Synthesis, structure, and reactivity of AlMe$_2$(1-Me-CB$_{11}$F$_{11}$): An AlMe$_2^+$ cation-like species bonded to a superweak anion

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ABSTRACT

Treatment of AlMe$_3$ with [CPh$_3$][1-Me-CB$_{11}$F$_{11}$] in toluene produced the dimeric compound [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$ in 89% isolated yield. The compound was characterized by ^{1}H and ^{19}F NMR spectroscopy and by single crystal X-ray diffraction. The structure consists of a AlMe$_2^+$ cation-like species bonded to two F atoms from two 1-Me-CB$_{11}$F$_{11}^-$ superweak anions, forming an AlMe$_2$F$_2$ coordination unit with the unusually large H$_3$C–Al–CH$_3$ angle of 147.6(2)° (cf. the corresponding angle of 117.1(1)° in the AlMe$_2$F$_2^-$ anion in [N(n-Bu)$_4$][AlMe$_2$F$_2$]). This large angle is due in part to the long Al–F distances of 1.922(3) and 1.928(3) Å (cf. 1.711(1) and 1.7113(1) Å in [N(n-Bu)$_4$][AlMe$_2$F$_2$]), which is why the dimethylaluminum moieties in [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$ should possess a considerable degree of positive charge and should be considered as cation-like AlMe$_2^+$ species.

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1. Introduction

Cationic aluminum complexes are of considerable interest due to their potential use in a variety of organic and catalytic transformations [1–7]. The most reactive are undoubtedly the cation-like species AlR$_2^+$ bonded to carborane and borane superweak anions, which have been isolated and characterized by Reed and co-workers (AlEt$_2$(CB$_{11}$H$_6$Cl$_6$) and AlEt$_2$(CB$_{11}$H$_6$Br$_6$)) [7] and by Knapp and co-workers ((AlMe$_2$)$_2$(B$_{12}$Cl$_{12}$) and (AlEt$_2$)$_2$(B$_{12}$Cl$_{12}$)) [2]. We herein report the synthesis, structure, and reactivity of another such species, AlMe$_2$(1-Me-CB$_{11}$F$_{11}$). It is the first AlMe$_2^+$ cation-like moiety bonded to a fluoroanion, and as such its structure can be compared to the AlMe$_2$F$_2$ moiety in the [AlMe$_2$F]$_4$ tetramer [8] and to the AlMe$_2$F$_2^-$ anion in [N(n-Bu)$_4$][AlMe$_2$F$_2$] [9].

2. Results and discussion

The synthesis of [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$ was accomplished by reaction of AlMe$_3$ with [CPh$_3$][1-Me-CB$_{11}$F$_{11}$] in toluene,

as shown in the reaction below:

2AlMe$_3$ + 2[CPh$_3$][1-Me-CB$_{11}$F$_{11}$]

$\rightarrow$ [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$ + 2CPh$_3$Me
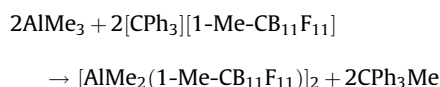
The yellow product AlMe$_2$(1-Me-CB$_{11}$F$_{11}$) is sparingly soluble in toluene and freely soluble in acetonitrile. It is not known whether the dimeric structure is maintained in toluene solution. What is known is that Al–F interactions are maintained in toluene solution, as evidenced by strong shielding of the ^{19}F NMR resonances of the free anion (δ −251.0, −256.0, and −257.2 for [N(n-Oc)$_4$][1-Me-CB$_{11}$F$_{11}$] in toluene-d$_8$, all sharp) in the aluminum compound (δ −233.0 (broad), −246.6 (broad), and −249.2 (sharp) in toluene-d$_8$). However, only a single set of 1:5:5 resonances was observed for a mixture of AlMe$_2$(1-Me-CB$_{11}$F$_{11}$) and [N(n-Oc)$_4$][1-Me-CB$_{11}$F$_{11}$] in toluene-d$_8$, suggesting fast intermolecular exchange of free and aluminum-bound anions. Furthermore, only a single aluminum-methyl resonance was observed in the ^{1}H NMR spectrum of a mixture of AlMe$_2$(1-Me-CB$_{11}$F$_{11}$) and AlMe$_3$ in toluene-d$_8$, suggesting fast methyl exchange between the AlMe$_2^+$ cation-like species and free AlMe$_3$. However, an adduct of AlMe$_3$ and [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$ was not isolated even when [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$ was crystallized from toluene containing a large excess of AlMe$_3$.

Table 1
Crystallographic data collection and refinement parameters.

Compound	$[AlMe_2(1\text{-Me-}CB_{11}F_{11})]_2$
Empirical formula	$C_8H_{18}Al_2B_{22}F_{22}$
Formula weight (g mol^{-1})	824.0
Habit, color	Thin plate, light yellow
Space group	Pnma
a (Å)	18.1097(2)
b (Å)	13.6505(1)
c (Å)	12.6612(2)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	3129.93(6)
Z	4
T (K)	127(2)
ρ_{calc} (g cm^{-3})	1.749
R(F) ($I > 2\sigma(I)$)[a]	0.0666
$wR(F^2)$ [all data][a]	0.1677

[a] $R(F) = \Sigma||F_o - F_c||/\Sigma|F_o|; wR(F^2) = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2])^{1/2}$.

The structure of $[AlMe_2(1\text{-Me-}CB_{11}F_{11})]_2$ is shown in Figs. 1 and 2. X-ray data collection and refinement parameters are listed in Table 1. The four F atoms that are "coordinated" to the Al atom (two long and two short bonds) are nearly co-planar, deviating from their least-squares plane by no more than 0.043 Å. The primary Al–F bonds are rather long, which is one of the reasons that the C–Al–C angle, at 147.6(2)°, is quite large. Compare the C–Al–C angles in Knapp's compound, $(AlMe_2)_2B_{12}Cl_{12}$, which is 133.8(4)° [2]). However, another reason that the angle is so large is that there are two weak Al···F interactions (together they account for only 3.8% of the sum of bond valences for Al; see below). There are two extremely weak Al···Cl interactions in Knapp's compound, 2.3961(5) and 2.4574(5) Å, but these add up to only 1% of the sum of Al bond valences and can therefore be ignored. The bond angle in the free $AlMe_2^+$ cation would undoubtedly be 180°, whereas in a tetrahedral aluminate species such as Roesky's $AlMe_2F_2^-$ anion, the C–Al–C angle is 117.1(1)°, only 8° higher than the tetrahedral angle [9]. Our F–Al–F angle is 82.53(8)°; Roesky's is 103.23(7)°, only 6° lower than the tetrahedral angle. The eight F···CH$_3$ distances in $[AlMe_2(1\text{-Me-}CB_{11}F_{11})]_2$, involving all four F atoms shown in Fig. 2, are all 3.0–3.1 Å.

DFT (B3LYP/6-31g*) calculations on this system indicate that an $AlMe_2(1\text{-Me-}CB_{11}F_{11})$ monomer would have an F–Al–F angle of 87.0° and a C–Al–C angle of 135.7°; the latter is close to Knapp's value of 133.8(4)°. Furthermore, the calculations show that an
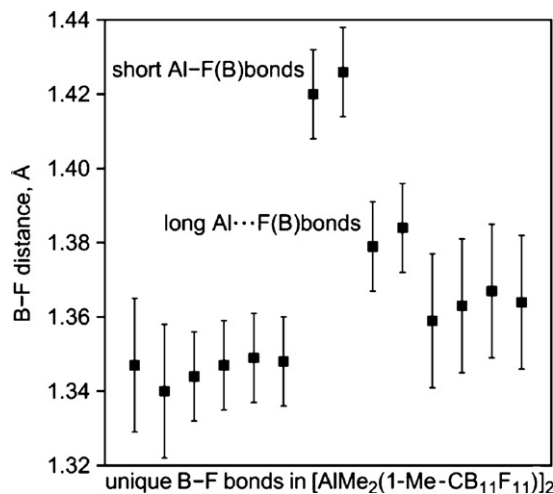
isolated dimer with the same overall structure as $[AlMe_2(1\text{-Me-}CB_{11}F_{11})]_2$ would have a C–Al–C angle of only 133.0°, even smaller than in the monomer, despite having an F–Al–F angle of 85.9°, quite close to the X-ray value of 82.53(8)°. Therefore, it seems likely that the greater C–Al–C angle of 147.6(2)° in $[AlMe_2(1\text{-Me-}CB_{11}F_{11})]_2$ (i.e., greater than ca. 135°) is in fact due to the presence of the weak intermolecular Al···F interactions in the solid state and is not due to the weaker basicity of $1\text{-Me-}CB_{11}F_{11}^-$ relative to $B_{12}Cl_{12}^{2-}$.

Several graphs based on the X-ray structure of $[AlMe_2(1\text{-Me-}CB_{11}F_{11})]_2$ are shown in Figs. 3 and 4 (the error bars in all three graphs are ±3σ but are smaller than the data points for two of the compounds in the upper graph in Fig. 4). The graph shown in Fig. 3 shows that the F atoms bonded to the Al atom have B–F distances that are significantly longer than the other B–F bonds, and it is almost true for the B–F bonds involved in secondary bonding to the Al atom. The two graphs in Fig. 4 show the tendency of the Al–CH$_3$ bonds to lengthen as the Al–F bonds shorten (from $[AlMe_2(1\text{-Me-}CB_{11}F_{11})]_2$ to $[AlMe_2F]_4$ to $[N(n\text{-Bu})_4][AlMe_2F_2]$, bottom graph) and the tendency of the H$_3$C–Al–CH$_3$ angle to decrease as the F–Al–F angle increases

Fig. 2. Two views of the coordination geometry around the unique Al atom in $[AlMe_2(1\text{-Me-}CB_{11}F_{11})]_2$ (50% probability ellipsoids except for H atoms), including the two secondary bonding interactions with F atoms from other $1\text{-Me-}CB_{11}F_{11}^-$ anions. The distances are in Ångstroms. In the drawing on the right, the plane of the page is the least-squares plane of the four F atoms, which deviate from this plane by no more than 0.043 Å.

Fig. 1. The structure of the $[AlMe_2(1\text{-Me-}CB_{11}F_{11})]_2$ dimer, which has crystallographic m symmetry (50% probability ellipsoids except for H atoms). The mirror plane is perpendicular to the plane of the page and includes the four C atoms in the two $1\text{-Me-}CB_{11}F_{11}^-$ anions. Selected interatomic distances (Å) and angles (deg): Al–CH$_3$, 1.922(3) and 1.928(3) Å; Al–F(B), 1.964(2) and 1.969(3) Å; H$_3$C–Al–CH$_3$, 147.6(2)°; F–Al–F, 82.53(8)°.
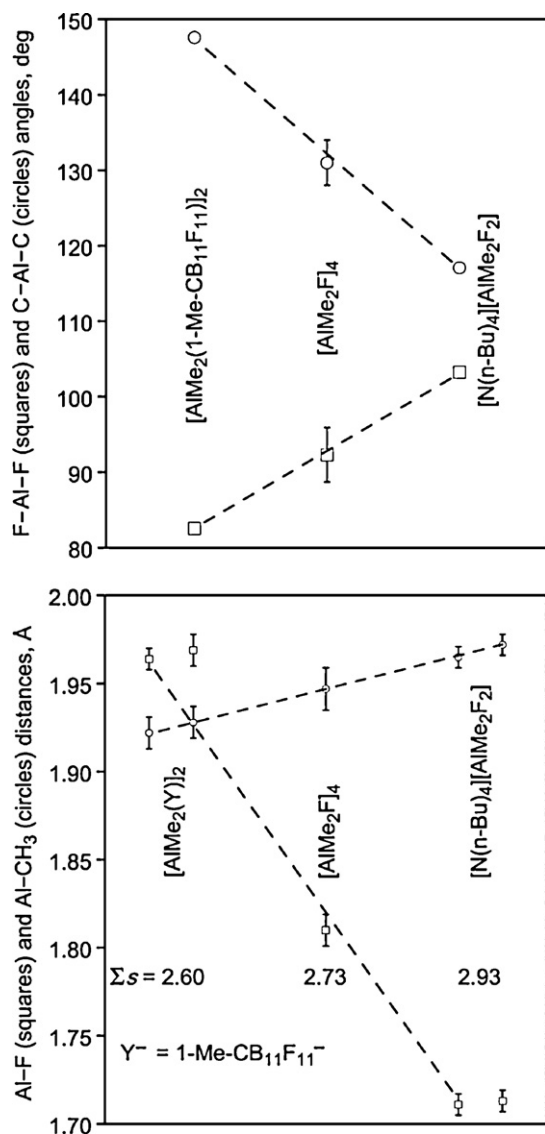

Fig. 3. Graph showing the 14 unique B–F bonds in $[AlMe_2(1\text{-Me-}CB_{11}F_{11})]_2$. The error bars shown are ±3σ.

Fig. 4. Graphs showing the Al–CH$_3$ and Al–F distances and F–Al–F and H$_3$C–Al–CH$_3$ angles in [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$, [AlMe$_2$F]$_4$, and [N(nBu)$_4$][AlMeF$_2$]. The error bars shown are ±3σ and in some cases are smaller than the data points. The Σs values are the sums of aluminum bond valences (see Table 2). The dotted lines are visual aids, not least-squares fits to the data.
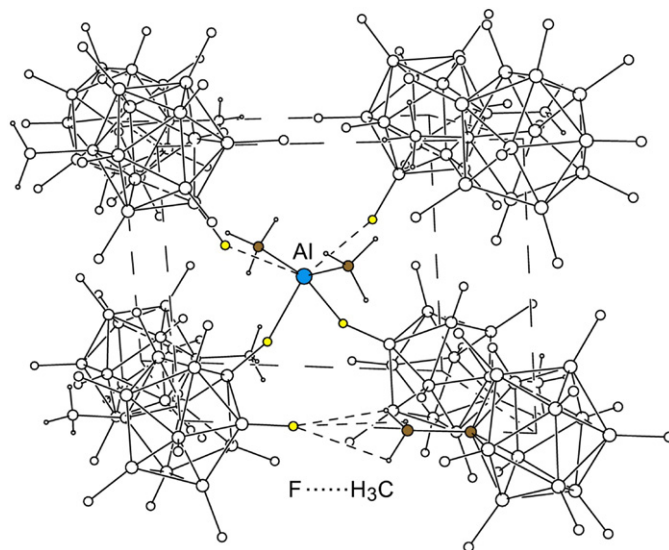
Table 2
Bond valence values for selected aluminum compounds with AlR$_2$ moieties.[a, b]

Compound	Bond, distance (Å)	Bond valence, s	Sum of bond valences, Σs
[AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$	Al–F, 1.964	0.322	
	Al–F, 1.969	0.318	
	Al–F, 2.623	0.054	
	Al–F, 2.703	0.044	
	Al–C, 1.922	0.940	
	Al–C, 1.928	0.925	2.603
[AlMe$_2$F]$_4$	Al–F, 1.810	0.489	
	Al–F, 1.810	0.489	
	Al–C, 1.947	0.878	
	Al–C, 1.947	0.878	2.734
[N(n-Bu)$_4$][AlMe$_2$F$_2$]	Al–F, 1.711	0.638	
	Al–F, 1.713	0.635	
	Al–C, 1.965	0.837	
	Al–C, 1.972	0.821	2.931
(AlMe$_2$)$_2$B$_{12}$Cl$_{12}$	Al–Cl, 2.457	0.317	
	Al–Cl, 2.396	0.374	
	Al–C, 1.916	0.955	
	Al–C, 1.920	0.945	2.618
(AlEt$_2$)$_2$B$_{12}$Cl$_{12}$	Al–Cl, 2.479	0.299	
	Al–Cl, 2.490	0.290	
	Al–C, 1.920	0.945	
	Al–C, 1.915	0.958	2.491
AlEt$_2$(CB$_{11}$H$_6$Cl$_6$)	Al–Cl, 2.400	0.332	
	Al–Cl, 2.430	0.341	
	Al–C, 1.930	0.920	
	Al–C, 1.934	0.910	2.502

[a] Aluminum bond valence values, s, are given by the equation $s = e^{(R_0-R)/0.37}$. The R_0 values for Al–F, Al–Cl, and Al–C bonds are 1.545, 2.032, and 1.899 Å, respectively (see Refs. [2,10] and references therein).
[b] The values in this table for the last three compounds first appeared in Ref. [2].

between anions that are almost perfectly dovetailed (the relevant dihedral angle is 84.5° instead of 90°; the four F···F distances are 2.697, 2.946, 2.978, and 3.083 Å). Interestingly, the 9.055 Å distance is between two anions that point directly at one another (see the highlighted F and C atoms near the bottom part of Fig. 5): the F atom of one anion points directly at the methyl C atom of the other anion, resulting in (B)F···H(C) distances of 2.708 (×2) and 2.711 Å.

(same order of compounds). In fact, for the distance graph, it is clear that a large change in Al–F distances causes only a small change in Al–CH$_3$ distances. However, as discussed below, the change from [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$ to [AlMe$_2$F]$_4$ to [N(n-Bu)$_4$][AlMe$_2$F$_2$] results in the sum of Al bond valences increasing from 2.60 to 2.73 to a normal value of 2.93 for the AlMe$_2$F$_2^-$ anion (relevant bond valence data are listed in Table 2 [2,10]). This suggests that the Al atoms in [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$ are more reactive (i.e., have a greater degree of positive charge, hence the "cation-like" designation) than the Al atoms in the AlMe$_2$F$_2^-$ anion. Note that the sum of Al bond valences are the same, 2.59–2.60, for both [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$ and (AlMe$_2$)$_2$B$_{12}$Cl$_{12}$.

The packing of ions in the structure of [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$ is shown in Fig. 5. Each AlMe$_2^+$ moiety is inside a rhomb with eight 1-Me-CB$_{11}$F$_{11}^-$ anions surrounding each cation (a distorted CsCl arrangement). The centroid of the ten upper- and lower-belt B atoms of each anion is designated ⊙. The rhomb has three ⊙···⊙ distances, 6.826, 7.495, and 9.055 Å. The short 6.826 Å distance is among the shortest observed for a 1-R-CB$_{11}$F$_{11}^-$ or B$_{12}$F$_{12}^{2-}$ compound [11–14], and this distance in [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$ is

Fig. 5. The CsCl-like anion-cation packing in [AlMe$_2$(1-Me-CB$_{11}$F$_{11}$)]$_2$. The anion centroid···centroid distances are 6.826, 7.495, and 9.055 Å.

3. Experimental

All reagents and solvents were reagent grade or better. All manipulations were carried out under an atmosphere of purified nitrogen using standard air-free techniques [15]. Toluene and toluene-d_8 were distilled from sodium. The compound $Ag(C_6H_6)(1\text{-Me-CB}_{11}F_{11})$ was prepared by a literature procedure [11]. The compound $[CPh_3][1\text{-Me-CB}_{11}F_{11}]$ was prepared by reacting $Ag(C_6H_6)(1\text{-Me-CB}_{11}F_{11})$ with CPh_3Cl. The synthesis of $[AlMe_2(1\text{-Me-CB}_{11}F_{11})]_2$ was first briefly reported in a U.S. Patent [16].

Fluorine-19 and ^1H NMR spectra were recorded on a Bruker WP-300 spectrometer. Chemical shifts (δ scale) are relative to internal $CFCl_3$ or $SiMe_4$. Crystals of $[AlMe_2(1\text{-Me-CB}_{11}F_{11})]_2$ were obtained by crystallization from toluene containing a large excess of $AlMe_3$. The compound is extremely air-sensitive; crystals for X-ray diffraction were examined at $-78\,^\circ C$ under an argon atmosphere. The diffraction data were obtained using a Siemens P4 diffractometer and computations were performed with standard crystallographic software. Data collection and refinement parameters are listed in Table 1.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2012.02.001.

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