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Facile and systematic access to the least-coordinating WCA [(R^{F}O)$_3$Al−F−Al(OR^F)$_3$]$^-$ and its more Lewis-basic brother [F−Al(OR^F)$_3$]$^-$ (R^F = C(CF$_3$)$_3$)

Useful starting materials with the anions [F−Al(OR^F)$_3$]$^-$ and [(R^{F}O)$_3$Al−F−Al(OR^F)$_3$]$^-$ (R^F = C(CF$_3$)$_3$) can be obtained by reaction of Me$_3$Si−F−Al(OR^F)$_3$ with the respective [PF$_6$]$^-$ salts in high purity and yield. [(R^{F}O)$_3$Al−F−Al(OR^F)$_3$]$^-$ 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(OR^F)$_3$]$^-$ is coordinating and may act as a hemi-labile ligand. [F−Al(OR^F)$_3$]$^-$ can be transformed into the fluoride bridged anion by addition of Me$_3$Si−F−Al(OR^F)$_3$.

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Facile and systematic access to the least-coordinating WCA [(R^FO)_3Al−F−Al(OR^F)_3]^− and its more Lewis-basic brother [F−Al(OR^F)_3]^− (R^F = C(CF_3)_3)†

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By reaction of the Lewis acid Me_3Si−F−Al(OR^F)_3 with a series of [PF_6]^− salts, gaseous PF_5 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^FO)_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_9]^+, oxidizing like [NO]^+, [NO_2]^+ or [Ag(X_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_4, S_8, S_12, Se_6, Se_12 or Se_19 could be stabilized.[1–5] One of the biggest advantages of this [Al(OR^F)_4]^− anion is its facile and fast synthesis in high yields.[6] Other commonly used WCAs are [B(C_6F_5)_4]^−, perhalogenated carborane anions [R−CB_11X_12]^− (X = F, Cl, Br) and the teflates [E(OTeF_5)_x]^− (E = B, Al, Sb, As, Bi, Nb; x = 4, 6).[7,8] However, the synthesis of these anions either require handling of explosive LiC_6F_5,[9] elaborate syntheses in small scales,[10] or handling of the toxic and hydrolysis sensitive HOTeF_5.[8,11] Yet, especially the carborane anions are chemically more stable against fierce electrophiles than [Al(OR^F)_4]^−, *e.g.* against small silylium ions.[12] As shown in eqn (1a), [Al(OR^F)_4]^− decomposes in the presence of small silylium ions [R_3Si]^+ above
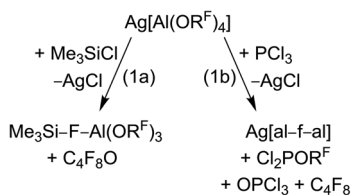
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† Electronic supplementary information (ESI) available: Experimental details, procedures, weights, 1D- and 2D-NMR spectra of the reactions are deposited. Details to the quantum chemical calculations are given together with crystallographic details. CCDC 1845808–1845817. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8sc02591f

Scheme 1 Overview to the anions presented in this paper and their abbreviations.

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−30 °C to give $R_3Si–F–Al(OR^F)_3$.[13,14] However, it is compatible with the bulky $[Si(C_6Me_5)_3]^+$ silylium ion.[15]

$$Ag[Al(OR^F)_4]$$

+ Me₃SiCl ╱ (1a)   (1b) ╲ + PCl₃
−AgCl   −AgCl

$Me_3Si–F–Al(OR^F)_3$ $Ag[al–f–al]$
+ C_4F_8O + Cl_2POR^F
                                 + $OPCl_3$ + C_4F_8

More general, very small and very potent electrophiles, like "$[PCl_2]^+$" or "$[SiCl_3]^+$" induce $[Al(OR^F)_4]^-$ decomposition, very often under formation of $[(R^FO)_3Al–F–Al(OR^F)_3]^-$ ($[al–f–al]^-$, eqn (1b)), which is even less coordinating than $[Al(OR^F)_4]^-$.[16] For more than a decade, access to a starting material with this anion was only accessible by decomposition of $Ag[Al(OR^F)_4]$. However, this synthesis proved to be delicate to reproduce, requires the two-step synthesis of $Ag[Al(OR^F)_4]$, and is combined with loss of Ag^+ and OR^F moieties. The bridging motif of $[al–f–al]^-$ may be seen in analogy to related bridged anions known to the literature,[17] e.g. as in $[(C_6F_5)_3B–CN–B(C_6F_5)_3]^-$, $[(C_6F_5)_3B–NH_2–B(C_6F_5)_3]^-$ and $[(C_6F_5)_3E–F–E(C_6F_5)_3]^-$ (E = B, Al, Ga).[18]

In some cases, where decomposition of $[Al(OR^F)_4]^-$ occurred, formation of $[al–f–al]^-$ could not be observed. Instead the formal $[F–Al(OR^F)_3]^-$ anion ($[f–al]^-$) was obtained, often as part of a neutral compound, like in $Me_3Si–F–Al(OR^F)_3$ or $Cp^*Be–F–Al(OR^F)_3$.[13,19] 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]

$Me_3Si–F–Al(OR^F)_3$ has already shown its usefulness for silylation reactions,[13,21] 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.[13,21] Therefore we investigated here, if it is possible to use $Me_3Si–F–Al(OR^F)_3$ 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(OR^F)₃

In order to establish optimized routes to the anions $[al–f–al]^-$ and $[f–al]^-$, we needed access to larger amounts of $Me_3Si–F–Al(OR^F)_3$. Therefore, we optimized this synthesis and performed an upscaling from 40 g (ref. 13) up to 85 g. Although we believe that further upscaling 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 Me_3SiF cost 364€ (ABCR), we elaborated a synthesis starting from Me_3SiCl and $[NH_4]_2[SiF_6]$ on the basis of ref. 22, yielding Me_3SiF in high purities at very low cost (see ESI† for details).

In order to maximize the yield and purity of $Me_3Si–F–Al(OR^F)_3$ 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 $AlEt_3$, the argon flow must be carefully controlled. If the argon flow is too high, the $AlEt_3$ may start to smoke due to swirling of ambient air. Additionally, the HOR^F has to be dried to a water content of less than 1 ppm, which can be achieved by stirring with P_4O_{10} 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 $Me_3Si–F–Al(OR^F)_3$ used for all syntheses in this paper was prepared according to the following optimized procedure: $AlEt_3$ (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 HOR^F (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 HOR^F, gas evolution (C_2H_6) was observed, the viscosity of the solution increased and small amounts of precipitate formed. After complete addition of the first HOR^F portion (typically within 1 hour), Me_3SiF (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 HOR^F (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 HOR^F (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.
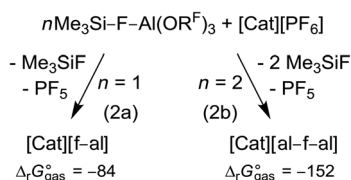
The quality of the $Me_3Si–F–Al(OR^F)_3$ can be verified by different methods: if the obtained powder seems to be moist, but cannot be completely dried, there are probably residual Al–Et groups present in the product. In this case, more HOR^F should be added. Another qualitative test for the purity of the product is by dissolving it in 1,2-difluorobenzene (o-DFB). A solution of pure $Me_3Si–F–Al(OR^F)_3$ is nearly colorless, while impurities (mainly residual Al–Cl groups stemming from the $AlEt_3$) induce a light yellow color. These impurities usually enrich at the top of the crystalized 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 CH_2Cl_2, let it cool and then filter it. Additionally, NMR spectra of the product should be taken in both, o-DFB and CH_2Cl_2. $Me_3Si–F–Al(OR^F)_3$ is only poorly soluble in CH_2Cl_2, but not its impurities. Therefore, if a NMR spectrum in CH_2Cl_2 shows only negligible amounts of impurities, the product can be considered pure. In o-DFB $Me_3Si–F–Al(OR^F)_3$ is highly soluble and here the signal intensity is increased compared to the impurities. Therefore, NMR spectra in CH_2Cl_2 may show a purity of only 60%, while the real purity is >90%, as can be seen from NMR spectra in o-DFB. Pure

$Me_3Si–F–Al(OR^F)_3$ 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_3C) can be obtained by reaction of 1 and 2 equiv. $Me_3Si–F–Al(OR^F)_3$, respectively, with [Cat][PF₆] at rt or 60 °C, depending on the solubility of the [PF₆]⁻ 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)).

$$nMe_3Si–F–Al(OR^F)_3 + [Cat][PF_6]$$

$$\swarrow \begin{array}{c} - Me_3SiF \\ - PF_5 \end{array} \; n = 1 \qquad n = 2 \; \begin{array}{c} - 2\, Me_3SiF \\ - PF_5 \end{array} \searrow$$

$$(2a) \qquad\qquad (2b)$$

$$[Cat][f–al] \qquad\qquad [Cat][al–f–al]$$

$$\Delta_r G°_{gas} = -84 \qquad\qquad \Delta_r G°_{gas} = -152$$

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 $Me_3Si–F–Al(OR^F)_3$ 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 PF₅ 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[PF₆] in o-DFB even at 60 °C, a donor has to be added. We chose Cl_3CCN 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(NCCCl₃)][f–al] could be obtained. As the only exception from eqn (2), the [al–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)ₓ][f–al]. However, strong donors are also able to coordinate to the $Al(OR^F)_3$ moiety of $Me_3Si–F–Al(OR^F)_3$, 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 $Me_3Si–F–Al(OR^F)_3$ first reacts with DMC to form DMC–$Al(OR^F)_3$ before the anion is formed (see ESI† for details).

Potassium salts. K[PF₆] 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 $Me_3Si–F–Al(OR^F)_3$ and formation of K[al–f–al] within 2 h.

The synthesis of K[f–al] proved to be more problematic. Compared to $Me_3Si–F–Al(OR^F)_3$, only little K[PF₆] 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 [PF₆]⁻ 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[PF₆] (2 eq.) the reaction mixture still contained 4% K[al–f–al]. Additionally, NMR spectra show signals of $K[OR^F]$ (6%) and $[F_{1+x}Al(OR^F)_{3-x}]⁻$ (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[PF₆] is also only poorly soluble in CH_2Cl_2, SO_2 and o-DFB at rt. Nonetheless, the formation of [Ag(L)ₓ][f–al] and [Ag(L)ₓ][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 crystallization 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 crystallized from o-DFB at rt, the cation is coordinated by three o-DFB molecules. Interestingly, when Ag[al–f–al] is crystallized 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 1 Reaction conditions for the synthesis of [Cat][f–al]⁻ and [Cat][al–f–al]⁻. When using 1 equiv. of $Me_3Si–F–Al(OR^F)_3$ the [f–al]⁻ anion is obtained. [al–f–al]⁻ is obtained by using 2 equiv. of $Me_3Si–F–Al(OR^F)_3$. The values in parentheses correspond to [Cat][f–al]

Cation	Solvent	Reaction time	Temperature	Yield	Cation (bulk)	Cation (single crystal)	CCDC number
Li⁺[a]	o-DFB/Cl₃CCN	4 h	60 °C	— (84%)	—	([Li(NCCCl₃)]⁺)	(1845808)
Li⁺[a]	DMC ((MeO)₂CO)	2 h	70 °C	— (86%)	([Li(DMC)₂]⁺)	([Li(DMC)₃]⁺)	(1845810)
K⁺[b]	o-DFB	2 h	60 °C	90%[b]	K⁺	—	
Ag⁺	CH₂Cl₂	1 h	rt	97% (98%)	[Ag(CH₂Cl₂)₃]⁺ ([Ag(CH₂Cl₂)]⁺)	—	
Ag⁺	SO₂	2 h	−20–0 °C	95% (98%)	Ag⁺ (Ag⁺)	—	
Ag⁺	o-DFB	30 min	rt	96% (70%)	[Ag(o-DFB)₂]⁺, ([Ag(o-DFB)ₓ]⁺; x = 0–2)	[Ag(o-DFB)₂]⁺, [Ag(o-DFB)₃]⁺ ([Ag(o-DFB)₃]⁺)	1845812, 1845817 (1845811)
[NO]⁺	SO₂	1 h	−35–0 °C	88% (90%)	[NO]⁺	[NO]⁺	18458114
[Ph₃C]⁺	o-DFB	1 h	rt	88% (95%)	[Ph₃C]⁺	—	

[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.

PF_5 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 $[NO][PF_6]$ in CH_2Cl_2 at rt, SO_2 has to be used as solvent. Here, the reaction is also carried out at −20 to −30 °C to allow the use of a bubbler for removal of the evolving PF_5. The reaction is then allowed to slowly warm up to 0 °C over the course of 45 min to ensure complete conversion, followed by removal of all volatiles *in vacuo*. Due to the incompatibility of $[NO]^+$ with *n*-pentane, a quantitative crystallization in analogy to the silver salts is not possible.

Trityl salts. When a few drops of *o*-DFB or CH_2Cl_2 are added to a mixture of $[Ph_3C][PF_6]$ and $Me_3Si–F–Al(OR^F)_3$, immediately a fierce evolution of PF_5 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 [al–f–al]$^-$ the ^{19}F NMR spectrum shows a broad signal for the bridging fluorine atom at −184.5 ppm and a resonance for the $C(CF_3)_3$ 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 ^{27}Al NMR spectrum, only a very broad resonance at about 37 ppm ($\Delta \nu_{1/2} = 1200$ Hz) is obtained. This broadness of the signal is caused by a fast relaxation of the Al atoms. As a result, the $^1J_{Al–F}$ coupling is not resolved neither in the ^{27}Al nor in the ^{19}F NMR spectra. The presence of this coupling can be deduced from the broadening of the signal of the bridging fluorine atom in the ^{19}F NMR spectrum. In the $^{19}F\{^{27}Al\}$ NMR spectrum this signal is sharp, which unambiguously proves that the broadening of this signal results from the $^1J_{Al–F}$

Fig. 1 Characteristic ^{19}F (Al–F range only) and ^{27}Al NMR signals of [f–al]$^-$ and [al–f–al]$^-$. The broad resonance at ∼60 ppm in the ^{27}Al NMR spectra is caused by the probe head; red: Ag[f–al] in *o*-DFB, blue: Ag[al–f–al] in *o*-DFB, the signals marked by the asterisk are caused by the NMR spectrometer.

coupling (see ESI† for details – investigations on the $Al(OR^F)_3$ exchange reactions).

By contrast, for [f–al]$^-$ the Al–F signal in the ^{19}F 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 $[SeCl_3]^+$ salts. The signal of the alkoxy 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 ^{27}Al NMR spectrum a sharp doublet at 41 ppm with ^1J(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 $[Al(OR^F)_4]^-$, [al–f–al]$^-$ and [f–al]$^-$ salts are shown in Fig. 2 and are discussed in reference to $Ag[Al(OR^F)_4]$. It should be noted that it is not possible to obtain a Raman spectrum of $[Ag(CH_2Cl_2)][Al(OR^F)_4]$, prepared from Li $[Al(OR^F)_4]$ and AgF in CH_2Cl_2, due to decomposition.[6] When this metathesis reaction is performed in SO_2, instead of CH_2Cl_2, donor-free $Ag[Al(OR^F)_4]$ 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 (ν_{as}(Al–F–Al)) and 862 cm^{-1} are visible for [al–f–al]$^-$, and at 762 (ν(Al–F)) and 808 cm^{-1} for [f–al]$^-$, when compared to $[Al(OR^F)_4]^-$. 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 $[Al(OR^F)_4]^-$. 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 blue shifted by up to 12 cm^{-1} compared to Ag[f–al]. Although a comparison of these compounds with the analogous $[Ph_3C]^+$ and $[Li(L)_x]^+$ salts would be interesting, it proved to be rather complicated, since the vibrational bands of these cations overlap with the ones of the anion.

Molecular structures of [f–al]$^-$ and [al–f–al]$^-$ salts

Although our commonly used $[Al(OR^F)_4]^-$ anion usually does not show significant coordination, very small cations, like Li^+ and $[Ag(L)]^+$ are able to be coordinated by its oxygen atoms.[4,5,23] As can be seen from Fig. 3, [f–al]$^-$ usually coordinates to the cation with the (Al–)F atom. In case of the dimeric $\{[Li(NCCCl_3)] [f–al]\}_2$ each (Al–)F atom is coordinated to two Li atoms and also
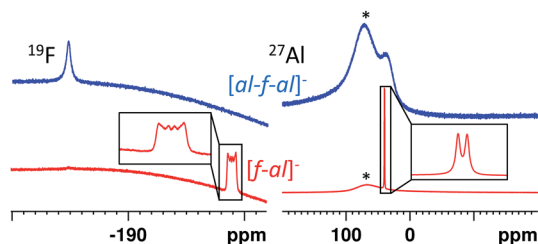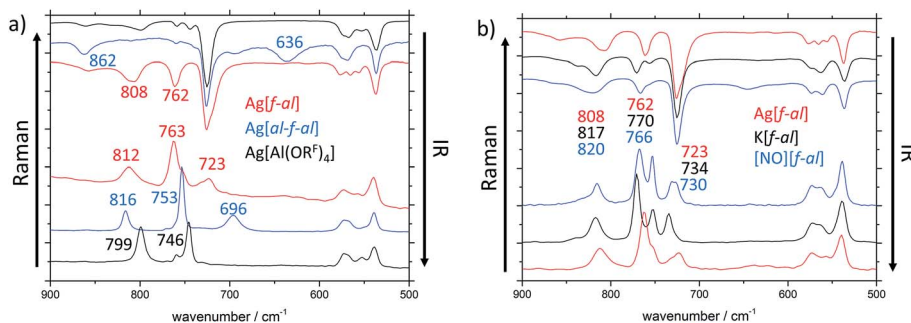
Fig. 2 IR (top) and Raman (bottom) spectra in the region between 900 and 500 cm^{-1} and frequencies of characteristic bands in cm^{-1} of (a) Ag[Al(OR^F)$_4$] (black), Ag[al−f−al] (blue) and Ag[f−al] (red); (b) Ag[f−al] (red), K[f−al] (black) and [NO][f−al] (blue).

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)$_3$][f−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 co-ordinate to these alkoxy groups.[2] Here, both Zn–O distances are nearly equal (209.8 pm on average), while in [ZnEt][Al(OR^F)$_4$] 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^F)$_4$]$^−$, but also for the inferior accessibility of the oxygen atoms.

Some aspects for single crystal X-ray diffraction refinements

For [Al(OR^F)$_4$]$^−$ 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 ShelXLe,[25] to facilitate the description of these often very complicated disorders.[26] 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^F)$_4$]$^−$ 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^F)$_4$]$^−$. Nevertheless, there are also cases, where the entire anion is disordered around the bridging fluorine atom (see ESI of ref. 21†).
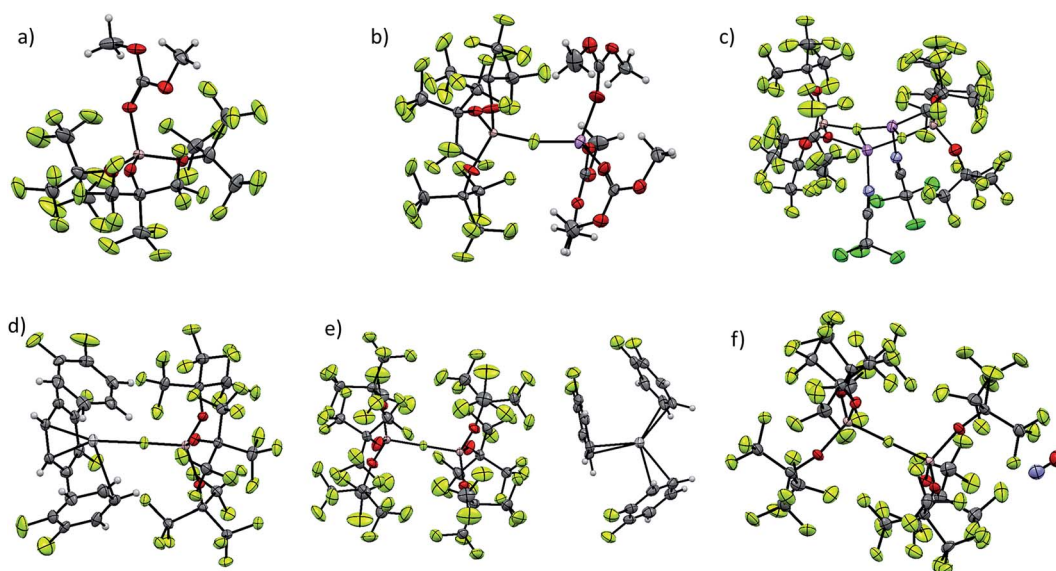

Fig. 3 Overview of molecular structures of some starting materials presented in this work. Disorder was omitted in all cases, for the sake of clarity. (a) DMC–Al(OR^F)$_3$; (b) [Li(DMC)$_3$][f−al]; (c) [Li(NCCCl$_3$)][f−al]; (d) [Ag(*o*-DFB)$_3$][f−al]; (e) [Ag(*o*-DFB)$_3$][al−f−al]; (f) [NO][al−f−al].

Table 2 Selected average Al–F, Al–O and anion–cation (A–Cat) distances (in pm) of different [f–al]⁻ and [al–f–al]⁻ salts

Anion	Cation	d(Al–F)	d(Al–O)	d(A–Cat)
[f–al]⁻	[Li(NCCCl₃)]⁺	171.2(2)	169.9(5)/177.4(4)	185.7(7)[a]/206.0(9)[b]/220(1)[c]
[f–al]⁻	[Li(DMC)₃]⁺	167.4(2)	171.9(2)	184.1(5)[a]
[f–al]⁻	[Ag(o-DFB)₃]⁺	168.7(1)	172.7(1)	242.0(1)[d]
[al–f–al]⁻	[Ag(o-DFB)₃]⁺	176.1(2)	169.3(2)	348.1(2)[e]
[al–f–al]⁻	[NO]⁺	176.7(2)	170.2(13)	273.0(3)[f]

[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/CDCl₃ showed several signals for the OR^F and Al–F moieties in the ¹⁹F NMR spectrum. This suggests a ligand scrambling reaction and formation of [AlF$_x$(OR^F)$_{4-x}$] (x = 1–3) and their F-bridged analogues. From the ¹¹B NMR spectrum only formation of BF(OR^F)₂ was visible. Since this solution contained lots of precipitate, another sample was prepared in C₆H₅F/acetone-d₆ in order to dissolve this precipitate. Here NMR spectra showed mainly the formation of unbridged [AlF$_x$(OR^F)$_{4-x}$]⁻ and several boron containing species. The formation of [AlF$_x$(OR^F)$_{4-x}$]⁻ 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(OR^F)₂] (see ESI† 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 good 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).[27] The same trend holds, when comparing the calculated [OR^F]⁻ 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 according reaction intermediate very likely involves Al–O(R^F)–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^F) and PF₄(OR^F), also should be considered, but this is rather a secondary effect. BF₂(OR^F) features a tricoordinated, planar boron atom, which is able to undergo π back bonding with the lone pairs of the alkoxy moiety. This back bonding is stronger than that of fluoride and leads to a considerable stabilization of this molecule. The BF₂(OR^F) is able to undergo a second ligand scrambling to form the observed BF(OR^F)₂. In PF₄(OR^F) 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^F)₄]⁻, [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)₃Al–F–Al(C₆F₅)₃]⁻. This is mainly due to the delocalization of the negative charge over 55 fluorine 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 [R^FO]⁻ abstraction than [Al(OR^F)₄]⁻ (see later).[16,28,29]

The reactions of Ag[Al(OR^F)₄] with halosilanes R₃SiX (R = Me, *t*Bu, Ph; X = Cl, Br, I) in CH₂Cl₂ were already described.[13,14] At rt these reactions yield R₃Si–F–Al(OR^F)₃, while at −50 °C the
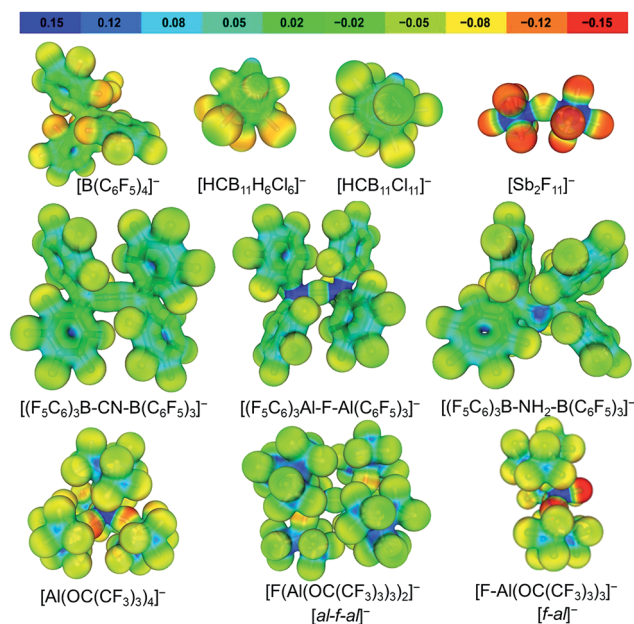

Fig. 4 Projection of the calculated electrostatic potential onto a 0.025 e⁻ Bohr⁻³ isodensity surface of commonly used WCAs and the anions presented in this work; BP86/def-SV(P).
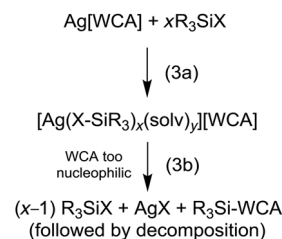
halide bridged bis-silylium ions $[R_3Si–X–SiR_3]^+$ were obtained. When we tried to reproduce these reactions with Ag[al–f–al] we noticed several curiosities. First of all, while $Ag[Al(OR^F)_4]$ is highly soluble in CH_2Cl_2 at low temperatures, Ag[al–f–al] is only poorly soluble in cold CH_2Cl_2, although a higher solubility would have been expected with the weaker interactions between cation and anion. Secondly, when Me_3SiCl, Ph_3SiCl or tBu_3SiBr were added to the reaction solution, no silver halide formed. NMR spectra also revealed almost quantitative retention of the anion and the halosilane. The ^{29}Si 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 tBu_3SiBr single crystals could be obtained and were identified as $[Ag(tBu_3SiBr)_2(CH_2Cl_2)_2]$[al–f–al] (Fig. 5). It is possible that related products may form with Me_3SiCl and Ph_3SiCl.

Although the formation of this cation is in agreement with the findings of Reed et al. that silylium ions are able to dissolve AgBr,[30] at the same time it is contradictory to the reactions of Ag $[Al(OR^F)_4]$, where halide abstraction from halosilanes was observed.[13,14] This leads to the conclusion that $[Al(OR^F)_4]^-$ cannot be innocent in these reactions as similar halide abstractions are observed with $Ag[ClO_4]$. Only when Me_3SiI was added to Ag[al–f–al] in toluene/1,2,3-$C_6H_3F_3$ in a 1 : 1 stoichiometry, the formation of AgI could be observed. NMR spectra of this solution predominantly showed decomposition of the anion and formation of $Me_3Si–F–Al(OR^F)_3$ next to other unidentified products.

Judged from these reactions and their solution NMR spectra, we propose that upon reaction of Ag[WCA] and halosilanes, R_3SiX, always the according silver complexes $[Ag(X–SiR_3)_x(solv)_y]^+$ are formed (eqn (3a)). These complexes contain an activated silicon and are strong silylating reagents. They react with nucleophiles (Nu) under formation of Nu–SiR_3 and AgX. It appears, that for anions like $[ClO_4]^-$ or even $[Al(OR^F)_4]^-$ 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 $[Ag(X–SiR_3)_x(solv)_y]^+$ cation increases, when going from X = Cl to I, mainly due to weakening of the Si–X bond. Overall, the lacking formation of AgX by reaction of Ag[al–f–al] with R_3SiX (X = Cl, Br) can be seen as first experimental proof for the less coordinating nature of $[al–f–al]^-$ with respect to $[Al(OR^F)_4]^-$ or other WCAs that react with halosilanes under separation of AgX.

$$Ag[WCA] + xR_3SiX$$
$$\downarrow \text{(3a)}$$
$$[Ag(X\text{–}SiR_3)_x(solv)_y][WCA]$$
$$\downarrow \text{(3b)} \quad \text{WCA too nucleophilic}$$
$$(x\text{–}1)\ R_3SiX + AgX + R_3Si\text{-}WCA$$
$$\text{(followed by decomposition)}$$

Another evidence for the weaker coordination and increased stability of $[al–f–al]^-$ compared to $[Al(OR^F)_4]^-$ is the intermediate synthesis of silylium ions by reaction of $[Ph_3C][WCA]$ with Me_3SiH in CH_2Cl_2. In case of $[WCA]^- = [Al(OR^F)_4]^-$ only $Me_3Si–F–Al(OR^F)_3$ 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 Me_3SiCl. 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 Me_3SiCl, it might be a chlorinated carbocation resulting from the solvent CH_2Cl_2. Exchanging the CH_2Cl_2 for o-DFB, we were not able to isolate silylium ions at rt by this route when using Me_3SiH or iPr_3SiH. Again, we mainly observed formation of $R_3Si–F–Al(OR^F)_3$ and other decomposition products, similar to the reaction of Ag[al–f–al] with Me_3SiI.

Thermodynamic stability of $[al–f–al]^-$

$[al–f–al]^-$ is stable against very strong silylating agents, such as $[Ag(X–SiR_3)_x(solv)_y]^+$ (X = Cl, Br), but not against small silylium ions. Therefore, we were interested in evaluating its general stability towards fluoride abstraction. This was done by calculating the decomposition reaction energies of $[al–f–al]^-$ and $[Al(OR^F)_4]^-$ using to the FIA procedure (Table 3).[31] Although this was already done in the literature,[28] we repeated these calculations with inclusion of the D3(BJ) dispersion correction (BP86-D3(BJ)/def-SV(P)). This seemed reasonable, since the strength of the Al–F–Al bond in $[al–f–al]^-$ is underestimated by $\Delta G^\circ_{(g)} = 66$ kJ mol^{-1} at BP86/def-SV(P) level. This also holds for the weak interaction between the evolving epoxide C_4F_8O and the corresponding Lewis acids. Yet, these calculations show only minor discrepancies to the literature.

Again, these calculations support the previous experiments and show that $[al–f–al]^-$ is more stable against fluoride abstraction than $[Al(OR^F)_4]^-$. Additionally, the decomposition of $[al–f–al]^-$ by $[Me_3Si]^+$ was calculated to be endergonic in CH_2Cl_2 by $\Delta G^\circ = 10$ kJ mol^{-1} and to be less favored than the decomposition of CH_2Cl_2. This is also in accordance to our reactions of $[Ph_3C][WCA]$ with Me_3SiH in CH_2Cl_2. It should be
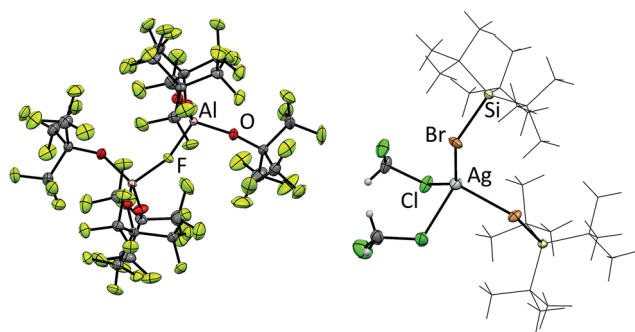

Fig. 5 Molecular structure of $[Ag(tBu_3SiBr)_2(CH_2Cl_2)_2]^+[al–f–al]^-$ at 100 K with thermal ellipsoids at 50% probability level. The $C(CH_3)_3$ moieties are shown in wireframe. Scheme: Ag (light gray), Br (brown), Si (yellow), Cl (green), Al (pink), O (red), F (light green), C (grey), H (white). Selected distances (pm) and bond angles (deg): Si1–Br1 231.87(7), Si2–Br2 231.88(6), Ag–Br1 265.68(5), Ag–Br2 268.33(5), Ag–Cl1 262.22(8), Ag–Cl2 276.0(1), Al1–F1 176.6(1), Al2–F1 176.9(1), Al1–F1–Al2 159.51(8).

Table 3 Calculated reaction enthalpies and free energies for the decomposition reactions of $[Al(OR^F)_4]^-$, $[al-f-al]^-$ and CH_2Cl_2 (BP86-D3(BJ)/def-SV(P)). The solvation free energy was calculated using the COSMO model ($\varepsilon = 8.93$). All values are given in kJ mol^{-1}

Decomposition reaction	$\Delta H^{\circ}_{(g)}$	$\Delta G^{\circ}_{(g)}$	$\Delta G^{\circ}(CH_2Cl_2)$
$[Al(OR^F)_4]^- \rightarrow F^- + C_4F_8O-Al(OR^F)_3$ [a]	605	561	324
$[al-f-al]^- \rightarrow F^- + C_4F_8O-Al(OR^F)_2-F-Al(OR^F)_3$ [a]	676	639	383
$[Al(OR^F)_4]^- + [Me_3Si]^+ \rightarrow Me_3SiF + C_4F_8O-Al(OR^F)_3$	−349	−336	−49
$[al-f-al]^- + [Me_3Si]^+ \rightarrow Me_3SiF + C_4F_8O-Al(OR^F)_2-F-Al(OR^F)_3$	−277	−257	10
$2CH_2Cl_2 + [Me_3Si]^+ \rightarrow Me_3SiCl + [(H_2)(Cl)C-Cl-CH_2Cl]^+$	−60	−4	0

[a] Thermodynamic values for F^- were calculated using the Sackur–Tetrode equation. Only the solvation free energy was calculated at DFT level.

noted, that the calculated reactions are only the first step in the decomposition of CH_2Cl_2, $[Al(OR^F)_4]^-$ and $[al-f-al]^-$ and are not the final reaction products. As a result, $[al-f-al]^-$ is not stable against small silylium 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 $[Al(OR^F)_4]^-$ seems to make it the anion of choice for the synthesis of reactive cations.[28] 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 Et_2O 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 $Et_2O-Al(OR^F)_3$ and $[f-al]^-$ remained. The fluoride bridged anion $[al-f-al]^-$ can thus be seen as an adduct of $[f-al]^-$ and the Lewis superacid $Al(OR^F)_3$.[32] 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 BF_3 (346 kJ mol^{-1}). This limits the choice of solvents: in basic solvents such as Et_2O and MeCN the equilibrium shown in Scheme 2 is on the side of $LB-Al(OR^F)_3$ and $[f-al]^-$. In SO_2, PhF, o-DFB, CH_2Cl_2 and $CHCl_2F$ the fluoride bridged anion $[al-f-al]^-$ was found to be completely intact by NMR spectroscopy. However, since $SO_2-Al(OR^F)_3$ and $Ph-F-Al(OR^F)_3$ are known to be relatively stable,[33] an equilibrium between $[al-f-al]^-$ and $LB-Al(OR^F)_3/[f-al]^-$ (here LB = SO_2, PhF) may be possible. For SO_2 this equilibrium was calculated to be on the side of $[al-f-al]^-$ by $\Delta G^{\circ}_{solv} = -66$ kJ mol^{-1} using the COSMO model ($\varepsilon = 16.3$) at BP86-D3(BJ)/def-SV(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 SO_2. 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 $Al(OR^F)_3$ moieties between $[f-al]^-$ and $[al-f-al]^-$ is expected. However, the presence of the $^1J_{Al-F}$ and $^5J_{F-F}$ 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.[34] Therefore,

we suggest using $CHCl_2F$, CH_2Cl_2, o-DFB, PhF and SO_2 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,[35] we were able to synthesize $[SeCl_3][WCA]$ by reaction of $Ag[WCA]$ ($[WCA]^- = [Al(OR^F)_4]^-$, $[al-f-al]^-$, $[f-al]^-$) with $SeCl_4$ 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 $[SeCl_3][Al(OR^F)_4]$, a simpler solution was obtained, when using $[f-al]^-$ and $[al-f-al]^-$ as anions at 100 K. Especially the crystal structure of $Cl_3Se-[f-al]$, which crystallized as a contact ion pair, showed no disorder at all and only contains one molecule in the asymmetric unit. The bond valence[36] (bv) of only 0.16 for the Se–F contact suggests a weak interaction between the cation and the
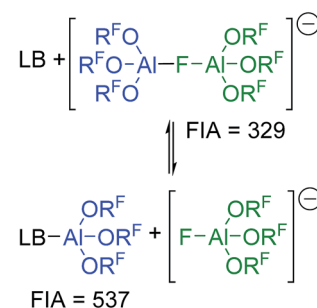
Scheme 2 Equilibrium between LB/$[al-f-al]^-$ and LB–Al(OR^F)$_3$/$[f-al]^-$; LB = Lewis base. Calculated FIAs refer to the free Lewis acids and are given in kJ mol^{-1}; BP86-D3(BJ)/def-SV(P).

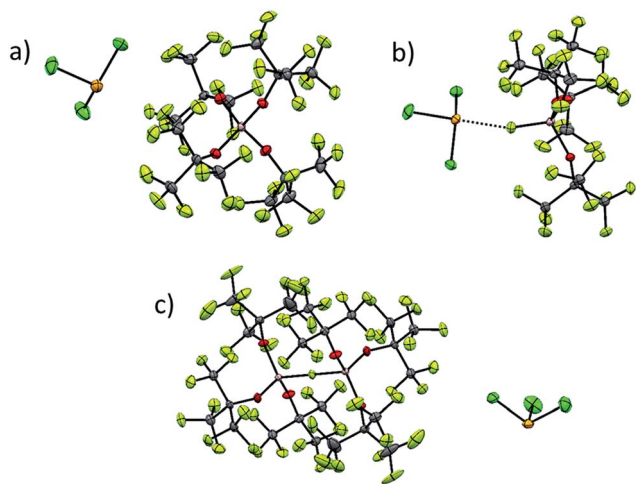**Fig. 6** Complete ion pairs cut out of the solid state structures of the three $[SeCl_3]^+[WCA]^-$ salts at 100 K with thermal ellipsoids drawn at 50% probability level. Disorder was omitted for clarity (see ESI† for details). (a) $[SeCl_3]^+[Al(OR^F)_4]^-$; (b) $Cl_3Se-[f-al]$; (c) $[SeCl_3]^+[al-f-al]^-$. Scheme: Se (orange), Cl (green), Al (pink), O (red), F (light green), C (grey).

anion (cf. bv(Al–F) = 0.68). Nevertheless, in the ^{19}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.[37] 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 $[B(CF_3)_3CN]^-$ and $[GaCl_4]^-$ (2288 and 2226 cm^{-1}).
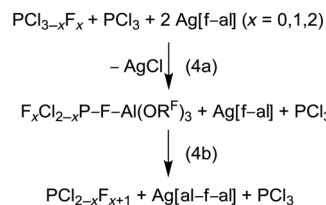
Additionally to crystallization, $[f-al]^-$ salts can be used as key intermediates towards $[al-f-al]^-$ salts. Since $[f-al]^-$ is compatible with nucleophiles, it can be used for the synthesis of cations, which require the presence of nucleophiles or coordinating solvents. The resulting product can then be transformed into the $[al-f-al]^-$ salt by addition of $Me_3Si-F-Al(OR^F)_3$. 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 $Me_3Si-F-Al(OR^F)_3$.

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]

Compound	Vibrational frequency
$[NO][GaCl_4]$	2226
$[NO][B(CF_3)_3CN]$	2288
$[NO][f-al]$	2313
$[NO][B(CF_3)_4]$	2337
$[NO][BF_4]$	2340
$[NO][Al(OR^F)_4]$	2340
$[NO][al-f-al]$	2340 (ref. 38)

Limits of $[f-al]^-$

To this point $[f-al]^-$ seemed to be rather stable against highly Lewis acidic cations, like $[SeCl_3]^+$ and $[Me_3Si]^+$ (FIA = 815 and 952 kJ mol^{-1}, respectively; BP86/def-SV(P)), due to formation of stable adducts. A comparison of the Al–F bond valences of 0.68 $(Cl_3Se-[f-al])$ and 0.50 $(Me_3Si-F-Al(OR^F)_3)$[13] already suggests, that extremely electrophilic cations might be able to abstract the Al-bound fluorine atom. Yet, the relatively high bv in $Me_3Si-F-Al(OR^F)_3$ is astonishing, considering the FIA of $[Me_3Si]^+$ is higher by 415 kJ mol^{-1} compared to $Al(OR^F)_3$ (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 $[Al(OR^F)_4]^-$ (eqn (1b)). When we treated $Ag[f-al]$ with PCl_3 in o-DFB we were expecting the formation of $Cl_2P-F-Al(OR^F)_3$ (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 $Ag[al-f-al]$, besides small signals of $PClF_2$ and PCl_2F. The presence of PF_xCl_{3-x} $(x = 1, 2, 3)$ and $[al-f-al]^-$ is evidence that $Cl_2P-F-Al(OR^F)_3$ 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_2F (eqn (4b)), analogous to the previously described reactions (eqn (2b)). The PCl_2F then further dismutated to PF_3, as described in eqn (4b). The ratio of the products also suggests that the halide abstraction from PF_xCl_{3-x} is preferred over PCl_3. Interestingly again, the $Ag[al-f-al]$ formed did not participate in further halide abstraction reactions (see our comments above).

$$PCl_{3-x}F_x + PCl_3 + 2\,Ag[f-al]\ (x = 0,1,2)$$
$$\downarrow -\,AgCl \quad (4a)$$
$$F_xCl_{2-x}P-F-Al(OR^F)_3 + Ag[f-al] + PCl_3$$
$$\downarrow \quad (4b)$$
$$PCl_{2-x}F_{x+1} + Ag[al-f-al] + PCl_3$$

As a conclusion, $[f-al]^-$ may be well suited for the stabilization of reactive cations as neutral ion-like $Cat-F-Al(OR^F)_3$ 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 $Cat-F-Al(OR^F)_3$ may be the reaction of Cat–F with $Al(OR^F)_3$ or its equivalent $Me_3Si-F-Al(OR^F)_3$.

Conclusion

By reaction of $Me_3Si-F-Al(OR^F)_3$ with different $[PF_6]^-$ salts we were able to selectively synthesize the anions $[(R^FO)_3Al-F-Al(OR^F)_3]^-$ $([al-f-al]^-)$ and $[F-Al(OR^F)_3]^-$ $([f-al]^-)$. In the presence of nucleophiles or coordinating solvents, however, $[al-f-al]^-$ was shown to react under formation of $[f-al]^-$ and $Nu-Al(OR^F)_3$. By intermediate generation of small silylium ions and isolation of $[Ag(tBu_3SiBr)_2(CH_2Cl_2)_2]^+$ we were able to support the role of $[al-f-al]^-$ as "least-coordinating-anion":[16] thus, the elimination of AgX from the formed solvated $[Ag(XSiR_3)_x]^+$ cation requires the back-side attack of a nucleophile (solvent,

anion). It appears that in non-basic solvents and in contrast to $[Al(OR^F)_4]^-$, the nucleophilicity of $[al–f–al]^-$ is too low to allow for AgX formation with $X = Cl$ and Br. These reactions and quantum-chemical calculations also show that $[al–f–al]^-$ is more stable against electrophiles than $[Al(OR^F)_4]^-$ and may be similar or in part also better than the borate $[B(C_6F_5)_4]^-$. However, the synthetic access to $[al–f–al]^-$ is now greatly facilitated compared to that of the borate $[B(C_6F_5)_4]^-$, which requires handling of explosive LiC_6F_5. Compared to $[Al(OR^F)_4]^-$, the refinement of single crystal X-ray diffraction data of $[al–f–al]^-$ and $[f–al]^-$ salts usually tends to be facilitated. This is due to less disorder of the $OC(CF_3)_3$ moieties for $[al–f–al]^-$ (increased bulk) and due to ion-pairing for $[f–al]^-$. The stronger coordination of $[f–al]^-$ could be used for the synthesis and crystallization of $Cl_3Se–[f–al]$ without any disorder. Additionally, we were able to show that $[f–al]^-$ salts can be transformed into $[al–f–al]^-$ salts by addition of $Me_3Si–F–Al(OR^F)_3$, if the salts exist as solvent separated ion pairs in solution.

Due to the facile synthesis of $Me_3Si–F–Al(OR^F)_3$ and the anions $[f–al]^-$ and $[al–f–al]^-$ 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 they may be suitable for catalytic processes. Here, the $[f–al]^-$ anion may 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.

Acknowledgements

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