Organometallics **2003,** *22,* 207−210

First Isolation and Structural Characterization of Triarylaluminum−Water and −Methanol Complexes

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Received October 7, 2002

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,[1] especially in organic synthesis,[2] olefin polymerization catalysis,[3] and polymerization of polar monomers.[4] There has been longstanding interest in the controlled reactions of water with aluminum trialkyl/triaryl compounds due to both scientific curiosity and technological importance.[5] The partial hydrolysis of trialkylaluminum (R_3Al) leads to formation of industrially important, oligomeric alumoxanes[6] that are potent activators for olefin polymerization[7] as well as active catalysts for polymerization of epoxides.[8] 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 ^1H NMR spectroscopic studies[10] have shown that the hydrolysis of R_3Al (R = Me, Et, ^iBu) proceeds with the formation of an alkylaluminum−water complex (**A**), which subsequently

$$\begin{array}{ccc} [R_3Al{\cdot}OH_2] & [R_2Al(\mu\text{-}OH)]_n & [RAl(\mu\text{-}O)]_n \\ \textbf{A} & \textbf{B} & \textbf{C} \end{array}$$

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 ^1H NMR studies, isolation and structural characterization of such a complex still remain a challenge.[5] The use of the bulky trimesityl ligand makes possible the isolation and structural characterization of the trimesitylgallium−water complex $Mes_3Ga{\cdot}OH_2{\cdot}2THF$, which is stabilized by two THF molecules.[11] 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,[5−11] and by the work of Green,[12a,b] Siedle,[12c] 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_2O, CH_3OH). Herein, we report the first isolation and structural characterization of triarylaluminum−water and −methanol complexes: $(C_6F_5)_3Al{\cdot}OH_2$ (**1**) and $(C_6F_5)_3Al{\cdot}OHCH_3$ (**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_2O with $(C_6F_5)_3Al$ 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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10.1021/om020834l CCC: $25.00
Publication on Web 12/06/2002

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} Torr), or in a argon-filled glovebox (<1.0 ppm O_2 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, ^{1}H; 282 MHz, ^{19}F) or a Varian Inova 400 spectrometer. Chemical shifts for ^{1}H spectra were referenced to internal solvent resonances and reported as parts per million relative to tetramethylsilane. ^{19}F NMR spectra were referenced to external $CFCl_3$.

Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was obtained as a research gift from Boulder Scientific Co. and used without further purification for preparative reactions. Tris(pentafluorophenyl)alane ($Al(C_6F_5)_3$, as a 0.5(toluene) adduct) was prepared according to the literature procedure.[13e,g] *Extra caution should be exercised when handling this material, due to its thermal and shock sensitivity.*

$(C_6F_5)_3Al·OH_2$ (1). To a rapidly stirred suspension of $(C_6F_5)_3Al·0.5$(toluene) (0.30 g, 0.52 mmol) in 10 mL of hexanes at −78 °C was added degassed H_2O (9.4 μL, 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 × 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). ^{1}H NMR (benzene-d_6, 23 °C): δ 3.82 (s). ^{1}H NMR (THF-d_8, 23 °C): δ 11.36 (s). ^{19}F NMR (benzene-d_6, 23 °C): δ −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.

$(C_6F_5)_3Al·OHCH_3$ (2). Complex **2** was synthesized in the same manner as for the synthesis of **1**; isolated yield 85%. ^{1}H NMR (benzene-d_6, 23 °C): δ 3.35 (q, J_{H-H} = 4.5 Hz, 1 H; OH), 2.48 (d, J_{H-H} = 4.5 Hz, 3H, CH_3). ^{19}F NMR (benzene-d_6, 23 °C): δ −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.[14] 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 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 $Me_3Al·OH_2$ (at −70 °C in Et_2O)[10] and 9.20 ppm in the putative $Mes_3Al·OH_2$ (at −60 °C in THF-d_8),[11] suggesting the observed highest degree of activation of the weak Brønsted acid H_2O by $(C_6F_5)_3$-Al.

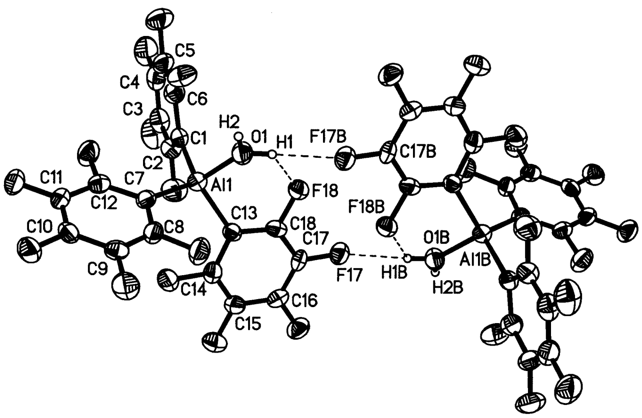

Figure 1. X-ray crystal structure of **1**. Selected bond lengths (Å) and angles (deg): Al1−O1 = 1.857(3), Al1−C1 = 1.987(3), Al1−C7 = 1.979(3), Al1−C13 = 1.978(3), O1−H1 = 0.857(10), H1···F17B = 2.13(2), H1···F18 = 2.32(3), O1−H2 = 0.855(10); C1−Al1−C7 = 115.15(14), C1−Al1−C13 = 112.85(14), C7−Al1−C13 = 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···F17B = 154.3(3), O1−H1···F18 = 120.3(3).

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)[15] 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,[13a] imidazole,[13b] toluene,[13c] and THF groups.[13h] 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[16] in **1** is manifested by the short distance H1···F17B = 2.13(2) Å and the large

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[14] Sheldrick, G. M. SHELXTL, Version 5; Siemens, Madison, WI, 1996.

[15] Crystallographic data for **1**: $C_{18}H_2AlF_{15}O·C_7H_8$, M_r = 638.31, 0.18 × 0.20 × 0.30 mm^3, monoclinic, space group $P2_1/n$, a = 10.318(3) Å, b = 16.319(5) Å, c = 14.427(4) Å, β = 100.902(5)°, V = 2402.1(12) Å^3, Z = 4, ρ_{calcd} = 1.765 Mg/m^3, θ range for data collection 3.12−23.28°, λ = 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^{-3}.

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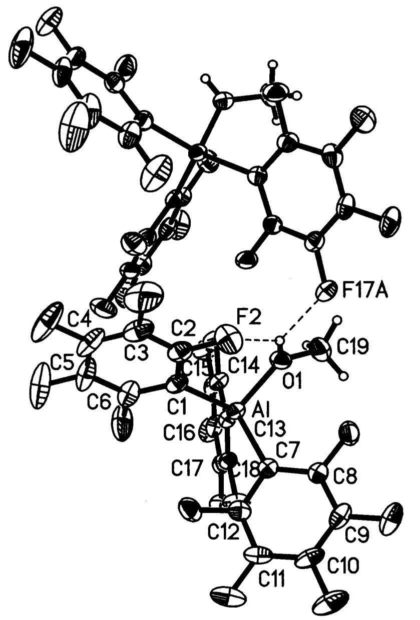

Figure 2. X-ray crystal structure of **2**. Selected bond lengths (Å) and angles (deg): Al−O1 = 1.858(2), Al−C1 = 1.977(3), Al−C7 = 1.985(3), Al−C13 = 1.994(3), O1−C19 = 1.462(4), O1−H1 = 0.81(4), H1···F17A = 2.22(4), H1···F2 = 2.23(4); C1−Al−C7 = 113.97(11), C1−Al−C13 = 114.63(12), C7−Al−C13 = 114.71(11), 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···F17A = 144(3), O1−H1···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)[17] are nearly identical with those in **1**; the methanol molecule in **2** also adopts a trigonal-planar 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 ^{1}H and^{19}F NMR spectroscopy. Figure 3 shows representative spectral changes in ^{19}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 ^{1}H NMR. The formation of an elimination product, C_6F_5H, can be readily detected by ^{19}F NMR (δ −139.20 (dd, *o*-F), −154.20 (t, *p*-F), −162.50 (tt, *m*-F)) and by ^{1}H NMR (δ 5.81 (m)). The coproduct, the putative hydroxide complex $[(C_6F_5)_2AlOH]_n$ (**3**, dimer or higher oligomer), is clearly seen from both the ^{1}H (δ 4.70 (s)) and ^{19}F NMR spectra (δ −123.33 (dd, *o*-F), −147.20 (t, *p*-F), −158.81 (t, *m*-F)). These ^{19}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 $[(C_6F_5)_2AlCl]_2$ (δ −122.82 (d, 4F, *o*-F), −145.91 (t, 2F, *p*-F), −158.80 (tt, 4F, *m*-F)).[18] 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 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_8, however, did not reveal any fluorine signals in the ^{19}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**): ^{1}H NMR, δ 3.60 (s)); ^{19}F NMR, δ −123.15 (dd, *o*-F), −145.15 (t, *p*-F), −159.19 (tt, *m*-F). The methoxide **4** exhibits

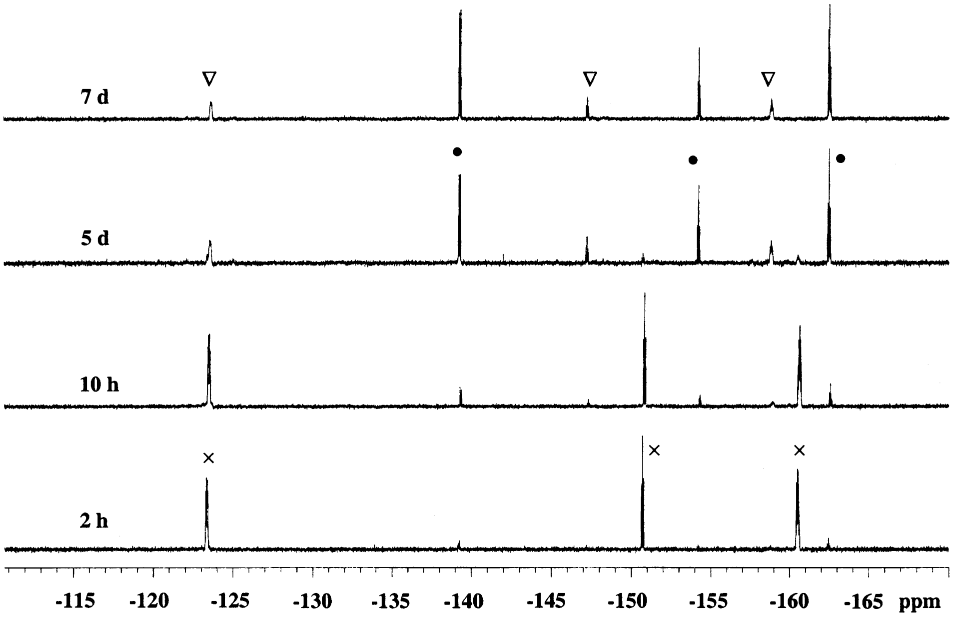

Figure 3. Selected ^{19}F NMR spectra of **1** in toluene-d_8 versus time at room temperature: (×) **1**; (●) C_6F_5H; (▽) **3**.

remarkable stability; there is no noticeable decomposition of **4** when its toluene solution is heated to 65 °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 $(C_6F_5)_3Al$ 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.

Acknowledgment. This work was supported by Colorado State University and the donors of the Petroleum Research Fund, administed by the American Chemical Society. We thank Ms. Susie M. Miller for the X-ray diffraction analysis and Prof. Oren P. Anderson for helpful discussions. E.Y.-X.C. gratefully acknowledges an Alfred P. Sloan Research Fellowship.

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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(17) Crystallographic data for **2**: $C_{19}H_4AlF_{15}O$, $M_r = 560.20$, 0.50 × 0.50 × 0.70 mm^3, monoclinic, space group $P2_1/n$, $a = 12.8362(19)$ Å, $b = 12.6834(19)$ Å, $c = 13.464(2)$ Å, $\beta = 114.830(2)°$, $V = 1989.4(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.870$ Mg/m^3, θ 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^{-3}.

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