Controlled Synthesis of Novel Aryloxide Polynuclear Aluminum Species. Study of Their Catalytic Properties in Polymerization Processes[†]

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The reaction of $AlMe_3$ with 3,5-$(CF_3)_2C_6H_3OH$ at room temperature renders the dinuclear $[AlMe_2(OR)]_2$ (**1**) (OR = 3,5-$(CF_3)_2C_6H_3O$), trinuclear $\{[AlMe_2(OR)]_2[AlMe(OR)_2]\}$ (**2**), or tetranuclear $\{[AlMe_2(OR)]_2[AlMe(OR)_2]_2\}$ (**3**) derivative depending on the reaction conditions (solvent and stoichiometry of the reagents). All compounds have been characterized by elemental analysis and NMR spectroscopy, and their crystal structures determined by X-ray diffraction methods. Catalytic studies reveal that these compounds show high activity in ring-opening polymerization of cyclohexene oxide (CHO). The activity in the catalytic process varies significantly with solvent and temperature conditions.

Introduction

Aluminum organometallic and coordination compounds generate great interest due to their key role in many catalytic reactions.[1–5] Since the discovery of MAO,[6,7] different alkylaluminoxanes have held a vital role as cocatalysts in Ziegler–Natta polymerization processes.[8–14] In addition, aluminum alkoxide derivatives have proven to be very efficient catalysts in many polymerization reactions, such as ring-opening polymerization.[15–20] The appeal of aluminum is complemented by a rich structural chemistry; thus aluminum derivatives of a vast nuclearity range have been described.[21–28]

In this note we report the synthesis and structural characterization of new aluminum aryloxide complexes. A large number of aluminum aryloxide compounds have been described,[29] containing in most cases nonfunctionalized aryl groups. Our work is focused on the study of new aryloxide derivatives with functionalized aryl moieties since we are interested in analyzing the influence of functionality on the compounds' properties. In this context, we have studied the reaction between the fluorinated phenol 3,5-$(CF_3)_2C_6H_3OH$ and $AlMe_3$. The outcome of the reaction depends strongly on the reaction conditions; varying the solvent, reaction time, and Al:phenol ratio allows the synthesis of di-, tri-, and tetrametallic derivatives. The behavior of these aluminum species in polymerization processes is also described.

Results and Discussion

Reactions of $AlMe_3$ with 3,5-$(CF_3)_2C_6H_3OH$. Trimethyl aluminum reacts with 3,5-$(CF_3)_2C_6H_3OH$ at room temperature,

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[†] In memory of Juan Antonio Delgado, deceased on July 14, 2007.

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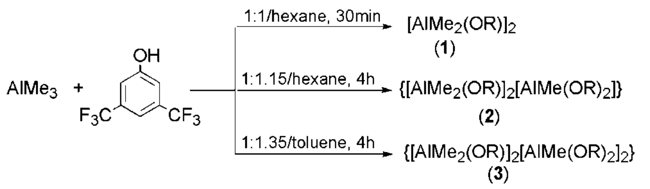
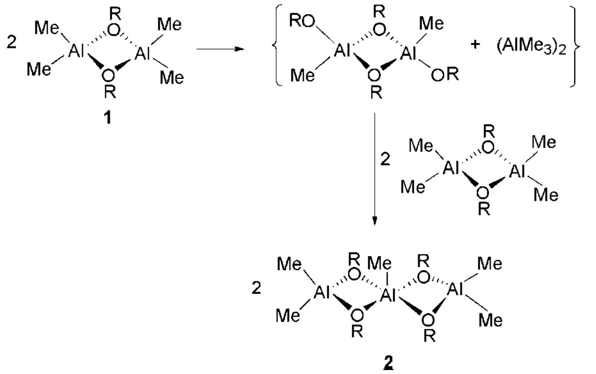
Scheme 1



Scheme 2



giving different products depending on the reaction conditions (Scheme 1), as frequently observed in the aluminum chemistry.[30,31] Thus, when the reaction was carried out in hexane with Al: phenol ratio 1:1, the dinuclear derivative $[AlMe_2(OR)]_2$ (**1**) (OR = 3,5-$(CF_3)_2C_6H_3O$) was formed after stirring the reaction mixture for 30 min. The same reaction using an Al:phenol ratio of 1:1.15 for longer reaction times affords the trinuclear derivative $\{[AlMe_2(OR)]_2[AlMe(OR)_2]\}$ (**2**). The transformation of compound **1** into **2**, with the elimination of $AlMe_3$ in the absence of free alcohol, has been observed, indicating that a possible route to **2** could involve an initial intermolecular phenoxide-methyl exchange between two molecules of **1**, generating intermediate diaryloxide species "$AlMe(OR)_2$". The reaction between this species and the remaining molecules of **1** would give **2** (Scheme 2). However, the proposed intermediate "$AlMe(OR)_2$" species have not been unequivocally identified. When a mixture of **1** and **2** is formed, fractional recrystallization from hexane solution affords a convenient separation method, as the trinuclear complex is less soluble than the dinuclear derivative. When toluene is used as reaction media and the ratio Al to phenol is 1:1.35, the formation of a precipitate containing a mixture of **2** and the tetranuclear derivative $\{[AlMe_2(OR)]_2[AlMe(OR)_2]_2\}$ (**3**) is observed after stirring the solution for 4 h. The tetranuclear compound is insoluble in hexane and barely soluble in toluene, so the mixture was separated by fractional recrystallization from a toluene solution.

Compounds **1–3** are air sensitive and should be stored under argon or dinitrogen. They were characterized by elemental analysis and multinuclear NMR spectroscopy. The analytical composition exactly fits the proposed formulation. The molecular structures of these compounds were determined by X-ray diffraction methods. In the $^{19}F\{^1H\}$ NMR spectra, only one signal was observed around δ 63, indicating all fluorine atoms are equivalent (δ 62.9 for **1**, δ 63.2 for **2**, δ 63.4 for **3**). The ^1H NMR spectra show the expected high-field shifted resonances for the protons of the methyl groups bonded to the aluminum. Interestingly, the resonances for the methyl protons bonded to the pentacoordinated aluminum atom in **2** and **3** (δ −0.21 for **2**, δ −0.19 for **3**) appear shifted low field with respect to the methyl protons linked to the tetracoordinated aluminum center (δ −0.53 for **2**, δ −0.52 for **3**), indicating a more acidic character for the pentacoordinated aluminum atom. The same spectroscopic features for the methyl groups bonded to the aluminum centers are observed in the $^{13}C\{^1H\}$ NMR spectra data.

Structural studies using single-crystal X-ray diffraction methods were performed and clearly confirmed the nuclearity of the species **1**−**3**. Figure 1 shows ORTEP views of the structures along with the atom-labeling schemes. Selected bond distances and bond angles with their standard deviations are listed in Table 1. In the dinuclear structure of compound **1**, the Al centers exhibit a typically tetrahedral coordination, being bonded to two methyl groups and two aryloxide bridging ligands. Al−O distances (1.8778(18) and 1.8829(19) Å) are within the usual range found for similar alkoxide aluminum derivatives.[32,33] The aryl rings are in a plane nearly perpendicular to the Al_2O_2 plane, a different disposition from that observed for the derivative $AlMe_2(OC_6F_5)$, where the aryl rings and the Al_2O_2 core adopt a nearly coplanar arrangement.[34]

Compound **2** shows a linear trinuclear structure formed by two Al_2O_2 rings sharing an Al atom. Two different environments are observed for the aluminum centers. The terminal dispositions exhibit tetrahedral geometry, whereas the central aluminum atom shows square-based pyramidal coordination geometry. The Al−C distances (average 1.953 Å) are similar for all the Al centers and are within the expected range.[3,35–37] Two different values are observed for the four Al−O distances around the pentacoordinated aluminum atom, two of which are longer (1.973 and 1.961 Å vs 1.867 and 1.863 Å). The phenyl rings are in parallel planes and could be affecting the angle between the Al_2O_2 planes, 119.49°. It is noteworthy that although several compounds with an AlO_2AlO_2Al linear core are known, in the majority the bridging groups are aliphatic or aromatic dialkoxide ligands,[3,33,35] no examples containing monoaryloxide bridging ligands have been described to date, and **2** is the first complex of this type to be fully characterized.

Compound **3** shows an unusual structure with a linear $AlO_2AlO_2AlO_2Al$ core formed by three quasi-planar Al_2O_2 rings linked by two Al atoms (Al(3) and Al(2)). The aluminum atoms shared by two rings display a pentacoordinated environment, similar to Al(2) in **2**. In this core, Al−C and Al−O bonds follow a pattern similar to that in **2**. The aryl rings located on each side of the core are placed in near-parallel planes and could have some influence on the disposition of the Al_2O_2 rings. In Figure 2, side views of the molecular structures of **2** and **3** are displayed, showing that in **3** the Al_4 core presents a distorted ladder structure, exhibiting different values for the dihedral angles between the Al_2O_2 planes (122.72° and 109.93°). The orientation of the Al_2O_2 rings forces the disposition of the methyl groups bonded to Al(3) and Al(2) to be located in opposite directions. It is interesting to point out the scarcity of examples

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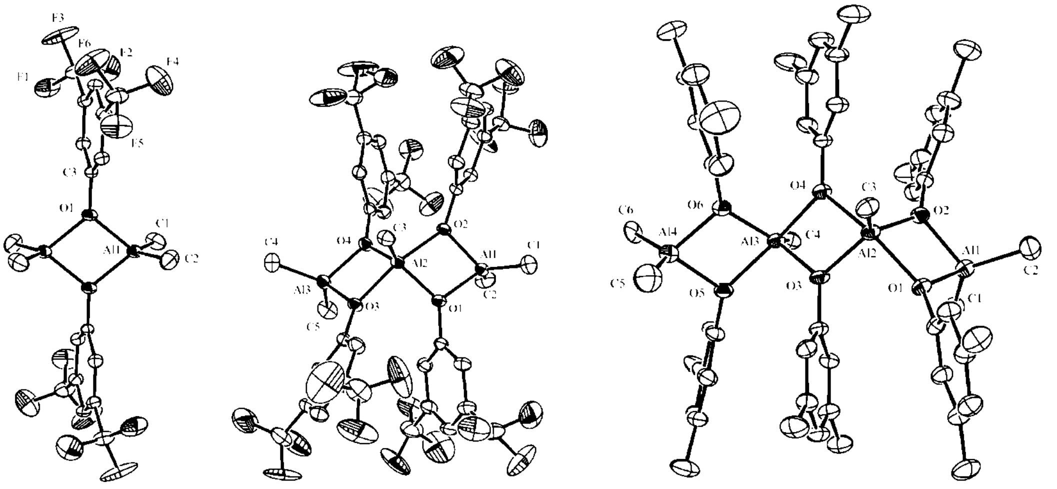

Figure 1. Molecular structures of **1**−**3**, showing thermal ellipsoid plots (30% probability). In **3** fluorine atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1–3[a]

				Compound **1**			
Al(1)−O(1)#1	1.8778(18)	Al(1)−C(1)	1.948(3)	O(1)#1−Al(1)−O(1)	78.68(8)		
Al(1)−O(1)	1.8829(19)	O(1)−C(3)	1.392(3)	Al(1)#1−O(1)−Al(1)	101.32(8)		
Al(1)−C(2)	1.945(3)						
				Compound **2**			
Al(1)−O(2)	1.855(2)	Al(2)−O(2)	1.973(2)	O(2)−Al(1)−O(1)	78.48(8)	C(3)−Al(2)−O(2)	102.82(12)
Al(1)−O(1)	1.881(2)	Al(3)−O(3)	1.875(2)	Al(1)−O(1)−Al(2)	104.33(9)	O(4)−Al(2)−O(2)	91.38(9)
Al(1)−C(1)	1.950(4)	Al(3)−O(4)	1.881(2)	Al(1)−Al(2)−Al(3)	127.07(4)	O(1)−Al(2)−O(2)	75.91(8)
Al(1)−C(2)	1.958(4)	Al(3)−C(4)	1.950(4)	O(3)−Al(3)−O(4)	77.56(9)	O(3)−Al(2)−O(2)	153.98(9)
Al(2)−O(4)	1.863(2)	Al(3)−C(5)	1.952(4)	O(4)−Al(2)−O(1)	120.77(10)	O(1)−Al(2)−O(3)	91.05(9)
Al(2)−O(1)	1.867(2)	O(1)−C(10)	1.406(3)	O(4)−Al(2)−O(3)	75.88(8)	Al(3)−O(3)−Al(2)	101.38(9)
Al(2)−O(3)	1.961(2)	O(3)−C(30)	1.379(3)	O(4)−Al(2)−C(3)	117.43(13)	Al(1)−O(2)−Al(2)	101.23(9)
Al(2)−C(3)	1.955(3)	O(2)−C(20)	1.388(3)	O(1)−Al(2)−C(3)	121.80(13)	Al(2)−O(4)−Al(3)	104.89(9)
		O(4)−C(41)	1.402(3)	O(3)−Al(2)−C(3)	103.18(12)		
				Compound **3**			
Al(1)−O(1)	1.854(5)	Al(3)−C(4)	1.950(7)	O(1)−Al(1)−O(2)	77.85(18)	O(3)−Al(3)−C(4)	116.1(3)
Al(1)−O(2)	1.884(4)	Al(3)−O(5)	1.972(4)	O(2)−Al(2)−O(3)	118.3(2)	C(4)−Al(3)−O(5)	98.4(2)
Al(1)−C(2)	1.919(8)	Al(3)−O(6)	1.862(4)	O(2)−Al(2)−O(4)	92.13(19)	O(6)−Al(3)−C(4)	123.6(3)
Al(1)−C(1)	1.945(7)	Al(4)−O(5)	1.853(5)	O(3)−Al(2)−O(4)	75.17(17)	O(4)−Al(3)−C(4)	103.7(2)
Al(2)−O(2)	1.883(5)	Al(4)−O(6)	1.892(5)	O(2)−Al(2)−O(1)	74.94(18)	O(3)−Al(3)−O(5)	95.33(18)
Al(2)−O(3)	1.896(4)	C(11)−O(1)	1.412(7)	O(3)−Al(2)−O(1)	92.13(18)	O(6)−Al(3)−O(5)	76.10(18)
Al(2)−O(4)	1.917(4)	C(61)−O(6)	1.404(7)	O(4)−Al(2)−O(1)	155.1(2)	O(4)−Al(3)−O(5)	158.0(2)
Al(2)−O(1)	1.976(4)	C(51)−O(5)	1.429(7)	O(2)−Al(2)−C(3)	125.7(3)	Al(1)−O(1)−Al(2)	102.27(19)
Al(2)−C(3)	1.953(7)	C(41)−O(4)	1.400(6)	O(3)−Al(2)−C(3)	115.9(3)	Al(1)−O(2)−Al(2)	104.7(2)
Al(3)−O(3)	1.861(4)	C(31)−O(3)	1.395(6)	O(4)−Al(2)−C(3)	103.2(2)	Al(3)−O(3)−Al(2)	106.60(19)
Al(3)−O(4)	1.947(4)	C(21)−O(2)	1.405(7)	O(1)−Al(2)−C(3)	101.6(2)	Al(3)−O(4)−Al(2)	102.45(18)
				O(3)−Al(3)−O(6)	120.2(2)	Al(4)−O(5)−Al(3)	101.03(19)
				O(3)−Al(3)−O(4)	75.24(17)	Al(3)−O(6)−Al(4)	103.7(2)
				O(6)−Al(3)−O(4)	91.30(19)		

[a] Symmetry transformations used to generate equivalent atoms: **1**: #1 $-x + 1, -y, -z$.

of tetranuclear metal alkoxide derivatives with this geometry; the few compounds reported occur mainly in group 13.[38,39]

Cyclohexene Oxide Polymerization. In pursuit of our aim to study the catalytic properties of the aluminum derivatives prepared, we investigated their behavior as cocatalysts in ethylene polymerization processes using $ZrCp_2Cl_2$ as a precatalyst. However, no activity was observed, and when the reaction of $ZrCp_2Cl_2$ with **2** was monitored by ^1H NMR spectroscopy, an alkoxide transfer reaction to the Zr center was observed with the formation of $ZrCp_2(OR)_2$. Since the ability of aluminum derivatives as catalysts in ring-opening polymerization processes is well-known,[15–20] we tried to study the activity of **1**–**3** in cyclohexene oxide (CHO) polymerization reactions.

The tests for the ROP were performed with a subtrate:catalyst molar ratio of 2000:1, during 30 min. The experiments were carried out at 25 and 0 °C, using methylene chloride or toluene as solvents. The catalyst was, first, dissolved at the appropriate temperature, and then CHO was slowly added to the vigorously stirred resultant solution. Yield values and polymer data are collected in Table 2.

The activity of the aluminum catalysts as initiators in the polymerization of cyclohexene oxide varies significantly with solvent and temperature conditions. The higher activity is exhibited at 25 °C in methylene chloride (Table 2, entries 3, 7, and 10). Under these conditions the three aluminum compounds show similar activities, generating comparable quantities of polymer. The polymerization yields are found to be practically quantitative (ca. 96% yield for **1**, 97% yield for **2** and **3**), with high molecular weights (102 866 g/mol for **1**, 43 043 g/mol for

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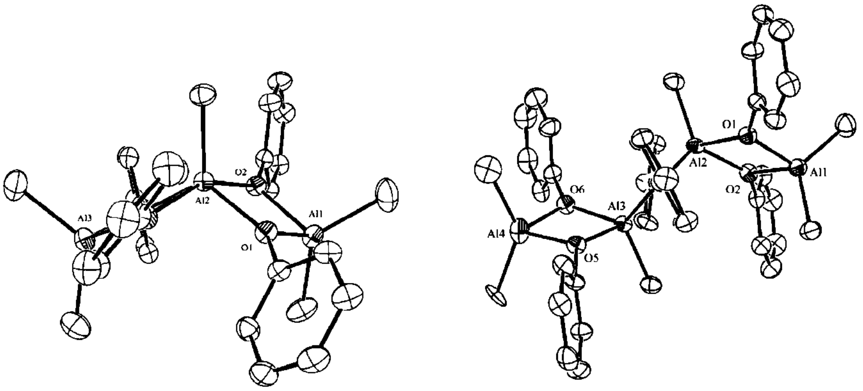

Figure 2. Side view of molecular structures of **2** and **3**, showing thermal ellipsoid plots (30% probability). CF_3 groups have been omitted for clarity.

Table 2. Cyclohexene Oxide Polymerization Results[a]

entry	catalyst	$n \times 10^5$ mol	T (°C)	solvent	yield (%)	M_n[b]	M_w[b]	M_w/M_n
1	**1**	3.6	25	toluene	75	53 851	97 461	1.8
2	**1**	3.6	0	toluene	70	40 552	70 533	1.7
3	**1**	3.6	25	CH_2Cl_2	96	68 837	102 866	1.5
4	**1**	3.6	0	CH_2Cl_2	90	51 068	80 532	1.6
5	**2**	1.9	25	toluene	85	36 048	65 569	1.8
6	**2**	1.9	0	toluene	72	18 748	31 103	1.6
7	**2**	1.9	25	CH_2Cl_2	97	2575	43 043	1.7
8	**2**	1.9	0	CH_2Cl_2	89	27 788	44171	1.6
9	**3**	1.3	25	toluene	95	45 045	76 707	1.7
10	**3**	1.3	25	CH_2Cl_2	97	55 711	105 765	1.8

[a] Experimental conditions: time 30 min, catalyst 21 mg, proportion catalyst/CHO 1/2000. [b] Determined by gel permeation chromatography relative to polystyrene standards.

2, and 105 765 g/mol for **3**). The narrow polydispersity indexes (1.5 with **1**, 1.7 with **2**, and 1.8 with **3**) and the long polymer chains suggest single-site behavior. Lower values of activity are reached in toluene (Table 2, entries 1, 5, and 9), and the yields vary significantly, from 75% for the dinuclear derivative **1** to 95% for the tetranuclear compound (**2** shows an intermediate value of 85%). Interestingly, the highest yield is observed for **3**, in agreement with the relatively higher Lewis acidity of the pentacoordinated aluminum atoms, as shown in the NMR spectroscopic studies. Nevertheless, although the catalytic activity is strongly influenced by the experimental conditions, the molecular weights and the polydispersity indexes are comparable in all cases.

In order to understand the role of the solvent in the reaction process, we have performed a series of CHO polymerization tests in toluene using benzenesulfonyl chloride as activator. Treatment of the initial solution of the catalysts in toluene with benzenesulfonyl chloride (catalyst:activator molar ratio 1:1) affords active polymerization catalytic species that give higher yields than in the absence of the chloride source. In the presence of the chloride-containing activator, the polymerization yield values increase from 75% to 88% for **1**, from 85% to 97% for **2**, and from 95% to 98% for **3** (Figure 3). Thus, the activities of the toluene/benzenesulfonyl system are similar to the values obtained for the same catalysts in methylene chloride (Table 2, entries 3, 7, and 10). Consequently, the presence of a chloride-containing activator in the reaction mixture increases the activity of these aluminum derivatives, as previously reported for other aluminum systems in ethylene polymerization.[4] An interaction between the aluminum catalyst and the chloride source or, alternatively, the direct activation of the monomer by the chloride reagent could be proposed as potential factors to explain the observed effect. More work is in progress to understand the exact nature of the intermediate species involved in these catalytic reactions.

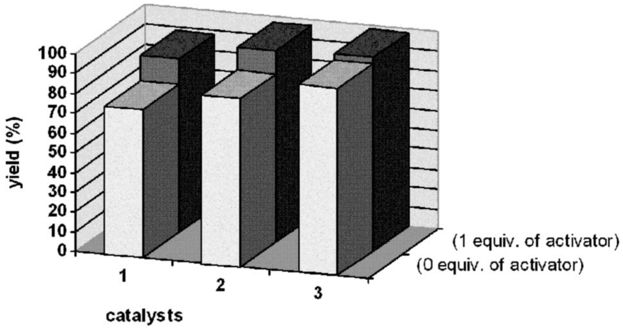

Figure 3. Comparative yields for the aluminum catalysts **1**, **2**, and **3** upon activation with benzenesulfonyl chloride.

The stereochemistry of the isolated poly(1,2-cyclohexene oxide) was investigated by ^1H NMR and ^{13}C NMR spectroscopic studies.[40–42] The ^1H NMR spectra of the polymers obtained in $CDCl_3$ with the three aluminum catalysts are identical. In the ^1H NMR spectra, the methine hydrogens in α-positions of the ether bridges appear around δ 3.5, while the protons of the methylene groups of the cyclohexyl fragment are located between δ 1.2 and 1.9. The signal of the methine protons appears in the form of three peaks (δ 3.52, 3.39, and 3.36), which can be attributed to syndiotactic (*rr*), heterotactic (*mr* and *rm*), and isotactic (*mm*) triads, respectively. Three main signals were found in the ^{13}C NMR spectra for the methine carbons at δ 80.0, 78.7, and 75.6, confirming the presence of several regions of different tacticity in the polymers. The remaining methylene groups of the cyclohexene moieties belonging to the polymer backbone were found in two set of resonances ranging from δ 30.0 to 37.1 and δ 24.8 to 20.8. Polydispersity values and stereochemistry of the isolated polymers are comparable to the reported data for polymers obtained using similar aluminum compounds as catalysts.[20]

In conclusion, we report here the synthesis and the structural characterization of new aryloxide aluminum compounds. The nature of the final product formed in the synthetic reactions strongly depends on the reaction conditions (solvent and stoichiometry of the alcohol reagent); hence it is possible to tune the nuclearity of the derivatives obtained. The aluminum compounds prepared showed no activity as cocatalysts in

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Table 3. Crystallographic Data for 1, 2, and 3

formula	$C_{20}H_{18}Al_2F_{12}O_2$	$C_{37}H_{27}Al_3F_{24}O_4$	$C_{54}H_{36}Al_4F_{36}O_6$
fw	572.30	1072.53	1572.75
color/habit	white/prism	white/prism	white/prism
cryst dimens, mm^3	0.43 × 0.41 × 0.37	0.48 × 0.46 × 0.45	0.55 × 0.48 × 0.37
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/a$	$P2_1/c$
a, Å	9.9720(16)	16.9230(15)	17.285(4)
b, Å	7.6787(10)	17.111(3)	12.598(3)
c, Å	17.488(3)	17.928(3)	30.701(6)
β, deg	92.638(15)	116.438(12)	90.248(13)
V, Å^3	1337.7(3)	4648.5(13)	6686(3)
Z	2	4	4
T, K	200	200	200
ρ_{calcd}, g cm^{-3}	1.421	1.533	1.563
μ, mm^{-1}	0.207	0.215	0.216
$F(000)$	576	2144	3136
θ range, deg	3.35−27.50	3.55–27.54	3.08−25.01
no. of rflns collected	27 149	101 993	60 568
no. of indep rflns/R_{int}	3035/0.0532	10 662/0.0692	11 709/0.0840
no. of obsd rflns ($I > 2\sigma(I)$)	1983	6534	7725
no. of data/restraints/params	3035/136/191	10 662/264/776	11 709/0/974
R_1/wR_2 ($I > 2\sigma(I)$)[a]	0.0555/0.1405	0.0593/0.1520	0.0746/0.1736
R_1/wR_2 (all data)[a]	0.0960/0.1593	0.1085/0.1867	0.1250/0.2140
extinction coeff	0.014(3)	0.0054(6)	0.0055(5)
GOF (on F^2)[a]	1.052	1.025	1.029
largest diff peak/hole, e Å^{-3}	+0.364/−0.343	0.538/−0.490	0.597/−0.347

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $\text{GOF} = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

Ziegler–Natta ethylene polymerization processes. Catalytic tests showed that these aluminum compounds are highly active in the ring-opening polymerization of cyclohexene oxide (CHO). Two different solvents were used, giving dissimilar results; thus, in toluene there is a clear increase in catalyst activity with the compound's nuclearity, but in dichloromethane the outcome is very similar for the three compounds. Overall, the process is more active in the halogenated solvent. Investigations to clarify the role of the solvent are continuing; we are also studying the extension of these studies to other functionalized monomers.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using standard Schlenk and glovebox techniques. Solvents were purified from appropriate drying agents. NMR spectra were recorded at 400.13 (^1H), 376.70 (^{19}F), and 100.60 (^{13}C) MHz on a Bruker AV400. Chemical shifts (δ) are given in ppm using C_6D_6 as solvent, unless otherwise stated. ^1H and ^{13}C resonances were measured relative to solvent peaks considering TMS = 0 ppm, while ^{19}F resonance were measured relative to external $CFCl_3$. Elemental analyses were performed on a Perkin-Elmer 240C. Cycloxene oxide was purchased from Fluka, distilled over CaH_2, and stored under an inert atmosphere prior to its use. All other reagents were commercially obtained and used without further purification.

$[AlMe_2(OR)]_2$, 1. A solution of $AlMe_3$ 2 M in toluene (2.07 mL, 4.14 mmol), was diluted in 10 mL of hexane. 3,5-$(CF_3)_2$-C_6H_3OH (0.6 mL, 4.14 mmol) was dissolved in 10 mL of hexane and added slowly to the $AlMe_3$ solution. Initially the reaction mixture heated up and some gas evolved. After stirring for 30 min the solvent was reduced under vacuum to ca. 5 mL. The resulting colorless solution was stored at −20 °C overnight, and some crystals were formed and identified as compound **1** (590 mg, 47% yield). ^1H NMR (C_6D_6): δ 7.40 (m, 2H, *p*-Ph), 7.32 (m, 4H, *o*-Ph), −0.54 (s, 12H, $(CH_3)_2$-AlO_2). ^{13}C NMR (C_6D_6): δ 151.8 (C_{ipso}-Ph), 134.2 (q, J_{C-F} = 34 Hz, CF_3), 124.0 (C_{para}-Ph), 118.6 (C_{orto}-Ph), 118.2 (C_{meta}-Ph), −10.8 (CH_3).$^{19}F\{^1H\}$ NMR (C_6D_6): δ 62.9 (s, CF_3). Anal. Calcd (%) for $C_{20}H_{18}Al_2F_{12}O_2$ (572.30): C 41.97, H 3.17. Found: C 42.06, H 2.94.

$\{[AlMe_2(OR)]_2[AlMe(OR)_2]\}$, 2. In a procedure similar to that described for compound **1**, $AlMe_3$ (1.8 mL, 3.6 mmol) reacted with 3,5-$(CF_3)_2C_6H_3OH$ (0.6 mL, 4.13 mmol) for 4 h. The solvent was reduced under vacuum to ca. 7 mL, and the solid produced was redissolved by heating the mixture. The colorless solution was stored at room temperature overnight, and some crystals of compound **2** were formed (800 mg, 72% yield). ^1H NMR (C_6D_6): δ 7.33 (m, 4H, *p*-Ph), 7.10 (m, 8H, *o*-Ph), −0.21 (s, 3H, CH_3-AlO_4), −0.53 (s, 12H, $(CH_3)_2$-AlO_2). ^{13}C NMR (C_6D_6): δ 151.9 (C_{ipso}-Ph), 134.0 (q, J_{C-F} = 34 Hz, CF_3), 123.7 (C_{para}-Ph), 120.5 (C_{orto}-Ph), 118.7 (C_{meta}-Ph), −10.8 (CH_3-AlO_4), −12.1 ($(CH_3)_2$-AlO_2). $^{19}F\{^1H\}$ NMR (C_6D_6): δ 63.2 (s, CF_3). Anal. Calcd (%) for $C_{37}H_{27}Al_3F_{24}O_4$ (1072.53): C 41.43, H 2.53. Found: C 41.35, H 2.76.

$\{[AlMe_2(OR)]_2[AlMe(OR)_2]_2\}$, 3. A solution of $AlMe_3$, 2 M in toluene (2.07 mL, 4.14 mmol), was diluted in 10 mL of toluene. 3,5-$(CF_3)_2C_6H_3OH$ (0.85 mL, 5.58 mmol) was dissolved in 10 mL of toluene, and the solution was added slowly to the $AlMe_3$ solution. Initially the reaction mixture heated up and some gas evolved. The solution was stirred for 4 h, the solid produced was redissolved by heating the mixture, the resulting colorless solution was stored at room temperature overnight, and some crystals of compound **3** were formed (211 mg, 15% yield). ^1H NMR (CD_2Cl_2): δ 7.37 (m, 6H, *p*-Ph), 7.16 (m, 12H, *o*-Ph), −0.19 (s, 6H, CH_3-AlO_4), −0.52 (s, 12H, $(CH_3)_2$-AlO_2). $^{19}F\{^1H\}$ NMR (C_6D_6): δ 63.4 (s, CF_3). The low solubility of **3** prevented us from obtaining ^{13}C NMR data. Anal. Calcd (%) for $C_{54}H_{36}Al_4F_{36}O_6$ (1572.75): C 41.24, H 2.31. Found: C 41.15, H 2.02.

General Procedure for the Polymerization Experiments. Typically, the catalyst was dissolved in dry solvent under argon at the appropriate temperature. CHO was then slowly added to the vigorously stirred catalyst solution. In all cases (dinuclear, trinuclear, and tetranuclear compounds) the reaction mixture rapidly became syrupy and the reaction was stirred for 30 min. In order to isolate the final poly(cyclohexene oxide) product of the reaction and separate it from the catalyst, the reaction mixture was further diluted with the solvent used for the polymerization reaction and added dropwise to a vigorously stirred methanol/HCl mixture. The polymer was vigorously stirred for 2 h, then filtered and dried under vacuum at 75 °C overnight.

Single-Crystal X-ray Structure Determination of Compounds 1, 2, and 3. Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in Table

3. Suitable single crystals of **1**, **2**, and **3** for the X-ray diffraction study were selected. The crystals covered with perfluorinated ether oil were mounted on a Bruker-Nonius Kappa CCD single-crystal diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was performed at 200(2) K. Multiscan[43] absorption correction procedures were applied to the data. The structures were solved, using the WINGX package,[44] by direct methods (SHELXS-97) and refined using full-matrix least-squares against F^2 (SHELXL-97).[45] Hydrogen atoms were geometrically placed and left riding on their parent atoms. All non-hydrogen atoms were anisotropically refined apart from C5 on compound **3**, which was disordered. In compound **3**, C5 and C6 showed disorder that was treated. In the three compounds, fluorine atoms on the CF_3 groups were disordered around the local C_3 axis, and the disorder was partially modeled. Some restraints were applied (DELU). Compound **3** was refined as a racemic twin using the TWIN and BASF instructions; the final value of the BASF parameter was 0.36458. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-676066 [**1**], CCDC-676067 [**2**], and CCDC-676068 [**3**]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data in CIF format for complexes **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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