Synthesis of Organoaluminum Fluorides and of an Oxo-Centered Trinuclear Carboxylate of Aluminum

Dissertation zur Erlangung des Doktorgrades der Mathematisch-Naturwissenschaftlichen Fakultäten der Georg-August-Universität zu Göttingen

vorgelegt von

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Göttingen 2001

Hagen Hatop:

Synthesis of Organoaluminum Fluorides and of an Oxo-Centered Trinuclear Carboxylate of Aluminum / vorgelegt von Hagen Hatop

D7 Referent: Korreferent: Tag der mündlichen Prüfung:

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meinen lieben Eltern

Acknowledgments

This work was brought to fruition under the close guidance and following value-added advice from Professor Dr. Dr. h. c. mult. H. W. Roesky, Institute of Inorganic Chemistry, Georg-August-University Göttingen, between March 1998 and May 2001.

I hereby wish to profoundly thank my highly esteemed tutor,

Professor Dr. Dr. h. c. mult. H. W. Roesky,

for his unfailing interest in my work, his invariable support, encouragement, motivation, suggestions, and the working conditions conductive to the completion of this thesis. His inspiration largely accounts for the results achieved during this time.

I would also like to thank T. Labahn, Dr. M. Noltemeyer, H.-G. Schmidt, Dr. R. Herbst-Irmer, Prof. Dr. J. Magull, and Dr. A. Fischer for crystallographic measurements and Dr. M. Cimpoesu for doing electron density calculations.

I extend my thanks for spectroscopic and analytical investigations to Dr. D. Böhler (MS), T. Schuchardt (MS), R. Schöne (NMR), W. Zolke (NMR), Dr. G. Elter (NMR), M. Hesse (IR), and the staff of the Analytical Laboratory for their timely help and friendliness.

I thank all my colleagues of the research group for the good and motivating working atmosphere. I would particularly like to thank Dr. U. Ritter, Dr. C. Schnitter, J. Janssen, T. Blunck, J. Prust, A. Stasch, W. Zheng, H. Hohmeister, Dr. S. Kiel, Dr. T. Borrmann, H.-J. Schuster, Dr. M. Schormann, Dr. A. K. Mohamed, Dr. D. Chakraborty, Dr. S. Bhandari and Dr. P. Böttcher for useful discussions and creative working atmosphere.

I thank Dr. M. Witt for helpful discussions and final proof reading.

I want to express my special thanks to my lab colleagues Dr. A. Klemp and M. Schiefer for cooperative discussions and a friendly working atmosphere.

I want to thank for financial aid i obtained from the Gustav-Tammann-Award, a halftime job at the Georg-August-University Göttingen, and my parents.

I also want to thank Olesya for the support and inspiration I got from her :-)

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Abbreviations

Anal. Calcd	analysis calculated
av	average
<i>i</i> Bu	iso-butyl
tBu	<i>tert</i> -butyl
С	Celsius
Ср	η^5 -cyclopentadienyl
Cp'	substituted cyclopentadienyl
Cp*	η^5 -pentamethylcyclopentadienyl
Cyc	cyclohexyl
d	doublet
δ	chemical shift
DDP-H	2-{(2,6-diisopropylphenyl)amino}-4-{(2,6-diisopropylphenyl)imino}-
	2-pentene
deg	degree
diff. peak	difference peak
DBP-H	2,6-di- <i>tert</i> -butylphenol
DBMP-H	2,6-di- <i>tert</i> -butyl-4-methylphenol
ed.	edition
EI	electron ionization
Et	ethyl
eq	equivalent(s)
FAB	fast atom bombardement
Fw	formula weight
h	hours
HSAB	hard and soft acids and bases
nhexane	normal-hexane
Hz	Hertz

IR	infrared
J	coupling constant
Κ	Kelvin
λ	wavelength
М	metal
M^+	molecular ion
m	multiplet
MAO	methylaluminoxane
Me	methyl
4-Mepy	4-methylpyridine
min	minute
mp	melting point
MS	mass spectrometry
m/z	mass/charge
μ	bridging
NMR	nuclear magnetic resonance
0	degree
Ph	phenyl
ppm	parts per million
<i>i</i> Pr	iso-propyl
Ру	pyridine
R, R', R"	organic substituent
S	singlet
Subl. point	sublimation point
t	triplet
TBADF	tetra-nbutylammonium hydrogen difluoride
THF	tetrahydrofuran
Tris	tristrimethylsilylmethyl
Ζ	number of molecules in the cell

1. Introduction

1.1. Aluminum Halides - Aluminum Fluorides

Aluminum trifluoride is a colorless solid which is nearly insoluble in water, acids and bases. It differs from the other aluminum trihalides by having a much higher melting and sublimation point, having a greater heat of formation and finally in different coordination numbers [1].

	AlF ₃	AlCl ₃	AlBr ₃	AlI ₃
melting point/°C	1290	192	98	189
Subl. point (1 atm)/°C	1272	180	256	382
$\Delta H_{\rm f}^{\circ}/{\rm kJ}~{\rm mol}^{-1}$	1498	707	527	310



AlF₃ forms with other alkali and metal fluorides different anionic compositions [2,3,4]:
M[AlF₄] (NaAlF₄, (a)) sharing of 4 equatorial vertices, layer of octahedral {AlF₆} units
M₂[AlF₅] (Tl₂AlF₅, (b)) sharing of 2 opposite vertices, chain of octahedral {AlF₆} units
M₃[AlF₆] (Na₃AlF₆, (c)) no vertex is shared, isolated octahedral {AlF₆} units.
Edge or face sharing of octahedral {AlF₆} units are not observed.

In AlF₃ each aluminum is surrounded by six fluorine atoms to form a distorted octahedron. The coordination number six in solid AlCl₃ decreases at 192 °C to four in the molecular dimer Al₂Cl₆ accompanied by a dramatic increase in volume (plus 85 %). AlBr₃ and AlI₃ are also four-coordinated. The trihalides of aluminum form a large number of addition compounds or complexes [5] which are used in Friedel-Crafts catalysis [6] and AlCl₃ especially for polymerization reactions and olefin cracking in technical processes [2].

There is an extensive scope in the use of aluminum fluorides. The most important practical application is cryolite (Na_3AlF_6) as a commodity chemical for electrochemical industrial processes such as the electrolysis of aluminum oxide [1,2,7]. Another relevant use of aluminum fluorides is as catalysts for the synthesis of chlorofluorocarbon alternatives [8].

Several articles concerning aluminum fluorides have been reported. Metal fluoride salts were found to activate aluminum in water to react with carbonyl compounds to give pinacol coupling products [9]. Aluminum trifluoride shows several biological activities like inhibition of nitrogenase [10] or decreasing the number of some special calcium channels in cells [11]. Recently it has been shown that aluminum fluoride is a storage matrix for atomic hydrogen [12]. Organoaluminum fluorides are found among the pioneering work of Ziegler [13]. There is also potential importance of these compounds as models for certain catalytic reactions [14]. X-ray crystallography analysis gave structural proof for the existence of tetrahedral [AlF4]⁻ in organic cation salts of the tetrafluoroaluminate anion [15]. The reduction of $(C_5H_4Me)_2TiF_2$ with aluminum yields the Werner-type coordination compound $[(C_5H_4Me)_2TiF_2]_3Al$ (d) with six-coordinated aluminum in the center [16].



There are several examples for diorganoaluminum fluorides [17]. Organoaluminum difluorides are a new field of research. Until 1995 they were found to be only accessible in special cases and not structurally characterized [18]. This changed two years later with the synthesis and the crystal structure of the trimeric organoaluminum difluoride $[RAIF_2]_3$ (R = N(SiMe₃)2,6-*i*Pr₂C₆H₃) (e) [19].

1.2. Metallocene Complexes

Metallocene complexes [20] were found to be useful for catalysis in the polymerization of ethene [21-23]. The modification of the Cp ligand leads, on account of a stereorigid sphere around the metal center, to compounds that are able to produce syndiotactic or isotactic polypropene [24]. Sinn and Kaminsky reported in 1980 that methylalumoxane (MAO) increases enormously the activity of the metallocene catalysts [25]. MAO is always used in a great excess. The mode of action of MAO is due to a lack of model compounds not yet understood [26-28]. It was searched for other cocatalysts that coordinate weakly to the catalytic active $[Cp'_2MX]^+$ cation (M = Ti, Zr; X = Me, Cl, F) [29]. The first examples of X-ray structural characterized zirconocene complexes which polymerize propene with high activity are perfluorinated phenylboranates like $[Cp'_2ZrMe]^+[B(C_6F_5)_4]^-$ [30]. The perfluorinated phenylaluminum compound $[Al(C_6F_5)_3 \cdot THF]$, analogue to $B(C_6F_5)_3$, decomposes spontaneously and proved to be unusable for further experiments [31]. Marks *et al.* synthesized catalytically active zirconocenes with a bridging methyl group $[(1,2-Me_2C_5H_3)_2ZrMe](\mu-Me)[B(C_6F_5)_3]$ (**f**, fluorine atoms are omitted) by treatment of $(1,2-Me_2C_5H_3)_2ZrMe_2$ with $B(C_6F_5)_3$ [32].





Soluble early transition metal fluorides like Cp*ZrF₃ have been easy accessible for a few years [33, 34]. The small size of the fluorine atom and the high electron density cause a strong π -acceptor capability of the metal center [35] which gives high potential for use as MAO alternative cocatalysts. Fluorinated half-sandwich complexes of titanium, such as CpTiF₃, have been used as catalysts in syndiospecific styrene polymerization [36] and seem to be useful as model compounds for catalysis which are characterizable by X-ray single crystal structure analysis.

The reaction of Cp*ZrF₃ with AlMe₃ resulted in the complex *cis*-[Cp*ZrMe(μ -F)-(μ -F)₂AlMe₂]₂ (**g**) approaching the structural requirements of a catalytically active system. However, this compound is only active in the presence of MAO in the polymerization of olefins [37].

1.3. Connectivity of Fluorine

Fluorine, the first member of the halogen group, is expected to be monocovalent or single charged to form anions [38]. A linear symmetric bridge of fluorine was first indentified in dialuminum anions $[R_3Al(\mu-F)AlR_3]^-$ (R = Me, Et) by X-ray diffraction analysis of the compound KF·2AlEt₃ [39]. This bridging ability allows the encapsulation of fluorine atoms in cage compounds as in [(Cp'TiF₂)₅AlF₂(μ_6 -F)·THF] (Cp' = C₅H₄SiMe₃) (**h**) [38]. It also can be found in host-guest complexation, the template of the cation is structure directing and leads to interesting systems like [Ph₄P]⁺[(Cp*₂Ti₂F₇)₂Na]⁻ (**i**) [40].



1.4. Oxo-Centered Trinuclear Carboxylates

Oxo-centered trinuclear carboxylates are a well-established class of complexes, referred to as "basic carboxylates" of the general formula $[M_3(\mu_3-O)(\mu-O_2CR)_6L_3]$ (M = metal; L = ligand (for example: Pyridine derivative, THF, water, etc.); R = CH₃, Ph, CF₃, H).



There are various addition compounds of oxo-centered trinuclear carboxylates of transition metals (M = V, Cr, Mn, Fe, Co, Ru, Rh and Ir) [41]. More than 100 examples can be found for the iron derivatives, one is $[Fe_3(\mu_3-O)(\mu-O_2CCH_3)_6(py)_3]$ (j) (R = CH₃, L = Py) [42].

"Basic carboxylates" of aluminum are, due to a highly symmetric and a more simple electron configuration compared to transition metals, good model molecules for computational electron density analysis.

1.5. Aims of this Work

Based on the described material in the sections 1.1 - 1.4, it is obvious that organoaluminum fluorides are, due to the Lewis acid character of aluminum in organoaluminum fluorides and the bridging ability of the Lewis base fluoride, qualified precursors for syntheses of new interesting cluster compounds.

The aims of this work have been (1) the synthesis of Ziegler-Natta catalyst relevant systems $[Cp'_{2-y}ZrX_{1+y}](\mu-X')[RAlF_2]$ (Cp' = Cp or substituted Cp; X, X' = Me, Cl or F; R = Ligand; y = 0 or 1), (2) the generation of new bimetallic organoaluminum fluorides, (3) access to new organoaluminum fluorides and (4) to investigate the reaction of (Me_3Si)_3CAlMe_2.THF with CF_3COOH.

2. **Results and Discussion**

The trimeric compound $[(Me_3Si)_3CAIF_2]_3$ (1) is a Lewis acid capable of accepting fluoride ions [43] or other Lewis bases (Scheme 1).



Scheme 1. $R = C(SiMe_3)_3$. The reactivity of 1 versus the Lewis base THF.

Few composites with **1** and fluoride anions and different counter cations, which have been structurally characterized by X-ray analysis, are known (Scheme 2) [43-46]:

- $[\{(Me_3Si)_3C\}_4Al_4K_2(\mu-F)_2F_8(THF)_4](2),$
- $[Ag(toluene)_3]^+[\{((Me_3Si)_3C)_2Al_2(\mu-F)F_4\}_2Li]^-(3),$
- $[AlF_2(THF)_4]^+[\{(Me_3Si)_3C\}_2Al_2(\mu-F)F_4]^-(4),$
- [Li(Me₃Si)₃CAlF₃(THF)]₄ (5), and
- $[Me_3C_5H_2NH]^+[(Me_3Si)_3CAlF_3]^-$ (6).

These compounds contain the anions $[(Me_3Si)_3CAlF_3]^-$ (5 and 6) and $[(Me_3Si)_3CAlF_2(\mu-F)F_2-AlC(SiMe_3)_3]^-$ (2, 3, and 4) respectively. 4 and 6 contain non coordinating anions. Coordination of the anion with the cation in 4 is precluded by the use of the coordinating solvent THF, while in 6 the cation is coordinatively saturated. 2, 3 and 5 possess metal cations acting as structure directing templates [47]. In the synthetic strategy for 3 a hard (Li⁺) and a soft (Ag⁺) cation were used according to the HSAB concept of Pearson [48]. The Ag⁺ exhibits no interaction with the fluorine atoms of the anion. Special attention has been drawn to compositions containing a strong coordinating solvent like THF or a weakly coordinating solvent like toluene [49]. Only compounds without strong coordinating solvents are likely to be useful for Ziegler-Natta catalysis [50]. For **5** it is observed that the cube dissociates in THF to form a $[(Me_3Si)_3CAIF_3]^-$ anion and a $[Li(THF)_4]^+$ cation. However, sometimes THF and other coordinating solvents may be necessary for the crystallization in order to get structural informations [49].





Scheme 2. $R = C(SiMe_3)_3$.

2.1. Synthesis of $[Cp_2ZrMe](\mu$ -F) $[F_2AlC(SiMe_3)_3]$ (7) and $[Cp_2Zr(\mu$ -F)₂-FAlC(SiMe_3)_3]_2O (8)

Compounds of type $[Cp'_{2-y}ZrX_{1+y}](\mu-X')[F_2AIR]$ (Cp' = Cp or substituted Cp; X, X' = Me, Cl or F; R = Ligand; y = 0 or 1) are of particular interest as catalysts for olefin polymerization [51]. Marks *et al.* published a system with a weak bridging fluorine between an aluminum and a zirconium atom $[Cp*_2ZrMe(\mu-F)Al(C_{12}F_9)_3]$ [52] that shows catalytical activity for ethene polymerisation. The $[(Me_3Si)_3CAIF_3]^-$ anion should also be able to stabilize the $[Cp_2ZrMe]^+$ cation. Several reactions of **1** and $Cp_2MX'X''$ (M = Ti, Zr; X', X'' = Me, Cl, F) are described although no characterized products or structures of these composites are available [53].

The reaction between **1** and Cp₂ZrMeF yielded compound **7** (Figure 1, Table 1) as expected. Cp₂ZrMeF was prepared *in situ* using Cp₂ZrMe₂ and Me₃SnF (Scheme 3). Attempts to grow X-ray quality crystals of **7** from toluene/*n*hexane mixtures (5 : 1) were unsuccessful. Crystallization from a THF/toluene/*n*hexane (1 : 8 : 2) solution of **7** produced X-ray quality crystals at -20 °C after 4 weeks.

$$Cp_2ZrMe_2 + Me_3SnF \longrightarrow Cp_2ZrMeF + Me_4Sn$$

$$[(Me_3Si)_3CAlF_2]_3 + 3 Cp_2ZrMeF \longrightarrow 3 [Cp_2ZrMe](\mu-F)[F_2AlC(SiMe_3)_3]$$
7

Scheme 3

However, these crystals proved to be $[Cp_2Zr(\mu-F)_2FAlC(SiMe_3)_3]_2O$ (8) (Figure 2, Table 2, Scheme 4). Presumably the source of the oxygen atom can be considered either oxygen, water or presumably THF since group 13 Lewis acids are known to cleave aliphatic ethers [54-59]. The opening of the THF molecule and its coordination to aluminum was recently shown by an

X-ray structural analysis of its product [59]. The condensation of two molecules of **7** with elimination of the methyl groups and formation of the μ -oxygen bridge in **8** is the second step of this reaction. A comparable eight-membered Al₂F₄Zr₂ ring-system is found in *cis*-[Cp*ZrMe(μ -F)(μ -F)₂AlMe₂]₂ (**f**). However, in the latter compound the zirconium atoms are bridged by two μ -F units [37]. Compound **8** is insoluble in THF or toluene. A second attempt to produce compound **8** under the same conditions resulted in the formation of a 2 : 1 mixture of compounds **7** and **8**.

$$[Cp_2ZrMe](\mu-F)[F_2AlC(SiMe_3)_3] + THF \longrightarrow [Cp_2Zr(\mu-F)_2FAlC(SiMe_3)]_2O$$
8

Scheme 4

Compound 7 decomposes slowly at 200 °C.

The elemental analysis of 7 for C and H confirms the required composition of $C_{21}H_{40}AlF_3Si_3Zr$.

The ¹H NMR spectrum of **7** shows resonances of the protons for the zirconium bound methyl group at $\delta 0.56$ ppm which is 0.04 ppm shifted downfield in relation to the comparable methyl group of *cis*-[Cp*ZrMe(μ -F)(μ -F)₂AlMe₂]₂ (**f**) ($\delta 0.52$ ppm) [34]. The resonances of the Cp-protons appear at $\delta 6.36$ ppm also shifted downfield compared to Cp-protons of [Cp₂ZrMe]-(μ -F)[Al(C₁₂F₉)₃] ($\delta 5.56$ ppm) [52].

The ¹⁹F NMR shows signals with the correct ratio (2 : 1) at δ -165.4 ppm for the terminal aluminum bonded fluorine atoms and at δ -161.8 ppm for the aluminum zirconium bridging fluorine atom considerably shifted upfield compared to $[Cp_2ZrMe](\mu$ -F)[Al(C₁₂F₉)₃] (δ -138.11 ppm) [52].

The Zr(1')-F(1') distance (2.118(2) Å) in 7 (Figure 1, Table 1) is slightly longer than the Zr-F distances for the bridging fluorine in $[Cp*ZrF_3]_4$ (2.121 - 2.160 Å) [34]. The zirconium-carbon bond length of the methyl group [Zr(1')-C'' 2.238(3) Å] is comparable to that in $[Me_2Si(\eta^5-Me_4C_5(t-BuN))ZrMe]^+[(C_{12}F_9)_3AlF]^-$ (Zr-Me 2.21 Å) [52]. The Al-F(bridging) (Al(1')-F(1') 1.779(2) Å) distance in 7 is also similar to the Al-F(bridging) distance in $[Me_2Si(\eta^5-Me_4C_5(t-BuN))ZrMe]^+[(C_{12}F_9)_3AlF]^-$ (1.780 Å) [52].



Figure 1. Molecular structure of $[Cp_2ZrMe](\mu$ -F)[F₂AlC(SiMe₃)₃] (7).

Table 1. Selected bond lengths (Å) and angles (deg) for 7.

Al(1')-F(1')	1.779(2)	Zr(1')-F(1')	2.118(2)
Al(1')-F(2')	1.674(2)	Zr(1')-C''	2.238(3)
Al(1')-F(3')	1.678(2)	Al(1')-C(61')	1.965(3)

F(1')-Al(1')-F(2')	100.86(10)	F(1')-Zr(1')-C''	95.52(11)
F(2')-Al(1')-F(3')	108.08(12)	F(1')-Al(1')-C(61')	112.48(11)
F(1')-Al(1')-F(3')	100.53(10)	F(2')-Al(1')-C(61')	116.62(12)
Al(1')-F(1')-Zr(1')	152.00(10)	F(3')-Al(1')-C(61')	116.08(22)



Figure 2. Molecular structure of $[Cp_2Zr(\mu-F)_2FAlC(SiMe_3)_3]_2O(8)$.

The Al-F(terminal) distances (average 1.675 - 1.678 Å) in **8** (Figure 2, Table 2) are comparable to those Al-F(terminal) in $[(Me_3Si)_3CAlF_2]_3$ [59] (1.657 - 1.671 Å). The Al-F(bridging) bond lengths (1.735 - 1.779 Å) are shorter than those in $[(Me_3Si)_3CAlF_2]_3$ [59] (1.795 - 1.815 Å) and similar to those in **7**. The Zr-F(bridging) distances (2.312 - 2.359 Å) in **8** are somewhat longer than those in **7** (Zr(1')-F(1') 2.118(2) Å).

Zr#1-O	1.9499(7)	Al-F(1)	1.677(2)
Zr-F(2)#1	2.312(2)	Al-F(2)	1.743(2)
Zr-F(3)	2.359(2)	Al-F(3)	1.735(2)
Al-C(61)	1.963(2)	O-Zr	1.9499(7)
O-Zr-F(2)#1	76.48(5)	F(2)-Al-C(61)	115.31(11)
F(2)#1-Zr-F(3)	151.06(6)	Zr-O-Zr#1	180.0
O-Zr-F(3)	74.59(5)	F(1)-Al(1)-F(3)	104.87(9)
F(2)-Al-F(3)	103.56(9)	F(1)-Al(1)-F(2)	103.87(9)
F(3)-Al-C(61)	114.23(11)	F(1)-Al-C(61)	113.73(11)
Al-F(3)-Zr	136.59(9)	Al-F(2)-Zr#1	135.32(9)

Table 2. Selected bond lengths (Å) and angles (deg) for 8.

2.1.1. Investigations on the Catalytic Activity of 7

The catalytic activity test of ethene polymerization was carried out in a glass reactor (250 mL) in ethene-saturated (1 bar) toluene (80 mL) solution at room temperature. **7** (0.020 g, 36 mmol), dissolved in toluene (5 mL), was injected with a syringe. The mixture was stirred while ethene was vigorously bubbled through the solution. After 30 min the experiment was terminated by interupting the ethene supply and adding ethanol (10 mL). No formation of polyethene was observed under this condition [43].

2.2. Synthesis of $[Na(Me_3Si)_3CAIF_3(THF)]_4$ (9)

Compositions of **1** with the alkali metal fluorides LiF and KF (**5** and **2**) [43, 45] are known, although no information about the sodium derivative is available. The direct reaction of $(Me_3Si)_3CAIF_2$. THF with sodium fluoride failed. This is probably due to the higher lattice energy and the chemical inertness of the latter alkali metal fluoride [2]. The reaction of $(Me_3Si)_3CAIMe_2$. THF with Me_3SnF and NaCl affords **9** (Scheme 5). It was necessary to use a threefold excess of the *in situ* generated sodium fluoride to produce **9**. Attempts to reduce the reaction time of 4 days at room temperature failed. Unidentified by-products can be observed when the reaction is interupted after 2 days.



Scheme 5

The elemental analysis of **9** for the elements C and H confirms the required composition of $C_{56}H_{140}Al_4F_{12}Na_4O_4Si_{12}$ (look at Figure 3 for comments about the composition of the crystals of **9**).

The ¹H NMR spectrum of **9** shows a singlet for the protons of the trimethylsilyl ligand at $\delta 0.41$ ppm as is observed for **5**. The proton resonances of the coordinated THF molecule appear at $\delta 1.45$ ppm (OCH₂CH₂) and 3.68 ppm (OCH₂CH₂) which are shifted upfield in comparison to **5** ($\delta 1.55$ ppm) for the only carbon bonded methylene protons of THF (OCH₂CH₂) and shifted downfield ($\delta 3.91$ ppm) for the oxygen bonded methylene protons of the THF molecule, respectively.

The expected singlet in the ¹⁹F NMR spectrum is observed at δ -176.7 ppm for the fluorine atoms of the [(Me₃Si)₃CAlF₃]⁻ anion.



Figure 3. Molecular structure of $[Na(Me_3Si)_3CAlF_3(THF)]_4$ (9). Me₃Si groups are omitted for clarity. One of the THF molecules represents a position that is only 50 % occupied by THF to form $[Na(Me_3Si)_3CAlF_3(THF)]_4$. The other 50 % of this position is occupied by a toluene molecule to form $[{Na(Me_3Si)_3CAlF_3}_4(THF)_3(toluene)]$. Figure 3 shows only the THF molecule.

Crystals of 9 suitable for X-ray structural investigations were obtained from toluene/*n*hexane (5:1) at -20 °C. Compound 9 (Figure 3, Table 3) is isostructural with 5. The structure

consists of a cube formed of aluminum and sodium atoms alternating at the corners, which are bridged by fluorine atoms. The Na-F distances are in the range of 2.158 - 2.278 Å, which is shorter than in crystalline sodium fluoride (2.303 Å) [62]. The Al-F bond distances cover a small range (1.683 - 1.703 Å). These are comparable to those in **5** (av 1.687 Å) but considerably shorter than the Al-F(bridging) distances in **2** (av 1.805 Å) [43]. The Na-O distances (2.137 - 2.278 Å) are similar to those in $[Cp*_6Ti_6Na_7F_{19}(2.5THF)]$ (2.291 - 2.319 Å) [63] but slightly shorter than those in $[Na_4Bi_2(\mu_6-O)(OC_6F_5)_8(THF)_4]$ (2.326 - 2.496 Å) [64].

Table 3. Selected bond lengths (A)	Å) and angles (deg) for 9.
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Al(1)-F(1)	1.693(3)	F(3)-Na(2)	2.156(3)
Al(1)-F(5)	1.692(3)	F(4)-Na(1)	2.172(4)
Al(1)-F(2)	1.683(3)	F(5)-Na(4)	2.220(4)
Al(1)-C(1)	1.959(5)	F(6)-Na(2)	2.158(3)
Al(3)-F(8)	1.703(4)	F(7)-Na(2)	2.179(3)
Al(3)-F(9)	1.687(3)	F(8)-Na(1)	2.169(4)
Al(3)-F(10)	1.684(4)	F(9)-Na(4)	2.208(3)
Al(3)-C(21)	1.968(5)	F(10)-Na(3)	2.205(4)
Al(4)-F(6)	1.702(5)	F(11)-Na(3)	2.173(3)
Al(4)-F(11)	1.682(3)	F(12)-Na(4)	2.278(5)
Al(4)-F(12)	1.694(3)	Na(1)-O(1)	2.278(5)
Al(4)-C(31)	1.963(5)	Na(2)-O(2)	2.278(4)
F(1)-Na(1)	2.166(3)	Na(3)-O(3)	2.210(5)
F(2)-Na(2)	2.158(3)	Na(4)-O(4)	2.137(7)
F(2)-Al(1)-F(5)	104.1(2)	Al(1)-F(1)-Na(1)	144.0(2)
F(2)-Al(1)-F(1)	105.5(2)	Al(1)-F(2)-Na(2)	152.3(2)
F(1)-Al(1)-F(5)	105.4(2)	Al(2)-F(3)-Na(2)	148.4(2)

F(2)-Al(1)-C(1)	113.2(2)	Al(2)-F(4)-Na(1)	149.6(2)
F(5)-Al(1)-C(1)	115.3(2)	Al(1)-F(5)-Na(4)	137.3(2)
F(1)-Al(1)-C(1)	112.5(2)	Al(4)-F(6)-Na(2)	139.7(2)
F(3)-Al(2)-F(4)	105.4(2)	Al(2)-F(7)-Na(3)	134.8(2)
F(3)-Al(2)-F(7)	104.1(2)	Al(3)-F(8)-Na(1)	142.4(2)
F(4)-Al(2)-F(7)	103.9(2)	Al(3)-F(9)-Na(4)	157.5(2)
F(3)-Al(2)-C(11)	112.8(2)	Al(3)-F(10)-Na(3)	127.4(2)
F(4)-Al(2)-C(11)	113.9(2)	Al(4)-F(11)-Na(3)	167.7(2)
F(7)-Al(2)-C(11)	115.7(2)	Al(4)-F(12)-Na(4)	139.6(2)
F(8)-Al(3)-F(10)	102.3(2)	F(1)-Na(1)-F(8)	99.8(1)
F(9)-Al(3)-F(10)	105.3(2)	F(1)-Na(1)-F(4)	106.4(1)
F(8)-Al(3)-F(9)	105.5(2)	F(8)-Na(1)-F(4)	105.6(2)
F(10)-Al(3)-C(21)	114.9(2)	F(1)-Na(1)-O(1)	120.9(2)
F(9)-Al(3)-C(21)	113.1(2)	F(8)-Na(1)-O(1)	112.1(2)
F(8)-Al(3)-C(21)	114.6(2)	F(4)-Na(1)-O(1)	110.6(2)
F(11)-Al(4)-F(12)	105.1(2)	F(3)-Na(2)-F(2)	102.6(1)
F(11)-Al(4)-F(6)	104.3(2)	F(3)-Na(2)-F(6)	105.6(1)
F(12)-Al(4)-F(6)	103.9(2)	F(2)-Na(2)-F(6)	111.1(1)
F(11)-Al(4)-C(31)	113.5(2)	F(3)-Na(2)-O(2)	126.1(2)
F(12)-Al(4)-C(31)	115.3(2)	F(2)-Na(2)-O(2)	112.7(2)
F(6)-Al(4)-C(31)	113.5(2)	F(6)-Na(2)-O(2)	98.3(2)
F(11)-Na(3)-F(7)	108.0(1)	O(4)-Na(4)-F(9)	119.0(2)
F(11)-Na(3)-F(10)	96.0(1)	O(4)-Na(4)-F(5)	107.4(2)
F(7)-Na(3)-F(10)	130.7(2)	F(9)-Na(4)-F(5)	101.0(1)
F(11)-Na(3)-O(3)	121.0(2)	O(4)-Na(4)-F(12)	109.7(2)
F(7)-Na(3)-O(3)	102.9(2)	F(9)-Na(4)-F(12)	105.3(1)
F(10)-Na(3)-O(3)	100.3(2)	F(5)-Na(4)-F(12)	114.6(2)

2.3. Synthesis of $[{(Me_3Si)_3CAIF_2}_2(\mu-O)Li_2(THF)_4]$ (10)

There are only a few examples of aluminum fluorine oxygen clusters reported in the literature [58]. The combination of $(Me_3Si)_3CAIF_2$ ·THF with lithium oxide was anticipated to give new interesting aluminum fluorine-oxygen clusters. Therefore $(Me_3Si)_3CAIF_2$ ·THF was treated with lithium oxide in THF. A more convenient route to **10** is the *in situ* generation of $(Me_3Si)_3CAIF_2$ ·THF by the action of Me_3SnF with $(Me_3Si)_3CAIMe_2$ ·THF in the presence of lithium oxide (Figure 4, Table 4, Scheme 6).



Scheme 6. $R = C(SiMe_3)_3$. The two routes to generate 10.

The elemental analysis of **10** for the elements C and H confirms the required composition of $C_{36}H_{86}Al_2F_4Li_2O_5Si_6$.

The ¹H NMR spectrum shows a singlet for the protons of the trimethylsilyl ligand at $\delta 0.43$ ppm only slightly shifted downfield compared to **5** ($\delta 0.41$ ppm). The resonances of the protons of the coordinated THF molecule appear at $\delta 0.90$ ppm (OCH₂CH₂) and 3.79 ppm (OCH₂CH₂).

The ¹⁹F NMR spectrum shows only one signal for the fluorine atoms at δ -158.5 ppm.



Figure 4. Molecular structure of $[{(Me_3Si)_3CAIF_2}_2(\mu-O)Li_2(THF)_4]$ (10). Me groups are omitted for clarity. Only the ipso oxygens atom of THF are displayed.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 10.

Al(1)-O(1)	1.7083(18)	Li(1)-F(2)	1.854(4)
Al(1)-F(2)	1.7373(15)	Li(1)-F(4)	1.837(5)
Al(1)-F(3)	1.7316(15)	Li(2)-F(3)	1.850(5)

Al(1)-C(1)	1.994(2)	Li(2)-F(5)	1.835(5)
Al(2)-C(2)	2.004(3)	Li(1)-O(1T1)	1.948(5)
Al(2)-O(1)	1.7097(17)	Li(1)-O(1T2)	1.974(5)
Al(2)-F(4)	1.7356(16)	Li(2)-O(1T3)	1.946(5)
Al(2)-F(5)	1.7294(16)	Li(2)-O(1T4)	1.938(5)
O(1)-Al(1)-F(3)	107.10(8)	F(4)-Li(1)-O(1T2)	120.0(2)
O(1)-Al(1)-F(2)	106.14(8)	F(2)-Li(1)-O(1T2)	106.5(2)
F(3)-Al(1)-F(2)	100.71(8)	O(1T1)-Li(1)-O(1T2) 101.6(2)
O(1)-Al(1)-C(1)	120.75(10)	F(5)-Li(2)-F(3)	106.6(2)
F(3)-Al(1)-C(1)	109.17(9)	F(5)-Li(2)-O(1T4)	117.1(3)
F(2)-Al(1)-C(1)	111.06(10)	F(3)-Li(2)-O(1T4)	113.6(3)
O(1)-Al(2)-F(5)	106.48(8)	F(5)-Li(2)-O(1T3)	109.6(3)
O(1)-Al(2)-F(4)	105.08(8)	F(3)-Li(2)-O(1T3)	110.1(3)
F(5)-Al(2)-F(4)	102.50(8)	O(1T4)-Li(2)-O(1T3) 99.7(2)
O(1)-Al(2)-C(2)	122.34(10)	Al(1)-O(1)-Al(2)	125.45(10)
F(5)-Al(2)-C(2)	109.32(9)	Al(1)-F(2)-Li(1)	120.60(15)
F(4)-Al(2)-C(2)	109.31(9)	Al(1)-F(3)-Li(2)	128.51(17)
F(4)-Li(1)-F(2)	112.6(2)	Al(2)-F(4)-Li(1)	124.49(15)
F(4)-Li(1)-O(1T1)	103.9(2)	Al(2)-F(5)-Li(2)	126.64(17)
F(2)-Li(1)-O(1T1)	111.5(2)		

The structure of **10** consists of an eight-membered (Al-F-Li-F)₂ ring with a transannular Al-O-Al bridge. The Li-F bond lengths are in the range of 1.835(5) to 1.854(4) Å and comparable to the mean Li-F distances (1.852 Å) in [Li(Me₃Si)₃CAlF₃(THF)]₄ (**5**). The average Al-F bond length (1.733 Å) in **10** is slightly shorter than those in [Cp₂ZrMe](μ -F)-[F₂AlC(SiMe₃)₃] (bridging 1.779(2) Å). The Al-O distance (av 1.709 Å) is shorter than those in [{(Me₃Si)₃CAl}₄(μ -O)₂(μ -OH)₄] (1.79 Å) [65]. The C-Al-F angle ($109.17(9) - 111.06(10)^{\circ}$) is narrower than those in **5** (111.9 - 115.2°). Obviously, due to a lesser steric influence in **10** the angles at fluorine are in the range of $120.60(15) - 128.51(17)^{\circ}$ and much narrower than those at fluorine in **5** (140.0 - 162.9°). The O-Al-F angles in **10** (105.08(8) - 107.10(8)°) differ significantly from those in [{C(CH₂COOEt)₂-(COOEt)}OAIFMe]₂ (127.7° and 90.7 - 96.8°) [66].

The $[(Me_3Si)_3CAlF_2(\mu-O)F_2AlC(SiMe_3)_3]$ species in **10** is comparable to the $[(Me_3Si)_3CAlF_2(\mu-F)F_2AlC(SiMe_3)_3]$ part in **2**, **3**, and **4**, where two of these units coordinate to a metal center. The $[(Me_3Si)_3CAlF_2(\mu-O)F_2AlC(SiMe_3)_3]$ species contains two negative charges and is probably suited to generate weak coordinating anions as found in **3**.

2.4. Synthesis of $[{Li(Me_3Si)_3CAIF_3(THF)}_3LiF(THF)]$ (11)

After the successful introduction of fluoride at $(Me_3Si)_3CAlF_2 \cdot THF$ in the synthesis of **9** it was intriguing to learn if alcoholates, which are isolobal [67] to fluoride, are useful as precursors for aluminum fluoro oxygen cluster compounds. LiOCH(CF₃)₂ was chosen to study the behavior of the $(Me_3Si)_3CAlF_2 \cdot THF$ molecule with deprotonated alcoholes.

MeLi was reacted with $(CF_3)_2CH(OH)$ in THF to generate LiOCH $(CF_3)_2$. This mixture was added to a solution of $(Me_3Si)_3CAIF_2 \cdot THF$ in THF. However, the reaction of $(Me_3Si)_3CAIF_2 \cdot THF$ with LiOCH $(CF_3)_2$ afforded the unexpected compound $[{Li}(Me_3Si)_3CAIF_3(THF)]_3LiF(THF)]$ (11) in low yield (Figure 5, Table 5, Scheme 7). It is assumed that the four LiF molecules necessary for the formation of 11 are formed by an exchange reaction of $(CF_3)_2HCOLi$ with $(Me_3Si)_3CAIF_2 \cdot THF$ where the $(CF_3)_2HCO^-$ is replacing a F⁻. Up to now it was not possible to isolate a compound with composition like $[(Me_3Si)_3CAIF(OCH(CF_3)_2)] \cdot THF$ to prove this assumption (Scheme 8).

$$7 (Me_{3}Si)_{3}CAlF_{2} \cdot THF + 4 LiOCH(CF_{3})_{2} \longrightarrow [{Li(Me_{3}Si)_{3}CAlF_{3}(THF)}_{3}LiF(THF)] (11) + 4 [(Me_{3}Si)_{3}CAlF {OCH(CF_{3})_{2}}] \cdot THF$$

Scheme 7

The elemental analysis of 11 + THF for the elements C and H confirms the required composition of $C_{50}H_{121}Al_3F_{10}Li_4O_5Si_9$.

The ¹H NMR spectrum of **11** was recorded in THF-d₈ due to its poor solubility in benzene. Decomposition in this strong coordinating solvent is presumed [45]. The proton spectrum of **11** shows a singlet for the protons of the trimethylsilyl ligand at δ 0.15 ppm. The resonances for the THF protons appear as multiplets at δ 1.77 ppm (CH₂CH₂O) and 3.61 ppm (CH₂CH₂O).

The resonances of the fluorine atoms of **11** give a main singlet in the ¹⁹F NMR spectrum at δ -166.5 ppm, and a very small singlet at -202.8 ppm.

Compound **11** shows good stability in the gas phase which is demonstrated by a FAB experiment that gives an anion of **11** minus a lithium and a THF molecule.

$$(Me_{3}Si)_{3}CAlF_{2} \cdot THF + LiOCH(CF_{3})_{2} \xrightarrow{THF} [(Me_{3}Si)_{3}CAlF\{OCH(CF_{3})_{2}\}] \cdot THF + LiF ?$$

Scheme 8. Assumption for the formation of the LiF that is implemented in the cluster of 11.



Figure 5. Molecular structure of [{Li(Me₃Si)₃CAlF₃(THF)}₃LiF(THF)] (**11**). Me groups are omitted for clarity. Only the ipso oxygen atoms of THF are displayed.

The X-ray structural analysis reveals that **11** consists of three $[(Me_3Si)_3CAIF_3]^-$ anions interconnected with three Li-cations to form a twelve-membered ring. In the center on one side of this ring is a fluorine atom that is coordinated to three lithiums of the twelve-membered ring. The opposite side of the ring is occupied by a lithium atom that is coordinated to three fluorine atoms each of which is coordinated to an aluminum atom of the ring. The fourth coordination site of each of the Li atoms is occupied by an oxygen atom of a THF molecule. There is a threefold axis (Figure 5) going through Li(2) and F giving a molecule of high symmetry. The consequence of this symmetrical arrangement is that the three Li atoms of the twelve-membered ring form a perfect triangle of Li₃ (Li-Li-Li 60°). The Al-F bond distances are in a narrow range (1.694(2) - 1.701(2) Å). They are comparable to those in [Li(Me₃Si)₃CAlF₃(THF)]₄ (av 1.688 Å) [45] but are considerably shorter than the Al-F(bridging) distances in [(Me₃Si)₃CAlF₂]₃ (1.795 - 1.815 Å) [43]. The Li-F bond lengths are in the range of 1.801(6) - 1.873(6) Å and close to the Li-F distances in **10** (1.835(5) to 1.854(4) Å). The C-Al-F angles cover a range of 113.36(11) - 115.74(13)° and are wider than those in **10** (109.17(9) - 111.06(10)°). The Al-F-Li angles range from 125.3(2) to 149.6(3)° (**10** 120.60(15) - 128.51(17)°).

Table 5. Selected bond lengths (Å) and angles (deg) for 11.

F(1)-Al(1)	1.694(2)	F(2)-Li(1)	1.856(7)
F(2)-Al(1)	1.697(2)	F(3)-Li(2)	1.864(3)
F(3)-Al(1)	1.701(2)	C-Al(1)	1.971(3)
F-Li(1)	1.801(6)	Li(1)-O(1)	1.932(6)
F(1)-Li(1)#1	1.873(6)	Li(2)-O(2)	1.950(8)
Li(1)#2-Li(1)-Li(1)#1	60.000	Li(1)#1-F-Li(1)	119.64(5)
Al(1)-F(1)-Li(1)#1	125.3(2)	F-Li(1)-F(2)	108.3(3)
Al(1)-F(2)-Li(1)	128.9(2)	F-Li(1)-F(1)#2	112.1(3)
Al(1)-F(3)-Li(2)	149.6(3)	F(2)-Li(1)-F(1)#2	104.8(3)
F(1)-Al(1)-F(2)	103.28(12)	F(3)-Li(2)-F(3)#1	110.8(2)
F(1)-Al(1)-F(3)	104.47(13)	F-Li(1)-O(1)	117.2(3)
F(2)-Al(1)-F(3)	105.08(12)	F(2)-Li(1)-O(1)	112.2(3)
F(1)-Al(1)-C	113.36(11)	F(1)#2-Li(1)-O(1)	101.5(3)
F(2)-Al(1)-C	113.66(12)	F(3)-Li(2)-O(2)	108.1(2)
F(3)-Al(1)-C	115.74(13)		

The easy generation of **11** is due to its insolubility in toluene. Complex **11** illustrates the variety of possible structures obtainable by the combination of $[(Me_3Si)_3CAIF_2]_3$ and LiF. In the series of the alkali metals the lithium derivative **11** has a different structural arrangement compared to those of the analogous compounds of the heavier alkali metals.

2.5. Synthesis of $[{(Me_3Si)_3C}_2Al_2(\mu-F)F_4K]_{\infty}$ (12)

It is known that organoaluminum difluorides form various aggregates in the presence of THF due to the Lewis base character of this solvent and the Lewis acidity site of the aluminum. Consequently different structural arrangements were isolated when these systems were treated with THF [46]. Compound **2** for example contains four molecules of coordinated THF. Therefore it was interesting to investigate the THF free analogous compound. Additionally new interesting compositions could be produced by studying the bearing of **1** in the presence of reductive metals. The reduction of (Me₃Si)₃CAII₂·THF with sodium potassium alloy affords the tetrahedral aluminum(I) compound [(Me₃Si)₃CAI]₄ [59]. It is reported that **1** resists reduction to aluminum(I) with alkali alloys [68].

Compound **12** was prepared from **1** with water free potassium fluoride in toluene under reflux in moderate yield. Using potassium metal and **1** under reflux conditions in toluene surprisingly produced compound **12**, too (Scheme 9). The by-product of this reaction could not be characterized. The yield of **12** using the latter method is slightly higher than the first one.



Compound **12** is slightly soluble in toluene at room temperature. However the solubility increases when heated under reflux. **12** dissolves easily in THF but dissociates in this strong coordinating solvent [49].



Scheme 10. Drawing of **12**. The rectangle shows the single unit of the supramolecular chain. The asterisk marked fluorine atom shows the F(4) atom from the X-ray structural analysis which occupies the weak fifth coordination site of the potassium atom. $R = C(SiMe_3)_3$.

The elemental analysis for C and H confirms the required composition of $C_{20}H_{54}Al_2F_5KSi_6$. The proton resonance in the ¹H NMR spectrum is observed at $\delta 0.42$ ppm.

The ¹⁹F NMR spectrum of **12** shows resonances for the fluorine atoms at δ -157.5 ppm (s, 4 F, Al(μ -F)K), -157.3 ppm (s, 4 F, Al(μ -F)K), -156.9 ppm (s, 1 F) , and -152.8 ppm (m, 2 F, Al(μ -F)Al). It is assumed that the multiplet at δ -152.8 ppm is an unresolved quintet (J = 30 Hz) and the resonances at δ -157.5 ppm and δ -157.3 ppm are the associated doublets (J = 30 Hz) with the intensity ratio of 1 : 4 as is expected for the [(Me₃Si)₃CAlF₂(μ -F)F₂AlC(SiMe₃)₃]⁻ anion in **12**. This coupling is hard to recognize in the ¹⁹F NMR spectrum. The source for the resonance at δ -156.9 ppm is unknown. For compound **3** the resonances in the ¹⁹F NMR are reported in the same range (δ -158.8 (s, 4 F), -158.6 (s, 4 F), -158.0 (s, 1 F), and 154.5 (m, 2 F) ppm) while the resonance at δ -156.9 ppm is obviously produced by the same impurity.



Figure 6. Arrangement of **12** in the chain. The potassium atoms are in the paperplane. (blue atoms = aluminum, pink atoms = potassium, green atoms = fluorine)
Suitable single crystals for X-ray structural analysis of **12** (Figure 6, Table 6), were obtained from hot toluene. The structure of **12** consists of infinite potassium zig-zag chains with a K-K distance of 4.7800(7) Å which is slightly longer than that in potassium metal (av 4.54 Å) [41] (Figure 6). The potassium atoms are fourfold coordinated by terminal fluorine atoms of the $[(Me_3Si)_3CAIF_2(\mu-F)F_2AIC(SiMe_3)_3]^-$ anions (Figure 7). The K-F bond length ranges from 2.5990(17) to 2.6587(18) Å which is slightly shorter or comparable to that in KF (2.664 Å) [41] but in the range of those in 2 (2.610 - 2.860 Å). Within the four terminal fluorine atoms of 12 F(4) is weakly coordinating to a second potassium atom with a distance of 3.147(2) Å which is slightly (0.5 Å) longer than the other observed K-F distances in this molecule (Scheme 10). The Al-F(terminal) bond length (1.6820(18) - 1.6940(19) Å) is slightly longer than those in 3 (1.657 - 1.688 Å) and in 2 (1.672 - 1.677 Å) respectively. The Al-F(bridging) bond length (1.8028(17) - 1.8144(17) Å) is comparable to that in 3 (1.7881 - 1.802 Å) and in 2 (1.817 - 1.823 Å). The F-K-F angles are acute for F(2)#1-K(1)-F(4)#1 (73.30(5)°) and F(3)-K(1)-F(5) (72.57(5)°) and more open for F(3)-K(1)-F(4)#1 (114.14(6)°) and F(2)#1-K(1)-F(5)(109.56(6)°). All potassium atoms in the chain are in plane with a K-K-K angle of 137.74(3)° (Figure 6). The potassium in 2 is sixfold-coordinated by four fluorines and two oxygens of the THF molecules. In contrast, the potassium in 12 has the coordination number four with a fifth fluorine atom in a weak contact.



Figure 7. Van der Waals plot of a section of the infinite chain of **12**. The $C(SiMe_3)_3$ ligand is omitted for clarity. (blue atoms = aluminum, pink atoms = potassium, green atoms = fluorine)

These investigations indicate the activation of the Al-F bonds using KF in the absence of a coordinating solvent. This example is an interesting model for the activation of AlF_3 in the presence of KF. Fluorides of aluminum find use as catalysts for the sythesis of new chlorofluorocarbon alternatives [8].

K(1)-F(2)#1 2.6347(17) 1.8144(17) Al(1)-F(1)K(1)-F(3)2.5990(17) Al(1)-F(2)1.6940(19) K(1)-F(4)#1 2.6441(18) Al(1)-F(3)1.6820(18) K(1)-F(4)3.147(2)1.8028(17) Al(2)-F(1)K(1)-F(5)2.6587(18) Al(2)-F(4)1.6922(17) K(1)-Al(2)3.5933(11) Al(2)-F(5)1.6865(19) Al(1)-C(1)1.953(3) 1.948(3) Al(2)-C(2)F(3)-K(1)-F(2)#1 132.31(7) F(4)-Al(2)-F(1)97.56(8) F(3)-K(1)-F(4)#1114.14(6) Al(2)-F(1)-Al(1)129.47(9) F(2)#1-K(1)-F(4)#173.30(5) Al(1)-F(2)-K(1)#2 131.60(10) 72.57(5) F(3)-K(1)-F(5)Al(1)-F(3)-K(1)145.68(9) 109.56(6) F(2)#1-K(1)-F(5) Al(2)-F(4)-K(1)#2143.54(10)F(4)#1-K(1)-F(5) 168.62(6) Al(2)-F(4)-K(1)90.79(8) F(3)-K(1)-F(4)65.27(5) Al(2)-F(5)-K(1)109.54(8) F(2)#1-K(1)-F(4) 78.02(5) K(1)#2-F(4)-K(1)110.97(5) F(4)#1-K(1)-F(4)136.73(5) K(1)#2-K(1)-K(1)#1 137.74(3) F(5)-K(1)-F(4)53.89(5) F(3)-Al(1)-C(1)116.87(11) F(3)-Al(1)-F(2)106.66(10) F(2)-Al(1)-C(1)118.33(11) F(3)-Al(1)-F(1)98.73(9) F(1)-Al(1)-C(1)114.16(10) 99.01(9) F(2)-Al(1)-F(1)F(5)-Al(2)-C(2)118.42(11)

 Table 6. Selected bond lengths [Å] and angles [°] for 12.

F(5)-Al(2)-F(4)	104.21(9)	F(4)-Al(2)-C(2)	116.85(10)
F(5)-Al(2)-F(1)	100.46(9)	F(1)-Al(2)-C(2)	116.14(10)

2.6. Synthesis of New Organoaluminum fluorides

One of the primary objectives concerning fluorine based science in our research group has been the development of new fluorinating agents in recent years. AsF₃ was used, for example, successfully with Cp'TiCl₃ for the synthesis of Cp'TiF₃ (Cp' = C₅Me₄Et[70]) and for Cp*MF₄ (M = Nb [40], Ta [71]). However, the most reliable fluorinating agent for transition metals proved to be Me₃SnF. The metathesis of fluoride and chloride yields Me₃SnCl which can be recycled easily by using KF or NaF to gain the fluorinating agent Me₃SnF [34]. Me₃SnF also finds use in the synthesis of organoaluminum difluorides [19, 43]. But the

metathesis in these reactions of fluoride and a methyl produces Me_4Sn which cannot be recycled easily unlike Me_3SnCl (Scheme 11).



Scheme 11. M = Ti, Zr, Hf [34]; $R' = N(SiMe_3)(2,6-iPr_2C_6H_3) [19]$; $R'' = C(SiMe_3)_3 [43]$.

Alternatives to Me_3SnF like Ph_2PbF_2 and Ph_2BiF for the metathesis reactions of group 4 and 5 compounds has been described [72].

Alkali metal fluorides can be used for the synthesis of organofluoroaluminates. $Cs[iBu_3AlF]$ for example they can be obtained by the reaction of $Al(iBu)_3$ with CsF as a fluorination agent for organometallic compounds of the elements of group 13 in toluene [73].

Examples of organoaluminum difluorides are rare [18]. Roesky *et al.* synthesized the compounds **1** [43], [RAlF₂]₃ {(R = N(SiMe₃)(2,6-*i*Pr₂C₆H₃), N(S*it*BuMe₂)(2,6-Me₂C₆H₃)} [19], and [{N(SiMe₃)C(Ph)C(CiMe₃)₂}AlF(μ -F)]₂ [74] and characterized them by X-ray single crystal structural analysis.

2.6.1. Attempted Reaction of Me₃SnF with DDPAIMe₂

No reaction of Me₃SnF [75] with DDPAlMe₂ in a molar ratio 2 : 1 in THF has been observed $[DDPH = (2-{(2,6-diisopropylphenyl)amino}-4-{(2,6-diisopropylphenyl)imino}-2-pentene].$

2.6.2. Synthesis of (CycMe₂Si)(Me₃Si)₂CAlF₂·THF (13)

 $(Me_3Si)_3CAIF_2$ ·THF is available in a facile way by the reaction of $(Me_3Si)_3CAIMe_2$ ·THF with Me_3SnF . It seemed to be easy to react the compound $(CycMe_2Si)(Me_3Si)_2CAIMe_2$ ·THF [76] with Me_3SnF in a similar route.

 $(CycMe_2Si)(Me_3Si)_2CAlMe_2$ ·THF was treated with 2 equivalents Me_3SnF in THF (Scheme 12). The volatiles were evaporated in vacuum. Crystallization of the residue from THF at -20 °C afforded **13** (71 %) in moderate yield.

 $RAIMe_2 \cdot THF + 2 Me_3 SnF \longrightarrow R'AIF_2 \cdot THF + 2 Me_4 Sn$

Scheme 12. $R = (CycMe_2Si)(Me_3Si)_2C$.

The ¹H NMR resonances of **13** are found in the expected range differing only slightly from those of the heavier halide congeners (CycMe₂Si)(Me₃Si)₂CAlX₂·THF (X = Cl, Br, I) [76]. The ¹⁹F NMR shows a sharp resonance for the fluorine atoms (at δ -156.5 ppm). In the EI-MS of **13** the fragment (Me₃Si)₂CHSiMe₂ is observed (at *m/z* 217) with 100 %

intensity.

Attempts to grow suitable crystals (in toluene) for an X-ray diffraction analysis were unsuccessful. It was not possible to remove the THF of **13** *in vacuo* at high temperatures in a similar way as it is described for **1** (Scheme 1) due to the fact that **13** melts (108 °C) and decomposes. Further investigations on **13** seemed to be less interesting.

2.6.3. Attempted Synthesis of (2,6-*t*Bu₂C₆H₃O)AlF₂·THF

Me₃Al reacts with sterically hindered 2,6-di-*tert*-butyl-substituted phenols [77]. In the reaction of 2,6-di-*tert*-butyl-4-methylphenol (DBMP-H) with Me₃Al, the species observed are Me₃Al, Al₂Me₅DBMP, AlMe₂DBMP, and AlMeDBMP₂. It has been reported, that species of type DBPAlMeX·(NH₂*t*Bu) (DBP-H = (2,6-*t*Bu₂C₆H₃)OH; X = Me, Cl, Br) [78] or (DBMP)AlMe₂·(pyridine) [79] are characterizable by X-ray structure analysis. The synthesis of a similar difluoride analogue with coordinated THF was attempted. Up to now it was not possible to isolate the desired DBPAlF₂·THF product by reaction of DBPAlMe₂·THF with Me₃SnF in THF in a ratio of 1 : 2. Several resonances in the ¹⁹F NMR spectrum in the range δ -140 ppm to -170 ppm indicated a mixture of products.

2.6.4. Synthesis of (2,6-*t*Bu₂C₆H₃O)₂AlF·THF (14)

The compound $(DBP)_2AIMe$ is reported [76, 80]. The synthesis of a similar difluoride analogue with coordinated THF was attempted.

DBP₂AlMe [77] and Me₃SnF (1 eq) were stirred in THF for 24 h. All volatiles were removed *in vacuo*. Crystallization from THF at -20 °C resulted in products of the composition DBP₂AlF·THF (82 %). The colorless solid melts at 135 - 136 °C.

$$(2,6-tBu_2C_6H_3O)_2AIMe \cdot THF + Me_3SnF \longrightarrow (2,6-tBu_2C_6H_3O)_2AIF \cdot THF + Me_4Sn$$
14

Scheme 13

The elemental analysis for C and H confirms the composition $C_{32}H_{50}AIFO_3$. The ¹H NMR of **14** reveals resonances for the protons as expected for one (2,6-*t*Bu₂C₆H₃O) ligand together with resonances of one coordinated THF with correct relation of the integrals. The fluorine atoms show resonances (at δ -161.8 ppm) in the ¹⁹F NMR as sharp singlet. In the EI-MS spectrum, the molecule peak [at *m*/*z* 528] and the THF free molecule fragment [at *m*/*z* 456] are observed with the intensity of 20 and 60 %, respectively.

It was so far unsuccessful to obtain suitable single crystals for an X-ray structure analysis.

2.7. Synthesis of [*n*Bu₄N][(Me₃Si)₃CAIMeF₂] (15)

Group 13 difluorodiorganometalates have been known since 1955 [13,81]; however, only a few of these were spectroscopically and structurally characterized [73,82-85]. Furthermore, the synthesis of these anions was not straightforward.

The X-ray crystal structures and spectroscopic characterization of some difluorodiorganometalates, $[nBu_4N][Me_2MF_2]$ (M = Al, Ga, In) have been described [86]. The synthesis of these compounds is accomplished through protonolysis of trialkyl derivatives of the group 13 metals with tetra-*n*butylammonium hydrogen difluoride (TBADF) [87], which induces elimination of methane and addition of two fluoride ions. In the series of group 13 difluorodiorganometalates it was intriguing to synthesize an aluminum analogue with a bulky ligand like (Me₃Si)₃C instead of a small methyl group.

Treatment of $(Me_3Si)_3CAIMe_2$ ·THF with an equimolar amount of TBADF in THF at room temperature afforded $[nBu_4N][(Me_3Si)_3CAIMeF_2]$ (**15**) (Figure 8, Table 7) in high yield after subsequent work-up (Scheme 14).

$$(Me_3Si)_3CAIMe_2 \cdot THF + TBDAF \longrightarrow [nBu_4N][(Me_3Si)_3CAIMeF_2] + MeH$$

-THF 15

Scheme 14

Compound **15** crystallized with 0.5 molecules of toluene. Crystals used for the analysis of the elements C, H, Al, F, and N confirm the composition of $C_{30.5}H_{70}AlF_2NSi_3$.

In the ¹H NMR of **15** one resonance at δ -0.29 ppm as a triplet with a coupling constant J = 2.8 Hz and one resonance at δ 0.69 ppm for the (Me₃Si)₃C ligand are found for the anion in the appropriate ratio of integration in addition to the signals of the cation.



Figure 8. Molecular structure of $[nBu_4N][(Me_3Si)_3CAlMeF_2]$ (15).

 Table 7. Selected bond distances [Å] and angles [°] for 15:

Al(1)-C(1)	2.010(6)	Al(1)-F(1)	1.702(5)
Al(1)-C(2)	1.945(11)	Al(1)-F(2)	1.680(5)
F(1)-Al(1)-F(2)	106.0(3)	F(2)-Al(1)-C(1)	109.0(3)
F(1)-Al(1)-C(1)	110.6(3)	F(2)-Al(1)-C(2)	106.4(5)
F(1)-Al(1)-C(2)	107.0(4)	C(1)-Al(1)-C(2)	117.2(4)

The ¹⁹F NMR spectrum reveals a singlet at δ -145.9 ppm shifted downfield from the comparable resonance of [*n*Bu₄N][Me₂AlF₂] (δ -154.8 ppm) [86].

In the negative FAB-MS of **15**, the anion peak is observed (at m/z 311) with 100 % intensity. The IR spectrum shows two absorptions at 741 and 640 cm⁻¹ attributable to Al-F bond stretches [61]. The spectroscopic conclusions were corroborated through an X-ray diffraction study of **15**. Single crystals of **15** were grown from toluene within one week at -20 °C. Compound **15** crystallizes in the monoclinic space group $P2_1/c$. The metal center of the anion has a distorted tetrahedral coordination environment. The average Al-F bond distance in **15** (1.690 Å) is somewhat shorter compared to that in $[nBu_4N][Me_2AlF_2]$ (1.712 Å) and somewhat longer than the normal Al-F bonds (1.65 Å) [2]. The C-Al-C (117.2(4)°) bond angle of **15** is nearly identical to that of $[nBu_4N][Me_2AlF_2]$ (117.13(10)°) despite the presence of a more sterically demanding ligand in **15**; in addition, the F-Al-F bond angle is actually larger in **15** (106.0(5)°) than that in $[nBu_4N][Me_2AlF_2]$ (103.23°).

The fluoride transfer with TBADF is facile to carry out, and has also been demonstrated in the fluorination of trisubstituted silanes [88].

Following to the herein described difluorodiorganometalates the first phosphonate anions of aluminum - containing fluorine and an anionic bridged fluoroalkoxy derivative of titanium are realized using TBADF as a fluorinating agent [89].

 $[Me_4N][(iBu)_2AIF_2]$ and $[Ph_4P][AIF_4]$ have been prepared and characterized by X-ray structure analysis [90] using a similar synthetic approach as described for **15**. These compounds, containing the anions $[R_2AIF_2]^-$ and $[AIF_4]^-$, respectively, permitted a comparison of the hard and soft acid and base principle by means of *ab-initio* calculations. The therein described model allows rationalization of the tendencies of bond angle variation in $[R_2MX_2]$ systems containing a main group metal (M) in terms of hybridization and correlation with electronegativity and hardness of the ligands. The computed analysis surprisingly reveals that the Al-F bond in the $[R_2AIF_2]^-$ anion is weaker than the Al-Me bond. **15** contains a large C(SiMe_3)_3 ligand and a small Me group in comparison with the $[R_2AIF_2]^$ anion described. But these results may account for **15** too and have to be taken into consideration when bond distances of the anion in **15** are compared to those in the $[Me_2AIF_2]^$ anion. The Al-F bond distance in **15** is 0.02 Å shorter than the corresponding distance in $[nBu_4N][Me_2AlF_2]$. This may indicate that the Al-F bonds in $[nBu_4N][Me_2AlF_2]$ are weaker than those in **15**.

2.8. Reactions of (Me₃Si)₃CAlMe₂·THF with CF₃COOH

Several oxo-centered trinuclear carboxylates of transition metal complexes are described in the literature. On the other hand there are only a few examples of analogous main group compounds characterized by X-ray crystal structural analysis. The first group 13 derivative of this type is $[Ga_3(\mu_3-O)(\mu-O_2CC_6H_5)_6(4-Mepy)_3][GaCl_4]$ (j) (R = $O_2CC_6H_5$, L = 4-Mepy) (Scheme 15) [91] without precedent for an analogous aluminum compound. Therefore it was interesting to investigate the reaction of a (Me_3Si)_3CAIMe_2·THF with CF_3COOH.



Scheme 15. Drawing of $[Ga_3(\mu_3-O)(\mu-O_2CC_6H_5)_6(4-Mepy)_3]^+$. R = C₆H₅; L = 4-Mepy.

2.8.1. Reaction of (Me₃Si)₃CAlMe₂·THF with CF₃COOH in a 1 : 1 molar ratio. Synthesis of [(Me₃Si)₃CAlMe(O₂CCF₃)]₂ (16)

CF₃COOH (1 eq) was added to a solution of (Me₃Si)₃CAlMe₂·THF in toluene. The cloudy liquid was stirred for 1 d. The insoluble residue was filtered off and crystallized at -20 °C from THF. Small amounts of adherent solvent were removed *in vacuo*. The colorless solid decomposes at 210 °C.

The analyses of 16 for the elements C and H confirm the required composition $C_{26}H_{60}Al_2F_6O_4Si_6$.

The ¹H NMR (THF-d₈) shows resonances for the protons of an aluminum bounded methyl group at δ -0.47 ppm and for the protons of the C(SiMe₃)₃ ligand at δ 0.23 ppm. The relation of the integrals (3 : 27) reveals the generation of a compound of composition (Me₃Si)₃C-AlMe(O₂CCF₃).

Only one (δ -74.7 ppm) resonance for the fluorine atoms of the CF₃ group is observed in the ¹⁹F NMR spectrum.

The EI mass spectrum shows a peak assignable to a $(Me_3Si)_3CAl(O_2CCF_3)$ fragment (at m/z 371) with 100 % intensity. Another peak (at m/z 757, $[(Me_3Si)_3CAlMe(O_2CCF_3)]_2$ - Me) with 30 % intensity is indicative for the dimeric nature of **16**.

Attemps to grow crystals for X-ray structural analysis to prove the configuration were not successful. (Scheme 16).

2.8.2. Reaction of (Me₃Si)₃CAlMe₂·THF with CF₃COOH in a 1 : 2 molar ratio. Synthesis of [(Me₃Si)₃CAl(O₂CCF₃)₂]₂ (17)

CF₃COOH (1 eq) was added to a solution of $(Me_3Si)_3CAIMe_2$ ·THF in toluene (Scheme 16). The same cloudy liquid originated as observed for the reaction described in 2.8.1. Addition of a second equivalent CF₃COOH (1 eq) produced a clear solution which was stirred for 1 d. All solvents were evaporated *in vacuo*. The residue was treated with *n*hexane (20 mL) and filtered. The insoluble residue was dissolved in toluene and crystallized at -20 °C. A colorless solid (45 %) was isolated which decomposes at 170 °C.

The elemental analyses of 17 for C and H confirm the composition C₂₈H₅₄Al₂F₁₂O₈Si₆.

The ¹H NMR (THF-d₈) spectrum contains only one resonance for the protons of the $C(SiMe_3)_3$ ligand at $\delta 0.23$ ppm.

The resonances for the fluorine atoms in the ¹⁹F spectrum are observed at δ -74.8 ppm.

In the EI mass spectrum the 100 % peak due to the fragment $[(Me_3Si)_3CAl(O_2CCF_3)_2]_2$ - Me (*m*/z 953) is observed which provides evidence for a dimeric composition, but a trimeric aggregate cannot be ruled out ultimatively.

Up to now it was not possible to grow suitable crystals for an X-ray structural analysis to unravel the configuration of $[(Me_3Si)_3CAl(O_2CCF_3)_2]_2$.

$$2 (Me_3Si)_3CAIMe_2 THF + 2 CF_3COOH \xrightarrow{-2 THF} [(Me_3Si)_3CAIMe(O_2CCF_3)]_2 + 2 MeH$$
 16

$$2 (Me_3Si)_3CAIMe_2 THF + 4 CF_3COOH \xrightarrow{-2 THF} [(Me_3Si)_3CAI(O_2CCF_3)_2]_2 + 4 MeH$$

$$4 (Me_{3}Si)_{3}CAIMe_{2} THF + 11 CF_{3}COOH \xrightarrow{- THF} [(Al_{3}(\mu_{3}-O)(\mu-O_{2}CCF_{3})_{6}(THF)_{3}]^{+} [(Me_{3}Si)_{3}CAI(OC(O)CF_{3})_{3}]^{-} + 8 MeH + 3 (Me_{3}Si)_{3}CH + (CF_{3}CO)_{2}O$$

Scheme 16

2.8.3. Reaction of $(Me_3Si)_3CAIMe_2$ ·THF with CF₃COOH in a 1 : 3 molar ratio. Synthesis of $[Al_3(\mu_3-O)(\mu-O_2CCF_3)_6(THF)_3]^+[(Me_3Si)_3CAI(OC(O)CF_3)_3]^-$ (18)

CF₃COOH (3 eq) was added to a solution of $(Me_3Si)_3CAIMe_2$ ·THF in toluene and stirred for 1 d. All volatile substances were pumped off. The residue was dissolved in toluene/THF (5 : 1). Crystallization at -20 °C afforded **18** (Scheme 16) in low yield after 2 weeks (decomposing at 135 °C).

18 crystallized together with one molecule of toluene. These crystals were used for the elemental analysis of C and H and confirm the composition $C_{47}H_{59}Al_4F_{27}O_{22}Si_3$.

The NMR spectra were recorded in THF-d₈, though 18 may decompose in this solvent.

In the ¹H NMR spectrum one resonance at $\delta 0.26$ ppm and one small signal at $\delta 0.48$ ppm are observed.

The resonances of the fluorine atoms in the ¹⁹F NMR spectrum appear at δ -77.4, -75.9 and -75.8 ppm.

In the FAB-MS of **18**, the peak for the cation $[Al_3(\mu_3-O)(\mu-O_2CCF_3)_6(THF)_3]^+$ is observed (at m/z 991) with 10 % intensity whereas the anion $[(Me_3Si)_3CAl(OC(O)CF_3)_3]^-$ is detected (at m/z 597) with 100 % intensity.

Suitable single crystals for an X-ray structural analysis of **18** (Figure 9 and 10, Table 8) were obtained from a saturated toluene/THF solution (8 : 1) at -20 °C. The molecular structure of the complex cation is shown in Figure 9. The central Al₃O part consists of a planar triangular arrangement of aluminum atoms (120°). Each aluminum atom possesses a slightly distorted octahedral coordination sphere. The μ_3 -O atom shows equidistances (1.8529(11) Å) to the three aluminum centers which is somewhat longer than those in Pb₂Al₅(μ_3 -O)(μ_4 -O)-(μ -OiPr)₉(OiPr)₃(μ -OAc)₃ (Al-(μ_3 -O) 1.822 Å) [92]. The aluminum oxygen (THF) distances (1.948(3) Å) in **18** are somewhat longer than those in [(2,6-*i*Pr₂C₆H₃)N(SiMe₂*i*Pr)-SiO₃Al·THF]₄ (1.866 Å) [93]. The aluminum oxygen (carboxylate) distances (av 1.892 Å) in the solid state cation are somewhat shorter than those of the coordinated oxygen atoms of

THF in **18**. The aluminum oxygen distances in the anion of **18** (Figure 10) are short (178.4(3) Å) compared to those of the cation of **18**. The coordination sphere at the aluminum in the anion has a slightly distorted tetrahedral environment.



Figure 9. Molecular structure of the $[Al_3(\mu_3-O)(\mu-O_2CCF_3)_6(THF)_3]^+$ cation of **18**. Only the ipso oxygen atoms of THF are displayed.

The stepwise formation of compounds 16-18 can be rationalized as follows:

The first step is the exchange of a methyl group by CF_3COO^- followed by replacement of the second methyl by a second CF_3COO^- . Inadvertently present water or water generated from condensation of CF_3COOH in this strongly acidic solution then accounts for the cleavage of

the remaining Al-C bonds under formation of the cation. The anion results from addition of CF_3COO^- to **17**.

18 is the first X-ray structurally characterized oxo-centered trinuclear carboxylate of aluminum.



Figure 10. Molecular structure of the $[(Me_3Si)_3CAl(OC(O)CF_3)_3]^-$ anion of **18**. Me groups are omitted for clarity.

Table 8. Selected bond distances [Å] and angles [°] for 18.

Al(1)-O(1)	189.0(3)	O(1)-C(1)	123.5(5)
Al(1)-O(3)	189.5(3)	O(2)-C(2)	123.2(4)
Al(1)-O(6)	185.29(11)	Al(2)-O(41)	178.4(3)
Al(1)-O(5)	194.8(3)	Al(2)-C(3)	195.9(7)
C(1)-O(3)#2	123.0(5)		

O(6)-Al(1)-O(2)	95.77(12)	O(1)-Al(1)-O(5)	84.16(12)
O(6)-Al(1)-O(1)	95.27(13)	O(4)-Al(1)-O(5)	84.53(11)
O(2)-Al(1)-O(1)	168.95(13)	O(3)-Al(1)-O(5)	84.84(12)
O(6)-Al(1)-O(4)	95.31(12)	C(1)-O(1)-Al(1) 1	31.5(3)
O(2)-Al(1)-O(4)	87.57(13)	C(2)-O(2)-Al(1) 1	30.9(2)
O(1)-Al(1)-O(4)	91.70(15)	Al(1)-O(6)-Al(1)#1 1	19.999(2)
O(6)-Al(1)-O(3)	95.30(12)	O(3)#2-C(1)-O(1) 1	27.3(4)
O(2)-Al(1)-O(3)	92.14(14)	O(3)#2-C(1)-C(11) 1	17.3(4)
O(1)-Al(1)-O(3)	86.54(16)	O(1)-C(1)-C(11) 1	15.4(4)
O(4)-Al(1)-O(3)	169.36(13)	O(2)-C(2)-C(21) 1	16.8(3)
O(6)-Al(1)-O(5)	179.40(11)	O(41)-Al(2)-O(41)#1 1	06.11(13)
O(2)-Al(1)-O(5)	84.80(11)	O(41)-Al(2)-C(3) 1	12.66(12)

Infrared spectrum of 18 (Table 9) [94]:

The infrared spectra of **16**, **17**, and **18**, between 1100 and 3300 cm⁻¹, are dominated by bands attributable to the organic part of these compounds.

A monodentate acetate group is expected to have a carbon-oxygen bond with an enhanced double bond character ($\nu 1600 - 1750 \text{ cm}^{-1}$). Two bands ($\nu 1763 \text{ cm}^{-1}$, 1735 cm⁻¹) are characteristic for asymmetric COO-valence stretches in the anion of **18**. Bands at $\nu 1400 - 1550 \text{ cm}^{-1}$ indicate acetate groups which coordinate to identical metal atoms (**18**: $\nu 1521 \text{ cm}^{-1}$). It is not possible to discern if an acetate is bidentate coordinated to one metal atom or bridged to two identical atoms [41]. The difference of this stretches ($\Delta \nu \approx 200 \text{ cm}^{-1}$) indicates the existence of monodentate and bidentate CF₃COO⁻ groups. The absorption at $\nu 663 \text{ cm}^{-1}$ of **18** has been tentatively assigned to an asymmetric stretch of the M₃O unit ([Ga₃(μ_3 -O)-(μ -O₂CC₆H₅)₆(4-Mepy)₃][GaCl₄]: $\nu 655 \text{ cm}^{-1}$). The band at $\nu 566 \text{ cm}^{-1}$ of **18** occurs in almost all trimeric carboxylates ($\nu 550 \text{ cm}^{-1}$) and is assigned to a carboxylate mode [91].

16	17	18	
1732	1758	1763, 1735	$v_{\rm as}$ COO, COO valence vibration
1699	1690, 1668		COO valence vibration
		1521	COO valence vibration
1207	1260, 1220	1236, 1207	v _{as} C-F, v _s C-C
1170 , 1077	1168	1179, 1170	v _s C-F
		1008	
857	857	860, 803	
722	724	735	
672	675	663	$v_{\rm as}$ Al-C
		566	band of trimeric carboxylate
		452	δ MO ₄

Fable 9. Bands in the infrared	spectra of 16, 17,	, and 18 .	(Tentatively	y assignment)
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2.8.3.1. Electron Density Calculations for 18

18 offers an interesting insight into the bonding of the trinuclear frame. Al(III) as a light and diamagnetic ion is a study case, where the coordination bonds of carboxylate and oxo ligands can be analyzed free from the complicated effects of unpaired electrons on the metal ions, as in the case for transition metal systems. The cation of 18 is a model complex for the coordination in the class of oxo-centered trinuclear compounds [95, 96].



Figure 11. The Laplacian of electron density in one Al-carboxylate-Al coordination plane. The dark contours represent charge accumulation (lone pairs at oxygen and the C-O bonds) and the light ones the charge deficient zones (empty shells of the Al(III) ions) [95].

The actual computational analysis is a preliminary test for a hypothetical structure with formiate, $[Al_3(\mu_3-O)(\mu-O_2CH)_6(H_2O)_3]^+$. The accuracy of the quantum calculations is moderate due to the use of a non expansive low level 3-21G basis set [95,97-99].

A distinguished feature of the structure is the oxo ligand (Figure 11 + 12). The preliminary investigations on the hypothetical molecule $[Al_3(\mu_3-O)(\mu-O_2CH)_6(H_2O)_3]^+$ indicate sp² hybridization and increased electron density for the oxygen atom in the center. This will probably be the same for **18**. The Laplacian map in the Al₃O plane (Figure 12) shows the accumulation of electron density in the slightly deformed trigonal shape. The relatively small trigonal deformation of charge accumulated in the plane of the central oxygen can be interpreted as illustrating the hard nature of this ligand [95].

The orientation of the oxygen π orbitals of the carboxylate group (Figure 11, bright sphere around the formiate oxygens) is expected to be different in density calculations for **18** because the orientation of the oxygen π orbitals is a function of the group R of the carboxylate (RCOO⁻) [95].

The crystallographic data reveal a disorder in one of the CF_3 -groups in the cation which causes some problems in the electron density calculations. It was not yet possible to complete the calculation prior to completion of this thesis.

The acetate groups of the anion are totally disordered and not useful for electron density calculations [95].

In conclusion it has been shown that the cation of **18** is useful for simplified electron density calculations and can serve as a model compound to understand the bonding situation in innumerable analogue transition metal complexes in the class of oxo-centered trinuclear compounds.





The dark area in the center represents the electron rich μ_3 -O atom. The valence shell of aluminum is electron deficient (ionized metal). At the aluminum atoms two inner circular zones corresponding to the 2s2p and 1s core shells are distinguishable [95].

According to the bond order values, the strength of the ligand is the central oxo bridged carboxylate terminal ligand. The central oxygen seems to be strongly involved in π donation, a factor that stabilizes the planar symmetry of the (Al₃O) skeleton [95].

3. Summary and Outlook

3.1. Summary

The scope and aim of this work was the synthesis of complexes with relevance to Ziegler-Natta catalysts $[Cp'_{2-y}ZrX_{1+y}](\mu-X')[RAIF_2]$ (Cp' = Cp or substituted Cp; X, X' = Me, Cl or F; R = ligand; y = 0 or 1), the generation of new bimetallic organoaluminum fluorides, access to new organoaluminum fluorides and to investigate the reaction of (Me₃Si)₃CAlMe₂·THF with CF₃COOH.

The objective to synthesize Ziegler-Natta-Catalysis relevant systems was achieved by the synthesis of $[Cp_2ZrMe](\mu$ -F)[F₂AlC(SiMe₃)₃] (7).

 $[(Me_3Si)_3CAIF_2]_3 + 3 Cp_2ZrMeF \longrightarrow 3 [Cp_2ZrMe](\mu-F)[F_2AIC(SiMe_3)_3]$

An experiment demonstrated that **7** possesses no significant catalytic activity in the polymerization of ethene. The crystallization of **7** from THF produced compound $[Cp_2Zr(\mu-F)_2FAlC(SiMe_3)_3]_2O(8)$.



The compounds 9, 10, 11 and 12 are new bimetallic organoaluminum fluorides.

Compound **9** was generated by using an excess of *in situ* generated NaF on $[(Me_3Si)_3CAIF_2]_3$ in THF and is isostructural with $[Li(Me_3Si)_3CAIF_3(THF)]_4$ [45]. The central core consists of a cube formed of alternating aluminum and sodium atoms at the edges bridged by fluorine atoms.



Two different synthetic routes have been developed for **10**. The $[(Me_3Si)_3CAIF_2(\mu-O)-F_2AIC(SiMe_3)_3]$ species in **10** is comparable to the $[(Me_3Si)_3CAIF_2(\mu-F)F_2AIC(SiMe_3)_3]$ unit in $[\{(Me_3Si)_3C\}_4Al_4K_2(\mu-F)_2F_8(THF)_4]$ (**2**), $[Ag(toluene)_3]^+[\{((Me_3Si)_3C)_2Al_2(\mu-F)F_4\}_2Li]^-$ (**3**), $[AIF_2(THF)_4]^+[\{(Me_3Si)_3C\}_2Al_2(\mu-F)F_4]^-$ (**4**), and in $[\{(Me_3Si)_3C\}_2Al_2(\mu-F)F_4K]_{\infty}$ (**12**).



The $[(Me_3Si)_3CAIF_2(\mu-O)F_2AIC(SiMe_3)_3]^2$ species in formula **10** contains two negative charges in contrast to one negative charge in the $[(Me_3Si)_3CAIF_2(\mu-F)F_2AIC(SiMe_3)_3]^2$ part of the other bimetallic fluoro complexes.

The reaction of $(Me_3Si)_3CAlF_2$ ·THF with LiOCH $(CF_3)_2$ afforded the unexpected compound $[{Li(Me_3Si)_3CAlF_3(THF)}_3LiF(THF)]$ (11). Complex 11 illustrates the structural variety accessible by the combination of $[(Me_3Si)_3CAlF_2]_3$ and LiF. In the series of the alkali metals the lithium derivative 11 has a different structural arrangement compared to those of the analogous compounds of the heavier alkali metals.



The supramolecular chain **12** was obtained by treating $[(Me_3Si)_3CAIF_2]_3$ with potassium metal or potassium fluoride. The potassium in **12** has the coordination number four with a fifth fluorine atom in a weak contact. These investigations indicate the activation of the Al-F bond using KF in the absence of a coordinating solvent.

The new aluminum difluoride $(CycMe_2Si)(Me_3Si)_2CAIF_2$ ·THF (**13**) and an oxygen bounded aluminum fluoride of composition $(2,6-tBu_2C_6H_3O)_2AIF$ ·THF (**14**) were prepared.

The synthesis of $[nBu_4N][(Me_3Si)_3CAIMeF_2]$ (15) is a straightforward route for a structurally characterized difluorodiorganoaluminate. The synthesis of this compound is accomplished through protonolysis of the methyl group with tetra-*n*butylammonium hydrogen difluoride (TBADF), which induces elimination of methane and addition of two fluoride ions.



The reaction of $(Me_3Si)_3CAIMe_2$ ·THF with CF₃COOH in a 1 : 3 molar ratio afforded [Al₃- $(\mu_3-O)(\mu-O_2CCF_3)_6(THF)_3$]⁺[$(Me_3Si)_3CAI(OC(O)CF_3)_3$]⁻ (18) which is the first X-ray structurally characterized oxo-centered trinuclear carboxylate complex of aluminum. The trinuclear aluminum cation of 18 exhibits high symmetry and offers the possibility for simplified computer studies.



3.2. Outlook

The straighforward synthesis of $[Cp_2ZrMe](\mu-F)[F_2AlC(SiMe_3)_3]$ (7) may be applied to more bulky metallocenes. It can be seen that $[Cp_2ZrMe](\mu-F)[Al(C_{12}F_9)_3]$ exhibits negligible ethene polymerization activity. Increasing the bulkyness of the ancillary ligand (Cp* instead of Cp) results in a drastic increase of polymerization activity in $[Cp_2ZrMe](\mu-F)[Al(C_{12}F_9)_3]$ [52].

Further investigations have to prove if the identified $[(Me_3Si)_3CAIF_2(\mu-O)F_2AIC(SiMe_3)_3]$ species in **10** is useful for new bimetallic fluorine oxygen clusters. Probably it is possible to generate weakly coordinating anions according to the developed principle in $[Ag(toluene)_3]^+[\{((Me_3Si)_3C)_2Al_2(\mu-F)F_4\}_2Li]^-$ (**3**). Using the $[(Me_3Si)_3CAIF_2(\mu-O)F_2Al C(SiMe_3)_3]$ species similar to the established $[(Me_3Si)_3CAIF_2(\mu-F)F_2AIC(SiMe_3)_3]$ species in **3** would lead to a threefold charged anion. A threefold charged weak/non coordinating anion would be a great improvement in the research field of "weakly coordinating anions" [49].

An organoaluminum difluoride containing an alkali metal cation without coordinating solvents as in $[{(Me_3Si)_3C}_2Al_2(\mu-F)F_4K]_{\infty}$ (12) is synthesized and offers new possibilities to generate weakly coordinating anions and to study the activation of aluminum fluorine bonds. Further experiments may demonstrate whether a " $[(Cp'_2ZrMe)(\mu-F)(alkali-cation)(\mu-F)AlR]$ " (substituting THF in 5, 9 - 12 by Cp'_2ZrMe^+) species is a valid approach to alternatives for Ziegler-Natta catalysts.

The oxo-centered trinuclear carboxylate cation in $[Al_3(\mu_3-O)(\mu-O_2CCF_3)_6(THF)_3]^+$ $[(Me_3Si)_3CAl(O_2CCF_3)_3]^-$ (18) is of high symmetry. 18 is a model compound for the bonding situation in the class of oxo-centered trinuclear carboxylates. 18 allows simplified computional analysis of this type of compounds without complications by unpaired electrons as in transition metals. The electron density calculations are already in progress and will hopefully provide reliable results [95, 96].

4. Experimental Section

4.1. General Procedures

All experiments, unless stated otherwise, were performed using standard Schlenk techniques [100] under a dry nitrogen atmosphere due to the sensitive behavior of the reactants and products toward air and moisture. A Braun MB 150-GI Box was used to store the compounds and to prepare the samples for spectroscopic characterization. The O_2 and H_2O levels were normally kept below 5 ppm and 1 ppm, respectively. Commercial grade solvents were purified and freshly distilled from sodium/benzophenone and degassed prior to use [101].

4.2. Physical Measurements

Melting points were measured in sealed glass capillaries on a Büchi 540 instrument.

Elemental analyses were performed by the Analytical Laboratory of the Institute of Inorganic Chemistry, University of Göttingen.

NMR spectra were recorded on Bruker AM 200, Bruker Avance 200, Bruker AM 250, Bruker AS 400, and Bruker Avance 500 instruments. Chemical shifts were referenced to external standards, namely SiMe₄ for ¹H and ²⁹Si, LiCl for ⁷Li, and CFCl₃ for ¹⁹F. The chemical shifts referenced to C_6F_6 are converted to the CFCl₃ values (δ (CFCl₃) - δ (C₆F₆) = -162.28 ppm). All heteroatom NMR spectra were measured ¹H decoupled. Downfield shifts from the reference are quoted as positive and the upfield shifts as negative values. The solvents for NMR measurements were dried over sodium and distilled prior to use. The multiplicities of the signals are assigned as: s = singlet, d = doublet, t = triplet, m = multiplet.

Mass spectra were obtained on Finnigan MAT 8230 and Varian MAT CH 5 instruments by EI- and FAB-MS techniques. Only the strongest peak of any isotopic distribution is given.

Infrared spectra were recorded on a Bio Rad FTS-7 spectrometer as nujol mulls between KBr plates, as KBr pellets, or as CsI pellets. Only relevant absorptions are reported. The absorption intensities are assigned as: vs = very strong, s = strong, m = medium.

X-ray structure determinations: Suitable crystals were mounted on glass fibers in a rapidly cooled perfluoropolyether [102]. Data for the 2 : 1 mixture of compounds 7 and 8, 12, 15, and 18 were collected on a Stoe four circle diffractometer, for compound 8 on a Bruker AXS SMART CCD System, for compound 9 and 10 on a Stoe-Siemens-Huber four circle diffractometer with a Siemens SMART CCD area detector and for compound 11 on a Stoe IPDS II System. Mo-K α radiation ($\lambda = 0.71073$ Å) was used in all cases, performing ϕ and ω -scans. Data reduction and space group determination routines were carried out using Siemens SHELXTL programs [103]. The structures were solved by direct methods employing SHELXTL-93/96/97 programs. The structure refinements were carried out by full-matrix least-squares methods against F^2 using SHELXTL-93/96/97 [104]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The crystal data for compounds 7 - 12, 15 and 18 along with structure factors and refinement parameters are tabulated in Section 6.

4.3. Starting Materials

Cp₂ZrMe₂ [105], (Me₃Si)₃CAlMe₂·THF [65], Me₃SnF [106], (CycMe₂Si)(Me₃Si)₂C-AlMe₂·THF [76], DDPAlMe₂ [75], (2,6- $tBu_2C_6H_3O$)AlMe₂·THF [107], and (2,6- $tBu_2C_6H_3O$)₂AlMe [77] were prepared according to literature procedures. K, KF, NaCl, NaF, MeLi, and (CF₃)₂CHOH were purchased from Aldrich, Acros, or Fluka. (Preparation of the reagents: K was washed with *n*hexane. NaCl, NaF, and KF were heated at 250 °C to

remove moisture in *vacuo*. nBu_4NHF_2 (Fluka) was received as a 50 % solution in dichloromethane. The dichloromethane was removed *in vacuo* and the nBu_4NHF_2 was dissolved in THF.)

4.4. Improved Synthesis of [(Me₃Si)₃CAIF₂]₃ (1) [43, 109]

A mixture of (Me₃Si)₃CAlMe₂·THF (3.61 g, 10.0 mmol) and Me₃SnF (3.66 g, 20.0 mmol) in THF (30 mL) was stirred for 12 h. After the THF had been pumped off the residue was heated for 4 h at 150 °C *in vacuo*. Pale yellow **1** (2.95 g, 9.95 mmol, 99 %) remained.

¹H NMR (200 MHz, C₆D₆, ppm): δ 0.38 (s).

¹⁹F NMR (188 MHz, C₆D₆, ppm, external standard CFCl₃): δ -149.6 (s).

For more data see ref. [43].

4.5. Synthesis of $[Cp_2ZrMe](\mu$ -F) $[F_2AlC(SiMe_3)_3]$ (7) and $[Cp_2Zr(\mu$ -F)_2-FAlC(SiMe_3)_3]_2O (8)

Preparation of 7. A mixture of Me₃SnF (0.464 g, 2.54 mmol), **1** (0.750 g, 0.84 mmol, 1/3 eq) and Cp₂ZrMe₂ (0.640 g, 2.54 mmol) in toluene (40 mL) was stirred for 24 h at 0 °C. The solution was then allowed to warm to room temperature and stirred for another 3 days. After filtration the solid was recrystallized from toluene/*n*hexane (4 : 1) at -20 °C. **7** was obtained as a colorless solid (0.900 g, 1.63 mmol, 64 %) that decomposes slowly at 200 °C.

Anal. Calcd for C₂₁H₄₀AlF₃Si₃Zr (552.01): C, 45.69; H, 7.30. Found: C, 44.6; H, 6.9. ¹H NMR (250 MHz, C₆D₆, ppm): δ 0.48 (s, 27 H, SiCH₃), 0.56 (s, 3 H, ZrCH₃), 6.36 (s, 10 H, C₅H₅); ¹⁹F NMR (235 MHz, C₆D₆, ppm, external standard CFCl₃): δ -165.4 (s, 2 H, AlF₂), -161.8 (s, 1 H, Al(μ-F)Zr).

IR (KBr, Nujol, cm⁻¹): 1251 s, 1016 s, 863 s, 797 m, 770 s, 680 m, 615 m, 546 m.

Preparation of 8. 7 (0.200 g, 0.36 mmol) was dissolved in THF/toluene/nhexane (1 : 8 : 2).
Crystallization at -20 °C afforded 8 (0.010 g, 0.01 mmol) after four weeks as a colorless solid.
8 was only characterized by single crystal X-ray structure analysis.

Preparation of a crystalline 2 : 1 mixture of compounds 7 and 8. Dissolving **7** (0.200 g, 0.36 mmol) in a mixture of THF/toluene/*n*hexane (1 : 8 : 2) and cooling the solution at -20 °C for 4 weeks resulted in the formation of a mixture of crystals of composition of **7** and **8**. Only the crystals formed were used for the characterization of this mixture.

4.6. Synthesis of [Na(Me₃Si)₃CAlF₃(THF)]₄ (9)

A mixture of trimethyltin fluoride (2.19 g, 12.0 mmol), NaCl (0.470 g, 8.00 mmol) and $(Me_3Si)_3CAIMe_2(THF)$ (0.721 g, 2.00 mmol) in THF (20 mL) was stirred for 4 days. The solvent was evaporated *in vacuo*. The residue was washed with pentane (5 mL) and afterwards extracted with toluene (40 mL). All solvents were removed under reduced pressure. **9** (0.329 g, 0.20 mmol, 40 %) was obtained as a colorless solid, which can be heated to 300 °C without decomposition or melting.

Anal. Calcd for C₅₆H₁₄₀Al₄F₁₂Na₄O₄Si₁₂ (1642.62): C, 40.95; H, 8.59. Found: C, 40.0; H, 8.3. ¹H NMR (250 MHz, C₆D₆, ppm): δ0.41 (s, 27 H, SiCH₃), 1.45 (m, 4 H, OCH₂CH₂), 3.68 (m, 4 H, OCH₂CH₂).

 19 F NMR (235 MHz, C₆D₆, ppm, external standard CFCl₃): δ -176.7 (s).

²⁹Si NMR (50 MHz, C₆D₆, ppm): δ -3.5 (s).

IR (KBr, Nujol, cm⁻¹): 1260 s, 863 m, 726 m, 671 m.

4.7. Synthesis of $[{(Me_3Si)_3CAIF_2}_2(\mu-O)Li_2(THF)_4]$ (10)

First method: A mixture of **1** (0.589 g, 0.66 mmol) and Li_2O (0.030 g, 1.00 mmol) in THF (20 mL) was stirred for 2 days. The mixture was filtered. Crystallization at -20 °C resulted in a colorless crystalline solid **10** (0.619 g, 0.68 mmol, 68 %), mp 178 - 179 °C.

Second method: A mixture of (Me₃Si)₃CAlMe₂·THF (0.722 g, 2.00 mmol), Me₃SnF (0.732 g, 4.00 mmol) and Li₂O (0.030 g, 1.00 mmol) in THF (20 mL) was heated at reflux for 6 h. All solvents were removed *in vacuo*. The residue was dissolved in THF (20 mL) and filtered. Crystallization at -20 °C afforded **10** (0.735 g, 0.81 mmol, 81 %) as a colorless crystalline solid, mp 177 - 179 °C.

Anal. Calcd for C₃₆H₈₆Al₂F₄Li₂O₅Si₆ (911.43): C, 47.44; H, 9.51. Found: C, 46.8; H, 9.4.

¹H NMR (200 MHz, C₆D₆, ppm): δ 0.43 (s, 54 H, SiCH₃), 0.90 (m, 16 H, CH₂CH₂O), 3.79 (m, 16 H, CH₂CH₂O).

⁷Li NMR (97 MHz, C₆D₆, ppm): δ -0.8 (s).

 19 F NMR (188 MHz, C₆D₆, ppm, external standard C₆F₆): δ -158.5 (s).

²⁹Si NMR (50 MHz, C₆D₆, ppm): δ -3.4 (s).

IR (KBr, cm⁻¹): 2957 vs, 2903 vs, 1262 s, 1098 s, 1047 s, 1020 s, 855 vs, 718 vs, 674 m.

4.8. Synthesis of $[{Li(Me_3Si)_3CAIF_3(THF)}_3LiF(THF)]$ (11)

MeLi (3.75 mL, 1.6 *M* in Et₂O, 6.0 mmol) was added to $(CF_3)_2CH(OH)$ (1.01 g, 6.00 mmol) in THF (30 mL) and the mixture was stirred for 3 h. This solution was added to **1** (1.79 g, 2.00 mmol) in THF (30 mL) and the resulting mixture stirred for 3 days. All solvents were removed *in vacuo*. The residue was dissolved in toluene/THF (30 mL, 20 : 1) and filtered. Crystallization at -20 °C afforded **11** (0.302 g, 0.22 mmol, 11 %) after 2 weeks as a colorless crystalline solid, mp > 300 °C.

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For the elemental analysis the crystals of composition $\mathbf{11}$ + THF were used. Anal. Calcd for $C_{50}H_{121}Al_3F_{10}Li_4O_5Si_9$ (1353.98): C, 44.35; H, 9.01. Found: C, 44.8; H, 9.0.

¹H NMR (200 MHz, THF-d₈, ppm): δ0.15 (s, 81 H, SiC*H*₃), 1.77 (m, 16 H, C*H*₂CH₂O), 3.61 (m, 16 H, CH₂C*H*₂O).

⁷Li NMR (97 MHz, THF-d₈, ppm): δ -0.5 (s).

¹⁹F NMR (188 MHz, THF-d₈, ppm, external standard C₆F₆): at δ -166.5 (s) the main resonance, with a very small resonance at -202.8 (s).

²⁹Si NMR (99 MHz, THF-d₈, ppm): δ -1.8 (s).

MS (FAB_(neg)): *m/z* 1203 (2 %, *M* - Li - THF), 1057 (100 %, *M* - Li - 3 THF).

IR (KBr, cm⁻¹): 2978 vs, 2956 vs, 2900 vs, 1463 s, 1292 s, 1212 s, 1054 vs, 874 vs, 837 vs, 755 s, 724 s, 708 s, 674 vs, 626 s.

4.9. Synthesis of $[{(Me_3Si)_3C}_2Al_2(\mu-F)F_4K]_{\infty}$ (12)

First method: **1** (1.04 g, 1.16 mmol) and KF (0.093 g, 1.60 mmol) in toluene (20 mL) were heated under reflux for 6 h. After cooling the reaction mixture, the solvent was removed *in vacuo*. The residue was extracted with hot *n*hexane (20 mL) to remove excess **1**. The solid was again treated with toluene (20 mL) and heated under reflux for 1 h. Crystallization at ambient temperature resulted in 0.180 g of **12** (0.28 mmol, 18 %) as a colorless crystalline solid, mp >300 °C.

Second method: **1** (0.892 g, 1.00 mmol) and K(metal) (0.039 g, 1.00 mmol) in toluene (20 mL) were heated under reflux for 6 h. Crystallization at ambient temperature resulted in 0.150 g of **12** (0.23 mmol, 23 %) as a colorless crystalline solid with mp >300 °C. The colorless crystals were manually separated.

Anal. Calcd for C₂₀H₅₄Al₂F₅KSi₆ (651.22): C, 36.89; H, 8.36. Found: C, 37.1; H, 8.4. ¹H NMR (200 MHz, C₆D₆, ppm): δ0.42 (s). ¹⁹F NMR (188 MHz, C₆D₆, ppm, external standard C₆F₆): δ-157.5 (s, 4 F, Al(μ-F)K), -157.3 (s, 4 F, Al(μ-F)K), -156.9 (s, 1 F), -152.8 (m, 2 F, Al(μ-F)Al).

²⁹Si (99 MHz, C₆D₆, ppm): -3.4 (s).

MS (FAB_(neg)): *m*/*z* 669 (40 %, *M* + F), 315 (100 %, [(Me₃Si)₃CAlF₃]).

IR (CsI, cm⁻¹): 2958 s, 2904 s, 1202 vs, 1100 s, 1022 s, 857 vs, 688 s, 551 s, 406 s, 327 s.

4.10. Synthesis of (CycMe₂Si)(Me₃Si)₂CAlF₂·THF (13)

A mixture of $(CycMe_2Si)(Me_3Si)_2CAIMe_2 \cdot THF$ (2.00 g, 4.66 mmol) and Me_3SnF (1.70 g, 9.32 mmol) in THF (20 mL) was stirred for 12 h at room temperature. After removing all volatile components under vacuum the residue was dissolved in THF/*n*hexane (30 mL, 1 : 2). Crystallization at -20 °C afforded the colorless compound **13** (1.44 g, 3.29 mmol, 71 %) (mp 108 °C).

Anal. Calcd for C₁₉H₄₃AlF₂OSi₃ (436.78): C, 52.25; H, 9.92; Al, 6.18; F 8.70. Found: C, 51.5; H, 9.7; Al, 5.9; F 8.4.

¹H NMR (250 MHz, C₆D₆, ppm): δ0.40 (s, 6 H, SiCH₃), 0.45 (s, 18 H, SiCH₃), 0.90 (m, 4 H, OCH₂CH₂), 1.15 (m, 1 H, CH C1-Cyc), 1.35 (m, 2 H, CH₂ C4-Cyc), 1.80, 2.15 (m, 8 H, CH₂ C2-Cyc, C3-Cyc), 3.80 (m, 4 H, OCH₂CH₂).

¹⁹F NMR (250 MHz, C₆D₆, ppm, external standard CFCl₃): δ -156.5 (s).

²⁹Si NMR (99 MHz, C₆D₆, ppm): δ-3.2 (*Si*Me₃), 0.5 (*Si*CycMe₂).

MS (EI): *m/z* 217 (100 %, (Me₃Si)₂CHSiMe₂).

IR (KBr, cm⁻¹): 2957 s, 2920 s, 2849 m, 1448 m, 1254 s, 1097 m, 1045 m, 1011 m, 852 vs, 816 vs, 718 m, 673 s, 616 m.

4.11. Synthesis of (2,6-*t*Bu₂C₆H₃O)₂AlF·THF (14)

 $(2,6-tBu_2C_6H_3O)_2$ AlMe (4.52 g, 10.0 mmol) and Me₃SnF (1.82 g, 10.0 mmol) in THF (40 mL) were stirred for 24 h. All volatiles were evaporated and the residue extracted with toluene. Crystallization from THF at -20 °C resulted **14** (4.32 g, 8.17 mmol, 82 %) as a colorless solid (mp 135 - 136 °C).

Anal. Calcd for C₃₂H₅₀AlFO₃ (528.73): C, 72.69; H, 9.53. Found: C, 72.2; H, 9.5.

¹H NMR (200 MHz, C₆D₆, ppm): δ 0.98 (m, 4 H, CH₂CH₂O), 1.62 (s, 18 H, C(CH₃)₃), 3.58 (m, 4 H, CH₂CH₂O), 6.87 (t, *J* = 3 Hz, 1 H, 4-Ph*H*), 7.36 (d, *J* = 3 Hz, 2 H, 3,5-Ph*H*).

¹⁹F NMR (188 MHz, C₆D₆, ppm, external standard C₆F₆): δ -161.8 (s).

MS (EI): *m*/*z* 528 (20 %, *M*), 456 (60 %, *M* - THF), 42 (100 %, C(CH₃)₂).

IR (KBr, Nujol, cm⁻¹): 1262 s, 1101 m, 1021 m, 928 m, 756 m, 723 m, 626 m.

4.12. Synthesis of [*n*Bu₄N][(Me₃Si)₃CAlMeF₂] (15)

A solution of $(Me_3Si)_3CAIMe_2$ ·THF (3.00 g, 8.32 mmol) in THF was added dropwise to a solution of TBADF (2.34 g, 8.32 mmol) in THF (40 mL) at room temperature, and the mixture was stirred for 12 h. The solvent was removed in vacuo. The residue was redissolved in toluene (30 mL) and filtered. Crystallization at 0 °C for 3 days yielded 4.20 g (7.00 mmol, 84 %) of **15** as rhombic crystals (mp 108 °C).

For the elemental analysis crystals of composition 15 + 0.5 molecule of C₇H₈ were used. Anal. Calcd for C_{30.5}H₇₀AlF₂NSi₃ (600.13): C, 61.0; H, 11.8; Al, 4.5; F, 6.3; N, 2.3. Found: C, 61.8; H, 11.5; Al, 3.4; F, 5.5; N, 2.8.

¹H NMR (200 MHz, C₆D₆, ppm): δ -0.29 (t, J = 2.8 Hz, 3 H, AlCH₃), 0.69 (s, 27 H, SiCH₃), 0.91 (t, ² J_{HH} = 6.5 Hz, 12 H, CH₃), 1.12 - 1.31 (m, 16 H, CH₂ C2-Bu, C3-Bu), 2.91 (m, 8 H, CH₂ C1-Bu).

¹⁹F NMR (235 MHz, C₆D₆, ppm, external standard CFCl₃): δ -145.9 (s).

²⁹Si NMR (79 MHz, C₆D₆, ppm): δ -3.71 (s).

MS (EI): *m/z* 242 (100 %, Bu₄N), 100 (4 %, Bu(Me)NCH₂).

MS (FAB_{(neg})): *m*/*z* 311 (100 %, (Me₃Si)₃C(Me)AlF₂).

IR (KBr, cm⁻¹): 2965 st, 2898 st, 2878 m, 1488 m, 1466 m, 1382m, 1243 s, 1179 m, 1029 m, 869 st, 787 m, 754 m, 741 m, 709 m, 680 m, 664 m, 640 m, 575 m.

4.13. Reaction of (Me₃Si)₃CAlMe₂·THF with CF₃COOH in a 1 : 1 molar ratio. Synthesis of [(Me₃Si)₃CAlMe(O₂CCF₃)]₂ (16)

CF₃COOH (0.335 g, 2.94 mmol, 1 eq) was added to a solution of (Me₃Si)₃CAlMe₂·THF (1.06 g, 2.94 mmol) in toluene (20 mL). The cloudy liquid was stirred for 1 day. An insoluble residue was filtered off and crystallized at -20 °C in THF. Small amounts of adherent solvent were removed *in vacuo*. **16** (0.419 g, 0.54 mmol, 37 %) was obtained as a colorless solid (decomposing at 210 °C).

Anal. Calcd for C₂₆H₆₀Al₂F₆O₄Si₆ (773.23): C, 40.39; H, 7.82. Found: C, 41.1; H, 7.8. ¹H NMR (200 MHz, THF-d₈, ppm): δ -0.47 (s, 3 H, AlCH₃), 0.23 (s, 27 H, SiCH₃). ¹⁹F NMR (188 MHz, THF-d₈, ppm, external standard C₆F₆): δ -74.7 (s). ²⁹Si NMR (99 MHz, THF-d₈, ppm): δ -4.1 (s). MS (EI): *m*/*z* 757 (30 %, *M* - Me), 371 (100 %, *M*/2 - Me). IR (KBr, Nujol, cm⁻¹): 1732 m, 1699 s, 1207 m, 1170 m, 1077 m, 857 vs, 722 vs, 672 m.

4.14. Reaction of (Me₃Si)₃CAlMe₂·THF with CF₃COOH in a 1 : 2 molar ratio. Synthesis of [(Me₃Si)₃CAl(O₂CCF₃)₂]₂ (17)

CF₃COOH (0.860 g, 7.54 mmol, 2 eq) was added to a solution of $(Me_3Si)_3CAIMe_2$ ·THF (1.36 g, 3.77 mmol) in toluene (20 mL) and stirred for 1 day. All solvents were removed *in vacuo*. The remaining solid was treated with *n*hexane (20 mL) and filtered. Crystallization in toluene at -20 °C afforded **17** (1.66 g, 1.71 mmol, 45 %) as a colorless solid (decomposing at 170 °C).

Anal. Calcd for C₂₈H₅₄Al₂F₁₂O₈Si₆ (969.19): C, 34.70; H, 5.62. Found: C, 35.0; H, 5.7.

¹H NMR (200 MHz, THF-d₈, ppm): δ 0.23 (s).

¹⁹F NMR (188 MHz, THF-d₈, ppm, external standard C₆F₆): δ -74.8 (s).

²⁹Si NMR (99 MHz, THF-d₈, ppm): δ -3.1 (s).

MS (EI): *m/z* 953 (100 %, *M* - Me).

IR (KBr, Nujol, cm⁻¹): 1758 s, 1690 s, 1668 s, 1260 m, 1220 m, 1168 m, 857 vs, 724 m, 675 m.

4.15. Reaction of $(Me_3Si)_3CAIMe_2$ ·THF with CF₃COOH in a 1 : 3 molar ratio. Synthesis of $[Al_3(\mu_3-O)(\mu-O_2CCF_3)_6(THF)_3]^+[(Me_3Si)_3CAI(OC(O)CF_3)_3]^-$ (18)

CF₃COOH (1.99 g, 16.5 mmol, 3 eq) was added to a solution of $(Me_3Si)_3CAlMe_2$ ·THF (2.00 g, 5.50 mmol) in toluene (20 mL) and stirred for 1 day. All volatile substances were pumped off. The residue was dissolved in toluene/THF (5 : 1) and crystallized for one week at -20 °C. **18** was obtained in 10 % yield (0.180 g, 0.11 mmol) (decomposing at 135 °C).

For the elemental analysis crystals of composition $\mathbf{18}$ + one molecule of C₇H₈ were used. Anal. Calcd for C₄₇H₅₉Al₄F₂₇O₂₂Si₃ (1681.13): C, 33.58; H, 3.54. Found: C, 34.3; H, 3.8. ¹H NMR (200 MHz, THF-d₈, ppm): δ 0.26 (s). ¹⁹F NMR (188 MHz, THF-d₈, ppm, external standard C₆F₆): δ -77.4 (s, 1 F), -75.9 (s, 1 F), -75.8 (s, 1 F).

²⁹Si NMR (99 MHz, THF-d₈, ppm): δ-3.0 (s).

MS (FAB_(pos)): *m*/*z* 991 (10 %, [Al₃(μ₃-O)(μ-O₂CCF₃)₆(THF)₃]), 919 (100 %, [Al₃(μ₃-O)-(μ-O₂CCF₃)₆(THF)₂]).

MS (FAB_(neg)): *m/z*, 597 (100 %, [(Me₃Si)₃CAl(OC(O)CF₃)₃]).

IR (CsI, cm⁻¹): 2962 m, 1763 vs, 1735 vs, 1521 s, 1236 vs, 1179 vs, 1008 m, 860 vs, 803 vs, 735 m, 663 vs, 566 m, 452 m, 410 m, 369 vs.
5. Handling and Disposal of Wastes and Residual Wastes

The solvents were distilled or condensed into cold traps and disposed into halogen-free or halogen-containing solvent containers.

The used NMR solvents were classified into halogen-free or halogen-containing solvents and disposed as heavy metal wastes and halogen containing wastes respectively.

The heavy metal residues were dissolved in nitric acid and stored in special containers for heavy metal wastes after neutralization. Me₃SnCl and Me₄Sn residues were stored in special containers for organic tin waste.

The drying agents (CaCl₂, CaH₂, P₄O₁₀) were neutralized and disposed as base or acid wastes.

Metallic sodium used for drying solvents was collected and recycled [108]. The residual sodium wastes were carefully hydrolyzed in cold 2-propanol and used for cleaning glassware together with residues of drying agents (KOH) in the alkali bath.

The residue of the alkali bath used for cleaning glassware was disposed into the container for basic wastes.

The acid bath used for cleaning glassware was neutralized with Na₂CO₃ and the resulting NaCl solution was washed of in the water drainage system.

Amounts of various types of disposable wastes generated during work:

Metal containing wastes	15 L
Halogen-containing solvent wastes	5 L
Halogen-free solvent wastes	10 L
Acid wastes	10 L
Base wastes	10 L

6. Crystal Data and Refinement Details

Table CD1. Crystal data and structure refinement for the 2 : 1 mixture of compounds 7 + 8

 [110].

Empirical formula	$C_{82}H_{154}Al_{4}F_{12}OSi_{12}Zr_{4} \\$
Formula weight	2193.93
Temperature (K)	150(2)
Crystal size (mm ³)	1.0 x 0.4 x 0.2
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	9.560(2)
<i>b</i> (Å)	16.700(3)
<i>c</i> (Å)	17.537(4)
α (deg)	77.90(3)
β (deg)	87.61(3)
$\gamma(\text{deg})$	83.79(4)
Volume (Å ³)	2720.9(9)
Z	1
Density (calculated) (Mg/m ³)	1.339
Absorption coefficient (mm ⁻¹)	0.596
<i>F</i> (000)	1142
2θ range (deg)	7 - 50
Index ranges	$-11 \le h \le 11, -19 \le k \le 19, -15 \le l \le 20$
Reflections collected	10726
Independent reflections	9606 ($R_{\rm int} = 0.0547$)
Data / restraints / parameters	9593 / 0 / 539
Goodness-of-fit on F^2	1.055
<i>R1, wR</i> 2 [I>2 <i>o</i> (I)]	0.0362, 0.0932
R, wR2 (all data)	0.0432, 0.1032
Largest diff. peak and hole (e·Å ⁻³)	0.615 and -0.640

Empirical formula	$C_{40}H_{74}Al_2F_6OSi_6Zr_2$
Formula weight	1089.93
Temperature (K)	173(2)
Crystal size (mm ³)	0.5 x 0.5 x 0.2
Crystal system	triclinic
Space group	Pī
<i>a</i> (Å)	8.8011(2)
<i>b</i> (Å)	12.5412(4)
<i>c</i> (Å)	12.5572(4)
α (deg)	83.80(1)
β (deg)	79.25(1)
$\gamma(\text{deg})$	77.45(1)
Volume (Å ³)	1286.42(7)
Ζ	1
Density (calculated) (Mg/m ³)	1.407
Absorption coefficient (mm ⁻¹)	0.630
<i>F</i> (000)	566
2θ range (deg)	3 - 57
Index ranges	$-7 \le h \le 11, -15 \le k \le 16, -16 \le l \le 16$
Reflections collected	8746
Independent reflections	$6148 \ (R_{\rm int} = 0.0262)$
Data / restraints / parameters	6125 / 0 / 268
Goodness-of-fit on F^2	1.165
R1, wR2 [I>2 σ (I)]	0.0519, 0.1343
<i>R</i> , <i>wR</i> 2 (all data)	0.0611, 0.1552
Largest diff. peak and hole $(e \cdot Å^{-3})$	1.510 and -0.918

Table CD2. Crystal data and structure refinement for 8 [110].

Table CD3. Crystal data and structure refinement for 9 [110].

(0.5 molecules THF + 0.5 molecules toluene are coordinated to one of the sodium atoms)

Empirical formula	$C_{57.5}H_{140}Al_4F_{12}Na_4O_{3.5}Si_{12}$
Formula weight	1652.62
Temperature (K)	133(2)
Crystal size (mm ³)	0.5 x 0.4 x 0.4
Crystal system	monoclinic
Space group	P2(1)/c
a (Å)	26.465(2)
<i>b</i> (Å)	14.0333(11)
<i>c</i> (Å)	26.162(2)
α (deg)	90
β (deg)	97.766(4)
$\gamma(\text{deg})$	90
Volume (Å ³)	9627.3(13)
Ζ	4
Density (calculated) (Mg/m ³)	1.140
Absorption coefficient (mm ⁻¹)	0.273
<i>F</i> (000)	3540
2θ range (deg)	4 - 45
Index ranges	$-28 \le h \le 28, -9 \le k \le 15, -28 \le l \le 28$
Reflections collected	115448
Independent reflections	12574 ($R_{\rm int} = 0.1382$)
Data / restraints / parameters	12574 / 60 / 814
Goodness-of-fit on F^2	0.956
<i>R1</i> , <i>wR</i> 2 [I>2 <i>o</i> (I)]	0.0615, 0.1643
<i>R</i> , <i>wR</i> 2 (all data)	0.1089, 0.1793
Largest diff. peak and hole $(e \cdot A^{-3})$	0.943 and -0.636

Empirical formula	$C_{36}H_{86}Al_2F_4Li_2O_5Si_6$
Formula weight	911.43
Temperature (K)	133(2)
Crystal size (mm ³)	0.7 x 0.7 x 0.6
Crystal system	triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	12.953(2)
b (Å)	13.442(2)
<i>c</i> (Å)	16.391(2)
α (deg)	89.33(2)
β (deg)	88.04(2)
$\gamma(\text{deg})$	70.02(2)
Volume (Å ³)	2680.6(7)
Ζ	2
Z Density (calculated) (Mg/m ³)	2 1.129
Z Density (calculated) (Mg/m ³) Absorption coefficient (mm ⁻¹)	2 1.129 0.236
Z Density (calculated) (Mg/m ³) Absorption coefficient (mm ⁻¹) F(000)	2 1.129 0.236 988
Z Density (calculated) (Mg/m ³) Absorption coefficient (mm ⁻¹) F(000) 2θ range (deg)	2 1.129 0.236 988 4 - 50
Z Density (calculated) (Mg/m ³) Absorption coefficient (mm ⁻¹) F(000) 2θ range (deg) Index ranges	2 1.129 0.236 988 4 - 50 $-15 \le h \le 15, -16 \le k \le 11, -19 \le l \le 19$
ZDensity (calculated) (Mg/m³)Absorption coefficient (mm ⁻¹) $F(000)$ 2θ range (deg)Index rangesReflections collected	2 1.129 0.236 988 4 - 50 $-15 \le h \le 15, -16 \le k \le 11, -19 \le l \le 19$ 33521
ZDensity (calculated) (Mg/m³)Absorption coefficient (mm ⁻¹) $F(000)$ 2θ range (deg)Index rangesReflections collectedIndependent reflections	2 1.129 0.236 988 4 - 50 $-15 \le h \le 15, -16 \le k \le 11, -19 \le l \le 19$ 33521 9477 ($R_{int} = 0.0409$)
Z Density (calculated) (Mg/m ³) Absorption coefficient (mm ⁻¹) F(000) 2θ range (deg) Index ranges Reflections collected Independent reflections Data / restraints / parameters	2 1.129 0.236 988 4 - 50 $-15 \le h \le 15, -16 \le k \le 11, -19 \le l \le 19$ 33521 9477 ($R_{int} = 0.0409$) 9477 / 924 / 706
ZDensity (calculated) (Mg/m³)Absorption coefficient (mm⁻¹) $F(000)$ 2θ range (deg)Index rangesReflections collectedIndependent reflectionsData / restraints / parametersGoodness-of-fit on F^2	2 1.129 0.236 988 4 - 50 $-15 \le h \le 15, -16 \le k \le 11, -19 \le l \le 19$ 33521 9477 ($R_{int} = 0.0409$) 9477 / 924 / 706 1.049
ZDensity (calculated) (Mg/m³)Absorption coefficient (mm⁻¹) $F(000)$ 2θ range (deg)Index rangesReflections collectedIndependent reflectionsData / restraints / parametersGoodness-of-fit on F^2 $R1, wR2$ [I>2 σ (I)]	2 1.129 0.236 988 4 - 50 $-15 \le h \le 15, -16 \le k \le 11, -19 \le l \le 19$ 33521 9477 ($R_{int} = 0.0409$) 9477 / 924 / 706 1.049 0.0490, 0.1171
ZDensity (calculated) (Mg/m³)Absorption coefficient (mm⁻¹) $F(000)$ 2θ range (deg)Index rangesReflections collectedIndependent reflectionsData / restraints / parametersGoodness-of-fit on F^2 $R1$, $wR2$ [I> 2σ (I)] R , $wR2$ (all data)	2 1.129 0.236 988 4 - 50 $-15 \le h \le 15, -16 \le k \le 11, -19 \le l \le 19$ 33521 9477 ($R_{int} = 0.0409$) 9477 / 924 / 706 1.049 0.0490, 0.1171 0.0730, 0.1313

Table CD4. Crystal data and structure refinement for 10 [111].

Empirical formula	$C_{50}H_{121}Al_3F_{10}Li_4O_5Si_9$
Formula weight	1353.98
Temperature (K)	133(2)
Crystal size (mm ³)	0.6 x 0.6 x 0.6
Crystal system	rhombohedral
Space group	R3
<i>a</i> (Å)	14.899(2)
<i>b</i> (Å)	14.899(2)
<i>c</i> (Å)	30.472(6)
α (deg)	90
β (deg)	90
$\gamma(\text{deg})$	120
Volume (Å ³)	5857.9(16)
Ζ	3
Density (calculated) (Mg/m ³)	1.151
Absorption coefficient (mm ⁻¹)	0.247
<i>F</i> (000)	2184
2θ range (deg)	3 - 50
Index ranges	$-17 \le h \le 17, -17 \le k \le 17, -35 \le l \le 35$
Reflections collected	37248
Independent reflections	4425 ($R_{\rm int} = 0.0490$)
Data / restraints / parameters	4425 / 822 / 410
Goodness-of-fit on F^2	1.086
R1, wR2 [I>2 σ (I)]	0.0323, 0.0841
<i>R</i> , <i>wR</i> 2 (all data)	0.0336, 0.0873
Largest diff. peak and hole $(e Å^{-3})$	0.268 and -0.125

 Table CD5. Crystal data and structure refinement for 11 [111].

Empirical formula	$C_{20}H_{54}Al_2F_5KSi_6$
Formula weight	651.22
Temperature (K)	200(2)
Crystal size (mm ³)	0.6 x 0.2 x 0.2
Crystal system	orthorhombic
Space group	<i>P</i> 2(1)2(1)2(1)
<i>a</i> (Å)	8.9174(11)
<i>b</i> (Å)	15.976(2)
<i>c</i> (Å)	25.206(3)
$\alpha(\text{deg})$	90
β (deg)	90
$\gamma(\text{deg})$	90
Volume (Å ³)	3591.0(8)
Ζ	4
Density (calculated) (Mg/m ³)	1.205
Absorption coefficient (mm ⁻¹)	0.433
<i>F</i> (000)	1392
2θ range (deg)	7 - 50
Index ranges	$-10 \le h \le 10, -19 \le k \le 19, -30 \le l \le 30$
Reflections collected	10531
Independent reflections	$6330 (R_{\text{int}} = 0.0361)$
Data / restraints / parameters	6330 / 571 / 438
Goodness-of-fit on F^2	1.062
<i>R1, wR</i> 2 [I>2 <i>o</i> (I)]	0.0358, 0.0744
<i>R</i> , <i>wR</i> 2 (all data)	0.0447, 0.0796
Largest diff. peak and hole $(e \cdot Å^{-3})$	0.430 and -0.238

Table CD6. Crystal data and structure refinement for 12 [109].

Empirical formula	$C_{30.5}H_{70}AlF_2NSi_3$ (incl. 0.5 molecules of toluene)
Formula weight	600.13
Temperature (K)	213(2)
Crystal size (mm ³)	0.8 x 0.8 x 0.6
Crystal system	monoclinic
Space group	P2(1)/c
<i>a</i> (Å)	17.618(3)
<i>b</i> (Å)	12.917(2)
<i>c</i> (Å)	17.681(3)
α (deg)	90
β (deg)	101.32(2)
$\gamma(\text{deg})$	90
Volume (Å ³)	3.9451(12)
Ζ	4
Density (calculated) (Mg/m ³)	0.999
Absorption coefficient (mm ⁻¹)	0.169
<i>F</i> (000)	1316
2θ range (deg)	7 - 45
Index ranges	$-18 \le h \le 18, -13 \le k \le 13, -15 \le l \le 19$
Reflections collected	9891
Independent reflections	$5134 (R_{\rm int} = 0.0395)$
Data / restraints / parameters	5130 / 0 / 348
Goodness-of-fit on F^2	1.024
R1, wR2 [I>2 σ (I)]	0.1243, 0.3381
R, wR2 (all data)	0.1608, 0.3874
Largest diff. peak and hole $(e \cdot A^{-3})$	1.373 and -0.426

Table CD7. Crystal data and structure refinement for 15 [76].

Energiational formula	
Empirical formula	$C_{47}H_{59}AI_4F_{27}O_{22}SI_3$
Formula weight	1681.13
Temperature (K)	200(2)
Crystal size (mm ³)	1.0 x 0.7 x 0.5
Crystal system	rhombohedral
Space group	<i>R</i> -3
a (Å)	18.313(2)
<i>b</i> (Å)	18.313(2)
<i>c</i> (Å)	18.313(2)
α (deg)	53.472(17)
β (deg)	53.472(17)
$\gamma(\text{deg})$	53.472(17)
Volume (Å ³)	3679.3(7)
Ζ	2
Z Density (calculated) (Mg/m ³)	2 1.517
Z Density (calculated) (Mg/m ³) Absorption coefficient (mm ⁻¹)	2 1.517 0.246
Z Density (calculated) (Mg/m ³) Absorption coefficient (mm ⁻¹) F(000)	2 1.517 0.246 1708
Z Density (calculated) (Mg/m ³) Absorption coefficient (mm ⁻¹) F(000) 2θ range (deg)	2 1.517 0.246 1708 7 - 50
Z Density (calculated) (Mg/m ³) Absorption coefficient (mm ⁻¹) F(000) 2θ range (deg) Index ranges	2 1.517 0.246 1708 7 - 50 $-14 \le h \le 21, -21 \le k \le 21, -12 \le l \le 18$
ZDensity (calculated) (Mg/m³)Absorption coefficient (mm ⁻¹) $F(000)$ 2θ range (deg)Index rangesReflections collected	2 1.517 0.246 1708 7 - 50 $-14 \le h \le 21, -21 \le k \le 21, -12 \le l \le 18$ 4633
ZDensity (calculated) (Mg/m³)Absorption coefficient (mm ⁻¹) $F(000)$ 2θ range (deg)Index rangesReflections collectedIndependent reflections	2 1.517 0.246 1708 7 - 50 $-14 \le h \le 21, -21 \le k \le 21, -12 \le l \le 18$ 4633 4341 ($R_{int} = 0.1241$)
ZDensity (calculated) (Mg/m³)Absorption coefficient (mm ⁻¹) $F(000)$ 2θ range (deg)Index rangesReflections collectedIndependent reflectionsData / restraints / parameters	2 1.517 0.246 1708 7 - 50 $-14 \le h \le 21, -21 \le k \le 21, -12 \le l \le 18$ 4633 4341 ($R_{int} = 0.1241$) 4341 / 599 / 368
ZDensity (calculated) (Mg/m³)Absorption coefficient (mm ⁻¹) $F(000)$ 2θ range (deg)Index rangesReflections collectedIndependent reflectionsData / restraints / parametersGoodness-of-fit on F^2	2 1.517 0.246 1708 7 - 50 $-14 \le h \le 21, -21 \le k \le 21, -12 \le l \le 18$ 4633 4341 ($R_{int} = 0.1241$) 4341 / 599 / 368 1.013
Z Density (calculated) (Mg/m ³) Absorption coefficient (mm ⁻¹) F(000) 2θ range (deg) Index ranges Reflections collected Independent reflections Data / restraints / parameters Goodness-of-fit on F^2 $R1$, wR2 [I>2 σ (I)]	2 1.517 0.246 1708 7 - 50 $-14 \le h \le 21, -21 \le k \le 21, -12 \le l \le 18$ 4633 4341 ($R_{int} = 0.1241$) 4341 / 599 / 368 1.013 0.0712, 0.1918
Z Density (calculated) (Mg/m ³) Absorption coefficient (mm ⁻¹) F(000) 2θ range (deg) Index ranges Reflections collected Independent reflections Data / restraints / parameters Goodness-of-fit on F^2 $R1$, $wR2$ [I> 2σ (I)] R, $wR2$ (all data)	2 1.517 0.246 1708 7 - 50 $-14 \le h \le 21, -21 \le k \le 21, -12 \le l \le 18$ 4633 4341 ($R_{int} = 0.1241$) 4341 / 599 / 368 1.013 0.0712, 0.1918 0.0889, 0.2112

Table CD8. Crystal data and structure refinement for 18 + toluene [96].

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