

# New reagents to introduce weakly coordinating anions of type $\text{Al}(\text{OR}_F)_4^-$ : synthesis, structure and characterization of Cs and trityl salts

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Dedicated to the occasion of the 60th birthday of Prof. Dr. H. Schnöckel.

## Abstract

The facile synthesis of five reagents ( $\text{Cs}^+$  and  $\text{Ph}_3\text{C}^+$  salts) to introduce weakly coordinating anions (WCAs) of type  $\text{Al}(\text{OR}_F)_4^-$  ( $\text{OR}_F$ :  $\text{OC}(\text{H})(\text{CF}_3)_2$ ;  $\text{OC}(\text{CF}_3)_3$ ) or lithium bridged  $\{(\text{R}_F\text{O})_2\text{Al}(\mu\text{-OR}_F)_2(\mu\text{-Li})(\mu\text{-OR}_F)_2\text{Al}(\text{OR}_F)_2\}^-$  ( $\text{Ph}_3\text{C}^+$  salt,  $\text{OR}_F$ :  $\text{OC}(\text{H})(\text{CF}_3)_2$ ) is presented. All of the species were characterized spectroscopically, three of the species  $\{\text{Cs}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]^-$  (**1**);  $\text{Cs}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$  (**2**);  $[\text{Ph}_3\text{C}][\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]_2]^-$  (**4**) also by a X-ray single crystal structure determination. In contrast to the known  $\text{Ag}^+$  salts, the solid  $\text{Cs}^+$  salts **1–2** crystallize unsolvated which makes them suitable starting materials to introduce them as counterions for highly electrophilic and oxidizing cations (i.e. by metathesis with  $\text{MF}_6^-$  salts (M: As, Sb);  $\text{CsMF}_6$  is insoluble in  $\text{SO}_2$ ,  $\text{CH}_2\text{Cl}_2$ , etc.). The anions of **1–2** have thermochemical volumes of  $599 \text{ \AA}^3$  (**1**) and  $758 \text{ \AA}^3$  (**2**) with estimated low lattice potential energies of only 379 (**1**) and 358 (**2**) kJ/mol (cf. 759 kJ/mol for CsF). The trityl salts  $[\text{Ph}_3\text{C}][\text{Al}(\text{OR}_F)_4]^-$  ( $\text{R}_F$ :  $\text{OC}(\text{H})(\text{CF}_3)_2$  (**3**);  $\text{OC}(\text{CF}_3)_3$  (**5**)) and  $[\text{Ph}_3\text{C}][\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]_2]^-$  (**4**) are extremely robust and sealed NMR samples of **3–5** show no sign of decomposition even after storage at  $+70^\circ\text{C}$  for 3 months. The basicity of the anions decreases according to  $\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4^- > \text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]_2^- > \text{Al}(\text{OC}(\text{CF}_3)_3)_4^-$  © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Weakly coordinating anion; Cesium; Aluminum; Trityl; Metathesis; Hydride/alkyl abstraction

## 1. Introduction

Weakly coordinating anions (WCAs) are of great interest for both, applied and fundamental science, i.e. they were recently used to stabilize strongly acidic gas phase species (e.g.  $\text{HC}_{60}^+$ ), unusual electrophilic species (e.g.  $\text{AsBr}_4^+$ ) [2], weak Lewis acid base adducts (e.g.  $\text{Au}(\text{Xe})_4^{2+}$ ,  $\text{Ag}(\text{P}_4)_2^+$ ) [3,4] and to enhance the reactivity of cationic homogenous catalysts [5,6]. Several types of WCAs are now established: halogenated and trifluoromethylated carboranes  $\text{CB}_{10}\text{X}_n\text{H}_{12-n}^-$  ( $n = 1–12$ , X: F, Cl, Br, I,  $\text{CH}_3$ ,  $\text{CF}_3$ ) [2,7], polyfluorinated tetraarylborates  $\text{B}(\text{Ar}_F)_4^-$  ( $\text{Ar}_F$ :  $\text{C}_6\text{F}_5$ ,  $\text{C}_6\text{H}_3(\text{CF}_3)_2$ ) [7,8] and tetra- and hexa-teflato-metallates  $\text{M}(\text{OTeF}_5)_n^-$  ( $n = 4$ ; M: B [9,10];  $n = 6$ ; M: As, Sb, Bi, Nb [11,12]). A recent development is the use of poly- and (per)-fluorinated alkoxy ligands  $\text{OR}_F$  that prevent C–H bond activation and produce a smooth and

non-adhesive surface of the anion (a “teflon” coated anion), i.e. in  $\text{Al}[\text{OC}(\text{Ph})(\text{CF}_3)_2]_4^-$ , [13]  $\text{Al}(\text{OC}_6\text{F}_5)_4^-$ , [14]  $\text{Nb}(\text{OC}_6\text{F}_5)_6^-$ , [16] and  $\text{Nb}[\text{OC}(\text{H})(\text{CF}_3)_2]_6^-$  [14]. Recently, we published [16] the facile preparation of several Li and Ag salts of the  $\text{Al}(\text{OR}_F)_4^-$  anion ( $\text{R}_F$ :  $\text{OC}(\text{H})(\text{CF}_3)_2$ ,  $\text{OC}(\text{CH}_3)(\text{CF}_3)_2$ ,  $\text{OC}(\text{CF}_3)_3$ ). The  $\text{Al}[\text{OC}(\text{CF}_3)_3]_4^-$  anion, which is stable in nitric acid (35 wt.%), was shown to be amongst the most WCAs known. However, the  $\text{Ag}^+$  salts always coordinate solvent molecules that cannot be removed in a dynamic vacuum. This prevents their use as starting materials for highly electrophilic or oxidizing cations that react<sup>2</sup> with chlorinated solvents [17,18,25].

Here, we describe the facile synthesis of  $\text{Cs}[\text{Al}(\text{OR}_F)_4]^-$  ( $\text{R}_F$ :  $\text{OC}(\text{H})(\text{CF}_3)_2$ ,  $\text{OC}(\text{CF}_3)_3$ ) which are ideal and unsolvated

<sup>2</sup> A suitable example where Cs salts are needed is the chemistry of the homopolyatomic chalcogen cations which are known to react with all types of organic solvents. Moreover, the  $\text{S}_8^{2+}$  dication is only stable in the solid state (i.e. it is lattice stabilized) and good quality ab initio calculations [17] showed it to dissociate in the gas phase in a variety of equilibria into all the stoichiometrically possible combinations of sulfur monocations and/or other sulfur dications. Yet only  $\text{S}_4^{2+}$ ,  $\text{S}_8^{2+}$  and  $\text{S}_{19}^{2+}$  were structurally characterized [25]. It is believed, however, that by reducing the overall lattice energies by introducing large and weakly basic anions one may stabilize other, hitherto unknown sulfur cations [17].

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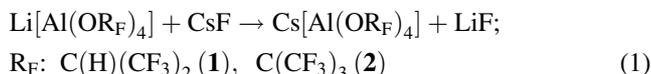
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<sup>1</sup> Brands, Koenig, Feuerhake prepared and characterized  $\text{Cs}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]^-$  (**1**), in partial fulfillment of their advanced inorganic chemistry lab demonstration [1].

starting materials to introduce the  $\text{Al}(\text{OR}_F)_4^-$  anion into  $\text{MF}_6^-$  salts (M: As, Sb) since  $\text{CsAsF}_6$  is insoluble in many solvents (e.g.  $\text{SO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ). The syntheses of  $[\text{Ph}_3\text{C}][\text{Al}(\text{OR}_F)_4]$  ( $\text{R}_F$ :  $\text{OC}(\text{H})(\text{CF}_3)_2$ ,  $\text{OC}(\text{CF}_3)_3$ ) and  $[\text{Ph}_3\text{C}]\{\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]_2\}$ , which are suitable starting materials to introduce the  $\text{Al}(\text{OR}_F)_4^-$  anion by hydride or alkyl abstraction reactions, is also presented (e.g. see synthesis of “ $\text{R}_3\text{Si}^+$ ” [19] or the activation of homogenous catalysts [6,15]).

## 2. Syntheses and spectroscopic characterization

The synthesis of  $\text{Cs}[\text{Al}(\text{OR}_F)_4]$  ( $\text{R}_F$ :  $\text{OC}(\text{H})(\text{CF}_3)_2$  (**1**),  $\text{OC}(\text{CF}_3)_3$  (**2**)) started from in  $\text{CH}_2\text{Cl}_2$  poorly soluble  $\text{Li}[\text{Al}(\text{OR}_F)_4]$  and  $\text{CsF}$  which react with ultrasonic enhancement at 40–50°C overnight to yield the more soluble  $\text{Cs}[\text{Al}(\text{OR}_F)_4]$  ( $\text{R}_F$ :  $\text{OC}(\text{H})(\text{CF}_3)_2$  (**1**),  $\text{OC}(\text{CF}_3)_3$  (**2**)) and  $\text{LiF}$  in almost quantitative yield (Eq. (1)).



This transformation is induced by the higher lattice energy of  $\text{LiF}$  (cf.  $\Delta H_{\text{latt}}$  ( $\text{LiF}$ ): 1049 kJ/mol versus  $\Delta H_{\text{latt}}$  ( $\text{CsF}$ ): 759 kJ/mol) [21]. According to elemental analyses, NMR and Raman spectra as well as X-ray crystal structure

determinations the  $\text{Cs}^+$  cation in **1–2** remained naked and, in contrast to the silver salts [16], coordinated no solvent molecules.

The syntheses of the yellow trityl salts started from  $\text{Ph}_3\text{CCl}$  and  $\text{M}[\text{Al}(\text{OR}_F)_4]$  (M: Li, Ag) in  $\text{CH}_2\text{Cl}_2$  solution at ambient temperature (RT). However,  $[\text{Ph}_3\text{C}][\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$  (**3**), was directly prepared from  $\text{Li}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$  (Eq. (2)) while only half of the lithium was accessible when starting from (dimeric [21])  $\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]$  and a dimeric anion formed in this reaction (Eq. (3)):  $[\text{Ph}_3\text{C}]\{\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]_2\}$  (**4**), in which the  $\text{Li}^+$  cation is coordinated by four oxygen atoms of two  $\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4^-$  units (see below, X-ray section). However, the simple lithium free trityl salt **5** was obtained by reacting  $\text{Ph}_3\text{CCl}$  with  $\text{Ag}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]$  (Eq. (4)).

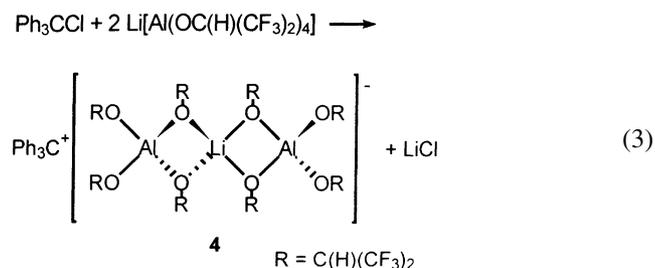
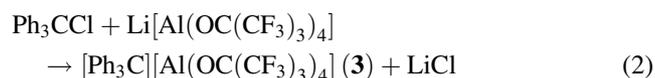


Table 1  
Crystallographic details on structure solution and refinement of **1**, **2** and **4**

Compound	<b>1</b>	<b>2</b>	<b>4</b>
Chemical formula	$\text{C}_{12}\text{H}_4\text{AlCsF}_{24}\text{O}_4$	$\text{C}_{16}\text{AlCsF}_{36}\text{O}_4$	$\text{C}_{43}\text{H}_{23}\text{Al}_2\text{F}_{48}\text{LiO}_8$
Form weight	828.05	1100.05	1640.51
Crystal size (mm)	$0.3 \times 0.3 \times 0.5$	$0.4 \times 0.5 \times 1.2$	$0.2 \times 0.5 \times 0.5$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)$	$Cc$	$P2(1)/c$
$a$ (Å)	9.980(2)	19.220(4)	19.373(4)
$b$ (Å)	12.845(3)	9.786(2)	9.290(2)
$c$ (Å)	10.046(2)	18.939(4)	33.057(7)
$\beta$ (°)	106.24(3)	119.21(3)	94.32(3)
$V$ (Å <sup>3</sup> )	1236.5(4)	3109.1(11)	5932.4(21)
$Z$	2	4	4
$\rho$ (Mg/m <sup>3</sup> ; calculated)	2.224	2.350	1.837
$\mu$ (mm <sup>-1</sup> )	1.733	1.464	0.250
$F(0\ 0\ 0)$	784	2080	3224
Index range	$-12 \leq H \leq 11, -15 \leq K \leq 15,$ $-12 \leq L \leq 12$	$-21 \leq H \leq 25, -12 \leq K \leq 0,$ $-21 \leq L \leq 25$	$-23 \leq H \leq 23, -10 \leq K \leq 11,$ $-40 \leq L \leq 40$
$2\theta$ (°)	51.96	56.24	52.02
Temperature (K)	180	223	190
Reflection collected	19229	4031	30009
Reflection unique	2486	3648	11053
Reflection observed ( $4\sigma$ )	2279	2441	6149
$R_{\text{int}}$	0.1631	0.0582	0.0804
Number of variables	380	553	883
Weighing scheme <sup>a</sup> $w/y$	0.0768/0.0000	0.1167/26.3419	0.0836/0.0000
GOOF	1.028	1.092	0.908
Final $R$ ( $4\sigma$ )	0.0358	0.0784	0.0562
Final $wR2$	0.0922	0.1944	0.1320
Largest resulting peak (e/Å <sup>3</sup> )	0.665	0.805	0.549

<sup>a</sup>  $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$ ;  $P = (F_o^2 + 2F_c^2)/3$ .

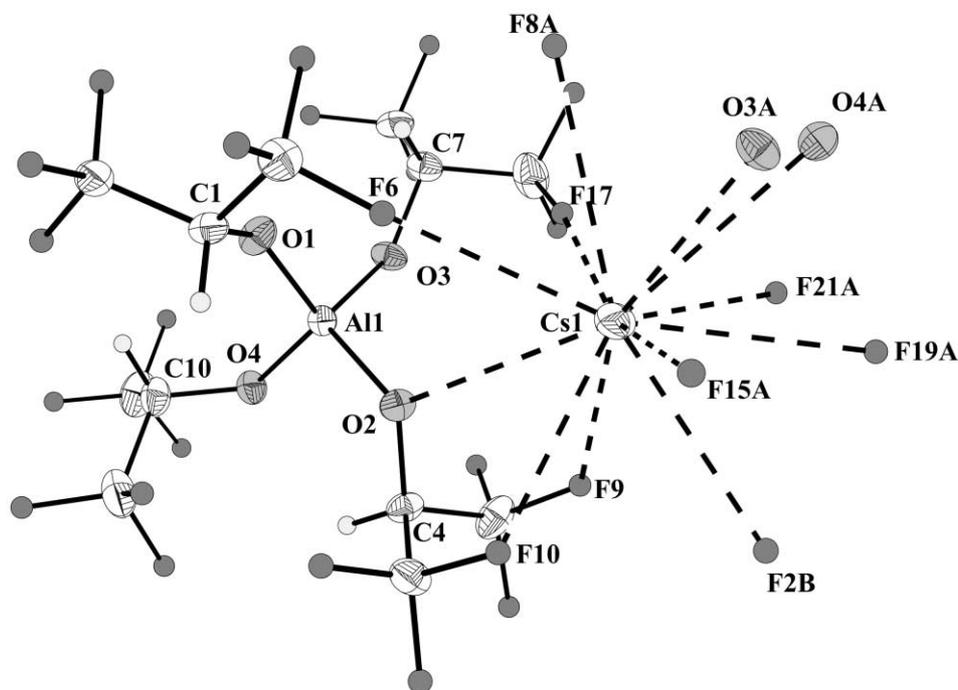
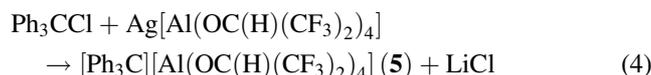


Fig. 1. Section of the solid state structure of **1** showing the anion, the cation and all cation–anion contacts of  $\text{Cs}^+$ . Hydrogen atoms (white) and fluorine atoms (dark gray) are shown as small circles of an arbitrary scale, thermal ellipsoids of carbon (white), oxygen (light gray), aluminum and cesium were drawn at the 25% probability level. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Cs1–F17 3.062(6), Cs1–F6 3.105(5), Cs1–F15A 3.109(6), Cs1–F10 3.116(5), Cs1–O3A 3.147(6), Cs1–F2B 3.278(5), Cs1–F9 3.294(8), Cs1–O4A 3.369(5), Cs1–F8A 3.392(7), Cs1–O2 3.399(5), Cs1–F19A 3.414(9), Cs1–F21A 3.465(9), Al1–O1 1.706(5), Al1–O3 1.734(5), Al1–O4 1.743(5), Al1–O2 1.753(5), C1–O1–Al1 138.8(5), C4–O2–Al1 125.7(4), C7–O3–Al1 130.7(5), C10–O4–Al1 129.8(5).



The reactions started already in the solid state as shown by the immediate color change to yellow upon mixing of the reagents. The dimeric  $\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]_2^-$  anion was found earlier by Strauss and co-workers in an imidazolium salt [21]. The chemical environment of the aluminum atoms in the  $\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4^-$  and the  $\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]_2^-$  anions is sufficiently different to allow the assignment of separate chemical shifts:  $\delta^{27}\text{Al}$  in **4** is 55.2 ppm and in **5** the signal appears at 59.7 ppm. Moreover, the lower symmetry of the central  $\text{AlO}_4$  unit of the dimeric anion in **4** becomes evident and consequently the linewidth of the  $^{27}\text{Al}$  NMR signal in **4** is 820 Hz and only 245 Hz in **5** [22].<sup>3</sup> Sealed NMR samples of **3–5** in  $\text{CDCl}_3$  were stored for 3 months at  $+70^\circ\text{C}$  without noticeable decomposition in the re-recorded  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{27}\text{Al}$ -NMR spectra.

### 3. Crystal structures

Details on the crystal structure solution and refinement are included in Table 1. Diffraction quality crystals of **1–2** were

<sup>3</sup>The line width of the quadrupolar nucleus  $^{27}\text{Al}$  ( $I = 5/2$ ) is very sensitive to a distortion of the local symmetry and, therefore, increased coordination of the  $\text{AlO}_4$  core by the lithium cation led to broader lines.

obtained by slowly cooling a warm ( $40^\circ\text{C}$ ) saturated  $\text{CH}_2\text{Cl}_2$  solution to RT while **4** was recrystallized from 1,3- $(\text{CF}_3)_2\text{C}_6\text{H}_4$  at  $-30^\circ\text{C}$ .

#### 3.1. $\text{Cs}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]$ (**1**)

The colorless needles of **1** crystallize in the chiral monoclinic space group  $P2(1)$  ( $Z = 2$ ). The structure of **1** (see Fig. 1) consists of naked  $\text{Cs}^+$  cations weakly coordinated by three  $\text{Cs} \cdots \text{O}$  and nine  $\text{Cs} \cdots \text{F}$  contacts at 3.147(6) to 3.399(5) Å (to O; average: 3.305 Å) and 3.062(6) to

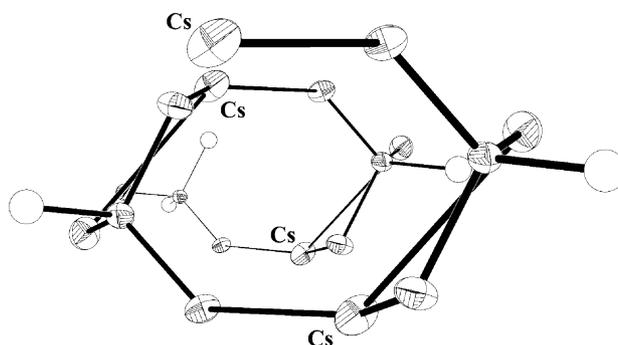


Fig. 2. Helical arrangement of **1** along the  $b$ -axis. All carbon, hydrogen and fluorine atoms were omitted for clarity, non-coordinated oxygen atoms are shown as white circles of an arbitrary size, thermal ellipsoids of the coordinated oxygen atoms, aluminum and cesium were drawn at the 25% probability level.

3.465(9) Å (to F; average: 3.248 Å) and  $\text{Al}[\text{OC}(\text{H})(\text{CF}_3)_2]_4^-$  anions. The Al–O distances and Al–O–C bond angles of the anion range from 1.706(5) to 1.753(5) Å (average: 1.734 Å) and 125.7(4) to 138.8(5)° (average: 131.3°) and are, therefore, in a range typical for this anion [16].

The overall structure of **1** consists of helices along the crystallographic *b*-axis formed by  $-\text{O}-(\text{Cs}-\text{O}-\text{Al}-\text{O})_n-\text{Cs}-$  linkages as shown in Fig. 2.

### 3.2. $\text{Cs}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$ (**2**)

The crystal system of the colorless blocks of **2** is monoclinic *c*-centered, space group *Cc* (*Z* = 4) and the structure consists of naked  $\text{Cs}^+$  cations weakly coordinated by 11  $\text{Cs}\cdots\text{F}$  contacts at 3.046(12) to 3.523(12) Å (average: 3.316 Å) and almost spherical  $\text{Al}[\text{OC}(\text{CF}_3)_3]_4^-$  anions (see Fig. 3). No  $\text{Cs}\cdots\text{O}$  contacts were found in this structure

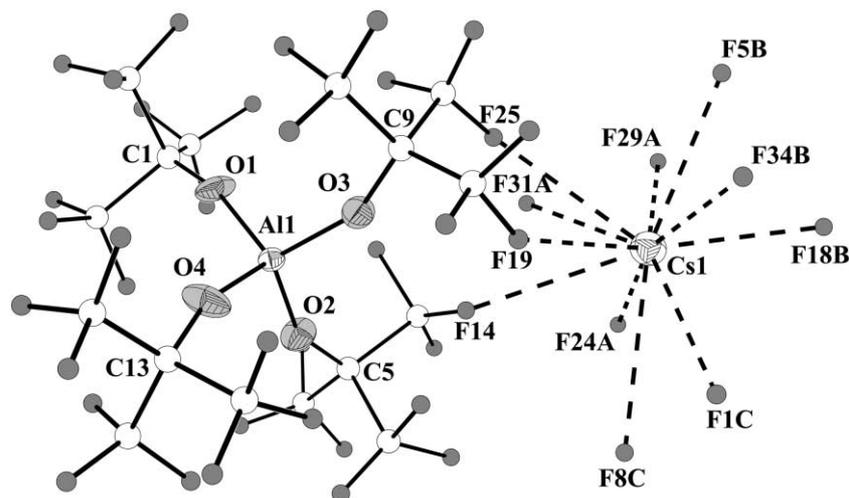


Fig. 3. Section of the solid state structure of **2** showing the anion, the cation and all cation–anion contacts of  $\text{Cs}^+$ . Carbon atoms (white) and fluorine atoms (dark gray) are shown as small circles of an arbitrary scale, thermal ellipsoids of oxygen (light gray), aluminum and cesium were drawn at the 25% probability level. Selected bond lengths (Å) and bond angles (°): Cs1–F18B 3.046(12), Cs1–F5B 3.157(12), Cs1–F14 3.261(13), Cs1–F29A 3.262(10), Cs1–F25 3.27(2), Cs1–F24A 3.28(2), Cs1–F34B 3.300(13), Cs1–F31A 3.409(12), Cs1–F8C 3.463(14), Cs1–F1C 3.505(11), Cs1–F19 3.523(12), Al1–O4 1.695(9), Al1–O3 1.699(10), Al1–O2 1.719(9), Al1–O1 1.728(9), C1–O1–Al1 164.2(9), C5–O2–Al1 152.2(8), C9–O3–Al1 153.6(9), C13–O4–Al1 161.1(11).

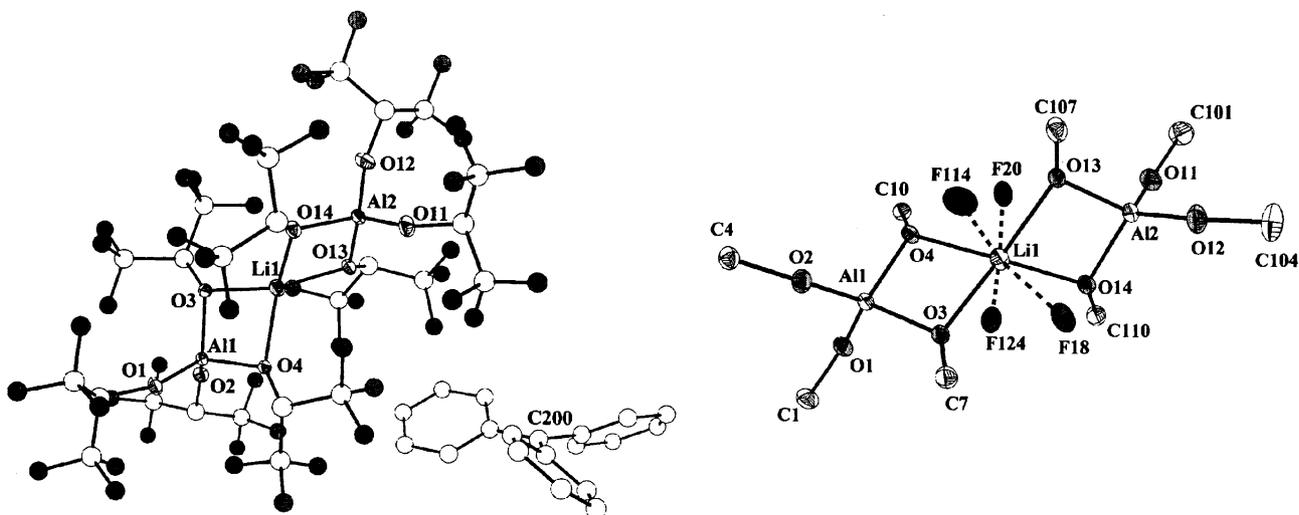


Fig. 4. Section of the solid state structure of **4** showing the anion and the cation (left) and the dimeric core of the anion (right). Carbon atoms (white) and fluorine atoms (dark gray) are shown as small circles of an arbitrary scale (left), thermal ellipsoids were drawn at the 25% probability level. Selected bond lengths (Å) and bond angles (°): Li1–O14 1.996, Li1–O13 1.996, Li1–O3 2.003, Li1–O4 2.038, Li1–F18 2.710, Li1–F124 2.750, Li1–F20 2.883, Li1–F114 2.928, O1–C1 1.371, O1–Al1 1.713, C1–O1–Al1 141.08, O2–C4 1.373, O2–Al1 1.708, C4–O2–Al1 143.30 O3–C7 1.388, O3–Al1 1.765, O3–Li1 2.003, C7–O3–Al1 128.40, C7–O3–Li1 129.81, Al1–O3–Li1 93.91, O4–C10 1.384, O4–Al1 1.771, O4–Li1 2.038, C10–O4–Al1 128.27, C10–O4–Li1 128.06, Al1–O4–Li1 92.51 O11–C101 1.355, O11–Al2 1.704, C101–O11–Al2 143.98, O12–C104 1.363, O12–Al2 1.698, C104–O12–Al2 145.77, O13–C107 1.386, O13–Al2 1.769, O13–Li1 1.996, C107–O13–Al2 125.30, C107–O13–Li1 131.90, Al2–O13–Li1 93.59, O14–C110 1.386, O14–Al2 1.769, O14–Li1 1.996, C110–O14–Al2 127.11, C110–O14–Li1 130.74, Al2–O14–Li1 93.59. S.D. of bond lengths (Å): Al–O 0.005, Li–O 0.006, C–O 0.004 and bond angles (°): 0.1–0.3.

in agreement with the lower nucleophilicity of this anion [16]. The Al–O distances and Al–O–C bond angles of the anion are shorter than in **1** and range from 1.695(9) to 1.728(9) Å (average: 1.710 Å) and 152.2(8) to 164.2(9)° (average: 157.8°), a range typical for this anion [16]. The solid state packing of **2** is determined by the large anion which forms a slightly distorted cubic closed packing where the Cs<sup>+</sup> cations occupy half of the tetrahedral interstices (ZnS structure). The observed ZnS packing of **2** is in agreement with the radius ratio rules ( $r_{\text{cat}}/r_{\text{an}} = 0.349$ , see in the following sections) which require a ratio between  $0.225 < r_{\text{cat}}/r_{\text{an}} < 0.414$  [23].

### 3.3. $[\text{Ph}_3\text{C}]\{\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]\}_2$ (**4**)

Yellow block like single crystals of **4** are *c*-centered monoclinic, space group *Cc* ( $Z = 4$ ). The solid state structure consists of isolated  $\text{CPh}_3^+$  cations and  $\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]^-$  anions. The geometry of the trityl cation is typical and shall not be discussed. In the anion the polarizing central Li<sup>+</sup> cation coordinates two  $\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4^-$  anions that serve as tetradentate  $\text{O}_2\text{F}_2$  ligands (see Fig. 4). The primary Li–O coordination ( $d(\text{Li–O}) = 1.996(6)$  to  $2.038(6)$  Å, average: 2.008 Å) is distorted tetrahedral and the two planar four membered  $\text{AlO}_2\text{Li}$  rings include an angle of 69.6°. The coordination environment of the Li<sup>+</sup> cation is further saturated by four weak Li···F contacts at 2.710(7) to 2.928(7) Å (average: 2.818 Å) giving a distorted square antiprismatic environment of Li<sup>+</sup>. The  $\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4^-$  anions exhibit two sets of Al–O distances and Al–O–C bond angles to di- and tri-coordinated oxygen atoms at  $1.706 \pm 0.008$  Å ( $\text{O}_{\text{di}}$ ) and  $1.769 \pm 0.004$  Å ( $\text{O}_{\text{tri}}$ ) as well as  $143.5 \pm 2.4^\circ$  ( $\text{O}_{\text{di}}$ ) and  $127.3 \pm 2^\circ$  ( $\text{O}_{\text{tri}}$ ). The structural parameters of the anion in **4** are similar to the ones observed in the only previous example [21].

## 4. Assignment of thermochemical radii and volumes to $\text{Al}(\text{OR})_4^-$

Thermochemical volumes and radii, which are needed for thermodynamic calculations [24,25]<sup>4</sup>, were established for **1–2**. The shortest Cs–Al separation in the structure of **2** is 6.375 Å and with the Goldschmidt radius [26] of Cs<sup>+</sup> of 1.65 Å a thermochemical radius 4.725 Å followed for the  $\text{Al}[\text{OC}(\text{CF}_3)_3]_4^-$  anion. Compound **1** does not form an ionic lattice which precludes the determination of a thermochemical radius of the  $\text{Al}[\text{OC}(\text{H})(\text{CF}_3)_2]_4^-$  anion. However, a thermochemical volume can be assigned to both anions. With the knowledge of the thermochemical volume of the Cs<sup>+</sup> cation ( $18.82 \text{ \AA}^3$ ) [26] a volume of 758 (599) Å<sup>3</sup> followed for the  $\text{Al}[\text{OC}(\text{CF}_3)_3]_4^- \cdot (\text{Al}[\text{OC}(\text{H})(\text{CF}_3)_2]_4^-)$  anion and, utilizing Jenkins' and Passmore's volume based modified Kapustinskii equation [26] the lattice potential energy of **1** (**2**) was calculated to be 379 (359) kJ/mol.

These values may be compared to the lattice potential energy of CsF of 759 kJ/mol and add evidence to our previous comment that by using large anions the overall lattice energies are reduced and gas phase conditions are approached in the solid state.

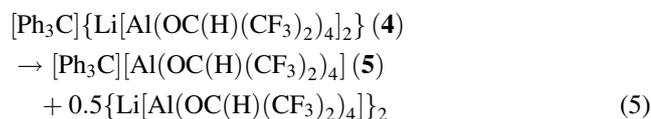
## 5. Discussion

Solid state structures of unsolvated simple salts of WCAs are very rare and, therefore, **1–2** are important examples of this kind that additionally allowed the assignment of thermochemical (an)-ionic radii and volumes. With the thereby estimated lattice potential enthalpies the stability of existing and hypothetical salts can be judged by Born–Fajans–Haber cycle calculations (for examples, see the following sections and [16,17,25]). The unsolvated nature of Cs<sup>+</sup> in **1–2** is very important when the  $\text{Al}(\text{OR})_4^-$  anions shall be introduced as counterions for highly electrophilic and/or strongly oxidizing cations that react with the coordinated solvent molecules, i.e. as found in the solid state structures of  $\text{Ag}[\text{Al}(\text{OR})_4]$  [16]. The coordination number of 11–12 of the Cs cation in **1–2** may be compared to  $\text{Cs}(\text{LiF}_2)^5$  [27] (and  $\text{Cs}(\text{SbF}_6)$ ) [28]. In the latter salts the Cs atom is coordinated by six shorter Cs···F contacts at 2.96–3.15 Å (3.12 Å) and two (six) longer contacts at 3.50 and 3.53 Å (3.38 Å) which are close to the distances found in **1–2** or CsF (coordination number = 8,  $d(\text{Cs–F}) = 2.936$  Å). However, the average lengths of the Cs contacts in **1–2** (3.29 and 3.32 Å) are slightly longer than those in  $\text{Cs}(\text{LiF}_2)$  and  $\text{Cs}(\text{SbF}_6)$  (3.17 and 3.25 Å) as well as the only other simple  $\text{Cs}^+\text{A}^-$  structure with a very large and weakly coordinating anion A<sup>−</sup>:  $\text{Cs}[\text{Sb}(\text{OTeF}_5)_6]$  (3.24 Å) [29]. This again underlines the weakly basic character of the anions in **1–2**.

The assignment of the ionic volumes of the  $\text{Al}(\text{OR})_4^-$  anions allowed to establish the solid state enthalpy of reaction for Eq. (1) in a suitable Born–Fajans–Haber cycle [30]<sup>6</sup>:

$$\Delta H \text{ (Eq. (1), solid state)} = -317 \text{ kJ/mol (1); } \\ 288 \text{ kJ/mol (2)}$$

The existence of the dimeric  $\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]_2^-$  anion in **4** is remarkable and indicates that this mode of aggregation is more favorable than the disproportionation according to Eq. (4):



<sup>5</sup> Containing tetrahedral  $\text{LiF}_4$  moieties.

<sup>6</sup> Utilizing the experimental [30] lattice energies of LiF (1049 kJ/mol), CsF (759 kJ/mol) and the calculated [26] lattice energies of  $\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]$  (382 kJ/mol),  $\text{Cs}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]$  (379 kJ/mol),  $\text{Li}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$  (361 kJ/mol) and  $\text{Cs}[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]$  (359 kJ/mol) [ $V_{\text{thermochem}}(\text{Li}^+) = 1.99 \text{ \AA}^3$ ].

<sup>4</sup> See [17,25,26] for examples.

The dissociation energy of the  $\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]_2^-$  anion must be large to account for this phenomenon, since the lattice potential energy of **5** [31]<sup>7</sup> was estimated [26] to be larger than that of **4** (348 versus 310 kJ/mol) and on the left side 0.5 additional molecules of (dimeric)  $\{\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]\}_2$  are formed. With a suitable Born–Fajans–Haber cycle (see footnote 6,7) the gaseous dissociation energy of  $\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]_2^-$  giving 0.5  $\{\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]\}_2$  and  $\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4^-$  was estimated to be greater than 204 kJ/mol. This shows that the dimeric  $\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]_2^-$  anion is a suitable candidate for a large and robust WCA. The basicity of the three different anions in **3–5** may be established by a comparison of the <sup>13</sup>C NMR shifts of the “cationic” central carbon atom  $\text{C}^+(\text{Ph})_3$  which follow  $\mathbf{5} < \mathbf{4} < \mathbf{3}$  or  $210.8 < 211.1 < 211.6$  (all spectra run in  $\text{CDCl}_3$ ; cf. 210,0 in acetone-*d*<sub>6</sub> in  $\text{CPh}_3^+[\text{CB}_{11}\text{Br}_6\text{H}_6]^-$  [32]). The least coordinated trityl cation containing the least coordinating anion of this series will presumably appear at lowest field and in agreement with earlier results [16] for the anions in **3** and **5** — the basicity of the anions decreases as follows:  $\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4^- > \text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]_2^- > \text{Al}(\text{OC}(\text{CF}_3)_3)_4^-$ . Therefore, and in contrast to other trityl salts which have to be stored at lower temperatures to prevent decomposition (i.e.  $[\text{Ph}_3\text{C}][\text{BF}_4]$ ), **3–5** are extremely robust.

## 6. Conclusion

The synthesis and characterization of five new reagents to introduce WCAs was achieved. Preliminary investigations show that the  $\text{Al}[\text{OC}(\text{CF}_3)_3]_4^-$  anion appeared to be stable in the presence of the extremely electrophilic and oxidizing  $\text{S}_4^{2+}$  cation [33]<sup>8</sup> which would react with  $\text{CH}_2\text{Cl}_2$ . This shows that the  $\text{Al}[\text{OC}(\text{R})(\text{CF}_3)_2]_4^-$  anions (R: H,  $\text{CF}_3$ ), introduced by metathesis of **1–2** or hydride or alkyl ion abstraction using **3–5**, are useful counterions to stabilize highly reactive hitherto unknown cationic species in many areas of synthetic chemistry and catalysis.

## 7. Experimental

### 7.1. General experimental procedures

All manipulations were performed using standard Schlenk or dry box techniques in an atmosphere of purified

dinitrogen or argon ( $\text{H}_2\text{O}$  and  $\text{O}_2 < 1$  ppm). All solvents were rigorously dried by standard procedures, distilled, degassed prior to use and stored under  $\text{N}_2$ . NMR spectra were recorded on a Bruker AC250 spectrometer and referenced against external  $\text{SiMe}_4$  (<sup>1</sup>H, <sup>13</sup>C) and aqueous  $\text{AlCl}_3$  (<sup>27</sup>Al). Raman spectra were recorded on a Bruker IFS 66v spectrometer equipped with the Raman module FRA106 in sealed mp capillaries. Elemental analyses were performed by the analytical laboratory of the institute.  $\text{LiAl}[\text{OC}(\text{R})(\text{CF}_3)_2]_4$  were prepared according to the literature [27].

### 7.2. General procedure for the syntheses of $\text{CsAl}[\text{OC}(\text{R})(\text{CF}_3)_2]_4$

1.3–1.5 equivalents of CsF and 1.0 equivalents of  $\text{LiAl}[\text{OC}(\text{R})(\text{CF}_3)_2]_4$  were weighed into a single piece two-bulb frit plate vessel closed with Young valves. Approximately 10 ml  $\text{CH}_2\text{Cl}_2$  per 1 g of Lithium salt were added and the resulting suspension was exposed to ultrasound over night (heating to about 40–50°C) (caution:  $\text{CH}_2\text{Cl}_2$  has a bp of 40°C). A colorless solution over some colorless precipitate formed which is best filtered warm (40°C). After five or six washings of the colorless precipitate all soluble Cs salt has been separated from the insoluble LiF. Upon removal of all the volatiles in vacuo, the in  $\text{CH}_2\text{Cl}_2$  medium soluble Cs salts were isolated in 87–89% yield.

### 7.3. $\text{CsAl}[\text{OC}(\text{H})(\text{CF}_3)_2]_4$ (**1**)

$\text{LiAl}[\text{OC}(\text{H})(\text{CF}_3)_2]_4$  (2.097 g, 2.998 mmol), CsF (0.684 g, 4.5 mmol), yield: 2.160 g (87%) of mp 83–85°C. Three attempts to obtain a Raman spectrum of **1** failed.

<sup>1</sup>H-NMR (250 MHz,  $\text{CD}_2\text{Cl}_2/5\%$  THF, 25°C):  $\delta = 4.44$  (<sup>3</sup>*J*<sub>H,F</sub> = 6.20 Hz); <sup>13</sup>C-NMR (63 MHz,  $\text{CD}_2\text{Cl}_2/5\%$  THF, 25°C):  $\delta = 72.7$  (<sup>2</sup>*J*<sub>C,F</sub> = 32.12 Hz), 125 (<sup>1</sup>*J*<sub>C,F</sub> = 286.4 Hz); <sup>27</sup>Al-NMR (78 MHz,  $\text{CD}_2\text{Cl}_2/5\%$  THF, 25°C):  $\delta = 61.7$  (*h*<sub>1/2</sub> = 748 Hz); anal. calc. for  $\text{C}_{12}\text{H}_4\text{Al}_1\text{O}_4\text{F}_{24}$  (828.05): C 17.41, H 0.49; found: C 17.15, H 0.63.

### 7.4. $\text{CsAl}[\text{OC}(\text{CF}_3)_3]_4$ (**2**)

$\text{LiAl}[\text{OC}(\text{CF}_3)_3]_4$  (4.302 g, 4.417 mmol), CsF (1.006 g, 6.625 mmol), yield: 4.337 g (89%) of mp 272–274°C.

<sup>13</sup>C-NMR (63 MHz,  $\text{CD}_2\text{Cl}_2$ , 25°C):  $\delta = 121.8$  (<sup>1</sup>*J*<sub>C,F</sub> = 292.1 Hz); <sup>27</sup>Al-NMR (78 MHz,  $\text{CD}_2\text{Cl}_2$ , 25°C):  $\delta = 34.7$  (*h*<sub>1/2</sub> = 28 Hz); FT-Raman:  $\nu(\%) = 798$  (100), 763 (20), 744 (83), 570 (13), 560 (17), 543 (7), 536 (47), 330 (sh), 321 (80), 288 (20), 233 (20); anal. calc. for  $\text{C}_{16}\text{Al}_1\text{Cs}_1\text{O}_4\text{F}_{36}$  (1100.05): C 17.47; found: C 16.60.

### 7.5. $[\text{Ph}_3\text{C}]\{\text{Al}[\text{OC}(\text{CF}_3)_3]_4\}$ (**3**)

$\text{LiAl}[\text{OC}(\text{CF}_3)_3]_4$  (1.413 g, 1.451 mmol) and  $\text{Ph}_3\text{CCl}$  (0.405 g, 1.451 mmol) were weighed into a Schlenk vessel (yellow coloring). Upon addition of 15 ml  $\text{CH}_2\text{Cl}_2$  a yellow solution over little colorless precipitate had formed. After

<sup>7</sup> With the knowledge of the unit cell volume of **4** of 1483 Å<sup>3</sup> followed a lattice potential energy of 310 kJ/mol. The unit cell volume of **5** was estimated by subtracting the known [16,25] thermochemical volumes of  $\text{Li}^+$  (2 Å<sup>3</sup>) and  $\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4^-$  (599 Å<sup>3</sup>) from the volume of **4** ( $V(\mathbf{5}) = 882 \text{ \AA}^3$ ) giving a lattice potential energy of **5** of 348 kJ/mol. The sublimation enthalpy of the dimeric  $\{\text{Li}[\text{Al}(\text{OC}(\text{H})(\text{CF}_3)_2)_4]\}_2$  was estimated based on a previously [16] employed formula as 333 kJ/mol.

<sup>8</sup> Introduced via a metathesis reaction with **2**; Passmore, personal communication.

stirring the mixture over night the suspension was filtered, all volatiles were removed from the filtrate in vacuo and the remaining yellow material was washed with three portions of *n*-pentane (5 ml). Yield: 1.611 g (92%) of mp 135–140°C (dec.). Recrystallization of part of this yellow material from 1,3(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> gave yellow crystals which were apparently twinned (hexagonal cell:  $a = b = 16.095 \text{ \AA}$ ,  $c = 14.627 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 120^\circ$ ).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 7.65$  (d, 6H), 7.89 (t, 6H), 8.28 (t, 3H); <sup>13</sup>C-NMR (63 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 121.4$  (q, CF<sub>3</sub>, <sup>1</sup>J<sub>C,F</sub> = 293.0 Hz), 131 (Ph), 140 (Ph), 142.6 (Ph), 143.8 (Ph), 211.6 (Ph<sub>3</sub>C<sup>+</sup>); <sup>27</sup>Al-NMR (78 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 34$  ( $h_{1/2} = 16$  Hz); anal. calc. for C<sub>35</sub>H<sub>15</sub>Al<sub>1</sub>O<sub>4</sub>F<sub>36</sub> (1210.44): C 34.73, H 1.25; found: C 34.02, H 1.64.

#### 7.6. [Ph<sub>3</sub>C]{Li[Al[OC(H)(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub>]} (4)

LiAl[OC(H)(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (6.371 g, 9.075 mmol) and Ph<sub>3</sub>CCl (1.265 g, 4.538 mmol) were weighed into a Schlenk vessel (yellow coloring). Upon addition of 30 ml CH<sub>2</sub>Cl<sub>2</sub> a yellow solution over larger amounts of colorless precipitate had formed. After stirring the mixture over night the suspension was filtered, all volatiles of the filtrate were removed in vacuo and the remaining solid yellow material was washed with three portions of *n*-pentane (5 ml); yield 2.015 g (27%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 4.41$  (sept., 8H, <sup>2</sup>J<sub>H,F</sub> = 5.8 Hz), 7.64 (d, 6H), 7.87 (t, 6H), 8.26 (t, 3H); <sup>13</sup>C-NMR (63 MHz, CDCl<sub>3</sub>):  $\delta = 70.8$  (sept., OC, <sup>2</sup>J<sub>C,F</sub> = 33.1 Hz), 122.3 (q, CF<sub>3</sub>, <sup>1</sup>J<sub>C,F</sub> = 284.1 Hz), 130.1 (Ph), 139.9 (Ph), 142.2 (Ph), 143.8 (Ph), 211.1 (Ph<sub>3</sub>C<sup>+</sup>); <sup>27</sup>Al-NMR (78 MHz, CDCl<sub>3</sub>):  $\delta = 55.2$  ( $h_{1/2} = 820$  Hz).

#### 7.7. [Ph<sub>3</sub>C]{Al[OC(H)(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub>} (5)

AgAl[OC(H)(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> (1.151 g, 1.433 mmol) and Ph<sub>3</sub>CCl (0.408 g, 1.463 mmol) were weighed into a Schlenk vessel (yellow coloring). Upon addition of 15 ml CH<sub>2</sub>Cl<sub>2</sub> a yellow solution over little colorless precipitate had formed. After stirring the mixture over night the suspension was filtered, all volatiles were removed in vacuo and the remaining solid yellow material was washed with three portions of *n*-pentane (5 ml); yield 1.381 g (83%).

<sup>1</sup>H-NMR (250 MHz, CDCl<sub>3</sub>, 25°C):  $\delta = 4.42$  (sept., 4H, <sup>2</sup>J<sub>H,F</sub> = 6.0 Hz), 7.62 (d, 6H), 7.88 (t, 6H), 8.25 (t, 3H); <sup>13</sup>C-NMR (63 MHz, CDCl<sub>3</sub>):  $\delta = 70.9$  (sept., OC, <sup>2</sup>J<sub>C,F</sub> = 32.5 Hz), 122.7 (q, CF<sub>3</sub>, <sup>1</sup>J<sub>C,F</sub> = 284.4 Hz), 130.8 (Ph), 139.9 (Ph), 142.4 (Ph), 143.8 (Ph), 210.8 (Ph<sub>3</sub>C<sup>+</sup>); <sup>27</sup>Al-NMR (78 MHz, CDCl<sub>3</sub>):  $\delta = 59.7$  ( $h_{1/2} = 245$  Hz).

#### 7.8. X-ray crystal structure determinations

Data collection for X-ray structure determinations were performed on a STOE STADI4 four circle (2) or a STOE IPDS diffractometer (1,4) using graphite-monochromated

Mo K $\alpha$  (0.71073 Å) radiation. Single crystals were mounted in perfluoroether oil on top of a glass fiber and then brought into the cold stream of a low temperature device so that the oil solidified. All calculations were performed on PCs using the Siemens SHELX93 software package. The structures were solved by the Patterson heavy atom method (Cs salts) or direct methods (trityl salt) and successive interpretation of the difference Fourier maps, followed by least-squares refinement. Crystals of 1 were racemically twinned (ratio 52:48). One OC(CF<sub>3</sub>)<sub>3</sub> ligand of 2 showed a rotational disorder and three additional carbon positions with a 24% occupation had to be defined. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions by a riding model using fixed isotropic parameters. Relevant data concerning crystallography, data collection and refinement details are compiled in Table 1. Further details on the crystal structure determination are deposited at the Cambridge Crystallographic Data Centre as supplementary publication number CCDC153359-153362. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.<sup>9</sup>

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