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Tetrahydrofurfuryloxide Derivatives of Alkyl Aluminum Species

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Tetrahydrofurfuryl alcohol (H-OTHF) was successfully reacted with a series of aluminum alkyls (AlR_3) to yield compounds of the general formula $[R_2Al(\mu\text{-OTHF})]_2$ where R = CH_3 (**1**), CH_2CH_3 (**2**), and $CH_2CH(CH_3)_2$ (**3**). Further, reactivity studies showed that the alkyls for **1** were easily exchanged, forming compounds of the general formula $[Me(OR)Al(\mu\text{-OTHF})]_2$ where OR = $OC_6H_3(Me)_2$-2,6 (**4**), $OC_6H_3(CMe_3)_2$-2,6 (**5a**), and $OSi(C_6H_5)_3$ (**6**). For **5a**, reflux temperatures were required to get the full exchange; otherwise the asymmetric derivative $[Me(OR)Al(\mu\text{-OTHF})_2AlMe_2]$ (**5b**) was isolated. The bulk powders of **1**−**6** were found to be in agreement with the crystal structures on the basis of elemental analyses and multinuclear solid state NMR studies. Multinuclear solution state NMR studies indicate that the alkyl OTHF derivatives have *cis/trans* isomers due to the chiral proton on the OTHF ligand.

Introduction

The family of trialkyl aluminum (AlR_3) reagents has found extensive use in catalyst, organic synthesis, materials production, and many other complex systems. We are interested in exploring the utility of these precursors for the production of H-storage materials. To exploit the properties of the starting precursors for any of these systems, it is necessary to understand the role of AlR_3. Therefore, numerous structurally characterized compounds that possess an AlR_3 moiety as a co-ligand have been reported in the literature.[1] Two predominant binding modes for this compound have been observed: (i) coordination through a bridging five-coordinate carbon center and (ii) reactively binding through loss of a proton to bind a methylene group.[2−14] Control over the final structures of these precursors is limited due to the high reactivity of AlR_3.

One method often employed to garner control during synthesis is to selectively introduce steric bulk around the metal center. For early transition metals, this has led to the dominant use of cyclopentadienyl ligands; however, introduction of the cyclopentadienyl ligand[15,16] has not been as successful in controlling structure properties for Al^{3+} compounds. Alternatively, alkoxide ligands have also proven to be a useful ligand set, since their steric bulk can be easily manipulated. Numerous alkoxy aluminum alkyl systems have been reported in the literature.[17]

Of these, one report revealed the use of 8-thiophenemethanol ($H\text{-}OCH_2\text{-}2\text{-}C_4H_3S$, H-OTPM)-modified $AlMe_3$, which led to the isolation of $[(Me_2Al)_3(\mu\text{-}OCH_2\text{-}2\text{-}C_4H_3S)_6Al$.[18] This compound contained both four- and six-coordinated Al metal centers and was of interest since the alkyl ligands were still accessible while the remainder of the molecule was sterically hindered. An identical structure for 2-furanmethanol (tetrahydrofurfuryl alcohol, $H\text{-}OCH_2\text{-}2\text{-}C_4H_8O$, H-OTHF) was proposed.[18] This species is of interest to us, since again the core of the structure would be isolated from the external reactive species and thus could be used as a template to build large, more complex species. In addition, the OTHF ligand is of more interest than the OTPM ligand since there are no potential S contaminants after processing.

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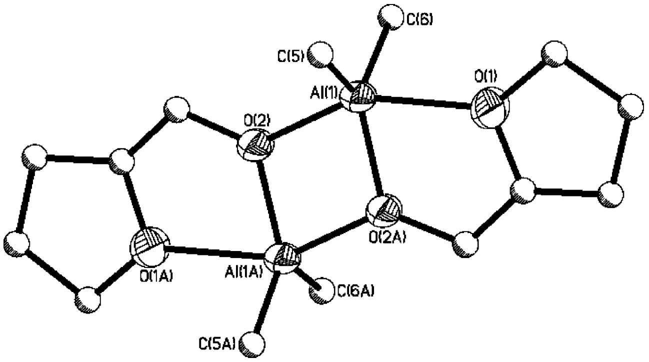

Figure 1. Plot of **1**. Thermal ellipsoids are drawn for heavy atoms at the 30% level, and carbon atoms are drawn as ball and sticks for clarity.

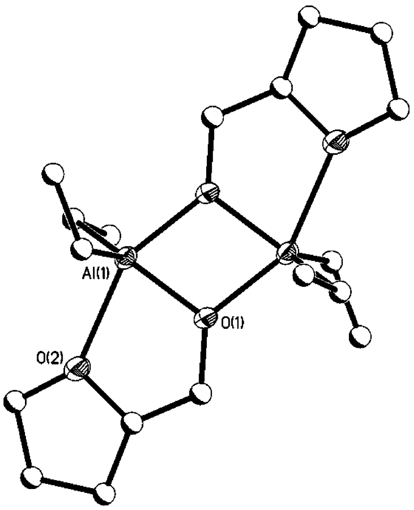

Figure 2. Plot of **2**. Thermal ellipsoids are drawn for heavy atoms at the 30% level, and carbon atoms are drawn as ball and sticks for clarity.

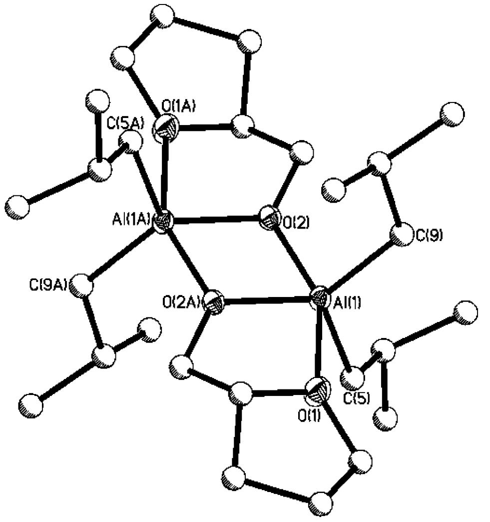

Figure 3. Plot of **3**. Thermal ellipsoids are drawn for heavy atoms at the 30% level, and carbon atoms are drawn as ball and sticks for clarity.

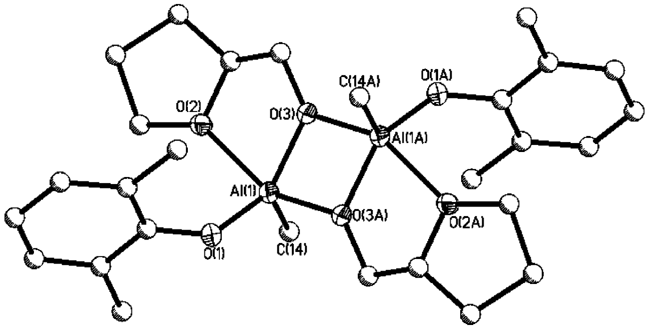

Figure 4. Plot of **4**. Thermal ellipsoids are drawn for heavy atoms at the 30% level, and carbon atoms are drawn as ball and sticks for clarity.

The product isolated from our attempts of the literature preparation[18] had been heated and stirred for a longer time than the original reaction and had several analytical results that were not consistent with the proposed structure. Therefore, we isolated crystals from the reaction and found the resultant material was [$Me_2Al(\mu\text{-OTHF})]_2$ (**1**, Figure 1). The elevated temperatures and longer stir times allow for greater ligand redistribution and may explain the variations between the observed products and the literature product.[18]

$$AlR_3 + \text{H–OTHF} \rightarrow [R_2Al(\mu\text{-OTHF})]_2 \qquad (1)$$
$$R = Me, Et, Bu^i$$

Once isolated, the general reactivity of **1** was investigated. Due to the presence of the OTHF ligand, the remainder of the molecule could be selectively reacted in an effort to build controlled complex precursors. This report details the synthesis and characterization of a novel family of aluminum alkyl compounds using the OTHF template, including $[R_2Al(\mu\text{-OTHF})]_2$ (R = CH_3 (**1**, Me); CH_2CH_3 (**2**, Et); $CH_2CH(Me)_2$ (**3**; Bu^i)) and $(OR)_xMe_{4-x}Al_2(\mu\text{-OTHF})_2$ [$x = 2$: OR = $OC_6H_3(Me)_2$-2,6 (**4**, DMP), $OC_6H_3(CMe_3)$-2,6 (**5a**, DBP), $OSi(C_6H_5)_3$ (**6**, TPS); $x = 1$, OR = DBP (**5b**)] shown in Figures 2–6.

Experimental Section

All compounds described below were handled with rigorous exclusion of air and water using standard Schlenk line and glovebox techniques. All solvents were stored under argon and used as received (Aldrich) in Sure Seal bottles. The following chemicals were used as received from (Aldrich) under argon atmosphere: $AlMe_3$, $AlEt_3$, 1 M $AlBu^i_3$ (toluene), H-OTHF, H-DMP, H-DBP, and H-TPS. *Note! Extreme care must be taken in the handling and storage of aluminum alkyl compounds and the subsequent waste due to the inherent pyrophoricity of these precursors*.

FT-IR data were obtained on a Bruker Vector 22 instrument using KBr pellets under an atmosphere of flowing nitrogen. Elemental analysis was performed on a Perkin-Elmer 2400 CHN-S/O elemental analyzer. Melting points were determined on samples sealed in a glass tube under an atmosphere of argon using an Electrothermal melting point apparatus. Thermal gravimetric analysis/differential thermal analysis (TGA/DTA) data were acquired on a Universal V3.0G TA instrument by heating from room temperature to 650 °C at a ramp rate of 5 °/min under an argon atmosphere.

All NMR samples were prepared from dried crystalline materials that were handled and stored under an argon atmosphere and redissolved in the appropriate deuterated solvent (toluene-d_8) at saturated solution concentrations. All solution spectra were obtained on a Bruker DRX400 spectrometer at 399.8, 100.1, and 104.2 MHz for ^1H, ^{13}C, and ^{27}Al experiments, respectively. A 5 mm broadband probe was used for all experiments. The ^1H NMR spectra were obtained using a direct single pulse excitation, with a 10 s recycle delay and eight signal averages. The $^{13}C\{^1H\}$ NMR spectra were obtained using a WALTZ-16 composite pulse ^1H decoupling, a 5 s recycle delay, and a $\pi/4$ pulse excitation. The ^{27}Al NMR spectra were

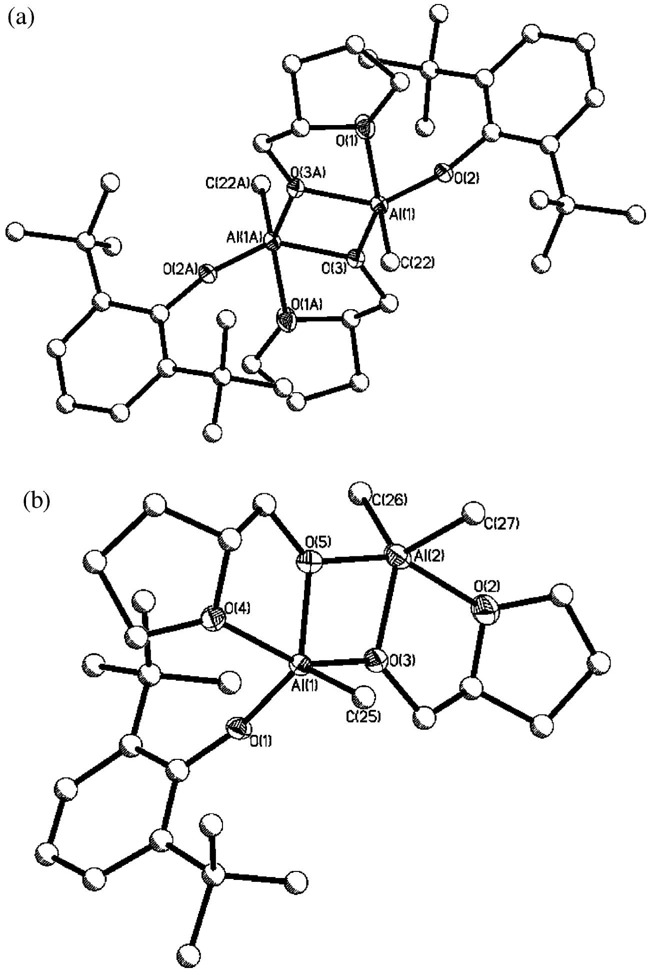

Figure 5. Plots of (a) **5a** and (b) **5b**. Thermal ellipsoids are drawn for heavy atoms at the 30% level, and carbon atoms are drawn as ball and sticks for clarity.

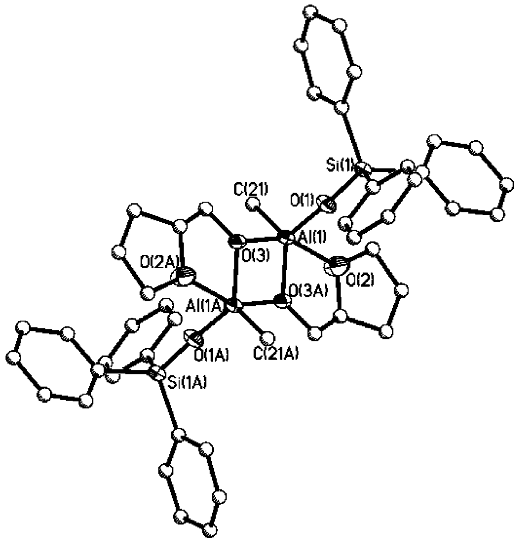

Figure 6. Plot of **6**. Thermal ellipsoids are drawn for heavy atoms at the 30% level, and carbon atoms are drawn as ball and sticks for clarity.

obtained using a WALTZ-16 composite pulse ^{1}H decoupling, a 500 ms recycle delay, a $\pi/2$ pulse excitation, and 128 signal averages.

The solid state ^{13}C NMR MAS and cross-polarization (CP) MAS NMR experiments were collected on a Bruker Avance400 NMR spectrometer with a 4 mm broadband probe at a spinning frequency of 4 kHz. Typical ^{13}C acquisition conditions utilized a direct single pulse Bloch decay with a 4.5 μs $\pi/2$ pulse, with two-phase modulation (TPPM) ^{1}H decoupling,[20] 128−432 scan averages, and a 240 s recycle delay. Acquisition conditions for the ^{13}C cross-polarization (CP) MAS NMR spectra included a 1 ms CP contact pulse, TPPM ^{1}H decoupling, 1024 scan averages, and a 10 s recycle delay. The ^{13}C NMR data were referenced to the carbonyl of the secondary standard glycine (δ = 176 ppm with respect to TMS δ = 0 ppm).

General Reaction. The appropriate AlR$_3$ was added to toluene (or hexanes) and stirred under an argon atmosphere. H-OTHF was added dropwise to this mixture (*note* the reaction is very exothermic and large volumes of gas are generated), followed by stirring for 12 h. If after this time, a precipitate was present, the reaction mixture was heated until the solution was clear and then allowed to sit at glovebox temperatures or cooled to −35 °C until X-ray quality crystals formed.

[Al(Me)$_2$(OTHF)]$_2$ (1). AlMe$_3$ (15.0 g, 20.8 mmol), H-OTHF (21.3 g, 20.8 mmol), and 20 mL of toluene were used. Yield: 29.0 g (88.1%). FT-IR (KBR, cm^{-1}): 2980(s), 2926(s), 2889(s), 2872(s), 2824(s), 1466(w), 1450(w), 1361(w), 1333(w), 1260(w), 1185(s), 1133(w, sh), 1108(m, sh), 1075(s, br), 1063(s,br), 1014(m), 993(m), 959(w). ^{1}H NMR (399.8 MHz, tol-d_8): δ 3.67(1H, m, OTHF), 3.63(1H, m, OTHF), 3.46(1H, m, OTHF), 3.54(1H, m, OTHF), 3.12(1H, m, OTHF) 1.39 to 1.19(3.0H, m, OTHF), 0.89(1H,m, OTHF), −054(6H, m, CH_3). ^{13}C{^{1}H} NMR (100.1 MHz, tol-d_8): δ 79.3, 67.3, 63.1, 26.9, 26.1 (OTHF), −9.3 (CH$_3$). ^{27}Al (104.2 MHz, tol-d_8): δ 120.3, 63.1, 0.8. Anal. Calcd for C$_7$H$_{15}$AlO$_2$: 53.15 C, 9.55 H. Found: 53.33 C, 9.41 H.

[Al(Et)$_2$(OTHF)]$_2$ (2). AlEt$_3$ (10.0 g, 87.6 mmol), H-OTHF (8.95 g, 87.5 mmol), and 20 mL of toluene were used. Yield: 10.9 g (67.2%). FT-IR (KBR, cm^{-1}): 2981(s, sh), 2926(s), 2886(s), 2853(s), 2791(s), 2715(m), 1466(m), 1460(m), 1412(m), 1358(w), 1331(w), 1261(m), 1230(w), 1187(m), 1077(s), 1063(s), 1017(m), 991(m), 946(m), 918(m), 640(s, br). ^{1}H NMR (399.8 MHz, tol-d_8): δ 3.78(1H, m, OTHF), 3.64(1H, dq, OTHF), 3.53(1H, m, OTHF), 3.38(1H, q, OTHF), 3.15(1H, q, OTHF), 1.36 to 1.28(9H, m, OTHF and CH$_2$CH_3), 0.90(1H, m, OTHF), 0.09(4.5H, m, CH_2CH$_3$). ^{13}C{^{1}H} NMR (100.1 MHz, tol-d_8): δ 79.5, 68.1, 64.5, 26.9, 21.1(OTHF), 10.9(CH$_2$$CH_3$), 1.32($CH_2CH_3$). ^{27}Al (104.2 MHz, tol-d_8): δ 131.2, 63.9, 5.1. Anal. Calcd for C$_9$H$_{19}$AlO$_2$: 58.05 C, 10.28 H. Found: 58.13 C, 9.97 H.

[Al(Bu^i)$_2$(OTHF)]$_2$ (3). AlBu$^i_3$ (1.0 M, 32.5 mL, 32.5 mmol), H-OTHF (3.33 g, 32.5 mmol), and 20 mL of toluene were used. Yield: 6.83 g/7.84 (87.1%). FT-IR (KBR, cm^{-1}): 2940(s), 2888(s), 2858(s), 2782(s), 1460(m), 1405(w), 1372(w), 1356(m), 1331(w), 1313(w), 1259(w), 1179(m), 1064(s), 1014(s), 991(m), 939(m), 921(w), 828(m), 817(m), 672(s), 642(s), 594(w), 562(w), 513(w), 469(w), 444(m), 420(w). ^{1}H NMR (399.8 MHz, tol-d_8): δ 3.81(1H, m, OTHF), 3.69−3.56(3H, m, OTHF), 3.37(1H, m, OTHF), 3.19(1H, q, OTHF), 1.19(29.0H, m, OTHF and (CH_2)$_3$CH$_3$), 0.90(1H, m, (CH_2)$_3$CH$_3$), 0.081(6H, m, (CH$_2$)$_3$CH_3). ^{13}C{^{1}H} NMR (100.1 MHz, tol-d_8): δ 79.3, 68.1, 64.7, 30.9, 29.9 (OTHF) 27.3, 27.0, 26.5, 24.1, 23.7, 23.2 (CH$_2$)$_3$$CH_3$). ^{27}Al (104.2 MHz, tol-d_8): δ 121.9, 65.1. Anal. Calcd for C$_{13}$H$_{27}$AlO$_2$: 64.43 C, 11.23 H. Found: 64.60 C, 10.95 H.

General Alkoxylation Reaction. Under an atmosphere of argon, compound **1** was dissolved in toluene, and the appropriate H-OR dissolved in toluene was slowly added by pipet. The reaction is exothermic, but the rate of methane gas evolution is highly dependent on the alcohol used. After stirring for 12 h, the mixture was heated to ensure complete exchange and/or to redissolve any precipitates that may have formed. After this, the mixture was allowed to cool slowly and then set aside to slowly evaporate until X-ray quality crystals formed.

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[Al(Me)(DMP)(OTHF)]$_2$ (4). Compound **1** (0.500 g, 1.58 mmol), H-DMP (0.386 g, 3.16 mmol), and 20 mL of toluene were used. Yield: 0.65 g (77.7%). FT-IR (KBR, cm^{-1}): 3070(w, sh), 3005 (w, sh), 2980(m, sh), 2927(s, br), 2892(m), 2877(m), 2825(w, sh), 1618(m), 1470(s, br), 1432(s), 1288(s), 1240(m), 1190(s), 1074(s), 1015(m), 994(m), 917(w), 888(m), 934(m, br), 769(m), 752(m), 754(m), 6801(s, br), 587(w), 561(w), 509(w). ^{1}H (399.8 MHz, tol-d_8): δ 7.07(2H, d, OCMe-2,6, $J_{\mathrm{H-H}}$ = 3.6 Hz), 6.72(1H, t, OCMe-2,6, $J_{\mathrm{H-H}}$ = 7.6 Hz), 3.77−3.42(4H, m, OTHF), 3.29−2.95(3.0H, m, OTHF), 2.83(0.2H, t, OTHF, $J_{\mathrm{H-H}}$ = 10 Hz), 2.41(8.4H, m, $\mathrm{OC_6H_3(C}H_3)_2$), 1.33−0.51(8.2H, m, OTHF), −0.42, −0.44, −0.46,−0.53, −0.61(3.5H, s, $\mathrm{C}H_3$). ^{13}C{^{1}H} (100.1 MHz, tol-d_8): δ 131.2, 128.8, 127.4, 127.3, 118.0, 117.9($\mathrm{O}C_6\mathrm{H_3(CH_3)_2}$), 80.3, 80.2, 80.1, 80.0, 79.5, 79.4, 68.7, 68.6, 68.3, 68.1, 68.0, 63.7, 63.6, 63.5, 63.4, 63.3, 32.4, 26.9, 26.1, 26.0, 25.8, 23.5(OTHF, $\mathrm{OC_6H_3(}C\mathrm{H_3)_2}$), 18.7, 18.6, 18.5($C\mathrm{H_3}$). ^{27}Al (104.2 MHz, tol-d_8): δ 69.6. Anal. Calcd for $C_{28}H_{42}Al_2O_6$: 63.62 C, 8.00 H. Found: 63.15 C, 7.81 H.

[Al(Me)(DBP)(OTHF)]$_2$ (5a). This reaction mixture was heated at reflux temperatures for 12 h prior to attempting to grow crystals. Compound **1** (1.00 g, 3.16 mmol), H-DBP (1.31 g, 6.37 mmol), and 20 mL of toluene were used. Yield: 1.85 g (83.4%). FT-IR (KBR, cm^{-1}): 2957(s), 2926(s), 2889(s), 2874(s), 1363(w), 1261(w), 1184(m), 1100(m, sh), 1076(s, br), 1063(s, br), 1016(s), 806(m), 747(m), 680(s, br), 465(w). ^{1}H (399.8 MHz, tol-d_8): δ 7.38−7.30(1.2H, m, $\mathrm{OC_6}H_3\mathrm{(C(CH_3)_3)_2}$), 7.11(0.7H, d, $\mathrm{OC_6}H_3\mathrm{(C(CH_3)_3)_2}$, $J_{\mathrm{H-H}}$ = 4 Hz), 6.81(0.6H, t, $\mathrm{OC_6}H_3\mathrm{(C(CH_3)_3)_2}$, $J_{\mathrm{H-H}}$ = 5.2 Hz), 3.97−2.99(4.5H, M, OTHF), 1.66, 1.648, 1.62(11.3H, s, $\mathrm{OC_6H_3(C(C}H_3)_3)_2$), 1.33(7.6H, s, $\mathrm{OC_6H_3(C(C}H_3)_3)_2$), −0.20, −0.30, −0.31, −0.32, −0.48, −0.50, −0.53, −0.54, −0.55(2H, s, $\mathrm{C}H_3$). ^{13}C{^{1}H} (100.1 MHz, tol-d_8): δ 139.6, 125.9, 125.6, 120.7, 117.6 ($OC_6\mathrm{H_3(C(CH_3)_3)_2}$)), 87.9, 81.9, 79.3, 79.1, 69.9, 64.1, 63.2, 62.8, 36.1, 35.8, 34.7, 32.4, 32.1, 30.7, 31.6, 23.5 (OTHF, $\mathrm{OC_6H_3(C(C}H_3)_3)_2$), 14.5 ($C\mathrm{H_3}$). Anal. Calcd for $C_{20}H_{33}AlO_5$: 68.94 C, 9.55 H. Found: 68.83 C, 9.38 H.

$Al_2(Me)_3(OTHF)_2(DBP)$ (5b). Compound **1** (1.00 g, 3.16 mmol), H-DBP (0.653 g, 3.16 mmol), and 10 mL of toluene were used. Reflux temperatures are not necessary to isolate **5b**. Yield: 1.40 g (86.9%). FT-IR (KBr, cm^{-1}): 3034(w), 2956(s), 2927(s), 2873(m), 1720(w), 1655(w), 1561(w), 1466(m), 1460(m), 1420(s), 1288(s), 1280(s), 1188(m), 1071(s), 1018(m, sh), 902(m), 883(m), 819(m), 752(m), 701(s), 670(s), 623(m), 473(m). ^{1}H (399.8 MHz, tol-d_8): δ 7.38, 7.36(d, $\mathrm{OC_6}H_3\mathrm{(C(CH_3)_3)_2}$, $J_{\mathrm{H-H}}$ = 4.0 Hz), 6.81, 6.08(t, $\mathrm{OC_6}H_3\mathrm{(C(CH_3)_3)_2}$, $J_{\mathrm{H-H}}$ = 8.0 Hz), 3.90−2.98(5.4H, m, OTHF), 1.66, 1.63, 1.61(10.4H, s, $\mathrm{OC_6H_3(C(C}H_3)_3)_2$), −0.21, −0.30, −0.32, −0.39, −0.49, −0.53, −0.54, −0.56(4.3H, s, CH_3). ^{13}C{^{1}H} (100.1 MHz, tol-d_8): δ 139.1, 125.9, 125.5, 117.5, 117.4 ($\mathrm{O}C_6\mathrm{H_3(C(CH_3)_3)_2}$), 79.6, 19.2, 78.9, 68.9, 68.7, 67.7, 64.2, 63.1, 62.8, 35.8, 32.4, 32.1, 31.9, 31.6, 31.6, 30.7, 27.1, 25.8, 25.6, 23.5 (OTHF, $\mathrm{O}C_6\mathrm{H_3(}C(C\mathrm{H_3)_3)_2}$), 14.7($C\mathrm{H_3}$). ^{27}Al (104.2 MHz, tol-d_8): δ 63.8. Anal. Calcd for $C_{27}H_{48}Al_2O_5$: 64.01 C, 9.55 H. Found: 64.01 C, 9.34 H.

[Al(Me)(TPS)(OTHF)]$_2$ (6). Compound **1** (0.500 g, 1.58 mmol), H-TPS (0.874 g, 3.16 mmol), and 20 mL of toluene were used. Yield: 1.25 (85.1%). FT-IR (KBR, cm^{-1}): 3134(s), 3066(s), 3047(s), 3021(s), 2997(s), 2926(s, br), 2877(s), 1428(s), 1261(w), 1192(w), 1113(s), 1076(s, br), 1064(s, br), 1026(m), 998(m), 825(m), 744(s), 705(s), 663(m, br), 560(w), 516(s), 468(m), 424(w). ^{1}H (399.8 MHz, tol-d_8): δ 7.85, 7.19(2.5H, br m, $C_6\mathrm{H_5}$), 3.6−2.8, 2.50, 1.25−0.87(1.0H, m, OTHF), −0.34, −0.37, −0.40, −0.42, and −0.57(0.5H, m, $\mathrm{C}H_3$). ^{13}C{^{1}H} (100.1 MHz, tol-d_8): δ 140.9, 140.3, 140.1, 137.2, 136.2, 136.1, 136.0, 136.0, 129.6, 129.4, 128.8, 128.1, 126.0($\mathrm{OSi(}C_6\mathrm{H_5)_3}$) 81.9, 79.5, 79.3, 79.1, 68.0, 67.7, 66.2, 64.3, 64.2, 63.3, 32.5, 26.8, 25.8, 25.7, 23.4 (OTHF), 14.6 ($C\mathrm{H_3}$). ^{27}Al (104.2 MHz, tol-d_8): δ 70.5. Anal. Calcd for $C_{55}H_{62}Al_2O_6Si_2$: 71.09 C, 6.73 H. Found: 71.12 C, 6.77 H.

Table 1. Data Collection Parameters for 1−3

	1	**2**	**3**
chemical formula	$C_{14}H_{28}Al_2O_4$	$C_{18}H_{38}Al_2O_4$	$C_{26}H_{54}Al_2O_4$
fw	314.32	372.44	484.65
temp (K)	273(2)	203(2) K	293(2)
space group	monoclinic *C*2/*c*	monoclinic *P*2(1)/*n*	triclinic $P\bar{1}$
a (Å)	16.242(4)	15.3187(16)	9.298(2)
b (Å)	9.887(2)	7.9024(8)	9.535(2)
c (Å)	13.764(3)	18.3558(19)	10.182(3)
α (deg)			91.508(4)
β (deg)	123.231(4)	96.019(2)	109.772(4)
γ (deg)			115.180(4)
V (Å^3)	1848.7(7)	2209.8(4)	753.3(3)
Z	4	4	1
D_{calcd} (Mg/m^3)	1.129	1.119	1.068
μ(Mo Kα) (mm^{-1})	0.166	0.148	0.122
R1[a] (%) (all data)	8.74 (11.68)	7.63 (9.45)	6.98 (7.71)
wR2[b] (%) (all data)	24.72 (27.60)	19.11 (20.64)	18.08 (18.82)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o| \times 100$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(w|F_o|^2)^2]^{1/2} \times 100$.

Table 2. Data Collection Parameters for 4

chemical formula	$C_{28}H_{42}Al_2O_6$
fw	528.58
temp (K)	203(2)
space group	triclinic $P\bar{1}$
a (Å)	7.9767(8)
b (Å)	13.2255(13)
c (Å)	14.4924(15)
α (deg)	85.607(2)
β (deg)	81.167(2)
γ (deg)	76.769(2)
V (Å^3)	1469.3(3)
Z	2
D_{calcd} (Mg/m^3)	1.195
μ(Mo Kα) (mm^{-1})	0.136
R1[a] (%) (all data)	7.83 (9.16)
wR2[b] (%) (all data)	17.85 (18.85)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o| \times 100$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(w|F_o|^2)^2]^{1/2} \times 100$.

General X-ray Crystal Structure Information. Each crystal was mounted onto a thin glass fiber from a pool of Fluorolube and immediately placed under a liquid N_2 stream, on a Bruker AXS diffractometer. The radiation used was graphite-monochromatized Mo Ka radiation (λ = 0.7107 Å). The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination and data collection were carried out using SMART Version 5.054 software. Data reduction was performed using SAINT Version 6.01 software. The structure refinement was performed using XSHELL 3.0 software. The data were corrected for absorption using the SADABS program within the SAINT software package. Data collection parameters are given in Tables 1−4 for **1**−**3**, **4**, **5a**,**b**, and **6**, respectively.

Each structure was solved using direct methods. This procedure yielded the heavy atoms, along with a number of C, N, and O atoms. Subsequent Fourier synthesis yielded the remaining atom positions. In cases in which the C, N, and O atoms were not significantly disordered, the hydrogen atoms were fixed in positions of ideal geometry and refined within the XSHELL software. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic *U* of the C atoms to which they were bonded. Therefore, idealized hydrogen bond distances were excluded from the finalized structural tables. In cases in which the atoms were not significantly disordered, the final refinement of each compound included anisotropic thermal parameters on all non-hydrogen atoms. Additional information concerning the data collection and final structural solutions of **1**−**6** can be found in the Supporting Information. Any

Table 3. Data Collection Parameters for 5a and 5b

	5a	5b
chemical formula	$C_{40}H_{66}Al_2O_6$	$C_{27}H_{48}Al_2O_5$
fw	696.89	506.61
temp (K)	203(2)	203(2)
space group	monoclinic $P2(1)/n$	monoclinic $P2(1)/n$
a (Å)	9.6840(16)	12.793(2)
b (Å)	12.117(2)	14.875(3)
c (Å)	17.288(3)	16.615(3)
β (deg)	92.609(3)	110.777(3)
V (Å^3)	2026.4(6)	2956.2(9)
Z	2	4
D_{calcd} (Mg/m^3)	1.142	1.138
μ(Mo Kα) (mm^{-1})	0.114	0.130
R1^a (%) (all data)	6.30 (7.82)	7.46 (10.79)
wR2^b (%) (all data)	15.85 (14.14)	15.60 (14.22)

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| \times 100$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(w|F_o|^2)^2]^{1/2} \times 100$.

Table 4. Data Collection Parameters for 6

chemical formula	$C_{55}H_{62}Al_2O_6Si_2$
fw	929.19
temp (K)	203(2)
space group	monoclinic $C2/c$
a (Å)	11.542(3)
b (Å)	19.145(5)
c (Å)	23.515(6)
β (deg)	98.444(4)
V (Å^3)	5140(2)
Z	4
D_{calcd} (Mg/m^3)	1.201
μ(Mo Kα) (mm^{-1})	0.151
R1^a (%) (all data)	8.18 (21.49)
wR2^b (%) (all data)	11.89(23.71)

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| \times 100$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(w|F_o|^2)^2]^{1/2} \times 100$.

variations from standard structural solution associated with the representative compounds are discussed below.

Results and Discussion

While the previous literature report indicated the structure of the H-OTHF substituted-$AlMe_3$ was $[(Me_2Al)_3(\mu\text{-OTHF})_6]Al$,[18] under the conditions reported here, which differed by higher synthesis temperatures and longer reaction times, the product isolated was determined to be **1**. A literature search of other H-OTHF Al adducts indicates that there are only a few structurally characterized species that use both this metal and ligand;[21,22] however, these structures involve either other metals or halide ligands that may be undesired for materials synthesis. Another Al complex with similar ligand constructs involves the quinaldinato ligand, yielding the dinculear complexes $[(Bu^i)_2Al(\mu\text{-O-8-}C_{10}H_9N)]_2$ and $[(Bu^i)Al(\mu\text{-O-8-}C_{10}H_9N)_2]_2$,[23] which exhibited strong fluorescent emissions. Our initial investigations explored the effect that the steric bulk of the alkyl group would have on the structure and investigated the ability to exchange OR on the central core of **1**. The following shows the results of these studies.

Synthesis. H-OTHF dissolved in toluene was *slowly* added via pipet to a solution of AlR_3 in the same solvent (eq 1, *note*: this reaction is very exothermic!). After addition was complete, the reaction was stirred for 0.5 h and then was warmed until the reaction boiled to ensure complete exchange. For the DBP derivative where $n = 2$, the reaction required longer reflux times. After this, the reaction was allowed to cool to room temperature and set aside until crystals formed. No change in color was noted throughout the reaction. FTIR data indicated that the alcohol had been de-protonated and was coordinated to the Al metal center. To characterize these species, X-ray crystallographic studies were undertaken. The products from each of these reactions were isolated as **1**−**6**, and the plots are shown in Figures 1−6, respectively.

Solid State Structure. The solid state structures of compounds **1**−**6** are all dinuclear with each Al adopting a five-coordinated distorted square base pyramidal (SBP) geometry. The bond distances and angles are consistent within this family and with what was reported in the literature for similar Al/OTHF systems.[21−23] The OTHF ligand acts as a chelating bridging moiety where the alcohol oxygen acts as the bridge and the THF oxygen coordinates to the metal. The remaining two sites are filled by either the starting alkyl or modifying alkoxides. The degree of substitution is controlled by the steric bulk of the ligand. For instance, the H-DMP and H-TPS reagents easily add 2 equiv to the Al metal centers, forming **4** and **6** at room temperature; however, we were not able to isolate the monosubstituted species for this ligand set under these conditions. However, reflux temperatures were required to obtain the disubstituted species **5a**, whereas room-temperature conditions with DBP-H led to the monosubstituted species **5b**. Additional substitution becomes difficult for any of the ligands investigated, and we have not been able to isolate a fully substituted aryloxide species. The IR spectra show the expected loss of OH stretch and the various substituents for the different substitutions.

Thermal Properties. The high reactivity of the alkyls does not appear to affect their stability at high temperatures, since the elemental analyses of these species are, surprisingly, in full agreement with the crystal structure. The melting point was determined for each of the alkyl derivatives: **1** at 145 °C, **2** at 65 °C, **3** at 85 °C.

TGA/DTA data obtained on these compounds shows almost complete volatilization of **1**−**3** before 300 °C in a single step in the TGA. The observed TGA weight loss for conversion to the expected Al_2O_3 is substantially beyond the theoretical amount. The DTA reveals an endotherm at ∼150, 73, and 88 °C for **1**−**3**, respectively, which correlates with the observed melting points, vide infra. This is followed by another endotherm for **1** around 200 °C but two exotherms for **2** and **3** at 260/300 and 287/328 °C associated with the weight loss. The TGA weight loss revealed only a very small amount of material was left in the sample holder upon completion of the thermal treatment. These traits (high volatility, low melting point, and low decomposition temperature) make **1**−**3** suitable candidates for metal organic chemical vapor deposition (MOCVD) precursors or for nanoparticle generation. Additional work to verify this is underway.

Thermal analysis of **4**−**7** showed multistep weight loss in the TGA coupled with an exothermic event in

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[21] Sobota, P.; Utko, J.; Brusilovets, A. I.; Jerzykiewicz, L. B. *J. Organomet. Chem.* **1998**, *553*, 1998.

[22] Sobata, P.; Utko, J.; Ejfler, J.; Jerzykiewics, L. B. *Organometallics* **2000**, *19*, 4929.

[23] Toulokhonova, I. S.; Guzei, I.; Kavana, M.; West, R. *Main Group Met. Chem.* **2002**, *25*, 489.

the DTA profile for each sample. The DBP derivative shows two exothermic peaks in the DTA. The weight loss of the species is less than calculated for complete conversion to Al_2O_3. The additional weight observed is most likely a result of the presence of amorphous carbon due to incomplete combustion, which is consistent with the final black-colored powder isolated. The alkoxide derivatives all exhibit a small endotherm associated with melting of the precursor. Decomposition of the precursor is initiated after 250 °C, and complete weight loss is achieved prior to 500 °C with no further thermal events.

Solution State NMR. Crystalline material of **1**−**6** was dried and then redissolved in the appropriate solvent to investigate the solution behavior of these compounds. Several characteristics of the OTHF ligand were known to complicate the solution behavior of these compounds. Once bound to the Al metal center through the alcohol atom, the OTHF ligand has nine protons that are no longer equivalent. In addition, the β-hydrogen can be oriented above or below the plane defined by the Al_2O_2 central core, leading to the formation of *cis*/*trans* isomers. Furthermore, an equilibrium between the solid state dinuclear and mononuclear species of **1**−**6** may also occur.

For the *iso*-structural compounds **1**−**3**, the observed ^1H NMR spectra were, as expected, very similar, revealing eight multiplets for the OTHF. Additional peaks representing the different pendant hydrocarbon alkyl groups (methyl, ethyl, or iso-butyl) were also observed. For **1**, three types of methyl groups were observed in the negative ^1H chemical shift region. For **2** and **3**, the alkyl shifts are further upfield than a normal shift but not as significant as observed for the directly bound methyls of **1**. The $^{13}C\{^1H\}$ for each shows the expected five resonances associated with the OTHF, but the majority of these peaks are present as multiplets or as broad singlets. The $^{13}C\{^1H\}$ methyl chemical shifts of **1** are again negative and very broad. For **2** and **3** similar duplicate resonances are noted and broad alkyl peaks observed.

Combined, these data indicate that in solution either there are different isomers present or an equilibrium exists. Due to the chiral proton on the THF ring, isomers with the methoxy substituent either *cis* (both up or down) and/or *trans* (one up and one down) may be present. Variable-temperature ^1H NMR spectra were obtained to differentiate between these two explanations. Upon warming compound **1** to 70 °C in tol-d_8, minor changes in the different spectra were observed, with the relative chemical shift differences between the different ^1H resonances narrowing slightly. No broadening or coalescence due to dynamic ligand exchange behavior was observed. This demonstrates that the two isomeric species present in solution do not interconvert on the NMR time scale, arguing against the dynamic equilibrium description.

The ^1H NMR spectrum of the methyl region of **1** reveals three resonances at room temperature in the approximate 1.0:2.2:1.0 ratio, but is not a multiplet due to J coupling. The observed fine structure in the methyl region of the ^1H NMR is the result of three distinct, overlapping proton species produced from the presence of *cis*/*trans* isomers. Since the VT experiments show that a rapid equilibrium between the different species is not present, the *cis*/*trans* isomers must be present in an almost 1:1 ratio.

VT analysis of **2** shows a simplification of the CH_2-CH_3 region upon warming to 95 °C. The initial 12−14 proton resonances partially coalesce into six somewhat overlapping resonances. This spectral simplification reflects some dynamic equilibrium within the system (perhaps monomer/dimer interconversion), but the retention of multiple resonances at elevated temperatures suggests that the *cis*/*trans* isomers do not interconvert. The spectral variations observed therefore are more likely related to an equilibration of the ethyl group configuration on **2**. The major peaks have been tentatively assigned as the overlapping inequivalent methylene resonances of the inequivalent *cis*/*trans* isomers. Due to the increased complexity of the NMR spectrum of **3** over **2**, VT NMR measurements were not obtained.

To further elucidate the solution behavior, ^{27}Al NMR data were collected. For **1**−**3**, two broad peaks were noted at around δ 118 and 63 ppm. The relative amount of the upfield (δ 118 ppm) resonance becomes larger with increasing temperature. If the *cis*/*trans* species are present, they would have the same coordination and two very similar peaks should be present. Since ^{27}Al NMR chemical shifts are very dependent upon coordination, assignments based on the chemical shift can be made. Four-coordinated Al metal centers are in agreement with the resonance at δ 118 ppm, while the 65 ppm resonance is the result of an increase in Al coordination. The NMR experiments reflect that there is a change in coordination due to the coordination and subsequent loss of the oxygen of the THF ring of the OTHF ligand. An additional minor, very sharp peak around δ +5 ppm was noted for some samples, which is most likely a decomposition product due to the high reactivity of these compounds and may correspond to an AlO_6 species. This indicates that the THF ring coordinates more as the temperature is lowered prior to crystallization. Interestingly this variation in the coordination does not allow for the interconversion between *cis*/*trans*, which is confirmed by the ^1H NMR studies.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **4**−**6** reveal resonances associated with OTHF, but there is significantly more fine structure than was noted for the simple dialkyl derivatives. In addition, there are numerous Me resonances in the negative chemical shift region. The presence of multiple resonances observed in the ^1H NMR is also carried over into the data observed for the ^{13}C NMR spectra. The large number of resonances observed for these species implies that *cis*/*trans* isomers are present. Due to the asymmetry of the alkoxy molecules, a number of arrangements are possible and potentially reflected in the NMR spectrum.

Initial solid state NMR data for **1**[24] suggest that the Al is indeed in an asymmetric bonding environment with a ^{27}Al quadrupolar coupling constant (C_Q) of ~22 MHz and an asymmetry parameter (η_Q) of ~1. These experimental results are consistent with the predicted C_Q based on the crystal structure of **1**. The size of C_Q is consistent with other reported alkylaluminoxane bound Al environments.[25] Previous studies of methylaluminoxane (MAO) gels and related compounds determined

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[24] Schurko, R. W.; Alam, T. M.; Boyle, T. J. Unpublished results.

C_Q ranging from 12 to 37 MHz for the methylaluminum oxane subunits and aminato- and propanolato-aluminum clusters. Additional wide-line analyses of the spectra of these compounds are currently being investigated.[24]

Summary and Conclusions

We have developed a family of alkyl-OTHF aluminum species with characteristics that are promising for materials synthesis (i.e., MOCVD and nanoparticle production). These derivatives form the identical dinuclear species $[R_2Al(\mu\text{-OTHF})]_2$. The systematic substitution of the alkyls was demonstrated for the first two equivalents forming $[R(OR)Al(\mu\text{-OTHF})_2AlR_2]$ or $[R(OR)Al(\mu\text{-OTHF})]_2$ depending on the steric bulk of the alkoxide ligand. The bulk powders were investigated by multinuclear NMR and elemental analyses and found to be consistent with the single-crystal X-ray structures. This system offers a scaffold to build more complex metal alkoxides with the ubiquitous Al cation in a controlled manner due to an accessible reactive site on the Al metal center.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures **1**−**6** are available free of charge via the Internet at http://pubs.acs.org.

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