Group 13 Elements | *Hot Paper*

Synthesis and Characterization of Tetrakis(pentafluoroethyl)aluminate

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Abstract: While perfluorinated aryl, aryloxy and alkoxy aluminum species are well-established as weakly coordinating anions (WCAs), corresponding perfluoroalkyl aluminum derivatives are virtually unknown. Reaction of $Si(C_2F_5)_3CH_3$ with $Li[AlH_4]$ afforded the tetrakis(pentafluoroethyl)aluminate, $[Al(C_2F_5)_4]^-$. Several salts of the $[Al(C_2F_5)_4]^-$ ion were synthesized and characterized by NMR spectroscopic methods, mass spectrometry, X-ray diffraction studies and elemental analysis.

Several tetrakis(perfluoroaryl) and -(alkyl) derivatives of group 13 elements B, Al and Ga are known to date. A wide variety of these compounds are functioning as very efficient and popular weakly coordinating anions (WCAs) and have found application in room temperature ionic liquids (RTILs), as electrolytes for lithium-ion batteries or in catalytic processes.[1,2]

Probably the most popular perfluoroaryl substituted WCA is the commercially available tetrakis(pentafluorophenyl)borate, $[B(C_6F_5)_4]^-$, which is used in catalysis.[3,4] Although the corresponding gallate $[Ga(C_6F_5)_4]^-$[5] and the aluminate $[Al(C_6F_5)_4]^-$[6] tend to decompose, they are employed in olefin polymerization processes.[4,7]

Particularly in aluminum chemistry the alkoxy (OR^F) and aryloxy (OAr^F) substituted WCAs $[Al(OR^F)_4]^-$ and $[Al(OAr^F)_4]^-$ are highly prominent due to their stability and facile synthesis from $Li[AlH_4]$ and the corresponding alcohols.[2,8] The resulting lithium salts are suitable for various metathesis reactions. Several boron analogues were also synthesized and are possibly useful as electrolytes in lithium-ion batteries.[2,9]

A further category of WCAs is based upon group 13 pentafluorotellurates (teflates). While $[B(OTeF_5)_4]^-$ is known since 1981,[10] the higher homologues $[Al(OTeF_5)_4]^-$[11] and $[Ga(OTeF_5)_4]^-$[12] have only recently been synthesized and have led to a considerable extension of WCA chemistry.

The tetrakis(trifluoromethyl)borate anion, $[B(CF_3)_4]^-$, which is accessible through fluorination of $[B(CN)_4]^-$ with ClF_3, is a surprisingly stable WCA that can be handled even in aHF.[13] The analogous $[Ga(CF_3)_4]^-$ was generated in 1991 and characterized by ^{19}F NMR spectroscopy.[14] Recently we reported on the tetrakis(pentafluoroethyl)gallate, $[Ga(C_2F_5)_4]^-$, which features a comparable stability to $[B(CF_3)_4]^-$.[15] Aluminum perfluoroalkyls however are virtually unknown. So far, a few perfluoropropyl aluminum species could be detected by ^{19}F NMR spectroscopy but due to their instability they could not be isolated.[16] In addition, numerous computational studies were performed on the Lewis acidity of $Al(CF_3)_3$ whereby, to the best of our knowledge, neither $Al(CF_3)_3$ nor its corresponding anion $[Al(CF_3)_4]^-$ are known to date.[17]

Due to their tendency to eliminate difluorocarbene, trifluoromethylated inorganic compounds with E–CF_3 bonds (with E = B,[18] Si,[19,20] Sn,[21] Ge,[22] P,[23] or Cd[24]) generally exhibit a limited thermal and chemical stability. In contrast to this, their pentafluoroethyl analogues are remarkably more stable.[25] This increased stability already becomes perceivable by the comparison of trifluoromethyllithium, $LiCF_3$, and pentafluoroethyllithium, LiC_2F_5. While $LiCF_3$ decomposes even at −78 °C,[26,27] the corresponding LiC_2F_5 is stable up to −40 °C and therefore serves as a well-established transfer reagent for pentafluoroethyl groups.[28] With regard to this, the pentafluoroethyl group appears to be a promising candidate for the synthesis of the yet unknown aluminum tetrakis(perfluoroalkyls). Herein we give an account on the synthesis and molecular structure of the tetrakis(pentafluoroethyl)aluminate $[Al(C_2F_5)_4]^-$.

As demonstrated by the Finze group in a parallel study, the reaction of aluminumtrichloride, $AlCl_3$, with LiC_2F_5 leads to the generation of the tetrakis(pentafluoroethyl)aluminate ion, $[Al(C_2F_5)_4]^-$.[29]

During our investigations of hydridosilicates we encountered a very efficient synthesis by accident. With the aim to generate the hydridosilicate $[Si(C_2F_5)_3H_2]^-$, the corresponding silane $Si(C_2F_5)_3H$ was treated with $Li[AlH_4]$. Here instead of the anticipated silicate, the tetrakis(pentafluoroethyl)aluminate ion, $[Al(C_2F_5)_4]^-$, was formed.

Since the synthesis of $Si(C_2F_5)_3H$ is elaborate,[30] the more readily accessible $Si(C_2F_5)_3CH_3$ was utilized for further investigations. $Si(C_2F_5)_3CH_3$ results from pentafluoroethylation of $SiCl_3(CH_3)$ with LiC_2F_5 in one step.[20] When four equivalents of $Si(C_2F_5)_3CH_3$ are treated with $Li[AlH_4]$, the formation of the tet-

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rakis(pentafluoroethyl)aluminate ion, $[Al(C_2F_5)_4]^-$, occurs immediately (Scheme 1).

In addition, hydridosilanes are identified in the reaction mixture. By analogy to the Ruppert–Prakash trifluoromethylation reaction,[26,31] it is conceivable that a hydride ion adds to $Si(C_2F_5)_3CH_3$, thus activating a $Si–C_2F_5$ bond with subsequent transfer of the pentafluoroethyl group to aluminum (Scheme 2).

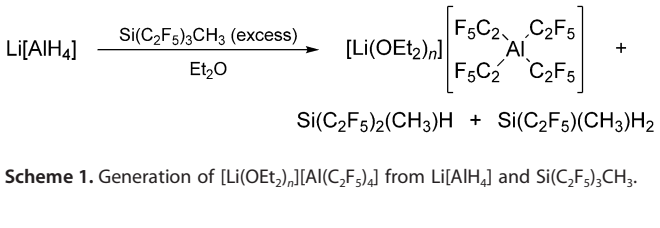
Due to the fast rate of this transfer, spectroscopic proof of neither pentafluoroethyl-hydrido aluminates nor silicates as intermediates in the reaction mixture was possible. Removal of all volatile components gives a colorless, extremely sensitive solid that slowly decomposes within days at room temperature. A cation exchange with $[PPh_4]Cl$, $[NBu_4]Cl$ and [PNP]Cl (PNP = bis(triphenylphosphine)iminium) affords the corresponding salts. While $[PPh_4][Al(C_2F_5)_4]$ and $[NBu_4][Al(C_2F_5)_4]$ slowly decompose at room temperature, the corresponding PNP salt exhibits an increased thermal stability.

Weakly coordinating phosphazenium cations, as originally introduced by Schwesinger et al.,[32] are outstanding in stabilizing reactive anions like for example the hydroxide trihydrate anion $[OH(OH_2)_3]^-$.[33] Consequently we employed $[\{(Et_2N)_3P=N\}_3PN(H)tBu]Cl$ ($[EtP_4H]Cl$) for a cation exchange to obtain $[EtP_4H][Al(C_2F_5)_4]$ in an overall yield of 85% (Scheme 3). The salt decomposes above 110 °C. This thermal stability of $[EtP_4H][Al(C_2F_5)_4]$ allowed a characterization of the $[Al(C_2F_5)_4]^-$ anion by elemental analysis (found for $C_{48}H_{100}AlF_{20}N_{13}P_4$: 41.59% C, 7.56% H and 13.33% N; calcd 41.47% C, 7.25% H, 13.10% N) underlining the identity and purity of the salt.

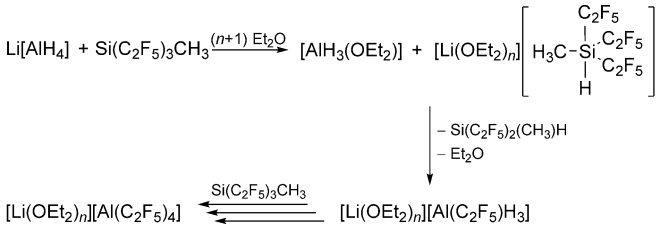
In the ^{27}Al NMR spectrum (Figure 1) the resonance of the $[Al(C_2F_5)_4]^-$ ion is observed as a nonet at $\delta = 107.7$ ppm with a $^2J(^{27}Al, ^{19}F)$ coupling constant of 32 Hz. In the ^{19}F NMR spectrum a singlet at $\delta = -83.5$ ppm for the CF_3 groups is observed. Due to the nuclear spin quantum number of $I = 5/2$ for aluminum, the signal for the CF_2 units appears as a six-line multiplet at $\delta = -127.7$ ppm (Figure 2).

The identity of the $[Al(C_2F_5)_4]^-$ ion is also evidenced by accurate mass measurement of the parent peak of $[Al(C_2F_5)_4]^-$ at $m/z = 502.9505$ (calcd 502.95016 for $C_8F_{20}Al^-$). Fragmentation occurs by extrusion of C_2F_4 units, revealing characteristic peaks at m/z (%) = 402.95 (73) $[Al(C_2F_5)_3F]^-$, 302.96 (11) $[Al(C_2F_5)_2F_2]^-$, 202.97 (2) $[Al(C_2F_5)F_3]^-$ and 102.97 (< 1) $[AlF_4]^-$.

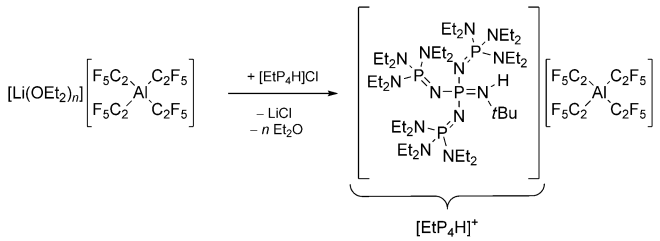
Single crystals of $[PPh_4][Al(C_2F_5)_4]$ suitable for X-ray diffraction were grown by diffusion of *n*-hexane into a dichloromethane solution of the salt at −40 °C. Just like the higher homologue $[PPh_4][Ga(C_2F_5)_4]$,[15] $[PPh_4][Al(C_2F_5)_4]$ crystallizes in the tetragonal space group $I4_1/a$ with 4 formula units per unit cell, meaning both ions exhibit S_4 symmetry (Figure 3).[34] The tetrahedral coordination sphere around the aluminum atom is



Scheme 1. Generation of $[Li(OEt_2)_n][Al(C_2F_5)_4]$ from $Li[AlH_4]$ and $Si(C_2F_5)_3CH_3$.



Scheme 2. Formation of $[Al(C_2F_5)_4]^-$ via the activation of $Si(C_2F_5)_3CH_3$ by $Li[AlH_4]$.



Scheme 3. Synthesis of $[EtP_4H][Al(C_2F_5)_4]$ by cation exchange.

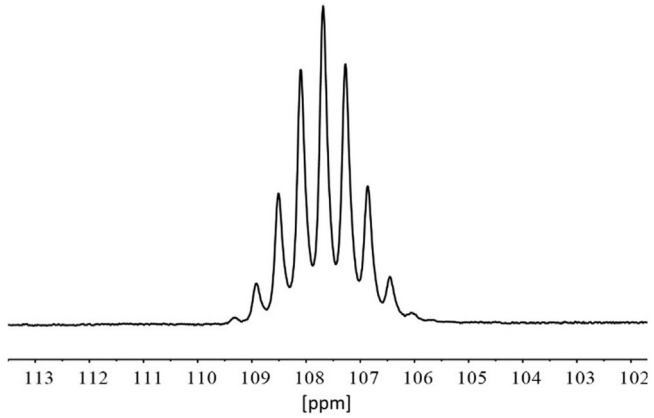


Figure 1. ^{27}Al NMR spectrum of $[EtP_4H][Al(C_2F_5)_4]$ in Et_2O with acetone-$[d_6]$ as external standard in a capillary.

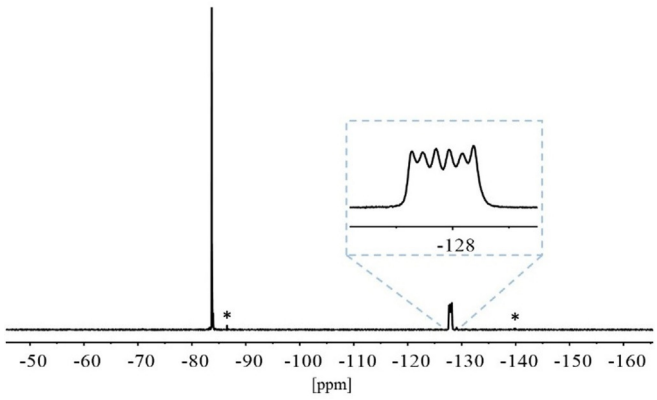


Figure 2. ^{19}F NMR spectrum of $[PPh_4][Al(C_2F_5)_4]$ in Et_2O with acetone-$[d_6]$ as external standard in a capillary. *Signals for HC_2F_5.

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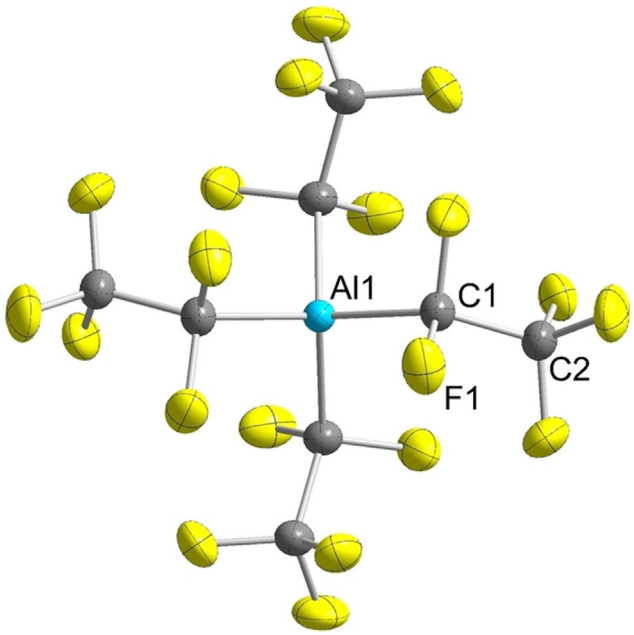

Figure 3. Molecular structure of the anion in $[PPh_4][Al(C_2F_5)_4]$. The cation is omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [pm] and angles [°]: Al1–C1 204.0(2), C1–F 137.9(2)–138.8(2), C2–F 132.8(2)–134.2(3), C1–C2 152.1(3); C1-Al-C1^1 105.4(1), C1-Al-C1^2 111.6(1), Al1-C1-C2 120.3(2). Symmetry codes: 1 = 1−X, 3/2−Y, +Z; 2 = 5/4−Y, 1/4+X, 1/4−Z.

slightly distorted as evident from the C1-Al-C1^1 and C1-Al-C1^2 angles of 105.4(1)° and 111.6(1)°. The Al–C1 bond length of 204.0(2) pm is well comparable to those of the anion $[Al(C_2H_5)_4]^-$ in alkali metal salts (201–203 pm)[35] and to $[Al(C_6F_5)_4]^-$ (200–203 pm).[36]

We presented a convenient synthesis of $[Al(C_2F_5)_4]^-$ salts by reaction of $Si(C_2F_5)_3CH_3$ with $Li[AlH_4]$. Subsequent cation exchange with $[PPh_4]Cl$, $[NBu_4]Cl$ and $[PNP]Cl$ affords the corresponding $[Al(C_2F_5)_4]^-$ salts. Utilizing the weakly coordinating phosphazenium cation $[EtP_4H]^+$, it was possible to increase the yield up to 85% and to enhance the thermal stability. The salt decomposes above 110 °C. To the best of our knowledge, these salts represent the first examples of perfluoroalkyl aluminum derivatives that were isolated and fully characterized.

Experimental Section

Materials and apparatus: All reactions were performed in the absence of water and air by use of standard *Schlenk* techniques. Chemicals were obtained from commercial sources and used without further purification. NMR spectra were either recorded on a Bruker Avance III 300 or Bruker Avance III 500 HD in the indicated solvent with acetone-$[d_6]$ as lock substance in a capillary. Positive shifts are downfield from the external standards (TMS for ^1H and ^{13}C, H_3PO_4 for ^{31}P, CCl_3F for ^{19}F and $Al(NO_3)_3$ for ^{27}Al). IR spectroscopic measurements were performed on a Bruker Alpha-FT-IR spectrometer with a diamond crystal. ESI mass spectra were recorded using a *ZQ2000* single quadrupole mass spectrometer (Waters, Manchester, UK) equipped with an ESI source (3.5 kV spray voltage). Accurate mass nano-ESI measurements were performed using a Q-IMS-TOF mass spectrometer Synapt G2Si (Waters Limited, Manchester, UK) in resolution mode, interfaced to a nano-ESI ion source. The melting point was measured on a Mettler Toledo Mp70 Melting Point System. C, H, N analysis was conducted with a HEKAtech Euro EA 3000 apparatus. SCXRD was performed on a Rigaku Supernova diffractometer.

$[EtP_4H][Al(C_2F_5)_4]$: A sample of $Si(C_2F_5)_3CH_3$ (2.84 g, 7.10 mmol) was dissolved in Et_2O (10 mL) and combined with a 1 M solution of $Li[AlH_4]$ in Et_2O (1.26 g, 1.77 mmol) at rt. The reaction mixture was evaporated to dryness to give a colorless solid. The residue was redissolved in Et_2O and treated with $[EtP_4H]Cl$ (1.65 g, 1.79 mmol). The reaction mixture was stirred for 17 h at rt and the precipitate was filtered off. $[EtP_4H][Al(C_2F_5)_4]$ was recrystallized from the filtrate and isolated as a colorless solid in an 85% (2.09 g, 1.50 mmol) yield.

m.p. 112 °C (only decomposition); **^{19}F NMR** (282.4 MHz, Et_2O, rt): $\delta = -83.5$ (s, 12 F, CF_3); −127.9 ppm (six-line multiplet, $^2J(^{19}F, ^{27}Al) \approx 32$ Hz, 8 F, CF_2); **^{27}Al NMR** (78.2 MHz, Et_2O, rt): $\delta = 107.7$ ppm (non, $^2J(^{19}F, ^{27}Al) \approx 32$ Hz, Al); **^{31}P NMR** (202.5 MHz, Et_2O, rt): $\delta = 8.4$ (dm, $^2J(^{31}P, ^{31}P) = 71$, $^3J(^1H, ^{31}P) = 10$ Hz, 3 P, $(Et_2N)_3P$), −33.0 ppm (qd, $^2J(^{31}P, ^{31}P) = 71$, $^2J(^1H, ^{31}P) = 7$ Hz, 1 P, P=NH); **^1H NMR** (500.2 MHz, Et_2O, rt): $\delta = 3.44$ (m, 36 H, $(CH_3CH_2)_2NP$), 2.37 (d, $^2J(^1H, ^{31}P) = 7$ Hz, 1 H, NH), 1.58 (s, 9 H, $P=NC(CH_3)_3$), 1.39 ppm (m, 54 H, $(CH_3CH_2)_2NP$); **$^{13}C\{^1H\}$ APT NMR** (125.8 MHz, Et_2O, rt): $\delta = 50.8$ (d, $^2J(^{13}C, ^{31}P) = 4$ Hz, $P=NC(CH_3)_3$), 39.3 (d, $^2J(^{13}C, ^{31}P) = 6$ Hz, $(CH_3CH_2)_2NP$), 31.3 (d, $^3J(^{13}C, ^{31}P) = 5$ Hz, $P=NC(CH_3)_3$), 13.0 ppm (d, $^3J(^{13}C, ^{31}P) = 4$ Hz, $(CH_3CH_2)_2NP$); **IR** (ATR): $\tilde{\nu} = 2970$ (w), 2934 (w), 2872 (w), 1462 (w), 1379 (w), 1351 (w), 1268 (m), 1199 (m), 1173 (vs), 1096 (m), 1017 (vs), 938 (s), 848 (w), 792 (m), 736 (m), 702 (s), 612 (m), 534 (m), 510 (s), 438 cm^{-1} (m); **MS** (ESI, pos., THF): *m/z* (%): 886.9 (100) $[EtP_4H]^+$; **MS** (ESI, neg., THF): *m/z* (%): 503.1 (6) $[Al(C_2F_5)_4]^-$; **elemental analysis** calcd (%) for $C_{48}H_{100}AlF_{20}N_{13}P_4$: C 41.47, H 7.25, N 13.10; found: C 41.59, H 7.56, N 13.33.

$[PPh_4][Al(C_2F_5)_4]$: Analogously to the synthesis of $[EtP_4H][Al(C_2F_5)_4]$, the reaction of $Si(C_2F_5)_3CH_3$ (8.28 g, 20.7 mmol), $Li[AlH_4]$ (6.26 g, 8.75 mmol), and $[PPh_4]Cl$ (3.30 g, 8.80 mmol) afforded $[PPh_4][Al(C_2F_5)_4]$ in a 63% yield (4.62 g, 5.48 mmol); **^{19}F NMR** (282.4 MHz, Et_2O, rt): $\delta = -83.5$ (s, 12 F, CF_3); −127.7 ppm (six-line multiplet, $^2J(^{19}F, ^{27}Al) \approx 32$ Hz, 8 F, CF_2); **^{27}Al NMR** (78.2 MHz, Et_2O, rt): $\delta = 107.7$ ppm (non, $^2J(^{19}F, ^{27}Al) \approx 32$ Hz, Al); **$^{31}P\{^1H\}$ NMR** (121.5 MHz, Et_2O, rt): $\delta = 23.9$ ppm (s, $^1J(^{31}P, ^{13}C) = 89$ Hz, P); **^1H NMR** (500.2 MHz, Et_2O, rt): $\delta = 8.67$ (m, 4 H, *para*-CH), 8.51 (m, 8 H, *meta*-CH), 8.40 ppm (m, 8 H, *ortho*-CH); **$^{13}C\{^1H\}$ APT NMR** (125.8 MHz, Et_2O, rt): 136.3 (d, $^4J(^{13}C, ^{31}P) = 3$ Hz, *para*-CH), 135.0 (d, $^3J(^{13}C, ^{31}P) = 11$ Hz, *meta*-CH), 131.3 (d, $^2J(^{13}C, ^{31}P) = 13$ Hz, *ortho*-CH), 118.4 ppm (d, $^1J(^{13}C, ^{31}P) = 89$ Hz, *ipso*-C); **IR** (ATR): $\tilde{\nu} = 1587$ (w), 1485 (w), 1438 (w), 1306 (m), 1286 (w), 1176 (s), 1097 (s), 1008 (m), 996 (m), 928 (m), 847 (w), 753 (m), 722 (s), 689 (s), 634 (w), 584 (w), 526 (vs), 437 cm^{-1} (s); **HRMS** (ESI, neg.): *m/z* calcd for $C_8F_{20}Al^-$: 502.95016; found: 502.9505. fragmentation: *m/z* (%): 402.95 (73) $[Al(C_2F_5)_3F]^-$, 302.96 (11) $[Al(C_2F_5)_2F_2]^-$, 202.97 (2) $[Al(C_2F_5)F_3]^-$, 102.97 (<1) $[AlF_4]^-$.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aluminum · perfluoroalkyl · phosphazenium cation · silane · weakly coordinating anions

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