Alcoholysis of Aluminum Alkyls Supported by Bulky Phenoxide Ligands: Synthesis, Characterization, and ε-Caprolactone Polymerization Activity of Two Dimeric Aluminum Isopropoxides

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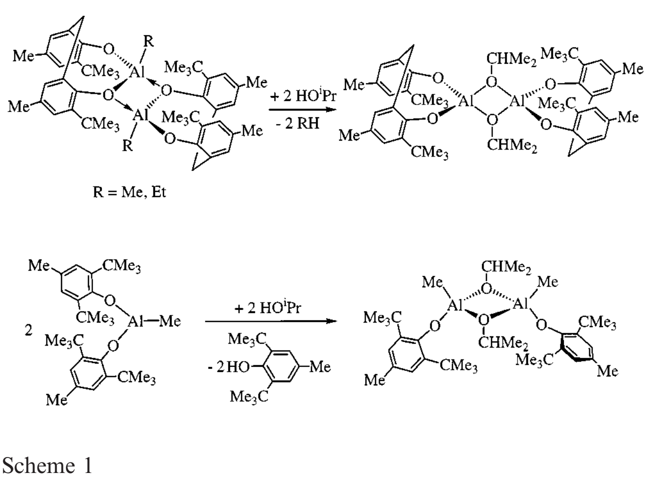
Reaction of trialkylaluminum Al_2R_6 (R = Me, Et) with 2,2′-methylenebis(6-*tert*-butyl-4-methylphenol) (mbmpH_2) gives the dimeric mono(alkyl) complex $[Al(mbmp)R]_2$ with bridging oxygen atoms. Reaction of $[Al(mbmp)R]_2$ with one equiv. of 2-propanol results in the formation of the dimeric isopropoxide $[Al(mbmp)(\mu\text{-O}i\text{Pr})]_2$. Single-crystal X-ray analysis shows a C_{2h}-symmetric structure with a planar Al_2O_2 core. Monomeric methylbis(2,6-di-*tert*-butyl-4-methylphenolato)aluminum, $AlMe(OC_6H_2\text{-}2,6\text{-}t\text{Bu}_2\text{-}4\text{-Me})_2$ (MAD), was found to react with one equiv. of 2-propanol to give a dimeric isopropoxide $[AlMe(OC_6H_2\text{-}2,6\text{-}t\text{Bu}_2\text{-}4\text{-Me})(\mu\text{-O}i\text{Pr})]_2$ in which the bulky phenolate, instead of the methyl group, has been displaced. According to the single-crystal X-ray structure analysis, the molecule contains a similar Al_2O_2 core, but the two 2,6-di-*tert*-butyl-4-methylphenolato ligands are *cis*- and orthogonally arranged to each other. ε-Caprolactone is polymerized at 50 °C in toluene in a controlled manner by $[Al(mbmp)(\mu\text{-O}i\text{Pr})]_2$, to give poly(ε-caprolactone) with high molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.50$). The low efficiency values (number of polymer chains initiated per aluminum atom) imply that $[Al(mbmp)(\mu\text{-O}i\text{Pr})]_2$ exists in a monomer–dimer equilibrium. The polymerization of ε-caprolactone by $[AlMe(OC_6H_2\text{-}2,6\text{-}t\text{Bu}_2\text{-}4\text{-Me})(\mu\text{-O}i\text{Pr})]_2$ is faster, but somewhat less controlled.

Introduction

Aluminum tri(isopropoxide) is a readily available compound that, among various applications in organic synthesis, has been employed as an efficient initiator for the ring-opening polymerization of aliphatic cyclic esters such as ε-caprolactone.[1] In the crystalline state it is a tetranuclear aggregate in which one six-coordinate aluminum center is surrounded by three bridging $Al(\text{O}i\text{Pr})_4$ units.[2] In solution, several other species including a trimer are present and the thermodynamics as well as the kinetics of their interconversion evidently complicates the polymerization mechanism.[1d,e] We anticipated that a *monomeric* aluminum alkoxide supported by bulky phenoxide ligands[3] would furnish a structurally well-defined initiator for ring-opening polymerization, and be amenable to mechanistic investigation. By employing the mono(alkyl) complexes with the chelating mbmp ligand [mbmp: 2,2'-methylenebis(6-*tert*-butyl-4-methylphenolato)] and its nonchelating analog 2,6-di-*tert*-butyl-4-methylphenolato, we attempted the synthesis of mono(isopropoxide) complexes. We present here the somewhat unexpected outcome of the alcoholysis reactions as well as the reactivity of the resulting products.[4]

Results and Discussion

When the sterically demanding chelating bisphenol mbmpH_2 [2,2'-methylenebis(6-*tert*-butyl-4-methylphenol)] was treated with trimethylaluminum in hexane, vigorous evolution of methane was observed and the monomethyl complex $[Al(mbmp)Me]_2$ was formed in high yields as air- and moisture-sensitive colorless crystals. The aluminum-bound methyl group occurred as broad signals in the ^{1}H and ^{13}C NMR spectra at δ = –0.39 and –7.36, respectively. The resonances of the mbmp ligand are all doubled, suggesting an unsymmetric structure in which the two halves of the mbmp ligand are inequivalent. We propose that a centrosymmetric dimer forms in which the Lewis-acidic aluminum center is coordinated to one phenoxy oxygen of the neighboring mbmp ligand (Scheme 1). By engaging in a bridging mode, for which the lone pair of the phenoxy oxygen is well suited, the coordinative unsaturation at the aluminum center is alleviated. Although, to the best of our knowledge, this bonding mode is unprecedented for the



Scheme 1

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Table 1. Experimental Data for the Crystal Structure [Al(mbmp)(μ-O*i*Pr)]$_2$ and [AlMe(OC$_6$H$_2$-2,6-*t*Bu$_2$-4-Me)(μ-O*i*Pr)]$_2$

	[Al(mbmp)(μ-O*i*Pr)]$_2$	[AlMe(OC$_6$H$_2$–2,6-*t*Bu$_2$-4-Me)(μ-O*i*Pr)]$_2$
Crystal data		
Empirical formula	$C_{26}H_{37}AlO_3$	$C_{38}H_{66}Al_2O_4$
Molecular mass	424.54	640.87
Crystal color	colorless	colorless
Crystal size, mm	0.50 × 0.40 × 0.15	0.30 × 0.60 × 0.80
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a [Å]	12.597(3)	9.7655(7)
b [Å]	16.762(3)	29.170(2)
c [Å]	16.029(3)	14.032(1)
β [deg]	108.23(3)	96.579(6)
V [Å^3]	3215(1)	3970.8(5)
Z	4	4
$\rho_{calc.}$ [g cm^{-3}]	0.877	1.072
μ [mm^{-1}] (Cu-K_α)	0.684	0.918
$F(000)$	920	1408
Wavelength	Cu-K_α (1.5418 Å)	Cu-K_α (1.5418 Å)
T [K]	173	296
θ-range [deg]	4–55	3–75
Index ranges	–13 h 13 –18 k 2 –17 l 17	–12 h 11 –14 k 36 –17 l 17
Solution and Refinement		
Number of reflections measured	8077	8170
Number of independent reflections	4034	8170
Number of observed reflections	2978	5030
ext coefficient	0.0006(2)	0.0021(2)
GOF	0.739	1.126
R [$I > 2\sigma(I)$]	0.0647	0.0588
wR_2 [$I > 2\sigma(I)$]	0.1802	0.1322
largest e-max, e-min, [eÅ^{-3}]	0.228, –0.341	0.294, –0.271

bulky bisphenolato ligand mbmp,[5] this type of bridging has been frequently observed in aluminum compounds with phenoxy[6] and chelating ligands in which at least one alkoxy function is present.[7] Addition of a Lewis base such as diethyl ether, THF, and pyridine, results in the formation of a mononuclear adduct with a four-coordinate aluminum center, as observed by NMR spectroscopy. The ethyl derivative [Al(mbmp)Et]$_2$ can be obtained in an analogous fashion from triethylaluminum, and isolated as colorless crystals. Due to the diastereotopicity, the methylene protons of the ethyl groups appear as a high-order multiplet, but give rise to a binomial quadruplet upon formation of the C_s-symmetric pyridine adduct [Al(mbmp)Et(py)]. The ethylene-linked bisphenol ebmpH$_2$[8] also forms a dimeric methyl complex [Al(ebmp)Me]$_2$ with NMR spectroscopic features similar to that of [Al(mbmp)Me]$_2$.

When precisely two equiv. of 2-propanol is added to an ethereal solution of the alkyl [Al(mbmp)R]$_2$ (R = Me, Et), the isopropoxide [Al(mbmp)(μ-O*i*Pr)]$_2$ is formed with concomitant alkane evolution and can be isolated as colorless crystals in 79% yield (Scheme 1). This compound can be independently prepared by reacting commercially available aluminum tri(isopropoxide) with one equiv. of mbmpH$_2$. The ^{1}H and ^{13}C NMR spectra indicate a molecule with a mirror plane bisecting the mbmp ligand, while the parent ion in the EI mass spectrum suggests a dimeric structure.

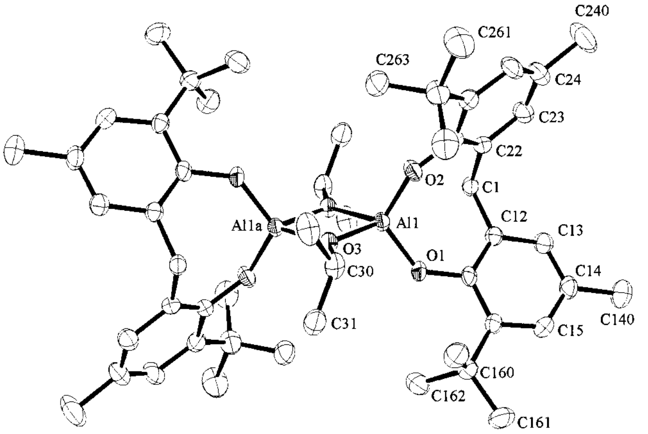

Figure 1. ORTEP diagram of the molecular structure of [Al(mbmp)(μ-O*i*Pr)]$_2$. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for the sake of clarity; selected bond lengths [Å] and angles [°]: Al1–O1 1.698(2), Al1–O2 1.694(3), Al1–O3 1.822(2), Al1–O3a 1.813(2); Al1–O1–C11 134.8(2), Al1–O2–C21 141.0(2), O1–Al1–O2 116.4(1), O1–Al1–O3 112.2(1), O3–Al1–O3a 81.1(1), Al1–O3–Al1a 99.0(1).

The single-crystal X-ray diffraction (Table 1, Figure 1) confirms the centrosymmetric dimeric structure with pseudo C_{2h} symmetry. The average Al–O bond lengths of 1.696(2) Å for the chelate is somewhat longer than those observed in AlMe(OC$_6$H$_2$-2,6-*t*Bu$_2$-4-Me)$_2$ (MAD) (1.686 Å), and the angles at the phenoxy oxygens of 134.8(2) and 141.0(2)° are

Table 2. Polymerization of ε-caprolactone (εCl) in toluene at 50 °C by [Al(mbmp)(μ-O*i*Pr)]$_2$ (run no. 1 to 4) and [AlMe(OC$_6$H$_2$–2,6-*t*Bu$_2$-4-Me)(μ-O*i*Pr)]$_2$ (run no. 5 to 10)

run no.	[εCl]/[Al]	time [h]	M_n(calcd.)	M_w(GPC)	M_n(GPC)	M_w/M_n	efficiency[a]
1	30	3.5	3424	9570	8820	1.09	0.39
2	50	3.0	5707	17010	16020	1.06	0.36
3	80	3.0	9132	39190	26140	1.50	0.35
4	150	3.5	17122	74850	53420	1.40	0.32
5	30	0.5	3424	48140	14660	3.28	0.23
6	50	0.5	5707	56270	31310	1.79	0.18
7	80	0.5	9132	84140	44970	1.87	0.20
8	100	0.5	11415	112900	60620	1.86	0.18
9	200	0.5	22829	163100	80700	2.02	0.28
10	500	0.5	57073	287000	155900	1.84	0.37

[a] Efficiency is defined as the fraction of active initiators, calculated from the observed number of polymer chains relative to the theoretical ones, assuming that each aluminum initiates one polymer chain.

smaller [average 143.6(2)° in MAD].[3a] These features may reflect the diminished double-bond character of the aluminum-oxygen bond within the mbmp chelate ring.[9] The two Al(mbmp) moieties with tetrahedrally-coordinated aluminum centers are linked by two isopropoxide groups. The geometry of the planar Al$_2$O$_2$ ring [average Al–O distance 1.818(2) Å; O–Al–O angle 81.1(1)°] corresponds to that of similar dimeric aluminum alkoxides such as [Al(OC$_6$H$_2$-2,4,6-*t*Bu$_3$)$_2$(μ−OEt)]$_2$ with Al–O distance of 1.845(2) Å and O–Al–O = 77.7(1)°,[10a] [AlH$_2$(μ−O*t*Bu)]$_2$ [Al–O = 1.810(3) Å and O–Al–O = 81.0(2)°],[10b] or [(η^1-C$_5$H$_5$)$_2$Al(μ-O-*i*Pr)]$_2$ [Al–O = 1.829(1) Å and O–Al–O = 80.85(1)°].[10c]

Molecular weight measurements in nonpolar solvents were inconclusive, probably due to the presence of a monomer–dimer equilibrium. As expected, molecular weight determination by vapor-pressure osmometry in THF indicated a mononuclear structure. By ^{1}H NMR spectroscopy, the formation of a 1:1 adduct with Lewis bases such as pyridine and γ-butyrolactone Al(mbmp)(O*i*Pr)(L) can be observed.

When monomeric AlMe(OC$_6$H$_2$-2,6-*t*Bu$_2$-4-Me)$_2$ is treated with 2-propanol, methane formation does not occur. Rather, under kinetic control, one equiv. of the bulky phenol HOC$_6$H$_2$-2,6-*t*Bu$_2$-4-Me is displaced to give [AlMe(OC$_6$H$_2$–2,6-*t*Bu$_2$-4-Me)(μ-O*i*Pr)]$_2$ as colorless crystals in high yields. The methyl group at the aluminum is recorded in the ^{1}H NMR spectrum at δ = –0.48. In the ^{13}C NMR spectrum the corresponding signal could not be detected, probably due to excessive broadening. Over the temperature range of +80 to –80 °C there is no significant change in the signal pattern. Molecular weight measurements in nonpolar solvents were inconclusive, but the dimeric structure can be inferred from the parent ion in the EI mass spectrum.

Single-crystal X-ray structural analysis (Table 1, Figure 2) showed a dimeric structure with two isopropoxo bridges and the ligands at the two aluminum centers arranged in a *cis* fashion. Metrical parameters such as Al–CH$_3$ [1.938(4), 1.945(4) Å] and Al–O distances of the phenoxy ligands [1.708(2), 1.698(2) Å] are within the expected ranges,[3a,10a,11] as are the values for the Al$_2$O$_2$ ring [average Al–O distance = 1.842(2) Å; O–Al–O angle = 99.1(1)°]. Most notably, the phenyl ring of one OC$_6$H$_2$-2,6-*t*Bu$_2$-4-Me ligand is turned in such a way as to bisect the plane formed by the Al$_2$O$_2$ lozenge [angle between the planes 82.4(1)°]. The other phenyl ring is in an almost orthogonal arrangement, the angle between the two aromatic rings amounting to 80.4(1)°. The two isopropyl groups of both of the bridging ligands are turned so that the methine hydrogens point toward the aluminum bearing the orthogonal aromatic ring. Evidently, the two aluminum fragments have to undergo substantial "gear-meshing" to alleviate the steric strain caused by the dimerization.

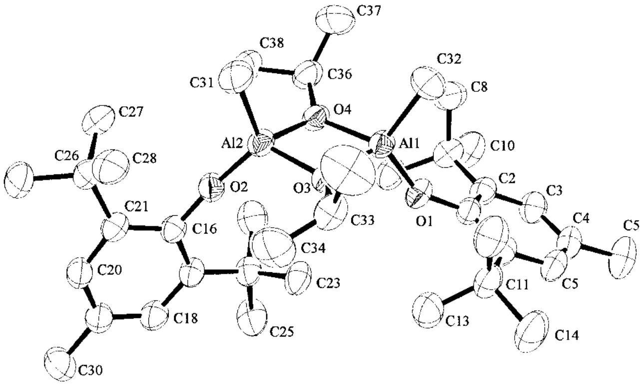

Figure 2. ORTEP diagram of the molecular structure of [AlMe(OC$_6$H$_2$–2,6-*t*Bu$_2$-4-Me)(μ-O*i*Pr)]$_2$. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for the sake of clarity; selected bond lengths [Å] and angles [°]: Al1–C32 1.938(4), Al1–O1 1.708(2), Al1–O3 1.839(2), Al1–O4 1.855(2), Al2–C31 1.945(4), Al2–O2 1.698(2), Al2–O3 1.837(2), Al2–O4 1.835(2); Al1–O1–C1 149.2(2), Al2–O2–C16 167.5(2), O1–Al1–C32 116.0(2), O1–Al1–O3 112.0(1), O3–Al1–O4 80.1(1), Al1–O3–Al2 99.3(1), Al1–O4–Al2 98.8(1), O2–Al2–C31 120.5(2), O2–Al2–O3 116.0(1).

Both the isopropoxo complexes are highly active initiators for the ring-opening polymerization of ε-caprolactone.[1] As summarized in Table 2, high molecular weights can be achieved in toluene at 50 °C, [AlMe(OC$_6$H$_2$–2,6-Bu$_2$-4-Me)(μ-O*i*Pr)]$_2$ being particularly active (complete conversion of a 2.0 M solution of monomer within 30 min). Moreover, the chelate complex [Al(mbmp)(μ-O*i*Pr)]$_2$ behaves in a controlled manner, as judged by the low molecular weight distribution values. The number-averaged molecular weights increase linearly with conversion, as well as with monomer to initiator ratio. Notably, since the efficiency, reflecting the number of chains started per aluminum, has a value of about 0.36 (run no. 1–4), we suggest that, under the conditions studied, the equilibrium between the dimer and the monomer Al(mbmp)(μ-O*i*Pr) is not completely on the side of the monomer.[12] The equilibrium constant for the dissociation in the presence of γ-butyrolactone as a nonpolymerizable lactone at 50 °C can be estimated to be $K_{eq} = 0.15$ mol L^{-1}. However, we cannot exclude the possibility that the dimeric species is also capable of initiating polymerization. Polymerization initiated by $[AlMe(OC_6H_2–2,6\text{-}t Bu_2\text{-}4\text{-}Me)(\mu\text{-}O i Pr)]_2$ is noticeably less controlled, as can be judged by the higher molecular weight distribution values as well as by the rather erratic efficiencies. We suspect that initiation may occur both at the Al-Me and Al-O*i*Pr function.[13,14]

Experimental Section

General Considerations: All experiments were performed under argon using standard Schlenk or glovebox techniques. – THF, pentane, and hexane were purified by distillation from sodium/benzophenone ketyl. Toluene was distilled over sodium sand. ε-Caprolactone was dried over calcium hydride and distilled. Commercially available mbmpH_2 (Aldrich), trimethyl-, and triethylaluminum (WITCO) were used as received. $AlMe(OC_6H_2–2,6\text{-}t Bu_2\text{-}4\text{-}Me)_2$ was prepared according to a literature procedure.[3a] – NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 101 MHz) in $CDCl_3$ at 298 K, unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. – Mass spectra were recorded on a Finnigan 8230 spectrometer. – Elemental analyses were performed by the microanalytical laboratory of this department. – Gel permeation chromatographic (GPC) analyses of the polymers were performed using a SpectraSeries P100 pump, a SDV 5μ 60 cm column, two 100 A 5 μ columns, with lengths of 5 cm and 30 cm, respectively, and a Shodex-RI-71 detector. THF was used as eluent; flow rate: 1 mL/min. – Molecular weights were corrected by universal calibration relative to polystyrene standards.

[Al(mbmp)Me]$_2$: To a suspension of mbmpH_2 (10.0 g, 29.5 mmol) in 40 mL of hexane was slowly added a 2.0 M solution of trimethylaluminum in hexane (14.75 mL, 29.5 mmol). Instantaneous and vigorous evolution of methane and heat was observed. Upon cooling the reaction mixture, a colorless precipitate formed that was filtered off, washed with cold hexane (2 × 10 mL), and dried in vacuo to give colorless microcrystals; yield 10.76 g (95%). – ^{1}H NMR: δ = –0.39 (s, 3 H, $AlCH_3$), 1.14 [s, 9 H, $C(CH_3)_3$], 1.28 [s, 9 H, $C(CH_3)_3$], 2.15 (s, 3 H, 4-CH_3), 2.24 (s, 3 H, 4-CH_3), 3.34 (d, $^2J_{HH}$ = 13.7 Hz, 1 H, CH_2), 4.27 (d, $^2J_{HH}$ = 13.7 Hz, 1 H, CH_2), 6.88 (d, $^4J_{HH}$ = 2.0 Hz, 1 H, 5-H), 6.91 (d, $^4J_{HH}$ = 2.0 Hz, 1 H, 5-H), 6.96 (d, $^4J_{HH}$ = 2.0 Hz, 1 H, 3-H), 7.01 (d, $^4J_{HH}$ = 2.0 Hz, 1 H, 3-H). – ^{13}C{^{1}H} NMR: δ = –7.4 ($AlCH_3$), 21.2, (4-CH_3), 21.3 (4-CH_3), 29.7 [$C(\mathit{C}H_3)_3$], 32.1 [$C(\mathit{C}H_3)_3$], 34.7 [$\mathit{C}(CH_3)_3$], 35.2 [$\mathit{C}(CH_3)_3$], 36.3 (CH_2), 126.6 (C-3), 127.5 (C-3’), 127.7 (C-5), 128.1 (C-5’), 130.7 (C-4), 130.9 (C-4’), 133.1 (C-2), 134.7 (C-2’), 138.1 (C-6), 141.3 (C-6’), 144.7 (C-1), 151.6 (C-1’). – EI MS; *m*/*z* (%): 760 (48) [M^+], 380 (100) [$M/2^+$], 57 (78) [$C_4H_9^+$]. – $C_{24}H_{33}AlO_2$ (380.5): calcd. C 75.76, H 8.74; found C 76.71, H 9.64.

[Al(mbmp)Et]$_2$: This compound was synthesized in a manner analogous to that described for [Al(mbmp)Me]$_2$ using triethylaluminum and isolated as colorless microcrystals in 86% yield. – ^{1}H NMR: δ = 0.42 (m, 2 H, $AlC\mathit{H}_2CH_3$), 0.84 (t, $^3J_{HH}$ = 7.0 Hz, 3 H, $AlCH_2C\mathit{H}_3$), 1.26 [s, 9 H, $C(CH_3)_3$], 1.36 [s, 9 H, $C(CH_3)_3$], 2.20 (s, 3 H, 4-CH_3), 2.31 (s, 3 H, 4-CH_3), 3.56 (d, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2-bridge), 4.56 (d, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2-bridge), 6.95 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, 5-H), 7.09 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, 3-H), 7.21 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, 3-H). – ^{13}C{^{1}H} NMR: δ = 8.0 ($AlCH_2\mathit{C}H_3$), 21.3 ($Al\mathit{C}H_2CH_3$), 30.2, (4-CH_3), 30.3 (4’-CH_3), 32.3 [$C(CH_3)_3$], 35.0 [$C(CH_3)_3$], 35.6 [$C(CH_3)_3$], 35.9 (CH_2-bridge), 126.8 (C-3), 127.85 (C-3’), 128.3 (C-5), 129.9 (C-5’), 130.3 (C-4), 131.2 (C-4’), 133.5 (C-2), 134.9 (C-2’), 138.2 (C-6), 140.9 (C-6’), 152.9 (C-1). – EI MS; *m*/*z* (%): 788 (17) [M^+], 394 (74) [$M/2^+$]. – $C_{25}H_{35}AlO_2$ (394.5): calcd. C 76.11, H 8.94; found C 76.42, H 9.23.

Upon adding 10 equiv. of pyridine, the pyridine adduct Al(mbmp)Et(py) was formed. – ^{1}H NMR: δ = –0.41 (q, $^3J_{HH}$ = 6.4 Hz, 2 H, $AlC\mathit{H}_2CH_3$), 0.79 (t, $^3J_{HH}$ = 6.4 Hz, 3 H, $AlCH_2C\mathit{H}_3$), 1.13 [s, 18 H, $C(CH_3)_3$], 1.95 (s, 6 H, 4-CH_3), 3.08 (d, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2-bridge), 3.52 (d, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2-bridge), 6.42 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, 5-H), 6.64 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, 3-H), 6.98 (m, 2 H, py), 7.38 (m, 1 H, py), 8.33 (m, 2 H, py); – ^{13}C NMR: δ = 10.7 ($AlCH_2\mathit{C}H_3$), 16.1 ($Al\mathit{C}H_2CH_3$), 22.8 (4-CH_3), 31.9 [$C(CH_3)_3$], 35.4 [$C(CH_3)_3$], 36.8 (CH_2-bridge), 125.3 (C-3), 125.9 (py), 127.6 (C-5), 128.4 (py), 130.9 (C-4), 132.6 (C-2) 140.1 (C-6), 151.6 (py), 155.2 (C-1).

[Al(ebmp)Me]$_2$: This compound was synthesized in a manner analogous to that described for [Al(mbmp)Me]$_2$ and isolated as colorless microcrystals in 79% yield. – ^{1}H NMR: δ = –0.81 (s, 3 H, $AlCH_3$), 1.11 [s, 9 H, $C(CH_3)_3$], 1.43 [s, 9 H, $C(CH_3)_3$], 2.24 (s, 3 H, 4-CH_3), 2.31 (s, 3 H, 4’-CH_3), 2.71 (m, 3 H, CH_2CH_2), 3.27 (m, 1 H, CH_2CH_2), 6.81 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, 5-H), 6.89 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, 5-H), 6.93 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, 3-H), 7.10 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, 3-H). – ^{13}C NMR: δ = –5.5 ($AlCH_3$), 20.8 (4-CH_3), 20.9 (4-CH_3), 30.8 [$C(\mathit{C}H_3)_3$], 31.6 [$C(\mathit{C}H_3)_3$], 33.1 [$\mathit{C}(CH_3)_3$], 34.6 [$\mathit{C}(CH_3)_3$], 36.0 (CH_2-bridge), 37.9 (CH_2-bridge), 126.4 (C-6), 126.6 (C-3), 127.5 (C-6), 128.3 (C-4), 128.5 (C-4), 128.9 (C-4), 129.3 (C-5), 134.1 (C-2), 135.9 (C-2), 140.5 (C-1), 144.4 (C-1). – EI MS; *m*/*z* (%): 789 (100) [M^+], 774 (65) [$M^+ – C_4H_9$], 380 (24) [$M/2^+ – CH_3$]. – $C_{25}H_{35}AlO_2$ (394.5): calcd. C 76.11, H 8.94; found C 76.19, H 8.43.

[Al(mbmp)(μ-O*i*Pr)]$_2$: A suspension of [Al(mbmp)Me]$_2$ (4.66 g, 6.1 mmol) in 20 mL of diethyl ether was treated dropwise under vigorous stirring at room temperature with 2-propanol (0.9 mL, 12.1 mmol). After some minutes an exothermic gas evolution began. Upon cooling, a precipitate formed which was filtered, washed with hexane, and dried in vacuo; yield 4.07 g (79%) of colorless microcrystals. – ^{1}H NMR: δ = 1.39 [s, 18 H, $C(CH_3)_3$], 1.58 [d, $^3J_{HH}$ = 6.4 Hz, 6 H, $CH(CH_3)_2$], 2.18 (s, 6H, 4-CH_3), 3.69 (d, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2), 3.89 (d, $^2J_{HH}$ = 14.0 Hz, 1 H, CH_2), 4.66 [septet, $^3J_{HH}$ = 6.4 Hz, 1 H, $C\mathit{H}(CH_3)_2$], 6.97 (d, $^4J_{HH}$ = 2.0 Hz, 2 H, 5-H), 7.11 (d, $^4J_{HH}$ = 2.0 Hz, 2 H, 3-H). – ^{13}C{^{1}H} NMR: δ = 19.2 (4-CH_3), 23.4 [$CH(\mathit{C}H_3)_2$], 28.6 [$C(\mathit{C}H_3)_3$], 33.4 (CH_2), 69.7 [$\mathit{C}H(CH_3)_2$], 124.8 (C-3), 126.5 (C-5), 127.1 (C-4), 127.4 (C-6), 136.7 (C-2), 149.7 (C-1). – EI MS; *m*/*z* (%): 848 (6) [M^+]. – $C_{26}H_{37}AlO_3$ (424.6): calcd. C 73.55, H 8.78; found C 73.18, H 8.55.

Upon adding 10 equiv. of pyridine, the pyridine adduct Al(mbmp)(O*i*Pr)(py) was formed. – ^{1}H NMR: δ = 1.11 [d, $^3J_{HH}$ = 6.4 Hz, 6 H, $CH(C\mathit{H}_3)_2$], 1.56 [s, 18 H, $C(CH_3)_3$], 2.14 (s, 6 H, 4-CH_3), 3.31 (d, $^2J_{HH}$ = 14.1 Hz, 1 H, CH_2-bridge), 3.99 (d, $^2J_{HH}$ = 14.1 Hz, 1 H, CH_2-bridge), 4.81 [s, $^3J_{HH}$ = 6.4 Hz, 1 H, $C\mathit{H}(CH_3)_2$], 6.97 (d, $^4J_{HH}$ = 1.6 Hz, 2 H, 5-H), 7.18 (d, $^4J_{HH}$ = 1.8 Hz, 2 H, 3-H), 7.22 (m, 2 H, py), 7.62 (m, 1 H, py), 8.55 (m, 2

H, py). – ^{13}C NMR: δ = 21.3 (4-CH$_3$), 27.7 [CH(*C*H$_3$)$_2$], 30.4 [C(*C*H$_3$)$_3$], 34.2 (CH$_2$-bridge), 35.1 [*C*(CH$_3$)$_3$], 64.3 [*C*H(CH$_3$)$_2$], 125.3 (C-3), 126.0 (C-5), 126.2 (py), 129.4 (C-4), 130.7 (C-2), 138.21 (py), 40.1 (C-6), 149.9 (C-1), 153.8 (py).

[AlMe(OC$_6$H$_2$-2,6-*t*Bu$_2$-4-Me)(μ-O*i*Pr)]$_2$: To a suspension of MAD (2.63 g, 4.8 mmol) in 10 mL of diethyl ether was added over a period of 2 h 2-propanol (0.37 mL, 4.8 mmol) at room temperature. The reaction mixture was stirred overnight and the solvent volume reduced to half, resulting in a precipitate of a colorless solid. In order to complete the precipitation, hexane was added. The supernatant was filtered off, the precipitate washed with diethyl ether (2 × 10 mL), and dried in vacuo; yield 1.10 g (72%) of colorless crystals. – ^{1}H NMR: δ = –0.48 (s, 3 H, AlCH$_3$), 1.41 [s, 18 H, C(CH$_3$)$_3$], 1.44 [d, 6 H, $^3J_{HH}$ = 6.2 Hz, CH(CH$_3$)$_2$], 2.27 (s, 6 H, 4-CH$_3$), 4.93 [septet, $^3J_{HH}$ = 6.2 Hz, 1 H, CH(CH$_3$)$_2$], 7.03 (s, 2 H, C-3,5). – ^{13}C NMR: δ = 21.4 [CH(CH$_3$)$_2$], 25.3 (4-CH$_3$), 31.7 [C(*C*H$_3$)$_3$], 35.3 [*C*(CH$_3$)$_3$], 69.9 [*C*H(CH$_3$)$_2$], 126.5 (C-3,5), 126.9 (C-4), 139.0 (C-2,6), 153.4 (C-1). – EI MS; *m*/*z* (%): 640 (6) [M$^+$], 365 (61) [Al(OC$_{15}$H$_{24}$)(OC$_3$H$_7$)$_2^+$]. – C$_{19}$H$_{33}$AlO$_2$ (320.4): calcd. C 71.21, H 10.38; found: C 71.19, H 10.43.

Polymerization of μ-Caprolactone: An appropriate amount of the initiator was dissolved in toluene (5 mL) and heated to 50 °C. ε-Caprolactone was added to give a ca. 2 M solution of the monomer, and the polymerization initiated. The reaction mixture was worked up after complete conversion by dropwise adding it to a tenfold volume of methanol. The poly(ε-caprolactone)s were filtered off and dried in vacuo until the weight remained constant.

X-Ray Crystal Structure Analysis of [Al(mbmp)(μ-O*i*Pr)]$_2$ and [AlMe(OC$_6$H$_2$–2,6-*t*Bu$_2$-4-Me)(μ-O*i*Pr)]$_2$: Relevant crystallographic data for [Al(mbmp)(μ-O*i*Pr)]$_2$ and [AlMe(OC$_6$H$_2$-2,6-*t*Bu$_2$-4-Me)(μ-O*i*Pr)]2 are summarized in Table 1. Single crystals suitable for X-ray crystal structure analysis were obtained by slow cooling of concentrated pentane solutions. Data collections were performed on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu-K_α radiation. Data reductions were carried out using the program system XCAD4[15a] for [Al(mbmp)(μ-O*i*Pr)]$_2$ and MolEN[15b] for [AlMe(OC$_6$H$_2$-2,6-*t*Bu$_2$-4-Me)(μ-O*i*Pr)]$_2$. From the measured reflections, all independent reflections were used and the parameters were refined by full-matrix least-squares against all F_o^2 data (SHELXL-93).[15c] The structure was solved using direct methods (SHELXS-86)[15d] and difference-Fourier syntheses and refined with anisotropic thermal parameters for nonhydrogen atoms. The hydrogen atoms in [Al(mbmp)(μ-O*i*Pr)]$_2$ were calculated at their idealized positions, whereas those in [AlMe(OC$_6$H$_2$-2,6-*t*Bu$_2$-4-Me)(μ-O*i*Pr)]$_2$ were located and refined with isotropic parameters. Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-104970 for [Al(mbmp)(μ-O*i*Pr)]$_2$ and –133689 for [AlMe(OC$_6$H$_2$-2,6-*t*Bu$_2$-4-Me)(μ-O*i*Pr)]$_2$. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44 (1223)336–033 or E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk].

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