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Notes

Syntheses and Structures of New Organoaluminum Fluorides†

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Summary: This paper reports the synthesis of $(Cp_2ZrMe)(\mu\text{-}F)[(Me_3Si)_3CAlF_2]$ *(**1**),* $[(Cp_2Zr)(\mu\text{-}F)_2[(Me_3Si)_3CAlF]]_2O$ *(**2**), and* $[Na(Me_3Si)_3CAlF_3(THF)]_4$ *(**3**). **1** was prepared by the reaction of* $[(Me_3Si)_3CAlF_2]_3$ *with* Cp_2ZrMe_2 *and* Me_3SnF*. Compound **1** reacts with THF to form **2**. The reaction of* $(Me_3Si)_3CAlMe_2(THF)$ *with* Me_3SnF *and NaCl affords **3**. The molecular structures of compounds **1**−**3** have been determined by single-crystal X-ray structural analysis.*

Introduction

The trimeric compound $[(Me_3Si)_3CAlF_2]_3$ is a Lewis acid that is capable of accepting fluoride ions.[1] The resulting anions are $[(Me_3Si)_3CAlF_3]^-$ and $[((Me_3Si)_3C)_2Al_2(\mu\text{-}F)F_4]^-$. These anions, due to their ability to coordinate to a cationic metal center, offer the possibility of preparing cubic arrays such as $[Li(Me_3Si)_3CAlF_3(THF)]_4$,[2] the unusual complexes $[((Me_3Si)_3C)_4Al_4K_2(\mu\text{-}F)_2F_8(THF)_4]$,[1a] or compounds containing weakly coordinating anions such as $[Ag(toluene)_3]^+[\{((Me_3Si)_3C)_2Al_2(\mu\text{-}F)F_4\}_2Li]^-$.[1b] Compounds of the type $[Cp_{4-x}MX_{x-1}]^+[RAlX'_3]^-$ (X, X′ = alkyl, aryl, halide) are of particular interest as catalysts for olefin polymerization.[1a,3] The $[(Me_3Si)_3CAlF_3]^-$ anion should be able to stabilize the $[Cp_2ZrMe]^+$ cation. Therefore, we attempted to synthesize the compound containing this ion pair. In the following account we describe the synthesis and structures of $(Cp_2ZrMe)(\mu\text{-}F)[(Me_3Si)_3CAlF_2]$ (**1**), $[(Cp_2Zr)(\mu\text{-}F)_2[(Me_3Si)_3CAlF]]_2O$ (**2**), and $[Na(Me_3Si)_3CAlF_3(THF)]_4$ (**3**).

Experimental Section

General Data. All experiments were performed using standard Schlenk techniques 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. All solvents were distilled from sodium/benzophenone and degassed prior to use. $[(Me_3Si)_3CAlF_2]_3$,[1a] Cp_2ZrMe_2,[4] Me_3SnF,[5] and $(Me_3Si)_3CAlMe_2(THF)$[6] were prepared as described in the literature. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen.[7] NMR spectra were recorded on a Bruker AM 250 and were externally referenced to Me_4Si and $CFCl_3$, respectively (m_c = centered multiplet). FT-IR spectra were measured on a Bio-Rad FTS-7 as Nujol mulls between KBr plates in the range of 4000−400 cm^{-1}. Melting points were measured in sealed glass tubes and are not corrected.

Crystal structure solutions and refinements for a 2:1 mixture of compounds **1** and **2, 2**, and **3** are shown in Table 1. Data for a 2:1 mixture of compounds **1** and **2** were collected on a Stoe four-circle diffractometer, for compound **2** on a Bruker AXS SMART CCD system, and for compound **3** on a Stoe-Siemens-Huber four-circle diffractometer with a Siemens SMART CCD area detector. Mo Kα radiation (λ = 0.710 73 Å) was used in all cases. Semiempirical absorption corrections for **2** and **3** were performed using the program SADABS.[8] All structures were solved by direct methods[9] and refined anisotropically with SHELXTL. Hydrogen atoms were included using the riding model, with U_{iso} tied to the U_{iso} value of the parent atom.

Preparation of $(Cp_2ZrMe)(\mu\text{-}F)[(Me_3Si)_3CAlF_2]$ (1). A solution of trimethyltin fluoride (0.464 g, 2.54 mmol), $[(Me_3Si)_3CAlF_2]_3$ (0.750 g, 0.84 mmol, 0.33 equiv), and Cp_2ZrMe_2 (0.640 g, 2.54 mmol) in toluene (40 mL) was stirred for 24 h at 0 °C. The solution was then warmed to room temperature and stirred for another 3 days. After filtration, the solid was recrystallized from toluene/hexane (4:1) at −20 °C. **1** was obtained as a colorless solid (0.90 g, 68%) that decomposes slowly at 200 °C. ^1H NMR (250.130 MHz, C_6D_6): δ 6.36 (s, C_5H_5, 10H); 0.56 (s, Zr−CH_3, 3H); 0.48 (s, Si−CH_3, 27H). ^{19}F NMR (235.320 MHz, C_6D_6): δ −161.8 (s, Al(μ-F)Zr); −165.4

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† Dedicated to Professor Jürgen Wolfrum on the occasion of his 60th birthday.

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Table 1. Crystallographic Data for 2:1 Mixture of Compounds 1 and 2, 2, and 3

	2:1 mixture of **1** + **2**	**2**	**3**
empirical formula	$C_{82}H_{154}Al_4F_{12}OSi_{12}Zr_4$	$C_{40}H_{74}Al_2F_6OSi_6Zr_2$	$C_{57.5}H_{140}Al_4F_{12}Na_4O_{3.5}Si_{12}$
fw	2193.93	1089.93	1652.66
temp (K)	150(2)	173(2)	133(2)
cryst size (mm)	1.00 × 0.40 × 0.20	0.50 × 0.50 × 0.20	0.50 × 0.40 × 0.40
cryst syst	triclinic	triclinic	monoclinic
cryst group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	9.560(2)	8.8011(2)	26.465(2)
b (Å)	16.700(3)	12.5412(4)	14.0333(11)
c (Å)	17.537(4)	12.5572(4)	26.162(2)
α (deg)	77.90(3)	83.80(1)	90
β (deg)	87.61(3)	79.25(1)	97.766(4)
γ (deg)	83.79(4)	77.45(1)	90
cell vol (Å^3)	2720.9(9)	1286.42(7)	9627.3(13)
Z	1	1	4
ρ_c (g mm^{-3})	1.339	1.407	1.140
μ (mm^{-1})	0.596	0.630	0.273
F(000)	1142	566	3540
2θ range (deg)	3.53−25.04	1.65−28.27	2.05−22.50
no. of measd, unique data	10 726, 9606	8746, 6148	115 448, 12 574
R_{int}	0.0547	0.0262	0.1382
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0362, 0.0932	0.0519, 0.1343	0.0615, 0.1643
R1, wR2 (all data)	0.0432, 0.1032	0.0611, 0.1552	0.1089, 0.1793
goodness of fit, S[c]	1.055	1.165	0.956
no. of data/restraints/params	9593/0/539	6125/0/268	12 574/60/814
largest diff peak/hole (e Å^{-3})	0.615/−0.640	1.510/−0.918	0.943/−0.636

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)^2]/[\sum(n - p)]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [F_o^2 + 2F_c^2]/3$.

(s, AlF_2). IR (KBr, Nujol, cm^{-1}): 1251, 1016, 863, 797, 770, 680, 615, 546. Anal. Calcd for $C_{21}H_{40}AlF_3Si_3Zr$: C, 45.69; H, 7.30. Found: C, 44.6; H, 6.9.

Preparation of a Crystalline 2:1 Mixture of Compounds 1 and 2. Dissolving $(Cp_2ZrMe)(\mu\text{-}F)[(Me_3Si)_3CAlF_2]$ (**1**; 0.20 g, 0.36 mmol) in a mixture of THF/toluene/hexane (1:8:2) and cooling the solution to −20 °C for 4 weeks resulted in the formation of a mixture of crystals of composition of **1** and **2**. Only the crystals that formed were used for the characterization of this mixture.

Preparation of $[Na(Me_3Si)_3CAlF_3(THF)]_4$ (3). A mixture of trimethyltin fluoride (2.19 g, 12 mmol), NaCl (0.47 g, 8.0 mmol), and $(Me_3Si)_3CAlMe_2(THF)$ (0.72 g, 2.0 mmol) in THF (20 mL) was stirred for 4 days. The solvent was removed in vacuo. The residue was washed with pentane (5 mL). The solid was then extracted with toluene (40 mL), and the solvent was removed under reduced pressure. A colorless solid (0.33 g, 40%) was obtained, which can be heated to 300 °C without decomposition or melting. ^{1}H NMR (250.130 MHz, C_6D_6): δ 3.68 (m$_c$, 4 H, OCH_2CH$_2$), 1.45 (m$_c$, 4 H, OCH$_2$CH_2), 0.41 (s, 27 H, SiCH_3). ^{19}F NMR (235.320 MHz, C_6D_6): δ −176.68 (s). ^{29}Si NMR (49.693 MHz, C_6D_6): δ −3.47 (s). IR (KBr, Nujol, cm^{-1}): 1260, 863, 726, 671. Anal. Calcd for $C_{56}H_{140}Al_4F_{12}Na_4O_4Si_{12}$: C, 40.95; H, 8.59. Found: C, 40.0; H, 8.3.

Results and Discussion

The reaction between $[(Me_3Si)_3CAlF_2]_3$ and Cp_2ZrMeF yielded compound **1** as expected, since $[(Me_3Si)_3CAlF_2]_3$ is an excellent fluoride acceptor[1] (eq 1). Cp_2ZrMeF was prepared in situ using Cp_2ZrMe_2 and Me_3SnF (eq 2).

$$[(Me_3Si)_3CAlF_2]_3 + 3Cp_2ZrMeF \rightarrow \underset{\mathbf{1}}{3(Cp_2ZrMe)(\mu\text{-}F)[(Me_3Si)_3CAlF_2]} \quad (1)$$

$$Cp_2ZrMe_2 + Me_3SnF \rightarrow Cp_2ZrMeF + Me_4Sn \quad (2)$$

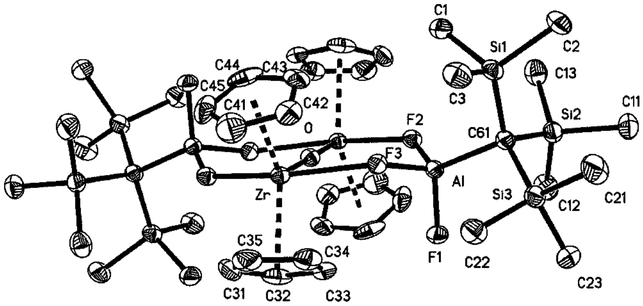

Figure 1. Molecular structure of $[(Cp_2Zr)(\mu\text{-}F)_2[(Me_3Si)_3CAlF]]_2O$ (**2**). Thermal ellipsoids are given at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(Cp_2Zr)(\mu\text{-}F)_2[(Me_3Si)_3CAlF]]_2O$ (2)

Zr−O	1.9523(4)	F(2)−Zr#1	2.345(2)
Zr−F(2)#1	2.345(2)	Zr−F(3)	2.324(2)
Al−F(1)	1.673(3)	Al−F(2)	1.735(3)
Al−F(3)	1.740(3)	O−Zr#1	1.9523(4)
O−Zr−F(3)	76.01(6)	O−Zr−F(2)#1	75.05(6)
F(3)−Zr−F(2)#1	150.98(8)	F(1)−Al−F(2)	104.59(14)
F(1)−Al−F(3)	104.56(14)	F(2)−Al−F(3)	104.00(13)
Al−F(2)−Zr#1	134.46(13)	Al−F(3)−Zr	135.22(13)
Zr−O−Zr#1	180.0		

Attempts to grow X-ray-quality crystals of **1** from toluene/hexane mixtures (5:1) were unsuccessful. Crystallization from a THF/toluene/hexane (1:8:2) solution of **1** did produce X-ray-quality crystals after 4 weeks at −20 °C. However, these crystals proved to be $[(Cp_2Zr)(\mu\text{-}F)_2[(Me_3Si)_3CAlF]]_2O$ (**2**) (Figure 1, Tables 2 and 3). Presumedly the source of the oxygen atom was oxygen,

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(Cp_2ZrMe)(\mu\text{-}F)[(Me_3Si)_3CAlF_2]$ (1) and $[(Cp_2Zr)(\mu\text{-}F)_2[(Me_3Si)_3CAlF]]_2O$ (2) (2:1 Mixture of Compounds 1 and 2)

Zr#1−O	1.9499(7)	Al(1′)−F(1′)	1.779(2)
Zr−F(3)	2.359(2)	Zr−F(2)#1	2.312(2)
Al−F(1)	1.677(2)	Al−F(3)	1.735(2)
Al−F(2)	1.743(2)	Al−C(61)	1.963(2)
O−Zr	1.9499(7)	Al(1′)−F(3′)	1.678(2)
Zr(1′)−F(1′)	2.118(2)	Al(1′)−C(61′)	1.965(3)
Al(1′)−F(2′)	1.674(2)	Zr(1′)−C″	2.238(3)

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#1−O−Zr	180.0
O−Zr−F(3)	74.59(5)	F(1′)−Zr(1′)−C″	95.52(11)
F(1)−Al(1)−F(3)	104.87(9)	F(2′)-Al(1′)-F(1′)	100.86(10)
F(3)−Al−F(2)	103.56(9)	F(2′)-Al(1′)-C(61′)	116.62(12)
F(3)−Al−C(61)	114.23(11)	F(1′)−Al(1′)−C(61′)	112.48(11)
Al−F(2)−Zr#1	135.32(9)	F(2′)−Al(1′)−F(3′)	108.08(12)
Al−F(3)−Zr	136.59(9)	F(3′)−Al(1′)−F(1′)	100.53(10)
F(1)−Al(1)−F(2)	103.87(9)	F(3′)−Al(1′)−C(61′)	116.08(22)
F(1)−Al−C(61)	113.73(11)	Al(1′)−F(1′)−Zr(1′)	152.00(10)

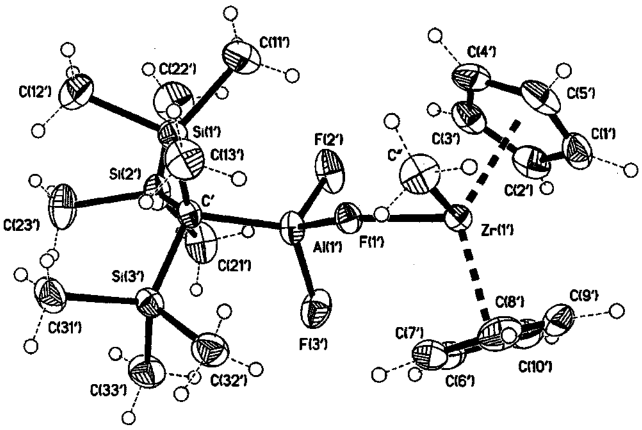

Figure 2. Molecular structure of $(Cp_2ZrMe)(\mu\text{-}F)[(Me_3Si)_3CAlF_2]$ (**1**). Thermal ellipsoids are given at the 50% probability level.

water, or THF, since group 13 Lewis acids are known to cleave aliphatic ethers.[10] The opening of the THF molecule and its coordination to aluminum was recently shown by an X-ray structural analysis of its product.[10f] The condensation of two molecules of **1** with elimination of the methyl groups to form the μ-oxygen bridge in **2** is the consequence of this transfer. A comparable eight-membered $Al_2F_4Zr_2$ ring system is found in $(Cp^*ZrF_3)_2(AlMe_3)_2$. However, in the latter compound the zirconium atoms are bridged by two μ-F units.[11] Compound **2** is not soluble in THF or toluene. A second attempt to produce compound **2** under the same conditions resulted in the formation of a 2:1 mixture of compounds **1** and **2**.

The Zr(1′)−F(1′) distance (2.118(2) Å) in **1** (Figure 2, Table 3) is slightly longer than the Zr−F distances for the bridging fluorine in $[Cp^*ZrF_3]_4$ (2.121−2.160 Å).[12] The zirconium−carbon bond length of the methyl group (Zr(1′)−C″ 2.238(3) Å) is comparable to that in $[Me_2Si(\eta^5\text{-}Me_4C_5(t\text{-}BuN))ZrMe]^+[(C_{12}F_9)_3AlF]^-$ (Zr−Me 2.21 Å).[3a] The Al−F(bridging) (Al(1′)−F(1′) = 1.779(2) Å) distance in **1** is also similar to the Al−F(bridging) distance in $[Me_2Si(\eta^5\text{-}Me_4C_5(t\text{-}BuN))ZrMe]^+[(C_{12}F_9)_3AlF]^-$ [3a] (1.780 Å).

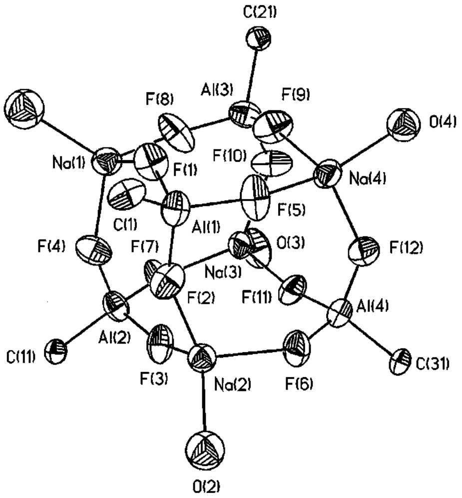

Figure 3. Molecular structure of $[Na(Me_3Si)_3CAlF_3(THF)]_4$ (**3**), containing only the connecting carbon of the $(Me_3Si)_3C$ group and the oxygen atoms of THF. Me_3Si groups and THF carbon atoms are omitted for clarity. Thermal ellipsoids are given at the 50% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Na(Me_3Si)_3CAlF_3(THF)]_4$ (3)

Al(1)−F(2)	1.683(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(1)	1.693(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(10)	1.684(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(8)	1.703(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(11)	1.682(3)	F(11)−Na(3)	2.173(3)
Al(4)−F(12)	1.694(3)	F(12)−Na(4)	2.278(5)
Al(4)−F(6)	1.702(5)	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(5)−Al(1)−F(1)	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(10)−Al(3)−F(9)	105.3(2)	F(1)−Na(1)−F(8)	99.8(1)
F(10)−Al(3)−F(8)	102.3(2)	F(1)−Na(1)−F(4)	106.4(1)
F(9)−Al(3)−F(8)	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)

The Al−F(terminal) distances (average 1.675−1.678 Å) in **2** (Figure 1, Tables 2 and 3) are comparable to those Al−F(terminal) in $[(Me_3Si)_3CAlF_2]_3$[1a] (1.657−1.671

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Å). The Al−F(bridging) bond lengths (1.735−1.779 Å) are shorter than those in $[(Me_3Si)_3CAlF_2]_3$[1a] (1.795−1.815 Å) and similar to those in **1**. The Zr−F(bridging) distances (2.312−2.359 Å) in **2** are somewhat longer than those in **1** (Zr(1′)−F(1′) = 2.118(2) Å).

Crystals of **3** for X-ray structural investigations were obtained from toluene/hexane (5:1) at −20 °C. Compound **3** (Figure 3, Table 4) is isostructural with $[Li(Me_3Si)_3CAlF_3(THF)]_4$.[2] The structure consists of a cube formed of aluminum and sodium atoms alternating at the edges, which are bridged by fluorine atoms. The Na−F distances are in the range 2.158−2.278 Å, which is comparable to those in crystalline sodium fluoride (2.303 Å).[13] The Al−F bond distances cover a small range (1.683−1.703 Å). These are comparable to those in $[Li(Me_3Si)_3CAlF_3(THF)]_4$ but are considerably shorter than the Al−F(bridging) distances in $[((Me_3Si)_3C)_4Al_4K_2(\mu\text{-}F)_2F_8(THF)_4]$ (average 1.805 Å).[1a] The Na−O distance (2.137−2.278 Å) is similar to those in $[Cp^*_6Ti_6Na_7F_{19}(THF)_{2.5}]$ (2.291−2.319 Å)[14] but slightly shorter than those in $[Na_4Bi_2(\mu_6\text{-}O)(OC_6F_5)_8(THF)_4]$ (2.326−2.496 Å).[15]

In summary, we have demonstrated by an X-ray structural investigation the ion pair formation of an organometallic zirconium cation and a fluorine-containing aluminum anion. With the facile access of $R_2AlF_2^-$ anions by the reaction of R_3Al with HF_2^-, a wide variety of anions is now available,[16] which are under investigation at present.

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Supporting Information Available: Tables giving positional and thermal parameters and estimated standard deviations for all atoms, bond distances and angles, and anisotropic thermal parameters for a 2:1 mixture of compounds **1** and **2**, **2,** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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