## First Isolation and Structural Characterization of Triarylaluminum–Water and –Methanol Complexes

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Summary: The structurally characterized  $(C_6F_5)_3Al \cdot OH_2$ (1) and  $(C_6F_5)_3Al \cdot OHCH_3$  (2) exhibit medium-strong intermolecular and weak intramolecular O-H···FC hydrogen bonds in the solid state. Both complexes have substantial stability in toluene solutions at room temperature, while the spectroscopic data of 1 show strong activation of the weak Brønsted acid  $H_2O$  by  $Al(C_6F_5)_3$ .

## Introduction

Organoaluminum complexes have played pivotal roles in many chemical processes,<sup>1</sup> especially in organic synthesis,<sup>2</sup> olefin polymerization catalysis,<sup>3</sup> and polymerization of polar monomers.<sup>4</sup> There has been longstanding interest in the controlled reactions of water with aluminum trialkyl/triaryl compounds due to both scientific curiosity and technological importance.<sup>5</sup> The partial hydrolysis of trialkylaluminum (R<sub>3</sub>Al) leads to formation of industrially important, oligomeric alumoxanes<sup>6</sup> that are potent activators for olefin polymerization<sup>7</sup> as well as active catalysts for polymerization of epoxides.<sup>8</sup> The controlled reaction of water with bulky trialkylaluminum compounds such as tri-tert-butylaluminum produces a series of structurally characterized tert-butylaluminum hydroxides, oxide hydroxides, and alumoxanes.9 Variable-temperature <sup>1</sup>H NMR spectroscopic studies<sup>10</sup> have shown that the hydrolysis of R<sub>3</sub>Al  $(R = Me, Et, ^{i}Bu)$  proceeds with the formation of an alkylaluminum-water complex (A), which subsequently

$$\begin{bmatrix} \mathbf{R}_{3} \text{Al} \cdot \text{OH}_{2} \end{bmatrix} \begin{bmatrix} \mathbf{R}_{2} \text{Al}(\mu - \text{OH}) \end{bmatrix}_{n} \begin{bmatrix} \mathbf{R} \text{Al}(\mu - \text{O}) \end{bmatrix}_{n}$$
  
**A B C**

eliminates an alkane to form a dialkylaluminum hydroxide (B). Hydroxide B normally associates to give dimers or trimers; warming the solution of **B** to room temperature induces further alkane elimination to give alkylalumoxanes (C) as the final products.

Although the existence of the alkylaluminum-water complex A was supported by the low-temperature solution <sup>1</sup>H NMR studies, isolation and structural characterization of such a complex still remain a challenge.<sup>5</sup> The use of the bulky trimesityl ligand makes possible the isolation and structural characterization of the trimesitylgallium-water complex Mes<sub>3</sub>Ga·OH<sub>2</sub>·2THF, which is stabilized by two THF molecules.<sup>11</sup> The analogous aluminum complex, however, is again thermally too unstable to isolate and characterize structurally.

Inspired by the above-mentioned work of Roesky, Barron, and others,<sup>5–11</sup> and by the work of Green,<sup>12a,b</sup> Siedle,<sup>12c</sup> and co-workers, in which  $B(C_6F_5)_3$  forms isolable and structurally characterizable adducts with water, we sought to utilize the electronic effects in attempts to isolate trialkyl/triaryl aluminum complexes with oxygen Brønsted acids in general (e.g., H<sub>2</sub>O, CH<sub>3</sub>-OH). Herein, we report the first isolation and structural characterization of triarylaluminum-water and -methanol complexes: (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ål·OH<sub>2</sub> (1) and (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Al·OHCH<sub>3</sub> (2). Complexes 1 and 2 have been isolated in good yields from the controlled reactions of the highly Lewis acidic alane  $Al(C_6F_5)_3^{13}$  with water and methanol. Unique properties of 1 and 2 include (1) substantial stability in toluene solutions at room temperature with half-lives of  $t_{1/2} = 33$ , 193 h, respectively, (2) strong activation of the weak Brønsted acid H<sub>2</sub>O with (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Al as shown by a 8.96 ppm downfield shift of the water proton in 1 versus the free water proton, and (3) in the solid state,

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exhibition by both complexes of medium-strong intermolecular and weak intramolecular O–H…FC hydrogen bonds.

## **Experimental Section**

Materials and Methods. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line  $(10^{-6}-10^{-7} \text{ Torr})$ , or in a argonfilled glovebox (<1.0 ppm O<sub>2</sub> and moisture). NMR-scale reactions were conducted in Teflon-valve-sealed sample J. Young tubes. Organic solvents were first saturated with nitrogen and then dried by passage through activated alumina and Q-5 catalyst (Englehardt Chemicals Inc.) in stainless steel columns prior to use. Benzene- $d_6$ , toluene- $d_8$ , and THF- $d_8$  were dried over sodium/potassium alloy and vacuum-distilled and/or filtered prior to use. NMR spectra were recorded on either a Varian Inova 300 (FT: 300 MHz, <sup>1</sup>H; 282 MHz, <sup>19</sup>F) or a Varian Inova 400 spectrometer. Chemical shifts for <sup>1</sup>H spectra were referenced to internal solvent resonances and reported as parts per million relative to tetramethylsilane. <sup>19</sup>F NMR spectra were referenced to external CFCl<sub>3</sub>.

Tris(pentafluorophenyl)borane, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, was obtained as a research gift from Boulder Scientific Co. and used without further purification for preparative reactions. Tris(pentafluorophenyl)alane (Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, as a 0.5(toluene) adduct) was prepared according to the literature procedure.<sup>13e,g</sup> *Extra caution should be exercised when handling this material, due to its thermal and shock sensitivity.* 

(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Al·OH<sub>2</sub> (1). To a rapidly stirred suspension of (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Al·0.5(toluene) (0.30 g, 0.52 mmol) in 10 mL of hexanes at -78 °C was added degassed H<sub>2</sub>O (9.4  $\mu$ L, 0.52 mmol). After being stirred at this temperature for 5 min, the reaction mixture was warmed to room temperature and stirred for an additional 1 h. The resulting suspension was filtered, and the solid collected was washed with 2  $\times$  2 mL of hexanes and dried in vacuo to afford 0.16 g of the product. When the filtrate was cooled to -35 °C, an additional crop of the product (0.05 g) was obtained. The total yield is 0.21 g (75% yield). <sup>1</sup>H NMR (benzene- $d_6$ , 23 °C):  $\delta$  3.82 (s). <sup>1</sup>H NMR (THF- $d_8$ , 23 °C):  $\delta$ 11.36 (s). <sup>19</sup>F NMR (benzene- $d_6$ , 23 °C):  $\delta$  -123.50 (dd, 6F, o-F), -150.66 (t, 3F, p-F), -160.56 (tt, 6F, m-F). Single crystals suitable for X-ray diffraction analysis were grown from a toluene solution layered with hexanes in the glovebox at -35°C.

(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Al·OHCH<sub>3</sub> (2). Complex 2 was synthesized in the same manner as for the synthesis of 1; isolated yield 85%. <sup>1</sup>H NMR (benzene- $d_6$ , 23 °C):  $\delta$  3.35 (q,  $J_{\rm H-H}$  = 4.5 Hz, 1 H; OH), 2.48 (d,  $J_{\rm H-H}$  = 4.5 Hz, 3H, CH<sub>3</sub>). <sup>19</sup>F NMR (benzene- $d_6$ , 23 °C):  $\delta$  -123.35 (dd, 6F, *o*-F), -150.57 (t, 3F, *p*-F), -160.52 (tt, 6F, *m*-F).

**X-ray Crystallography.** Data were collected at 173(2) K on a Siemens SMART CCD diffractometer. The structure was solved by direct methods and refined using the Siemens SHELXTL program library.<sup>14</sup> The structure was refined by full-matrix weighted least squares on  $F^2$  for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms on oxygen in both **1** and **2** were found in the difference Fourier map, and their positions were refined.

## **Results and Discussion**

Under controlled reaction conditions (see Experimental Section), 1:1 stoichiometric reactions of  $(C_6F_5)_3Al$ with  $H_2O$  and  $CH_3OH$  in aliphatic solvents such as hexanes produce crystalline solids. The spectroscopic



**Figure 1.** X-ray crystal structure of **1**. Selected bond lengths (Å) and angles (deg): Al1-O1 = 1.857(3), Al1-C1 = 1.987(3), Al1-C7 = 1.979(3), Al1-C13 = 1.978(3), O1-H1 = 0.857(10),  $H1\cdots F17B = 2.13(2)$ ,  $H1\cdots F18 = 2.32(3)$ , O1-H2 = 0.855(10); C1-Al1-C7 = 115.15(14), C1-Al1-C13 = 112.85(14), C7-Al1-C13 = 114.84(13), C1-Al1-O1 = 106.59(14), C7-Al1-O1 = 103.29(13), C13-Al1-O1 = 102.35(12), Al1-O1-H1 = 125(3), Al1-O1-H2 = 129-(3), H1-O1-H2 = 106(4),  $O1-H1\cdots F17B = 154.3(3)$ ,  $O1-H1\cdots F18 = 120.3(3)$ .

data of the isolated crystalline products are consistent with the anticipated  $H_2O$  and  $CH_3OH$  complexes **1** and **2**. Strong activation of the weak Brønsted acid  $H_2O$  by  $(C_6F_5)_3Al$  as a result of complexation is evident by the *significant downfield shift* of the water proton in **1** (11.36 ppm in THF- $d_8$ ) as compared to that of the free water proton (2.40 ppm in THF- $d_8$  at 23 °C). This value (11.36 ppm) is compared with 8.05 ppm for the water proton in the putative Me<sub>3</sub>Al·OH<sub>2</sub> (at -70 °C in Et<sub>2</sub>O)<sup>10</sup> and 9.20 ppm in the putative Mes<sub>3</sub>Al·OH<sub>2</sub> (at -60 °C in THF- $d_8$ ),<sup>11</sup> suggesting the observed highest degree of activation of the weak Brønsted acid H<sub>2</sub>O by (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-Al.

The molecular structures of the complexes 1 and 2 in the solid state are confirmed by X-ray diffraction studies (Figures 1 and 2). Hydrogen atoms on oxygen were located in the difference Fourier map, and their positions were refined. The structure of 1 (Figure 1)<sup>15</sup> features a distorted-tetrahedral geometry at aluminum with the sum of the C-Al-C angles of 342.84°. The average Al-C(aryl) distance (1.981 Å) compares well with those in other  $(C_6F_5)_3Al$  complexes with metallocene alkyl,<sup>13a</sup> imidazole,<sup>13b</sup> toluene,<sup>13c</sup> and THF groups.<sup>13h</sup> The water molecule adopts a trigonal-planar geometry, as evidenced by the sum of the angles around the oxygen of 360.0°, which implies that both lone pairs from the water oxygen atom are employed in the bonding to aluminum. Medium-strong intermolecular OH…FC hydrogen bonding<sup>16</sup> in **1** is manifested by the short distance H1···F17B = 2.13(2) Å and the large

<sup>(14)</sup> Sheldrick, G. M. SHELXTL, Version 5; Siemens, Madison, WI, 1996.

<sup>(15)</sup> Crystallographic data for 1:  $C_{18}H_2AIF_{15}O\cdot C_7H_8$ ,  $M_r = 638.31$ , 0.18 × 0.20 × 0.30 mm<sup>3</sup>, monoclinic, space group  $P2_1/n$ , a = 10.318(3)Å, b = 16.319(5) Å, c = 14.427(4) Å,  $\beta = 100.902(5)^\circ$ , V = 2402.1(12)Å<sup>3</sup>, Z = 4,  $\rho_{calcd} = 1.765$  Mg/m<sup>3</sup>,  $\theta$  range for data collection  $3.12-23.28^\circ$ ,  $\lambda = 0.710$  73 Å, T = 173(2) K, 15 041 reflections collected, 3450 independent reflections ( $R_{int} = 0.0873$ ), 386 refined parameters, goodness of fit on  $F^2$  0.979, R1 = 0.0462 ( $I > 2\sigma(I)$ ), wR2 = 0.0948, largest difference peak and hole 0.302 and -0.312 e Å<sup>-3</sup>.

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**Figure 2.** X-ray crystal structure of **2**. Selected bond lengths (Å) and angles (deg): Al-O1 = 1.858(2), Al-C1 = 1.977(3), Al-C7 = 1.985(3), Al-C13 = 1.994(3), O1-C19 = 1.462(4), O1-H1 = 0.81(4),  $H1\cdots F17A = 2.22(4)$ ,  $H1\cdots F2 = 2.23(4)$ ; C1-Al-C7 = 113.97(11), C1-Al-C13 = 114.63(12), C7-Al-C13 = 114.71(11), C1-Al-O1 = 102.58-(11), C7-Al-O1 = 106.72(11), C13-Al-O1 = 102.32(11), Al-O1-H1 = 118(3), Al-O1-C19 = 129.65(18), H1-O1-C19 = 112(3),  $O1-H1\cdots F17A = 144(3)$ ,  $O1-H1\cdots F2 = 130$ -(3).

angle O1-H1···F17B = 154.3(3)°. Furthermore, weak intramolecular hydrogen bonding is also shown to involve H1 with the distance H1···F18 = 2.32(3) Å and the angle O1-H1···F18 = 120.3(3)°.

The metrical parameters of the  $(C_6F_5)_3Al$  fragment in **2** (Figure 2)<sup>17</sup> are nearly identical with those in **1**; the methanol molecule in **2** also adopts a trigonalplanar geometry with the sum of the angles at oxygen of 359.65°. Analogous to the water complex **1**, there is also medium to weak intermolecular and intramolecular hydrogen bonding involving the OH hydrogen in **2**, as shown by the following short distances and large angles: intermolecular, H1…F17A = 2.22(4) Å, O1-H1…F17A = 144(3)°; intramolecular, H1…F2 = 2.23(4) Å, O1-H1…F2 = 130(3)°.

The solution stability of **1** and **2** in toluene- $d_8$  was investigated using <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy. Figure 3 shows representative spectral changes in <sup>19</sup>F NMR of **1** (0.030 M solution in toluene- $d_8$ ) versus time at ambient temperature for a period of 7 days. The toluene solution of **1** is fairly stable, with a half-life of  $t_{1/2} = 33$ h at room temperature, obtained from monitoring the spectral changes in its <sup>1</sup>H NMR. The formation of an elimination product, C<sub>6</sub>F<sub>5</sub>H, can be readily detected by <sup>19</sup>F NMR (δ –139.20 (dd, *o*-F), –154.20 (t, *p*-F), –162.50 (tt, *m*-F)) and by <sup>1</sup>H NMR ( $\delta$  5.81 (m)). The coproduct, the putative hydroxide complex  $[(C_6F_5)_2AIOH]_n$  (3, dimer or higher oligomer), is clearly seen from both the  $^1\mathrm{H}$  ( $\delta$ 4.70 (s)) and <sup>19</sup>F NMR spectra ( $\delta$  –123.33 (dd, *o*-F), -147.20 (t, p-F), -158.81 (t, m-F)). These <sup>19</sup>F NMR chemical shifts differ considerably from those in 1 (especially those chemical shifts for the para and meta fluorines) but compare well with the analogous, structurally characterized chloride-bridged dimer [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-AlCl]<sub>2</sub> (δ -122.82 (d, 4F, o-F), -145.91 (t, 2F, p-F), -158.80 (tt, 4F, *m*-F)).<sup>18</sup> After a toluene solution stood for an extended period (7 days) at room temperature, 1 completely vanished and was converted to two products  $(C_6F_5H \text{ and } 3)$ . Formation of further pentafluorophenyl elimination products is not observed at room temperature; when a toluene solution of 1 is heated to 65 °C for 15 h, insoluble precipitates formed. Redissolution of the precipitates in THF-d<sub>8</sub>, however, did not reveal any fluorine signals in the <sup>19</sup>F NMR spectrum. The methanol complex 2 is more stable than the water complex 1; the toluene solution of **2** has a half-life of  $t_{1/2} = 193$  h at room temperature. Decomposition of **2** follows the same manner as for 1, leading to the stable, putative methoxide-bridged complex  $[(C_6F_5)_2AlOMe]_n$  (4): <sup>1</sup>H NMR,  $\delta$  3.60 (s)); <sup>19</sup>F NMR,  $\delta$  -123.15 (dd, o-F), -145.15 (t, p-F), -159.19 (tt, m-F). The methoxide 4 exhibits



**Figure 3.** Selected <sup>19</sup>F NMR spectra of **1** in toluene- $d_8$  versus time at room temperature: (×) **1**; (•) C<sub>6</sub>F<sub>5</sub>H; ( $\nabla$ ) **3**.

remarkable stability; there is no noticeable decomposition of **4** when its toluene solution is heated to  $65 \, ^{\circ}C$  for 15 h.

To the best of our knowledge, complexes 1 and 2 represent the first examples of isolable and structurally characterizable triarylaluminum complexes of water and methanol. Two factors, namely, the high Lewis acidity of the ( $C_6F_5$ )<sub>3</sub>Al moiety and moderately strong OH···FC hydrogen bonding, are believed to contribute to the stability of these complexes. The structural characterization of the water complex confirms the proposed the alkyl/arylaluminum–water adduct **A**, an

elusive intermediate involved in the hydrolysis of alkyl/ arylaluminum compounds. Studies are underway to investigate the potential applications of the pronounced activation of weak Brønsted acids such as  $H_2O$  by  $(C_6F_5)_3Al$  in catalysis.

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**Supporting Information Available:** Tables giving crystallographic data for **1** and **2**; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(17)</sup> Crystallographic data for **2**:  $C_{19}H_4AlF_{15}O$ ,  $M_r = 560.20$ ,  $0.50 \times 0.50 \times 0.70$  mm<sup>3</sup>, monoclinic, space group  $P2_1/n$ , a = 12.8362(19) Å, b = 12.6834(19) Å, c = 13.464(2) Å,  $\beta = 114.830(2)^\circ$ , V = 1989.4(5) Å<sup>3</sup>, Z = 12.6834(19) Å, c = 12.464(2) Å,  $\beta = 12.6834(19)$  Å, c = 12.6834(19) Å, c = 12.464(2) Å,  $\beta = 12.6834(19)$  Å, c = 12.6834(19) Å, c = 12.68

<sup>= 4,</sup>  $\rho_{calcd}$  = 1.870 Mg/m<sup>3</sup>,  $\theta$  range for data collection 3.33–23.27°,  $\lambda$  = 0.710 73 Å, T= 173(2) K, 12 194 reflections collected, 2849 independent reflections ( $R_{int}$  = 0.0515), 329 refined parameters, goodness of fit on  $F^2$  1.081, R1 = 0.0443 ( $I > 2\sigma(I)$ ), wR2 = 0.1168, largest difference peak and hole 0.398 and -0.395 e Å<sup>-3</sup>.

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