

Aluminum Compounds | Hot Paper |

Pentafluoroethylaluminates: A Combined Synthetic, Spectroscopic, and Structural Study

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Abstract: Salts of the tetrakis(pentafluoroethyl)aluminate anion $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ were obtained from AlCl_3 and LiC_2F_5 . They were isolated with different counter-cations and characterized by NMR and vibrational spectroscopy and mass spectrometry. Degradation of the $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ ion was found to

proceed via 1,2-fluorine shifts and stepwise loss of $\text{CF}(\text{CF}_3)$ under formation of $[(\text{C}_2\text{F}_5)_{4-n}\text{AlF}_n]^-$ ($n=1-4$) as assessed by NMR spectroscopy and mass spectrometry and supported by results of DFT calculations. In addition, the $[(\text{C}_2\text{F}_5)_3\text{AlF}_3]^-$ ion was structurally characterized.

Introduction

Perfluoroalkyl-substituted borate anions are among the most weakly coordinating anions (WCAs), known to date.^[1,2] Especially, the homoleptic tetrakis(trifluoromethyl)borate anion $[\text{B}(\text{CF}_3)_4]^-$ (Figure 1)^[3-5] and related mixed perfluoroalkylfluoroborate anions $[\text{R}^x\text{BF}_{4-x}]^-$ ($x=1-3$; R^x = perfluoroalkyl)^[6,7] have found widespread applications, for example, for the stabilization of highly reactive cations,^[1,6] in catalysis,^[8] ionic liquids (ILs),^[9] and battery applications.^[4,10] In addition, perfluoroalkylboron compounds with functional groups were synthesized,^[6,7] for example, R^xBCO ($\text{R}^x = \text{CF}_3$,^[11] C_2F_5 ,^[12] C_3F_7 ,^[12]), $[(\text{CF}_3)_3\text{BCPnic}]^-$ ($\text{Pnic} = \text{N}$,^[13] P , As),^[14] $[(\text{C}_2\text{F}_5)\text{BX}_3]^-$ ($\text{X} = \text{H}$,^[15] CN ,^[16]), and the decomposition pathway of perfluoroalkylboranes, for example, $(\text{CF}_3)_3\text{B}$, was elucidated.^[17]

In contrast to perfluoroalkylboron derivatives, related perfluoroalkyl compounds of boron's higher homologues gallium, indium, and thallium have been rarely studied. The tetrakis(trifluoromethyl)gallate anion $[\text{Ga}(\text{CF}_3)_4]^-$,^[19] the gallane $\text{Ga}(\text{CF}_3)_3$,^[20] and some of its adducts $(\text{CF}_3)_3\text{Ga}\cdot\text{L}$ ($\text{L} = \text{PMe}_3$, AsMe_3)^[20] have been synthesized and characterized by NMR

spectroscopy. Recently, Hoge and co-workers reported on salts of the tetrakis(pentafluoroethyl)gallate anion $[\text{Ga}(\text{C}_2\text{F}_5)_4]^-$ (Figure 1) and its application in Li-ion batteries.^[18] In addition, first examples of related tris(pentafluoroethyl)gallane derivatives were described.^[18,21] Tris(trifluoromethyl)indium $\text{In}(\text{CF}_3)_3$,^[22] some donor-stabilized adducts $(\text{CF}_3)_3\text{In}\cdot\text{L}$ ($\text{L} = \text{PMe}_3$,^[22] DMF), and few additional perfluoroalkylindium compounds, for example, $(\text{CF}_3)_2\text{InCl}$,^[19] were reported.^[19,23,24] Perfluoroalkylindium compounds and partially fluorinated indium organyls were applied in synthetic organic chemistry.^[25] Similar to $(\text{CF}_3)_3\text{M}$ ($\text{M} = \text{Ga}$, In), tris(trifluoromethyl)thallium $(\text{CF}_3)_3\text{Tl}$ was obtained via metal vapor deposition synthesis.^[26] In addition, some adducts with donor molecules $(\text{CF}_3)_3\text{Tl}\cdot\text{PMe}_3$ ^[26] and $(\text{CF}_3)_3\text{Tl}\cdot 2\text{L}$ ($\text{L} = \text{DMF}$, DMSO , Py)^[19] and a few further thallium derivatives with one or more perfluoroalkyl groups were reported,^[24,26,27] including a NMR report on the homoleptic thallate anion $[\text{Tl}(\text{CF}_3)_4]^-$.^[24]

In case of perfluoroalkylaluminum, computational studies were performed, for example, on the Lewis acidity of $\text{Al}(\text{CF}_3)_3$,^[28] but to the best of our knowledge, neither AlR_3 nor the corresponding anions $[\text{AlR}_4]^-$ are known, to date. The sole experimental information on perfluoroalkylaluminum compounds provided in the literature are on the reaction of $\text{Li}[\text{AlH}_4]$ with perfluoropropyl iodide to give $\text{Li}[\text{Al}(\text{CF}_2\text{CF}_2\text{CF}_3)_2]^-$.^[29,30] However, only limited spectroscopic data were presented.^[30] The formation of trifluoromethyl alumi-

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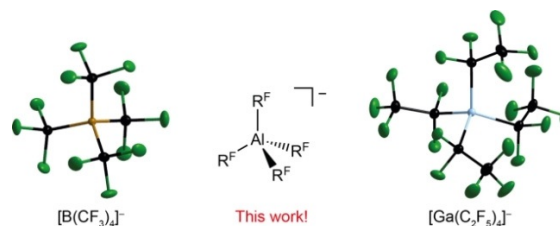


Figure 1. Homoleptic perfluoroalkylated anions of boron ($[\text{B}(\text{CF}_3)_4]^-$), aluminum, and gallium ($[\text{Ga}(\text{C}_2\text{F}_5)_4]^-$).

num compounds via metal vapor deposition was claimed but without any spectroscopic evidence.^[26,31]

Here, we report on salts of the tetrakis(pentafluoroethyl)aluminate anion $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ and present a detailed spectroscopic characterization. The degradation of the $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ ion via the pentafluoroethylfluoroaluminate ions $[(\text{C}_2\text{F}_5)_{4-n}\text{AlF}_n]^-$ ($n=1-3$) to give $[\text{AlF}_4]^-$ is described and the discussion is aided by results of DFT calculations.

Results and Discussion

Synthetic aspects

Pentafluoroethyl lithium was reacted with aluminum trichloride in diethyl ether to give $\text{Li}[\text{Al}(\text{C}_2\text{F}_5)_4]$ (Scheme 1). The pentafluoroethyl group was employed as substituent because of its high stability^[16,17,32] compared to the trifluoromethyl group, which tends to degrade via difluorocarbene elimination as shown for many trifluoromethylated compounds.^[17,32-36] The Hoge group has developed an alternative synthesis for $\text{Li}[\text{Al}(\text{C}_2\text{F}_5)_4]$ in parallel to our study using the silane $\text{Si}(\text{C}_2\text{F}_5)_3\text{H}$ and $\text{Li}[\text{AlH}_4]$ as starting materials.^[37] The crude product obtained from LiC_2F_5 and AlCl_3 in ether contained three aluminum-containing side products, the anions $[(\text{C}_2\text{F}_5)_3\text{AlF}]^-$, $[(\text{C}_2\text{F}_5)_2\text{AlF}_2]^-$, and, most likely, $[(\text{C}_2\text{F}_5)_3\text{AlOEt}]^-$ or less probable $(\text{C}_2\text{F}_5)_3\text{Al}\cdot\text{OEt}_2$, as assessed by multinuclear NMR spectroscopy. The best result with respect to the $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ content in the crude reaction mixture was achieved with a molar ratio of 1:3.0 to 1:3.5 for $\text{AlCl}_3\cdot\text{LiC}_2\text{F}_5$. More than 3.5 equivalents of LiC_2F_5 resulted in the formation of side products of unknown composition. The lithium salt $\text{Li}[\text{Al}(\text{C}_2\text{F}_5)_4]$ is stable in diethyl ether for several hours and such solutions were successfully employed in metatheses. Solid $\text{Li}(\text{OEt})_x[\text{Al}(\text{C}_2\text{F}_5)_4]$ was obtained by removal of all volatiles. However, $\text{Li}(\text{OEt})_x[\text{Al}(\text{C}_2\text{F}_5)_4]$ underwent fast decomposition in the solid state. Thus, immediate uptake of the solid in acetonitrile resulted in significant amounts of insoluble products and

after three days of storage of the solid all $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ had decomposed.

The reaction of aluminum trichloride with LiC_2F_5 in the presence of potassium or rubidium fluoride yielded $M[\text{Al}(\text{C}_2\text{F}_5)_4]$ ($M=\text{K}, \text{Rb}$) as solids with small amounts of $M[(\text{C}_2\text{F}_5)_3\text{AlF}]$ as side products (Scheme 1). Removal of $\text{Rb}[(\text{C}_2\text{F}_5)_3\text{AlF}]$ was achieved by further work-up to yield pure $\text{Rb}[\text{Al}(\text{C}_2\text{F}_5)_4]$ that was characterized by IR and Raman spectroscopy (Figure S23 in the Supporting Information). These salts showed slow decomposition in the solid state under an inert atmosphere inside a glovebox. Decomposition of these solids is much slower than of $\text{Li}(\text{OEt})_x[\text{Al}(\text{C}_2\text{F}_5)_4]$, which is rationalized by the high fluoride ion affinity of the lithium cation. Full decomposition of $M[\text{Al}(\text{C}_2\text{F}_5)_4]$ ($M=\text{K}, \text{Rb}$) was observed after approximately 2 months, only. According to elemental analysis of the solid remainder after 2 months, most of the fluoroorganic content had been lost. However, the NMR spectra of the solid remainder suspended in dichloromethane proved the formation of fluorinated substances during decomposition (vide infra).

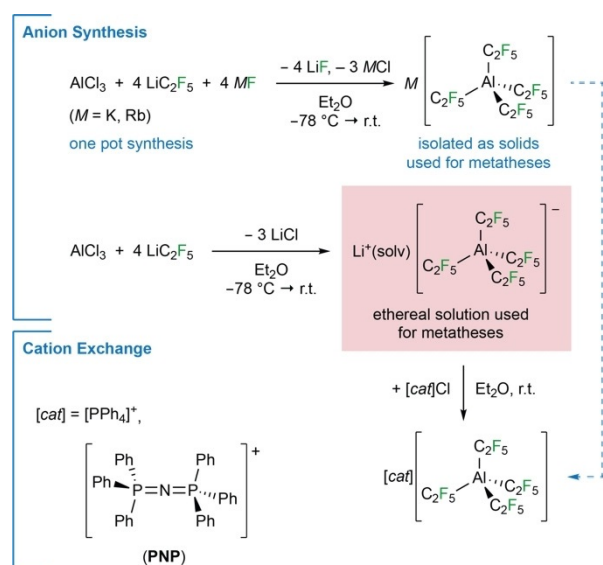
Metatheses using ethereal solutions of $\text{Li}[\text{Al}(\text{C}_2\text{F}_5)_4]$ and $\text{Rb}[\text{Al}(\text{C}_2\text{F}_5)_4]$ with $[\text{PPh}_4]\text{Cl}$ or **PNP**Cl (**PNP** = bis(triphenylphosphane)iminium) afforded the corresponding tetrakis(pentafluoroethyl)aluminates (Scheme 1). The highest stability of all $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ salts studied herein was found for **PNP** $[\text{Al}(\text{C}_2\text{F}_5)_4]$ that was stable over months in the solid state and has shown no decomposition up to 80 °C (DSC). In contrast, salts with less bulky cations such as $[\text{PPh}_4][\text{Al}(\text{C}_2\text{F}_5)_4]$ disclosed much faster degradation in the solid state.

Spectroscopic characterization of **PNP** $[\text{Al}(\text{C}_2\text{F}_5)_4]$

PNP $[\text{Al}(\text{C}_2\text{F}_5)_4]$ was characterized, in detail, by multinuclear NMR spectroscopy, vibrational spectroscopy, mass spectrometry, and elemental analysis. The ^{27}Al NMR signal of the $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ ion at 107.3 ppm is split into nine lines with $^2J(^{27}\text{Al}, ^{19}\text{F})$ of 32 Hz due to the coupling to four CF_2 groups (Figure 2). The ^{19}F NMR spectrum shows two signals in the solid state as well as in solution (Figure 2). In CD_2Cl_2 solution, the signal corresponding to the CF_3 groups is located at -83.9 ppm and the one for the CF_2 groups at -128.4 ppm. The latter signal is split into a sextet as a result of $^2J(^{27}\text{Al}, ^{19}\text{F})$ coupling of 31 Hz. In the solid-state ^{19}F NMR spectrum two broad singlets that are shifted to slightly higher resonance frequencies compared to the NMR spectrum in solution are observed. In the $^{13}\text{C}\{^{19}\text{F}\}$ NMR spectrum the signals of the CF_2 and CF_3 groups at 124.8 and 121.2 ppm are split into sextets with $^1J(^{27}\text{Al}, ^{13}\text{C})=123$ Hz and $^2J(^{27}\text{Al}, ^{13}\text{C})\approx 9$ Hz (Figure 2). In the solid state $^{13}\text{C}\{^{19}\text{F}\}$ CP/MAS NMR spectrum the signals are located at 125 and 122 ppm, respectively. Only the signal of the CF_2 groups shows the coupling to ^{27}Al with around 120 Hz.

Degradation of $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ via $[(\text{C}_2\text{F}_5)_{4-n}\text{AlF}_n]^-$ ($n=1-4$)

The degradation of tetraphenylphosphonium tetrakis(pentafluoroethyl)aluminate and of **PNP** $[\text{Al}(\text{C}_2\text{F}_5)_4]$ in diethyl ether was investigated by NMR spectroscopy. The reaction proceeds via successive loss of the pentafluoroethyl groups under formation



Scheme 1. Synthesis of tetrakis(pentafluoroethyl)aluminates.

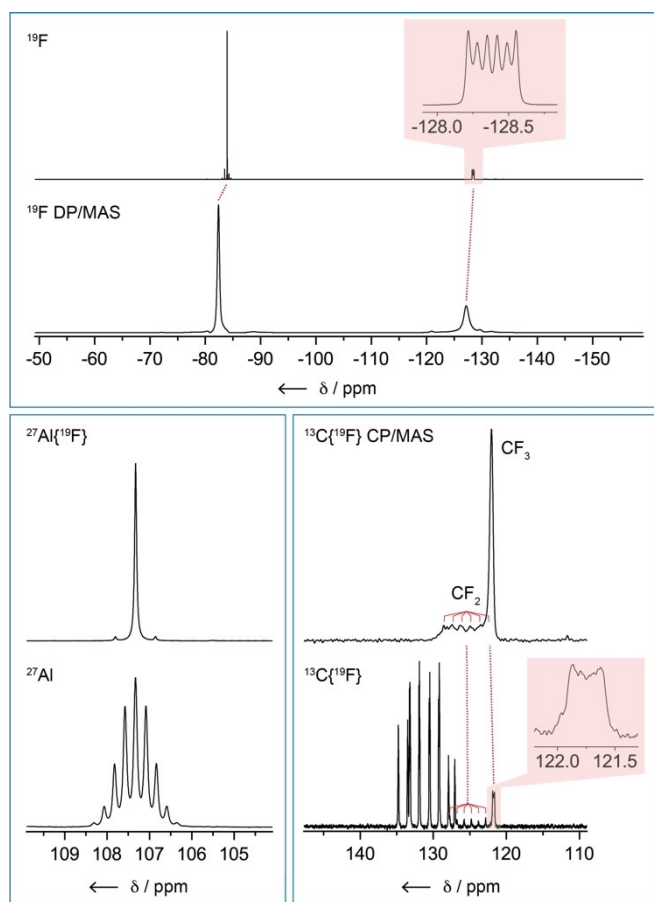


Figure 2. Selected NMR spectra of $\text{PNP}[\text{Al}(\text{C}_2\text{F}_5)_4]$ in CD_2Cl_2 .

of the anions $[(\text{C}_2\text{F}_5)_3\text{AlF}]^-$, $[(\text{C}_2\text{F}_5)_2\text{AlF}_2]^-$, $[(\text{C}_2\text{F}_5)\text{AlF}_3]^-$, and $[\text{AlF}_4]^-$ (Figure 3). In addition to the NMR spectroscopic characterization, all anions were identified by mass spectrometry (Figure S24 and S25 in the Supporting Information). The assignment of the ^{27}Al and ^{19}F NMR signals of the anions $[(\text{C}_2\text{F}_5)_{4-n}\text{AlF}_n]^-$ ($n=0-4$) is aided by correlation spectra, selective decoupling experiments, and NMR data calculated at the B3LYP/6-311++G(2d,p) level of theory (Table 1, Figure S26–S32 in the Supporting Information). The ^{19}F NMR chemical shifts of the anions $[(\text{C}_2\text{F}_5)_{4-n}\text{AlF}_n]^-$ ($n=0-4$) are in narrow ranges: CF_3 –83.6 to –84.6 ppm, CF_2 –127.7 to –133.1 ppm, and AlF –180.5 to –195.9 ppm. In contrast, $\delta(^{27}\text{Al})$ reveals a distinct trend along the series with a reduction of $\delta(^{27}\text{Al})$ of ca. 12–18 ppm per exchange of C_2F_5 against fluorine (Figure 3 and Table 1). An analogous behavior with larger differences was reported for $[(\text{CH}_3)_{4-n}\text{AlF}_n]^-$ ($n=1-4$).^[38,39] A further similar, univocal trend was found for $^1J(^{27}\text{Al},^{19}\text{F})$ that strongly decreases with decreasing number of pentafluoroethyl groups at aluminum. The coupling between ^{19}F of the CF_2 units and ^{27}Al shows a parallel but less pronounced trend, whereas $^1J(^{27}\text{Al},^{13}\text{C})$ reveals opposite behavior (Table 1). The decomposition of $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ in diethyl ether is accompanied by the formation of pentafluoroethylfluoroaluminium species with ethoxy groups and/or diethyl ether coordinated to aluminum as indicated by the NMR

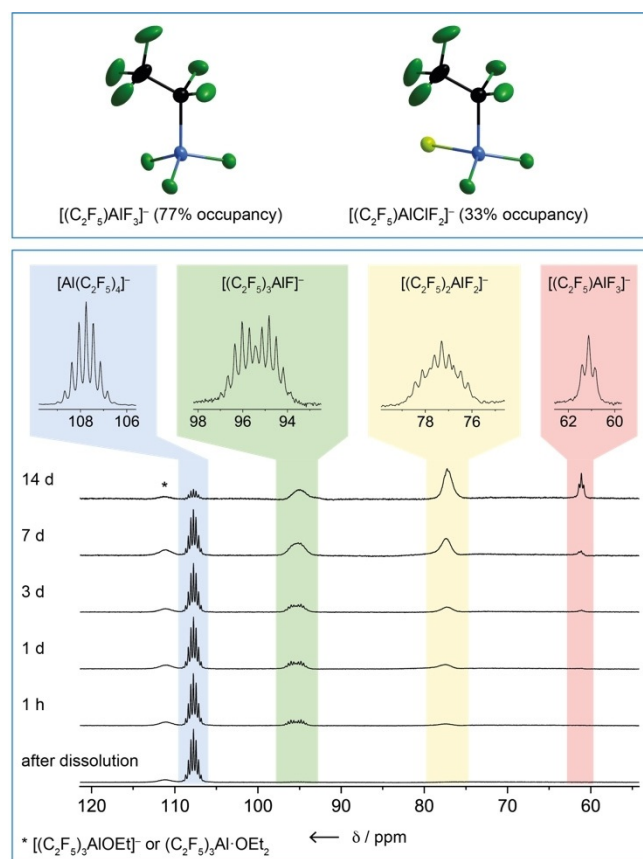


Figure 3. Decomposition of $[\text{PPh}_4][\text{Al}(\text{C}_2\text{F}_5)_4]$ in Et_2O monitored by ^{27}Al NMR spectroscopy (bottom) and the $[(\text{C}_2\text{F}_5)_3\text{AlF}]^-$ ion that is disordered with $[(\text{C}_2\text{F}_5)_2\text{AlClF}_2]^-$ in $\text{PNP}[(\text{C}_2\text{F}_5)_3\text{AlF}_3]\cdot\text{Et}_2\text{O}$ (top).

spectra depicted in Figure S28–S30 in the Supporting Information.

Crystallization of a decomposition mixture of $\text{PNP}[\text{Al}(\text{C}_2\text{F}_5)_4]$ afforded single crystals of $\text{PNP}[(\text{C}_2\text{F}_5)\text{AlF}_3]\cdot\text{Et}_2\text{O}$ and $\text{PNP}[\text{AlF}_4]$ providing additional evidence for the successive replacement of C_2F_5 by fluorine during degradation of $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$. In both crystals studied, partial disorder of $\text{Al}-\text{F}$ with $\text{Al}-\text{Cl}$ was observed. The presence of chlorine is due to $\text{PNP}[\text{AlF}_4]$ that was employed in metatheses. $\text{PNP}[(\text{C}_2\text{F}_5)\text{AlF}_3]\cdot\text{Et}_2\text{O}$ crystallizes in the triclinic space group $P\bar{1}$ with $Z=2$ and $\text{PNP}[\text{AlF}_4]$ in the monoclinic space group $P2_1/c$ with $Z=8$. The bond parameters of the $[(\text{C}_2\text{F}_5)\text{AlF}_3]^-$ anion (Figure 3) are in good agreement to values derived from DFT calculations (Table 2). A similar good agreement was achieved for experimental and calculated data of $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$,^[37] $[\text{AlF}_4]^-$,^[38,40,41] and $[\text{Ga}(\text{C}_2\text{F}_5)_4]^-$ ^[18] (Table 2). The crystal structure of $[\text{PPh}_4][\text{Al}(\text{C}_2\text{F}_5)_4]$ is reported in the parallel contribution by Hoge et al.^[37] The calculated bonding parameters of the anions $[(\text{C}_2\text{F}_5)_{4-n}\text{AlF}_n]^-$ ($n=0-4$) are very close. However, trends have been found for $d(\text{M}-\text{C})$ and $d(\text{M}-\text{F})$ that are predicted to decrease and increase, respectively, with decreasing number of C_2F_5 groups (Table 2). The experimental and calculated bond distances of $[\text{M}(\text{C}_2\text{F}_5)_4]^-$ ($\text{M}=\text{Al}, \text{Ga}$) are almost the same (Table 2), which nicely fits to the almost identical covalent radii of gallium (122 pm) and aluminum (121 pm).^[42]

Table 1. Experimental and calculated NMR parameters of $[(C_2F_5)_{4-n}AlF_n]^-$ ($n=0-4$).^[a,b]

anion	$[Al(C_2F_5)_4]^-$	$[(C_2F_5)_3AlF]^-$	$[(C_2F_5)_2AlF_2]^-$	$[(C_2F_5)AlF_3]^-$	$[AlF_4]^-$
$\delta(^{27}Al)^{[c]}$	107.7 (108.0) <i>115.4</i>	95.2 (95.1) <i>102.6</i>	77.3 (76.5) <i>81.1</i>	61.1 (61.0) <i>64.3</i>	49.1 ^[d,e] (50.3) <i>51.8</i>
$\delta(^{19}F)$ Al-F	–	–191.6 <i>–246.7</i>	–180.5 <i>–229.2</i>	–182.7 <i>–232.9</i>	–195.9 ^[d] <i>–250.5</i>
$\delta(^{19}F)$ CF ₂	–127.7 <i>–151.3</i>	–131.8 <i>–154.7</i>	–133.5 <i>–156.2</i>	–133.1 <i>–156.0</i>	–
$\delta(^{19}F)$ CF ₃	–83.6 <i>–103.8</i>	–83.9 <i>–104.1</i>	–84.3 <i>–104.6</i>	–84.6 <i>–105.0</i>	–
$\delta(^{13}C)$ CF ₂	124.8 ^[d] <i>135.6</i>	n.o. ^[f] <i>135.2</i>	n.o. <i>135.5</i>	n.o. <i>136.8</i>	–
$\delta(^{13}C)$ CF ₃	121.2 ^[d] <i>133.6</i>	n.o. <i>134.1</i>	n.o. <i>134.5</i>	n.o. <i>135.1</i>	–
$^1J(^{27}Al, ^{19}F)$	–	125	87	n.o. ^[g]	n.o. (38) ^[g]
$^2J(^{27}Al, ^{19}F)$	32	32	31	29	–
$^1J(^{27}Al, ^{13}C)$	123	135 ^[h]	149 ^[h]	n.o.	–

[a] Cation: $[PPh_4]^+$; solvent: Et₂O with a (CD₃)₂CO capillary. [b] Calculated values in italics; B3LYP/6-311 + G(2d,p)//B3LYP/6-311 + G(d,p). [c] Solid state NMR spectroscopic data in brackets. [d] Cation: PNP^+ ; solvent: CD₂Cl₂. [e] Literature data for $[AlF_4]^-$ in CD₃CN: $\delta(^{27}Al)$ = 49.2 ppm, $\delta(^{19}F)$ = –194.2 ppm, $^1J(^{27}Al, ^{19}F)$ = 37.8 Hz.^[40] [f] n.o. = not observed. [g] The fluoroaluminate anions undergo fluorine exchange as proven by ¹⁹F-¹⁹F EXSY experiments (Figure S31 and S32 in the Supporting Information). So, $^1J(^{27}Al, ^{19}F)$ coupling was not observed for $[(C_2F_5)AlF_3]^-$ and $[AlF_4]^-$, rarely for $[(C_2F_5)_2AlF_2]^-$, and in many spectra the signal of $[(C_2F_5)_3AlF]^-$ was broad without any resolved $^1J(^{27}Al, ^{19}F)$ coupling. A similar, concentration-dependent effect was reported for $[AlF_4]^-$.^[40] [h] ¹³C satellites of the ²⁷Al/¹⁹F NMR spectrum.

Table 2. Experimental and calculated bond distances of $[(C_2F_5)_{4-n}AlF_n]^-$ ($n=0-4$) and $[Ga(C_2F_5)_4]^-$.^[a,b]

Anion	$d(M-C)$	$d(C-C)$	$d(C-F_2)$	$d(C-F_3)$	$d(M-F)$
$[Al(C_2F_5)_4]^-$ ^[c]	204.0(2) <i>207.4</i>	152.1(3) <i>154.1</i>	138.4(3) <i>139.1</i>	133.6(3) <i>134.8</i>	–
$[Ga(C_2F_5)_4]^-$ ^[d]	204.14(11) <i>208.5</i>	152.6(2) <i>154.1</i>	137.72(13) <i>138.5</i>	133.4(2) <i>134.8</i>	–
$[(C_2F_5)_3AlF]^-$	207.3	153.9	139.3	134.9	170.3
$[(C_2F_5)_2AlF_2]^-$	206.9	153.8	139.5	135.0	170.5
$[(C_2F_5)AlF_3]^-$ ^[e]	200.6(6) <i>206.8</i>	149.9(8) <i>153.8</i>	141.4(7) <i>139.8</i>	134.0(10) <i>135.2</i>	166.6(3) <i>171.0</i>
$[AlF_4]^-$	–	–	–	–	164.7(2) ^[f] <i>171.7</i>

[a] Calculated values in italics; d in pm; mean values where applicable. [b] B3LYP/6-311 + G(d). [c] $[PPh_4][Al(C_2F_5)_4]$; Symmetry: S_4 .^[37] [d] $[PPh_4][Ga(C_2F_5)_4]$; Symmetry: S_4 .^[18] [e] $PNP[(C_2F_5)AlF_3]$; the $[(C_2F_5)AlF_3]^-$ anion is disordered with $[(C_2F_5)AlClF_2]^-$ ($d(Al-Cl)$ = 211.9(4) [exptl] and 217.2 pm [calcd]). [f] $[PPh_4][AlF_4]$.^[41]

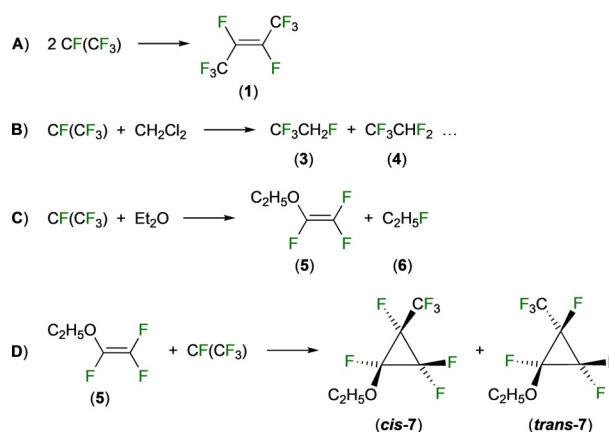
Fluoroorganic compounds are formed as byproducts of the degradation of $[(C_2F_5)_{4-n}AlF_n]^-$ ($n=0-3$) in solution and the solid state. In Scheme 2 the fluoroorganic molecules are depicted that were identified by NMR spectroscopy and in the Supporting Information the spectra and experimental as well as calculated data are provided (Figures S33–S46, Tables S2 and S3). The formation of all fluoroorganic derivatives assigned is rationalized by initial elimination of fluoro(trifluoromethyl)carbene $CF(CF_3)$ ^[43] from the pentafluoroethylaluminate anions: **A**) $trans-CF_3CF=CFCF_3$ (**1**) is the dimer of $CF(CF_3)$, **B**) 1,1,1,2-tetrafluoroethane (**3**) and pentafluoroethane (**4**) are formed from the carbene and dichloromethane, **C**) ethyl trifluorovinyl ether (**5**) and fluoroethane (**6**) are derived from $CF(CF_3)$ and diethyl

ether, and **D**) the diastereomeric cyclopropanes *cis-7* and *trans-7* are the result of the addition of $CF(CF_3)$ to **5** (Scheme 2).

Theoretical study on the degradation pathway of $[Al(C_2F_5)_4]^-$

Only limited information on decomposition pathways of pentafluoroethyl derivatives can be found in the literature. Pentafluoroethyltetrafluorophosphorane $(C_2F_5)PF_4$ was reported to extrude $CF(CF_3)$ on platinum at 240 °C.^[44] Thermolysis of pentafluoroethyltrifluorosilane $(C_2F_5)SiF_3$ at 160 °C gives both dimers of $CF(CF_3)$, *trans*- $CF_3CF=CFCF_3$ (**1**) and *cis*- $CF_3CF=CFCF_3$ in 92% yield, together with SiF_4 .^[35,43,45] Later, $(C_2F_5)_3SiF$ was found to result in *trans*- $CF_3CF=CFCF_3$ (**1**) and *cis*- $CF_3CF=CFCF_3$, together with SiF_4 , $(C_2F_5)SiF_3$, and further fluoroorganic compounds, upon thermolysis at 180 °C for 1 h.^[36] Silane $(C_2F_5)SiF_3$ was employed as source for $CF(CF_3)$ and in carbene trapping reactions,^[43] for example, with PF_3 .^[44] The formation of $CF(CF_3)$ from $(C_2F_5)SiF_3$ and $(C_2F_5)PF_4$ was explained by intramolecular 1,2-fluorine shifts ($C_\alpha-F$ activation) from CF_2 to silicon and phosphorus, respectively.^[35,43,44] The release of $CF(CF_3)$ from silane $(C_2F_5)SiF_3$ was predicted by DFT calculations to proceed barrierless and to be endergonic (141.8 kJ mol^{–1}).^[46] $C_\alpha-F$ activation and formation of fluorocarbenes $CF(CF_2R)$ is a general reaction of trifluorosilanes of the type $(RCF_2CF_2)SiF_3$ (e.g. $R=H$).^[43] An X-ray crystallographic study on pentafluoroethyl lithium provided evidence for a Li/F carbenoid,^[33] which can be regarded as a further indication for the favorable release of $CF(CF_3)$ upon degradation of pentafluoroethyl compounds.

The degradation of the $[Al(C_2F_5)_4]^-$ anion was modeled using DFT calculations (Figure 4). 1,2-fluorine shifts ($C_\alpha-F$ activation) via $CF(CF_3)$ extrusion and 1,3-fluorine shifts ($C_\beta-F$ activation)



Scheme 2. Experimentally confirmed (data are given in the Supporting Information) products of reactions of fluoro(trifluoromethyl)carbene $CF(CF_3)$, which was released from pentafluoroethylaluminate anions during degradation. For *cis-7* and *trans-7* only one of the two enantiomers is depicted, respectively.

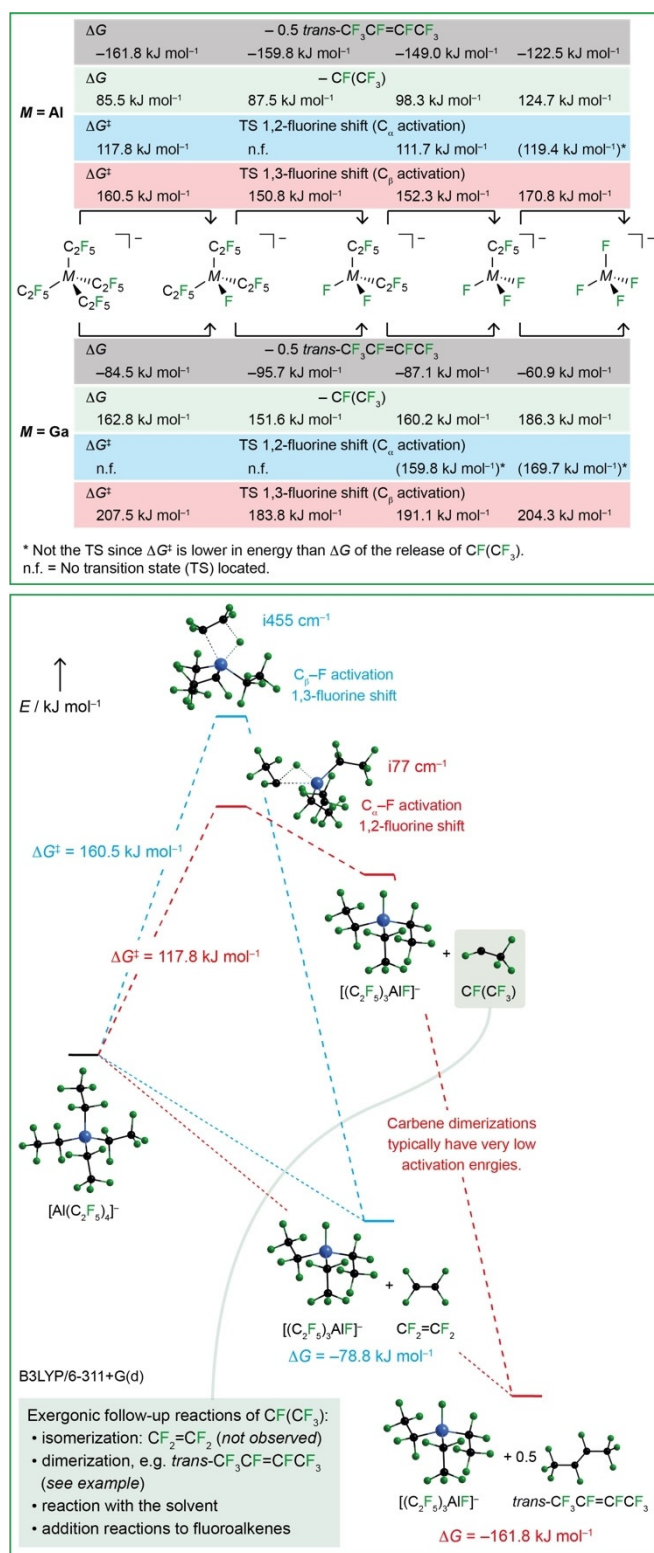


Figure 4. Calculated free reaction energies (ΔG) and free activation energies (ΔG^\ddagger) for the consecutive degradation of pentafluoroethylaluminum and pentafluoroethylgallate ions $[(C_2F_5)_{4-n}MF_n]^-$ ($n = 0-3$, $M = \text{Al, Ga}$) (top), and comparison of degradation of $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ via $\text{C}_\alpha\text{-F}$ or $\text{C}_\beta\text{-F}$ activation (bottom) (B3LYP/6-311 + G(d)).

via release of tetrafluoroethylene (TFE) were considered. The 1,2-fluorine shift of the degradation of the first C_2F_5 group of $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ has a significantly lower free activation energy

(ΔG^\ddagger) than the 1,3-fluorine shift. Thus, $\text{C}_\alpha\text{-F}$ activation is predicted to be favorable, which is in perfect agreement to the experimental findings (vide supra) because there is proof solely for the formation of $\text{CF}(\text{CF}_3)$ as an intermediate (Scheme 2) but no indication for the formation of TFE. Analogous results were obtained for the depletion of the remaining C_2F_5 groups at aluminum (Figure 4). In case of $[(\text{C}_2\text{F}_5)_3\text{AlF}_3]^-$ the release of $\text{CF}(\text{CF}_3)$ corresponds to the free activation energy since the transition state located is lower in energy than the separated species $[(\text{C}_2\text{F}_5)_3\text{AlF}_3]^-$ and $\text{CF}(\text{CF}_3)$. In summary, the extrusions of $\text{CF}(\text{CF}_3)$ are all endergonic but the follow-up reactions of the highly reactive carbene, for example, dimerization to *trans*- $\text{CF}_2\text{CF}=\text{CFCF}_3$ (1), make the full reaction sequence strongly exergonic.

The successive degradation of the related gallate anion $[\text{Ga}(\text{C}_2\text{F}_5)_4]^-$ (Figure 1)^[18] that exhibits a much higher thermal and chemical stability in its salts than $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ was studied by DFT calculations, as well (Figure 4). The data available show that the loss of $\text{CF}(\text{CF}_3)$ via an 1,2-fluorine shift is favored over TFE elimination via an 1,3-fluorine shift. This behavior parallels the findings for the related aluminate anions. Together with earlier reports on $(\text{C}_2\text{F}_5)_3\text{SiF}_3$,^[35,43,45,46] $(\text{C}_2\text{F}_5)_3\text{SiF}_2$,^[36] and $(\text{C}_2\text{F}_5)_2\text{PF}_4$,^[43,44] these results point toward a general mechanism for the decomposition of pentafluoroethyl element compounds. However, the extrusion of $\text{CF}(\text{CF}_3)$ requires significantly more energy for the pentafluoroethylgallate anions compared to the respective aluminate anions ($> 60 \text{ kJ mol}^{-1}$), which is the reason for the higher stability of $[\text{Ga}(\text{C}_2\text{F}_5)_4]^-$ compared to $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$.

Conclusions

The reaction of pentafluoroethyl lithium with aluminum trichloride provides a convenient synthetic entry to salts of the tetrakis(pentafluoroethyl)aluminate $[\text{Al}(\text{C}_2\text{F}_5)_4]^-$ ion with different cations. The combined experimental and theoretical study on the pentafluoroethylaluminate anions shows that the degradation proceeds via 1,2-fluorine shifts ($\text{C}_\alpha\text{-F}$ activation) and loss of $\text{CF}(\text{CF}_3)$. The much higher stability of the related gallate ions is rationalized by significantly higher barriers for the extrusion of the carbene $\text{CF}(\text{CF}_3)$.

Experimental Section

Full experimental details and characterization data for all compounds and details of the DFT calculations are included in the Supporting Information. Deposition Number(s) 1979821 (PNP $[(\text{C}_2\text{F}_5)_3\text{AlF}_3]\cdot\text{Et}_2\text{O}$) and 1979820 (PNP $[\text{AlF}_4]$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of interest

The authors declare no conflict of interest.

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