically, the [f-al]⁻ anion may also act as Lewis base here, i.e. when the [al-f-al]⁻ salt is contaminated with [f-al]⁻. In this case, an exchange of Al(ORF)₃ moieties between [f-al]⁻ and [al-f-al]⁻ is expected. However, the presence of the \( J_{\text{Al-F}} \) and \( J_{\text{F-F}} \) coupling for both anions in this mixture definitely excludes this exchange. We did also not observe such an exchange in the \(^{19}F,^{19}F\) EXSY NMR spectrum or by line shape analysis. In contrast to this, the analogous chloride bridged anion [al-cl-al]⁻ dissociates in PhF. Therefore, we suggest using CHCl₃, CH₂Cl₂, o-DFB, PhF and SO₂ as solvents of choice, as they are polar and feature low Lewis basicity.

Taking advantage of [f-al]⁻

As already discussed, [al-f-al]⁻ decomposes in presence of nucleophiles under formation of its more coordinating brother [f-al]⁻. This anion is less suited for the stabilization of reactive cations, since the anion is very likely to undergo ion pairing due to the strongly coordinating Al-bound fluorine atom. However, the characterization of reactive cations in combination with WCAs can be very demanding, e.g. because of bad crystallization behavior due to the very low Coulomb interactions between anion and cation. In these cases the use of [f-al]⁻ as a coordinating anion may be very helpful. Due to the stronger interaction between the anion and the cation, the crystallization of the reaction product may be facilitated. In a different project to be published with all details separately, we were able to synthesize [SeCl₃][WCA] by reaction of Ag[WCA] [(WCA)⁻ = Al(ORF)₃][al-f-al]⁻, [f-al]⁻] with SeCl₄ and to crystallize all three compounds (Fig. 6).

While single crystal X-ray diffraction measurements on these crystals yielded a superstructure at 100 K for [SeCl₃][Al(ORF)₃], a simpler solution was obtained, when using [f-al]⁻ and [al-f-al]⁻ as anions at 100 K. Especially the crystal structure of Cl₃Se-[f-al], which crystallized as a contact ion pair, showed no disorder at all and only contains one molecule in the asymmetric unit. The bond valence²⁶ (bv) of only 0.16 for the Se-F contact suggests a weak interaction between the cation and the

Table 3 Calculated reaction enthalpies and free energies for the decomposition reactions of [Al(ORF)₃]⁻, [al-f-al]⁻ and CH₂Cl₂ (BP86-D3(BJ)/def-SVP(P)). The solvation free energy was calculated using the COSMO model (\( \varepsilon = 8.93 \)). All values are given in kJ mol⁻¹

<table>
<thead>
<tr>
<th>Decomposition reaction</th>
<th>( \Delta H'_{\text{(g)}} )</th>
<th>( \Delta G'_{\text{(g)}} )</th>
<th>( \Delta G'_{\text{(CH₂Cl₂)}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Al(ORF)₃]⁻ + ( C_2F_2O_2Al(ORF)₃ )</td>
<td>605</td>
<td>561</td>
<td>324</td>
</tr>
<tr>
<td>[al-f-al]⁻ + ( C_2F_2O_2Al(ORF)₃ )</td>
<td>676</td>
<td>639</td>
<td>383</td>
</tr>
<tr>
<td>[Al(ORF)₃]⁻ + ( Me_3SiF + C_2F_2O_2Al(ORF)₃ )</td>
<td>-349</td>
<td>-336</td>
<td>-49</td>
</tr>
<tr>
<td>[al-f-al]⁻ + ( Me_3SiF + C_2F_2O_2Al(ORF)₃ )</td>
<td>-277</td>
<td>-257</td>
<td>10</td>
</tr>
<tr>
<td>( C_2H₂Cl₂ + Me_3SiF + [(H_2)Cl]C-Cl-CH₂Cl₂ )</td>
<td>-60</td>
<td>-4</td>
<td>0</td>
</tr>
</tbody>
</table>

*a Thermodynamic values for F⁻ were calculated using the Sackur-Tetrode equation. Only the solvation free energy was calculated at DFT level.
anion (cf. \(\text{bv}(\text{Al-F}) = 0.68\)). Nevertheless, in the \(^{19}\text{F}\) NMR spectrum the (Al–F) signal is shifted from \(-187\) to \(-145\) ppm. A related effect was also observed for [NO][f-al], which may be caused by coordination to the cation.

This coordination of [f-al]– to [NO]– can be evaluated by the Raman vibrational frequency of the N–O stretching vibration, since a strong coordination of the anion leads a redshift of this vibration.\(^{27}\) The N–O vibrational frequencies given in Table 4 suggest that [f-al]– (2313 cm\(^{-1}\)) is stronger coordinating than [BF\(_4\)]– and [B(CF\(_3\))\(_4\)]– (2340 and 2337 cm\(^{-1}\)), but less coordinating than [B(CF\(_3\))\(_2\)CN]– and [GaCl\(_4\)]– (2288 and 2226 cm\(^{-1}\)).

Additionally to crystallization, [f-al]– salts can be used as key intermediates towards [al–f-al]– salts. Since [f-al]– is compatible with nucleophiles, it can be used for the synthesis of cations, which require the presence of nucleophiles or coordinating solvents. The resulting product can then be transformed into the [al–f-al]– salt by addition of Me\(_3\)Si–F–Al(OR\(_3\))\(_3\). The only prerequisite for this transformation is that the cation and [f-al]– have to be separated in solution to some extent, i.e. as solvent separated ion pair providing access to small amounts of free [f-al]– for the reaction with Me\(_3\)Si–F–Al(OR\(_3\))\(_3\).

**Table 4** Raman vibrational frequencies of the N–O stretching vibration of different [NO][WCA] salts in cm\(^{-1}\). All values are taken from ref. 37, except those for [NO][f-al] and [NO][al–f-al]–.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vibrational frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>[NO][GaCl(_4)]</td>
<td>2226</td>
</tr>
<tr>
<td>[NO][B(CF(_3))(_2)CN]</td>
<td>2288</td>
</tr>
<tr>
<td>[NO][f-al]–</td>
<td>2313</td>
</tr>
<tr>
<td>[NO][B(CF(_3))(_4)]</td>
<td>2337</td>
</tr>
<tr>
<td>[NO][BF(_4)]–</td>
<td>2340</td>
</tr>
<tr>
<td>[NO][Al(OR(_3))(_3)]</td>
<td>2340</td>
</tr>
<tr>
<td>[NO][al–f-al]–</td>
<td>2340 (ref. 38)</td>
</tr>
</tbody>
</table>

### Limits of [f-al]–

To this point [f-al]– seemed to be rather stable against highly Lewis acidic cations, like [SeCl\(_3\)]+ and [Me\(_3\)Si]+ (FIA = 815 and 952 kJ mol\(^{-1}\), respectively; BP86/def-SVP(P)), due to formation of stable adducts. A comparison of the Al–F bond valences of 0.68 (Cl\(_{3}\)Se–[f-al]– and 0.50 (Me\(_3\)Si–F–Al(OR\(_3\))\(_3\))\(^{16}\) already suggests, that extremely electrophilic cations might be able to abstract the Al-bound fluorine atom. Yet, the relatively high hv in Me\(_3\)Si–F–Al(OR\(_3\))\(_3\) is astonishing, considering the FIA of [Me\(_3\)Si] is higher by 415 kJ mol\(^{-1}\) compared to Al(OR\(_3\))\(_3\) (FIA = 537 kJ mol\(^{-1}\)).\(^{32}\) Therefore, it seemed possible to stabilize an ion-like [PCl\(_2\)]+ cation (FIA = 1001 kJ mol\(^{-1}\))\(^{39}\) with [f-al]–, although it is not possible with [Al(OR\(_3\))\(_3\)]+ (eqn (1b)). When we treated Ag[f-al] with PCl\(_3\) in o-DFB we were expecting the formation of Cl\(_3\)P–F–Al(OR\(_3\))\(_3\) (eqn (4a)). As expected, after a few seconds a precipitate formed (AgCl). NMR spectra, however, did not show the formation of the expected product, but mainly signals of PF\(_3\), PCl\(_3\) and Ag[f-al]–, besides small signals of PCl\(_2\)F and PCl\(_2\)F. The presence of PCl\(_3\)Cl\(_3\)– (\(x = 1, 2, 3\)) and [al–f-al]– is evidence that Cl\(_3\)P–F–Al(OR\(_3\))\(_3\) was formed. But at the same time there was nucleophilic [f-al]– present in solution, which led to formation of [al–f-al]– and PCl\(_3\)F (eqn (4b)), analogous to the previously described reactions (eqn (2b)). The PCl\(_3\)F then further dismutated to PF\(_3\), as described in eqn (4b). The ratio of the products also suggests that the halide abstraction from PCl\(_3\)Cl\(_3\)– is preferred over PCl\(_3\). Interestingly again, the Ag[f-al]– formed did not participate in further halide abstraction reactions (see our comments above).

As a conclusion, [f-al]– may be well suited for the stabilization of reactive cations as neutral ion-like Cat–F–Al(OR\(_3\))\(_3\) compounds. However, the presence of another [f-al]– anion may also lead to formation of [al–f-al]– and release of Cat–F. In these cases the best way to obtain a desired Cat–F–Al(OR\(_3\))\(_3\) may be the reaction of Cat–F with Al(OR\(_3\))\(_3\) or its equivalent Me\(_3\)Si–F–Al(OR\(_3\))\(_3\).
anion). It appears that in non-basic solvents and in contrast to [Al(OR)], the nucleophilicity of [f–al] is too low to allow for AgX formation with X = Cl or Br. These reactions and quantum-chemical calculations also show that [f–al] is more stable against electrophiles than [Al(OR)], and may be similar or in part also better than the borate [B(C6F5)4]. However, the synthetic access to [f–al] requires handling of explosive LiC6F5. Compared to [f–al], we were able to show that [f–al]– was more stable against electrophiles than [Al(OR)]– and may be the refinement of single crystal X-ray diffraction data of [f–al]– and [f–al]– salts usually tends to be facilitated. This is due to less disorder of the OC(CF3)3 moieties for [f–al]– and due to ion-pairing for [f–al]–. The stronger coordination of [f–al]– could be used for the synthesis and crystallization of Cl2Se–[f–al] without any disorder. Additionally, we were able to show that [f–al]– salts can be transformed into [f–al]– salts by addition of Me3Si–F–Al(OR), if the salts exist as solvent separated ion pairs in solution.

Due to the facile synthesis of Me3Si–F–Al(OR), and the anions [f–al]– and [f–al]– in large scales and high yields, we believe that these anions will find wide-spread use for the generation and stabilization of reactive cations, but also suggest that these anions will even be helpful to stabilize in a hemilabile coordination scheme the resting state of the catalysis process.

Conflicts of interest

There are no conflicts to declare.

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