Oxygen-Stabilized Organoaluminum Compounds as Highly Active Cocatalysts for Ziegler−Natta Olefin Polymerization

Herbert Schumann,* Sebastian Dechert, Stefan Schutte, Ji-Young Hyeon,
Markus Hummert, and Birgit C. Wassermann

Institut für Chemie der Technischen Universität Berlin, Strasse des 17. Juni 135,
D-10623 Berlin, Germany

Walter Kaminsky* and Andrea Eisenhardt

Institut für Technische und Makromolekulare Chemie, Universität Hamburg,
Bundesstrasse 45, D-20146 Hamburg, Germany

Katrin Köhler* and Jens Eichhorn

Merck KGaA, Frankfurter Strasse 250, D-64293 Darmstadt, Germany

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The hydroalumination of the allyl ethers $CH_2{=}CHCH_2OR$ with $^iBu_2AlH$ yields the (3-alkoxypropyl)diisobutylaluminum complexes $^iBu_2Al(CH_2)_3OR$ (R = Me (**1**), Et (**2**), Bu (**3**)). Et_2AlCl and $^iBu_2AlCl$ react with (2-(methoxymethyl)phenyl)lithium and (2-methoxybenzyl)magnesium chloride, yielding (2-(methoxymethyl)phenyl)diethylaluminum (**4**), (2-(methoxymethyl)phenyl)diisobutylaluminum (**5**), and (2-methoxybenzyl)diisobutylaluminum (**7**), respectively. The reaction of $^iBu_2AlCl$ with (2-methoxyphenyl)lithium affords the dimeric bis((2-methoxyphenyl)diisobutylaluminum) (**6**). Et_2AlCl and (8-ethoxynaphthyl)lithium form (8-ethoxynaphthyl)diethylaluminum (**10**) along with a few crystals of bis(8-ethoxynaphthyl)aluminum chloride (**13**). $AlCl_3$ reacts with 2 equiv of (2-methoxybenzyl)magnesium chloride, yielding bis(2-methoxybenzyl)aluminum chloride (**9**). Ligand redistribution followed by metathesis was observed for the reactions of Me_2AlCl and Et_2AlCl with (2-methoxybenzyl)magnesium and (8-methoxynaphthyl)lithium, yielding bis(2-methoxybenzyl)methylaluminum (**8**), bis(8-methoxynaphthyl)methylaluminum (**11**), and bis(8-methoxynaphthyl)ethylaluminum (**12**), respectively. The new compounds have been characterized by elemental analysis, NMR spectroscopy, and mass spectrometry. The solid-state structures of **6**, **8**, **9**, and **11**−**13** were determined by single-crystal X-ray diffraction. The new aluminum alkyls are very active cocatalysts in the $TiCl_4$-catalyzed ethylene polymerization. **7** and **10** cause a higher productivity compared to the common cocatalyst Al_2Et_6. The activity depends strongly on the structure of the oxygen-stabilized aluminum alkyls and is also influenced by the Al/Ti ratio.

Introduction

In the course of the past few decades, numerous efforts have been made to find effective catalysts for the Ziegler−Natta olefin polymerization. In the meantime, a variety of highly efficient catalysts have been available, ranging from titanium(IV) chloride to structurally optimized metallocenes.[1] In a great majority of cases, addition of cocatalysts is necessary to obtain catalytic activity. Nowadays, the most frequently used catalyst/cocatalyst systems are combinations of metallocene and methylalumoxane (MAO), of $TiCl_4$ and trialkylaluminum compounds, and of $TiCl_4$ and alkylaluminum halides.[2] However, alkylaluminum compounds are very sensitive to air and moisture, and compounds such as trimethyl- and triethylaluminum even inflame spontaneously in the presence of only traces of oxygen. To solve this problem, a series of intramolecularly nitrogen- and sulfur-stabilized organoaluminum compounds[3] were synthesized and tested as cocatalysts in olefin polymerization. However, except for the fact that those complexes are less sensitive to air and moisture and therefore easier to handle, their activity was lower than that of the trialkylaluminum compounds industrially used up to now.[4]

In this paper we describe the synthesis of new intramolecularly oxygen-stabilized organoaluminum com-

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* To whom correspondence should be addressed. E-mail: H.S., schumann@chem.tu-berlin.de; W.K., kaminsky@chemie.uni-hamburg.de; K.K., katrin.koehler@merck.de.

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pounds and their application as cocatalysts to the $\mathrm{TiCl_4}$-catalyzed ethylene polymerization. The incorporation of coordinating oxygen functions into the ligand systems of the organoaluminum complexes causes a significant increase in cocatalytic activity. Some of these complexes show an activity even higher than that of commercial triethylaluminum. A further goal for our studies was to investigate the influence of the structure of the cocatalysts on the properties of the polymers formed.

Experimental Section

All operations involving organometallic compounds were carried out under an inert atmosphere of nitrogen using standard Schlenk techniques in dry, oxygen-free solvents. Melting points were measured in sealed capillaries with a Büchi 510 melting point determination apparatus and are uncorrected. The NMR spectra were recorded on a Bruker ARX 200 (^{1}H, 200 MHz; ^{13}C, 50.32 MHz) or ARX 400 (^{1}H, 400 MHz; ^{13}C, 100.64 MHz; ^{27}Al, 104.26 MHz) spectrometer at ambient temperature. Chemical shifts are reported in ppm relative to the ^{1}H and ^{13}C residues of the deuterated solvents. Signal assignments were deduced from ^{13}C-DEPT, ^{1}H,^{1}H, and ^{1}H,^{13}C correlation spectroscopy. ^{27}Al chemical shifts are given relative to $[\mathrm{Al(H_2O)_6}]^{3+}$. Mass spectra (EI, 70 eV) were recorded using a Varian MAT 311 A/AMD instrument. Only characteristic fragments containing the isotopes of the highest abundance are listed. Relative intensities are given in parentheses. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O 2400 analyzer. Allyl methyl ether,[5] allyl ethyl ether,[5] allyl butyl ether,[5] (8-methoxynaphthyl)lithium,[6] 1-ethoxynaphthalene,[7] (8-ethoxynaphthyl)lithium,[6] (2-methoxyphenyl)lithium,[8] (2-(methoxymethyl)phenyl)lithium,[9] (2-methoxybenzyl)magnesium chloride,[10] and $\mathrm{TiCl_4}$ supported on $\mathrm{MgCl_2}$[4d] were prepared according to published procedures. Diisobutylaluminum hydride, diisobutylaluminum chloride, diethylaluminum chloride, dimethylaluminum chloride, and aluminum trichloride were purchased from Aldrich or Merck and used as received.

(3-Methoxypropyl)diisobutylaluminum (1). To allyl methyl ether (5.00 g, 69.3 mmol) was added dropwise half of an *n*-hexane solution of $^i\mathrm{Bu_2AlH}$ (1 M, 34 mL, 34 mmol) at room temperature. After the mixture was heated to 45 °C, the remaining half of the $^i\mathrm{Bu_2AlH}$ solution was added dropwise and the whole reaction mixture was refluxed for 4 h. Then the solvent was removed under vacuum (0.2 mbar) and the crude product was fractionally distilled (0.2 mbar) to yield **1** as a colorless liquid (1.43 g, 20%); bp 55 °C (0.2 mbar). ^{1}H NMR (benzene-d_6, 200 MHz): δ 0.10−0.21 (m, 6 H, $(\mathrm{Me_2CHC}\mathit{H_2})_2\mathrm{AlC}\mathit{H_2}$), 1.16 (d, 12 H, $^3J = 6.5$ Hz, $((\mathrm{C}\mathit{H_3})_2\mathrm{CHCH_2})_2\mathrm{Al}$), 1.61−1.79 (m, 2 H, $\mathrm{AlCH_2C}\mathit{H_2}$), 1.98−2.18 (m, 2 H, $(\mathrm{Me_2C}\mathit{H}\mathrm{CH_2})_2\mathrm{Al}$), 2.77 (s, 3 H, $\mathrm{OC}\mathit{H_3}$), 2.98 (t, 2 H, $^3J = 6.0$ Hz, $\mathrm{AlCH_2CH_2C}\mathit{H_2}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 4.9 (br, $(\mathrm{Me_2CH}\mathit{C}\mathrm{H_2})_2\mathrm{Al}$), 22.5 (br, $\mathrm{Al}\mathit{C}\mathrm{H_2}$), 25.11 ($\mathrm{AlCH_2}\mathit{C}\mathrm{H_2}$), 26.91 ($(\mathrm{Me_2}\mathit{C}\mathrm{HCH_2})_2\mathrm{Al}$), 28.62 ($((\mathit{C}\mathrm{H_3})_2\mathrm{CHCH_2})_2\mathrm{Al}$), 58.20 ($\mathrm{O}\mathit{C}\mathrm{H_3}$), 79.27 ($\mathrm{AlCH_2CH_2}\mathit{C}\mathrm{H_2}$). ^{27}Al NMR (benzene-$d_6$, 104.26 MHz): δ 181 ($w_{1/2} = 3500$ Hz). MS (32 °C; m/z (%)): 214 (0.5) $[\mathrm{M}]^+$, 157 (100) $[\mathrm{M} - \mathrm{C_4H_9}]^+$, 101 (74) $[\mathrm{M} - \mathrm{C_4H_9} - \mathrm{C_4H_8}]^+$, 73 (63) $[\mathrm{C_4H_9O}]^+$. Anal. Calcd for $\mathrm{C_{12}H_{27}AlO}$ (mol wt 214.32): C, 67.25; H, 12.70. Found: C, 67.09; H, 12.55.

(3-Ethoxypropyldiisobutyl)aluminum (2). In analogy to the preparation of **1**, allyl ethyl ether (8.53 g, 99.0 mmol) was reacted with an *n*-hexane solution of $^i\mathrm{Bu_2AlH}$ (1 M, 43 mL, 43 mmol) at 20−65 °C to provide **2** as a colorless liquid (5.49 g, 56%); bp 55 °C (0.15 mbar). ^{1}H NMR (benzene-d_6, 200 MHz): δ 0.10 (ABX, 2 H, $^3J = 6.6$ Hz, $^2J = 14.0$ Hz, $(\mathrm{Me_2CHCH}\mathit{H'})_2\mathrm{Al}$), 0.18 (A$\mathit{B}$X, 2 H, $^3J = 6.6$, $^2J = 14.0$ Hz $(\mathrm{Me_2CHC}\mathit{H}\mathrm{H'})_2\mathrm{Al}$), 0.20 (t, 2 H, $^3J = 7.5$ Hz, $\mathrm{AlC}\mathit{H_2}$), 0.77 (t, 3 H, $^3J = 7.1$ Hz, $\mathrm{OCH_2C}\mathit{H_3}$), 1.16 (d, 6 H, $^3J = 6.5$ Hz, $((\mathrm{C}\mathit{H_3})(\mathrm{CH_3})\mathrm{CHCH_2})_2\mathrm{Al}$), 1.18 (d, 6 H, $^3J = 6.5$ Hz, $((\mathrm{CH_3})(\mathrm{C}\mathit{H_3})\mathrm{CHCH_2})_2\mathrm{Al}$), 1.74 (tt, 2 H, $^3J = 7.5$, $^3J = 7.1$, $\mathrm{AlCH_2C}\mathit{H_2}$), 2.02 (AB$\mathit{X}$, 2 H, $^3J = 6.5$ Hz, $^3J = 6.6$ Hz, $(\mathrm{Me_2C}\mathit{H}\mathrm{CH_2})_2\mathrm{Al}$), 3.05 (t, 2 H, $^3J = 6.0$ Hz, $\mathrm{AlCH_2CH_2C}\mathit{H_2}$), 3.18 (q, 2 H, $^3J = 7.3$ Hz, $\mathrm{OC}\mathit{H_2}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 4.8 (br, $(\mathrm{Me_2CH}\mathit{C}\mathrm{H_2})_2\mathrm{Al}$), 13.64 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_3}$), 23.1 (br, $\mathrm{Al}\mathit{C}\mathrm{H_2}$), 25.18 ($\mathrm{AlCH_2}\mathit{C}\mathrm{H_2}$), 26.04 ($(\mathrm{Me_2}\mathit{C}\mathrm{HCH_2})_2\mathrm{Al}$), 28.67 ($((\mathit{C}\mathrm{H_3})_2\mathrm{CHCH_2})_2\mathrm{Al}$), 67.86 ($\mathrm{O}\mathit{C}\mathrm{H_2CH_3}$), 75.93 ($\mathrm{AlCH_2CH_2}\mathit{C}\mathrm{H_2}$). ^{27}Al NMR (benzene-$d_6$, 104.26 MHz): δ 180 ($w_{1/2} = 4000$ Hz). MS (54 °C; m/z (%)): 171 (100) $[\mathrm{M} - \mathrm{C_4H_9}]^+$, 115 (97) $[\mathrm{M} - \mathrm{C_4H_9} - \mathrm{C_4H_8}]^+$. Anal. Calcd for $\mathrm{C_{13}H_{29}AlO}$ (mol wt 228.35): C, 68.38; H, 12.80. Found: C, 68.30; H, 12.86. Mol wt (cryoscopy in benzene): 236.

(3-Butoxypropyl)diisobutylaluminum (3). To allyl butyl ether (25 g, 219 mmol) was added dropwise an *n*-hexane solution of $^i\mathrm{Bu_2AlH}$ (1 M, 62 mL, 62 mmol) at 80 °C. The reaction mixture was refluxed for 16 h. The solvent was removed under vacuum (0.2 mbar), and the crude product was fractionally distilled (0.16 mbar) to yield **3** as a colorless liquid (8.77 g, 55%); bp 72 °C (0.16 mbar). ^{1}H NMR (benzene-d_6, 400 MHz): δ 0.10 (ABX, 2 H, $^3J = 6.6$ Hz, $^2J = 14.0$ Hz, $(\mathrm{Me_2CHCH}\mathit{H'})_2\mathrm{Al}$), 0.15 (A$\mathit{B}$X, 2 H, $^3J = 6.6$, $^2J = 14.0$ Hz, $(\mathrm{Me_2CHC}\mathit{H}\mathrm{H'})_2\mathrm{Al}$), 0.17 (t, 2 H, $^3J = 7.1$ Hz, $\mathrm{AlC}\mathit{H_2}$), 0.71 (t, 3 H, $^3J = 7.2$ Hz, $\mathrm{O(CH_2)_3C}\mathit{H_3}$), 0.89−1.00 (m, 2 H, $\mathrm{O(CH_2)_2C}\mathit{H_2}\mathrm{CH_3}$), 1.19 (d, 6 H, $^3J = 6.6$ Hz, $(((\mathrm{C}\mathit{H_3})(\mathrm{CH_3}))\mathrm{CHCH_2})_2\mathrm{Al}$), 1.21 (d, 6 H, $^3J = 6.6$ Hz, $(((\mathrm{CH_3})(\mathrm{C}\mathit{H_3}))\mathrm{CHCH_2})_2\mathrm{Al}$), 1.21−1.31 (m, 2 H, $\mathrm{OCH_2C}\mathit{H_2}\mathrm{CH_2CH_3}$), 1.77 (tt, 2 H, $^3J = 7.1$ Hz, $^3J = 6.0$ Hz, $\mathrm{AlCH_2C}\mathit{H_2}$), 2.02 (AB$\mathit{X}$, 2 H, $^3J = 6.6$ Hz, $^3J = 6.6$ Hz, $(\mathrm{Me_2C}\mathit{H}\mathrm{CH_2})_2\mathrm{Al}$), 3.14 (t, 2 H, $^3J = 6.0$ Hz, $\mathrm{AlCH_2CH_2C}\mathit{H_2}$), 3.27 (t, 2 H, $^3J = 7.3$ Hz, $\mathrm{OC}\mathit{H_2}$). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 4.9 (br, $(\mathrm{Me_2CH}\mathit{C}\mathrm{H_2})_2\mathrm{Al}$), 13.65 ($\mathrm{O(CH_2)_3}\mathit{C}\mathrm{H_3}$), 18.64 ($\mathrm{O(CH_2)_2}\mathit{C}\mathrm{H_2CH_3}$), 23.1 (br, $\mathrm{Al}\mathit{C}\mathrm{H_2}$), 25.24 ($\mathrm{AlCH_2}\mathit{C}\mathrm{H_2}$), 27.02 ($(\mathrm{Me_2}\mathit{C}\mathrm{HCH_2})_2\mathrm{Al}$), 28.67 ($((((\mathit{C}\mathrm{H_3})(\mathrm{CH_3}))\mathrm{CHCH_2})_2\mathrm{Al}$), 28.72 ($((((\mathrm{CH_3})(\mathit{C}\mathrm{H_3}))\mathrm{CHCH_2})_2\mathrm{Al}$), 30.06 ($\mathrm{OCH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$), 72.18 ($\mathrm{O}\mathit{C}\mathrm{H_2}$), 76.50 ($\mathrm{AlCH_2CH_2}\mathit{C}\mathrm{H_2}$). ^{27}Al NMR (benzene-$d_6$, 104.26 MHz): δ 182 ($w_{1/2} = 6000$ Hz). MS (54 °C; m/z (%)): 199 (100) $[\mathrm{M} - \mathrm{C_4H_9}]^+$, 143 (83) $[\mathrm{M} - \mathrm{C_4H_9} - \mathrm{C_4H_8}]^+$, 87 (17) $[\mathrm{M} - \mathrm{C_4H_9} - \mathrm{C_4H_8} - \mathrm{C_4H_8}]^+$. Anal. Calcd for $\mathrm{C_{15}H_{33}AlO}$ (mol wt 256.40): C, 70.26; H, 12.97. Found: C, 70.07; H, 13.10. Mol wt (cryoscopy in benzene): 269.

(2-(Methoxymethyl)phenyl)diethylaluminum (4). To a suspension of (2-(methoxymethyl)phenyl)lithium (7.74 g, 60.4 mmol) in toluene (120 mL) was added slowly an *n*-hexane solution of $\mathrm{Et_2AlCl}$ (1 M, 60.4 mL, 60.4 mmol) via a syringe at −50 °C. The solution was warmed to room temperature and stirred at 60 °C for 2 days. The solvent was removed under vacuum (0.05 mbar), and toluene (100 mL) was added. The mixture was filtered, and toluene was removed under vacuum (0.05 mbar), leaving a clear colorless liquid which was fractionally distilled (0.71 mbar) to yield **4** as a colorless oil (6.20

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g, 50%); bp 108 °C (0.71 mbar). ^{1}H NMR (benzene-d_6, 200 MHz): δ 0.24 (q, 4 H, ^3J = 8.2 Hz, $(CH_3CH_2)_2Al$), 1.26 (t, 6 H, ^3J = 8.2 Hz, $(CH_3CH_2)_2Al$), 2.88 (s, 3 H, OCH_3), 4.16 (s, 2 H, $C_6H_4CH_2O$), 6.67−6.78 (m, 1 H, H^{ar}), 7.12−7.26 (m, 2 H, H^{ar}), 7.71−7.80 (m, 1 H, H^{ar}). $^{13}C\{^1H\}$ NMR (benzene-d_6, 50.32 MHz): δ 0.12 (br, $(CH_3CH_2)_2Al$), 9.69 ($(CH_3CH_2)_2Al$), 58.54 (OCH_3), 81.09 ($C_6H_4CH_2O$), 120.87 (C^{ar}), 126.86 (C^{ar}), 127.04 (C^{ar}), 136.43 (C^{ar}), 142.16 (C^2), 147.2 (br, C^1). ^{27}Al NMR (benzene-d_6, 104.26 MHz): δ 184 ($w_{1/2}$ = 5000 Hz). MS (49 °C; m/z (%)): 177 (100) $[M - C_2H_5]^+$, 149 (56) $[M - C_2H_5 - C_2H_4]^+$, 119 (34) $[C_7H_8Al]^+$, 91 (29) $[C_7H_7]^+$. Anal. Calcd for $C_{12}H_{19}AlO$ (mol wt 206.26): C, 69.88; H, 9.28. Found: C, 69.51; H, 9.05.

(2-(Methoxymethyl)phenyl)diisobutylaluminum (5). In analogy to the preparation of **4**, (2-(methoxymethyl)phenyl)lithium (6.30 g, 49.2 mmol) was reacted with $^iBu_2AlCl$ (8.36 g, 47.3 mmol) at −50 to +20 °C for 12 h. The fractional distillation of the obtained crude product (0.37 mbar) yielded **5** as a colorless oil (7.40 g, 60%); bp 110 °C (0.37 mbar). ^{1}H NMR (benzene-d_6, 200 MHz): δ 0.22 (*A*BX, 2 H, ^3J = 6.9 Hz, ^2J = 14.0 Hz, $(Me_2CHCHH')_2Al$), 0.33 (A*B*X, 2 H, ^3J = 6.9 Hz, ^2J = 14.0 Hz, $(Me_2CHCHH')_2Al$), 1.12 (d, 12 H, ^3J = 6.5 Hz, $((CH_3)_2CHCH_2)_2Al$), 2.03 (AB*X*, 2 H, ^3J = 6.5 Hz, ^3J = 6.9 Hz, $(Me_2CHCH_2)_2Al$), 2.88 (s, 3 H, OCH_3), 4.17 (s, 2 H, $C_6H_4CH_2O$), 6.58−6.74 (m, 1 H, H^{ar}), 7.11−7.26 (m, 2 H, H^{ar}), 7.77−7.84 (m, 1 H, H^{ar}). $^{13}C\{^1H\}$ NMR (benzene-d_6, 50.32 MHz): δ 22.60 (br, $((CH_3)_2CHCH_2)_2Al$), 26.83 ($(((CH_3)_2CHCH_2)_2Al$), 28.51 ($(((CH_3C'H_3)CHCH_2)_2Al$), 28.62 ($(((CH_3CH_3)CHCH_2)_2Al$), 58.40 (OCH_3), 80.64 ($C_6H_4CH_2O$), 120.81 (C^{ar}), 126.91 (C^{ar}), 126.98 (C^{ar}), 136.47 (C^{ar}), 141.57 (C^2), 148.6 (br, C^1). ^{27}Al NMR (benzene-d_6, 104.26 MHz): δ 182 ($w_{1/2}$ = 7400 Hz). MS (29 °C; m/z (%)): 205 (89) $[M - C_4H_9]^+$, 149 (100) $[M - C_4H_9 - C_4H_8]^+$, 119 (32) $[C_7H_8Al]^+$, 91 (31) $[C_7H_7]^+$. Anal. Calcd for $C_{16}H_{27}AlO$ (mol wt 262.37): C, 73.25; H, 10.37. Found: C, 72.97; H, 10.26.

Bis((2-methoxyphenyl)diisobutylaluminum) (6). To a suspension of (2-methoxyphenyl)lithium (6.87 g, 60.3 mmol) in toluene (120 mL) was added dropwise $^iBu_2AlCl$ (10.65 g, 60.3 mmol) at −60 °C. The suspension was warmed to room temperature and stirred for 12 h. The solution was filtered from the precipitated LiCl. The solvent was removed under vacuum (0.05 mbar), and the remaining oily solid was suspended in *n*-heptane (40 mL). The residue was separated and washed with *n*-heptane (2 × 20 mL) to give a white solid. Recrystallization from toluene at 0 °C gave colorless crystals of **6** (9.12 g, 61%); mp 128 °C. ^{1}H NMR (THF-d_8, 400 MHz): δ 0.16 (d, 4 H, ^3J = 7.1 Hz, $(Me_2CHCH_2)_2Al$), 0.91 (d, 12 H, ^3J = 6.0 Hz, $((CH_3)_2CHCH_2)_2Al$), 1.89 (tsp, 2 H, ^3J = 6.0 Hz, ^3J = 7.1 Hz, $(Me_2CHCH_2)_2Al$), 3.70 (s, 3 H, OCH_3), 6.69 (d, 1 H, ^3J = 8.1 Hz, H^3), 6.77 (dd, 1 H, ^3J = 6.8 Hz, ^3J = 7.3 Hz, H^5), 7.10 (ddd, 1 H, ^3J = 8.1 Hz, ^3J = 7.3 Hz, ^4J = 1.9 Hz, H^4), 7.39 (dd, 1 H, ^3J = 6.8 Hz, ^4J = 1.9 Hz, H^6). $^{13}C\{^1H\}$ NMR (THF-d_8, 100.64 MHz): δ 22.77 (br, $((CH_3)_2CHCH_2)_2Al$), 27.43 ($(((CH_3)_2CHCH_2)_2Al$), 28.88 ($(((CH_3)_2CHCH_2)_2Al$), 54.66 (OCH_3), 108.60 (C^3), 120.99 (C^5), 129.04 (C^4), 139.27 (C^6), 139.5 (br, C^1), 167.22 (C^2). ^{27}Al NMR (THF-d_8, 104.26 MHz): δ 176 ($w_{1/2}$ = 7200 Hz); (benzene-d_6, 104.26 MHz): δ 220 ($w_{1/2}$ = 19500 Hz). MS (86 °C; m/z (%)): 191 (72) $[M - C_{15}H_{25}AlO - C_4H_9]^+$, 135 (100) $[C_{15}H_{25}AlO - C_4H_9 - C_4H_8]^+$, 108 (20) $[C_7H_8O]^+$, 105 (26) $[C_6H_6Al]^+$, 78 (16) $[C_6H_6]^+$, 65 (11) $[C_5H_5]^+$. Anal. Calcd for $C_{30}H_{50}Al_2O_2$ (mol wt 496.68): C, 72.55; H, 10.15. Found: C, 72.16; H, 9.87. Mol wt (cryoscopy in benzene): 376.

(2-Methoxybenzyl)diisobutylaluminum (7). $^iBu_2AlCl$ (6.83 g, 38.7 mmol) was dissolved in THF (250 mL) at 0 °C. A THF solution of (2-methoxybenzyl)magnesium chloride (0.26 M, 150 mL, 39 mmol) was added dropwise over a period of 3 h at 0 °C. The reaction mixture was slowly warmed to room temperature and stirred for 18 h. The solvent was removed under vacuum (0.05 mbar), and the remaining oily solid was suspended in *n*-pentane (125 mL). The suspension was filtered, and the residue was washed with *n*-pentane (75 mL). *n*-Pentane was removed from the combined solutions under vacuum (0.05 mbar), leaving a clear colorless liquid which was fractionally distilled (0.05 mbar) to yield **7** as a colorless oil (5.00 g, 49%); bp 85 °C (0.05 mbar). ^{1}H NMR (benzene-d_6, 200 MHz): δ 0.22 (d, 4 H, ^3J = 6.9 Hz, $(Me_2CHCH_2)_2Al$), 1.07 (d, 12 H, ^3J = 6.5 Hz, $((CH_3)_2CHCH_2)_2Al$), 1.45 (s, 2 H, $C_6H_4CH_2Al$), 1.99 (tsp, 2 H, ^3J = 6.5 Hz, ^3J = 6.9 Hz, $(Me_2CHCH_2)_2Al$), 3.18 (s, 3 H, OCH_3), 6.20−6.25 (m, 1 H, H^{ar}), 6.75−6.90 (m, 2 H, H^{ar}), 7.20−7.30 (m, 1 H, H^{ar}). $^{13}C\{^1H\}$ NMR (benzene-d_6, 50.32 MHz): δ 10.3 (br, $C_6H_4CH_2Al$), 22.3 (br, $((CH_3)_2CHCH_2)_2Al$), 26.74 ($(((CH_3)_2CHCH_2)_2Al$), 28.44 ($(((CH_3)_2CHCH_2)_2Al$), 55.78 (OCH_3), 109.20 (C^{ar}), 124.22 (C^{ar}), 125.06 (C^{ar}), 133.98 (C^{ar}), 134.57 (C^1), 155.62 (C^2). ^{27}Al NMR (benzene-d_6, 104.26 MHz): δ 195 ($w_{1/2}$ = 7300 Hz). MS (65 °C; m/z (%)): 262 (1) $[M]^+$, 205 (80) $[M - C_4H_9]^+$, 149 (100) $[M - C_4H_9 - C_4H_8]^+$, 148 (10) $[M - (C_4H_9)_2]^+$, 134 (16) $[C_7H_7AlO]^+$ 91 (10) $[C_7H_7]^+$. Anal. Calcd for $C_{16}H_{27}AlO$ (mol wt 262.37): C, 73.25; H, 10.37. Found: C, 72.61; H, 10.44.

Bis(2-methoxybenzyl)methylaluminum (8). In analogy to the preparation of **9**, Me_2AlCl (2.15 g, 23 mmol) was reacted with a THF solution of (2-methoxybenzyl)magnesium chloride (0.28 M, 90 mL, 26 mmol), forming a white solid, which could not be satisfactorily purified, to allow its analytical and spectroscopic characterization. Digesting of the solid with toluene, filtration of the mixture, and cooling of the clear toluene solution to −30 °C resulted in the precipitation of a few crystals, which were identified as **8** by X-ray structural analysis.

Bis(2-methoxybenzyl)aluminum Chloride (9). $AlCl_3$ (5.36 g, 40.2 mmol) was dissolved in THF (250 mL) at −30 °C. A THF solution of (2-methoxybenzyl)magnesium chloride (0.26 M, 150 mL, 39 mmol) was added dropwise over a period of 3.5 h at −30 °C. The reaction mixture was slowly warmed to room temperature and stirred for 3 days. The solvent was removed under vacuum (0.05 mbar), leaving a white solid which was suspended in diethyl ether (100 mL). The suspension was filtered, and the residue was washed with diethyl ether (50 mL). The diethyl ether was removed from the combined solutions under vacuum (0.05 mbar), and the white residue was dissolved in warm toluene (40 mL). Cooling the solution to room temperature gave colorless crystals of **9** (3.60 g, 29% based on $AlCl_3$, 60% based on 2-methoxybenzylmagnesium chloride); mp 167 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.40 (s, 4H, $(CH_2)_2Al$), 4.11 (s, 6 H, OCH_3), 6.90−7.20 (m, 6 H, H^{ar}), 7.30−7.35 (m, 2 H, H^{ar}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.32 MHz): δ 8.4 (br, $(CH_2)_2Al$), 55.23 (OCH_3), 108.84 (C^{ar}), 123.01 (C^{ar}), 125.11 (C^{ar}), 132.43 (C^1), 132.53 (C^{ar}), 154.86 (C^2). ^{27}Al NMR ($CDCl_3$, 104.26 MHz): δ 134 ($w_{1/2}$ = 7900 Hz). MS (126 °C; m/z (%)): 304 (16) $[M]^+$, 289 (38) $[M - CH_3]^+$, 183 (50) $[M - C_8H_9O]^+$, 167 (66) $[C_7H_5AlClO]^+$, 121 (38) $[C_8H_{10}O]^+$, 107 (49) $[C_7H_7O]^+$, 91 (100) $[C_7H_7]^+$, 77 (61) $[C_6H_5]^+$, 65 (41) $[C_5H_5]^+$. Anal. Calcd for $C_{16}H_{18}AlClO_2$ (mol wt 304.75): C, 63.06; H, 5.95. Found: C, 63.15; H, 5.83.

(8-Ethoxynaphthyl)diethylaluminum (10) and Bis(8-ethoxynaphthyl)aluminum Chloride (13). To a suspension of (8-ethoxynaphthyl)lithium (3.50 g, 19.6 mmol) in diethyl ether (50 mL) was added dropwise Et_2AlCl (2.36 g, 19.6 mmol) at −40 °C. The suspension was slowly warmed to room temperature and stirred for 12 h. The solution was decanted from the precipitated LiCl. The solvent was removed under vacuum (0.01 mbar), leaving a yellow oil which was fractionally distilled (0.01 mbar) to yield **10** as a light yellow oil (1.24 g, 25%); bp 146 °C (0.01 mbar). ^{1}H NMR (benzene-d_6, 200 MHz): δ 0.36 (*A*BX$_3$, 2 H, ^3J = 8.2 Hz, ^2J = 14.5 Hz, $(MeCHH')_2Al$), 0.41 (A*B*X$_3$, 2 H, ^3J = 8.2 Hz, ^2J = 14.5 Hz, $(MeCHH')_2Al$), 1.00 (t, 3 H, ^3J = 7.1 Hz, OCH_2CH_3), 1.30 (AB*X*$_3$, 6 H, ^3J = 8.2 Hz, $(CH_3CHH')_2Al$), 3.92 (q, 2 H, ^3J = 7.1 Hz, OCH_2CH_3), 6.22 (dd, 1 H, ^3J = 7.7 Hz, ^4J = 0.7 Hz, H^7), 7.03 (dd, 1 H, ^3J = 8.4 Hz, ^3J = 7.7 Hz, H^6), 7.38 (dd, 1 H, ^3J = 8.4 Hz, ^4J = 0.7 Hz, H^5), 7.45 (dd, 1 H, ^3J 8.4 = Hz, ^3J 6.4 Hz, H^3), 7.59 (dd, 1 H, ^3J = 8.4 Hz, ^4J = 1.3 Hz, H^4), 7.91 (dd, 1 H, ^3J = 6.4 Hz, ^4J =

Table 1. Crystal Structure Determination of 6, 8, and 9

	6	**8**	**9**
empirical formula	$C_{30}H_{50}Al_2O_2$	$C_{17}H_{21}AlO_2$	$C_{16}H_{18}AlClO_2$
fw	496.66	248.32	304.73
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbcn* (No. 60)	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
a (Å)	12.9941(1)	15.0362(7)	17.0545(3)
b (Å)	12.5007(2)	7.1516(3)	7.2033(1)
c (Å)	18.6822(2)	15.7713(6)	14.7905(3)
α (deg)	90	90	90
β (deg)	90	116.007(1)	123.464(1)
γ (deg)	90	90	90
V (Å^3)	3034.65(6)	1524.20(11)	1515.79(5)
Z	4	4	4
D(calcd) (g/cm^3)	1.087	1.239	1.335
μ(Mo Kα) (mm^{-1})	0.119	0.132	0.308
F(000)	1088	608	640
cryst size (mm^3)	0.46 × 0.36 × 0.33	0.42 × 0.20 × 0.08	0.42 × 0.20 × 0.06
$\theta_{\min}$, $\theta_{\max}$ (deg)	2.18, 26.00	2.87, 27.49	2.86, 27.49
index ranges	$-13 \leq h \leq 16$	$-11 \leq h \leq 19$	$-22 \leq h \leq 17$
	$-15 \leq k \leq 15$	$-9 \leq k \leq 9$	$-7 \leq k \leq 9$
	$-22 \leq l \leq 23$	$-20 \leq l \leq 19$	$-18 \leq l \leq 19$
no. of rflns collected	19 164	5561	5622
no. of indep rflns	2982 ($R_{\mathrm{int}} = 0.0981$)	1737 ($R_{\mathrm{int}} = 0.0813$)	1730 ($R_{\mathrm{int}} = 0.0728$)
max/min transmission	0.9741/0.4778	0.8383/0.4230	0.9781/0.7271
no. of data/restraints/params	2982/6/160	1737/0/94	1730/0/93
GOF on F^2	1.026	1.024	1.031
R indices ($I > 2\sigma(I)$)			
R1	0.0580	0.0602	0.0406
wR2	0.1447	0.1307	0.0975
R indices (all data)			
R1	0.0817	0.1035	0.0539
wR2	0.1599	0.1501	0.1048
residual electron density (e/Å^3)			
max	0.518	0.447	0.375
min	−0.403	−0.247	−0.332

1.3 Hz, H^2). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 0.33 (br, $(CH_3CH_2)_2Al$), 8.91 ($(CH_3CH_2)_2Al$), 12.85 (OCH_2CH_3), 66.41 (OCH_2CH_3), 102.81 (C^7), 123.33 (C^5), 123.71 (C^6), 125.28 (C^4), 127.45 (C^3), 132.39 (C$^{10/9}$), 133.17 (C$^{9/10}$), 133.59 (C^2), 144.9 (br, C^1), 153.27 (C^8). ^{27}Al NMR (benzene-d_6, 104.26 MHz): δ 189 ($w_{1/2}$ = 8200 Hz). MS (60 °C; *m*/*z* (%)): 256 (2) [M]$^+$, 227 (100) [M − C_2H_5]$^+$, 199 (56) [M − (C_2H_5) − (C_2H_4)]$^+$, 198 (23) [M − $(C_2H_5)_2$]$^+$, 171 (25) [M − $Al(C_2H_5)_2$]$^+$, 170 (36) [M − $(C_2H_5)_5$ − (C_2H_4)]$^+$, 144 (17) [$C_{10}H_8O$]$^+$, 116 (4) [C_9H_8]$^+$, 115 (8) [C_9H_7]$^+$. Anal. Calcd for $C_{16}H_{21}AlO$ (mol wt 256.32): C, 74.97; H, 8.26. Found: C, 74.71; H, 8.05.

The residue left after the distillation of **10** was disolved in toluene, and the solution was cooled to −30 °C. A few crystals precipitated, which were identified as **13** by X-ray structural analysis.

Bis(8-methoxynaphthyl)methylaluminum (11). To a suspension of (8-methoxynaphthyl)lithium (8.50 g, 51.8 mmol) in diethyl ether (100 mL) was slowly added an *n*-hexane solution of Me_2AlCl (1 M, 51.8 mL, 51.8 mmol) via a syringe at −78 °C. The solution was warmed to room temperature and stirred overnight. The solvent was removed under vacuum (0.05 mbar), and toluene (100 mL) was added. The mixture was filtered, and the toluene was removed under vacuum (0.05 mbar). The remaining residue was washed twice with *n*-heptane (2 × 10 mL) to yield **11** as a white solid (2.03 g, 11% based on Me_2AlCl, 22% based on (8-methoxynaphthyl)lithium); mp 250 °C dec. ^{1}H NMR (benzene-d_6, 200 MHz): δ −0.26 (s, 3 H, CH_3Al), 3.73 (s, 6 H, OCH_3), 6.41 (dd, 2 H, ^3J = 7.7 Hz, ^4J = 0.7 Hz, H^7), 7.17 (dd, 2 H, ^3J = 8.2 Hz, ^3J = 7.7 Hz, H^6), 7.47 (dd, 2 H, ^3J = 8.2 Hz, ^3J = 6.4 Hz, H^3), 7.48 (dd, 2 H, ^3J = 8.2 Hz, ^4J = 0.7 Hz, H^5), 7.69 (dd, 2 H, ^3J = 8.2 Hz, ^4J = 1.3 Hz, H^4), 7.74 (dd, 2 H, ^3J = 6.4 Hz, ^4J = 1.3 Hz, H^2). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ −10 (br, CH_3Al), 55.90 (OCH_3), 102.52 (C^7), 123.08 (C^5), 124.53 (C^6), 126.00 (C^4), 127.48 (C^3), 133.31 (C$^{10/9}$), 133.91 (C$^{9/10}$), 134.11 (C^2), 145.9 (br, C^1), 155.68 (C^8). MS (150 °C; *m*/*z* (%)): 341 (100) [M − CH_3]$^+$, 326 (89) [M − $(CH_3)_2$]$^+$, 311 (93) [M − $(CH_3)_3$]$^+$, 158 (41) [$C_{11}H_{10}O$]$^+$, 143 (21) [$C_{10}H_7O$]$^+$, 115 (45) [C_9H_7]$^+$. Anal. Calcd for $C_{23}H_{21}AlO_2$ (mol wt 356.39): C, 77.51; H, 5.94. Found: C, 77.21; H, 6.14.

Bis(8-methoxynaphthyl)ethylaluminum (12). In analogy to the preparation of **11**, (8-methoxynaphthyl)lithium (6.85 g, 41.7 mmol) suspended in diethyl ether (90 mL) was reacted with Et_2AlCl (5.03 g, 41.7 mmol), yielding **12** as a white solid (2.93 g, 19% based on Et_2AlCl, 37.9% based on (8-methoxynaphthyl)lithium); mp 190 °C. ^{1}H NMR (benzene-d_6, 200 MHz): δ 0.38 (q, 3H, ^3J = 8.1 Hz, CH_3CH_2Al), 1.18 (t, 3 H, ^3J = 8.1 Hz, CH_3CH_2Al), 3.77 (s, 6 H, OCH_3), 6.40 (dd, 2 H, ^3J = 7.7 Hz, ^4J = 0.7 Hz, H^7), 7.16 (dd, 2 H, ^3J = 8.2 Hz, ^3J = 7.7 Hz, H^6), 7.47 (dd, 2 H, ^3J 8.2 = Hz, ^3J = 6.4 Hz, H^3), 7.48 (dd, 2 H, ^3J = 8.2 Hz, ^4J = 0.7 Hz, H^5), 7.69 (dd, 2 H, ^3J = 8.2 Hz, ^4J = 1.3 Hz, H^4), 7.75 (dd, 2 H, ^3J = 6.4 Hz, ^4J = 1.3 Hz, H^2). ^{13}C{^{1}H} NMR (benzene-d_6, 50.32 MHz): δ 0.8 (br, CH_3CH_2-Al), 10.54 (CH_3CH_2Al), 56.04 (OCH_3), 102.31 (C^7), 123.06 (C^5), 124.55 (C^6), 126.01 (C^4), 127.46 (C^3), 133.42 (C$^{10/9}$), 133.85 (C$^{9/10}$), 134.25 (C^2), 145.1 (br, C^1), 155.83 (C^8). MS (143 °C; *m*/*z* (%)): 370 (0.5) [M]$^+$, 341 (100) [M − C_2H_5]$^+$, 326 (56) [M − C_2H_5 − CH_3]$^+$, 311 (61) [M − C_2H_5 − $(CH_3)_2$] $^+$ 158 (36) [$C_{11}H_{10}O$]$^+$, 143 (17) [$C_{10}H_7O$]$^+$, 115 (25) [C_9H_7]$^+$. Anal. Calcd for $C_{24}H_{23}AlO_2$ (mol wt 370.42): C, 77.82; H, 6.26. Found: C, 77.61; H, 6.40.

X-ray Structure Determination. The crystal data and details of the data collections of **6**, **8**, **9**, and **11**−**13** are given in Tables 1 and 2. The data were collected on a Siemens SMART CCD diffractometer[11] (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å) with an area detector by use of ω scans at 173 K. The structures were solved by direct methods and refined on F^2 using all reflections with the SHELX-97 software package.[12] Two methyl groups of one isobutyl group

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(11) SMART and SAINT: Data Collection and Processing Software for SMART System; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1995.

(12) Sheldrick, G. M. SHELX-97 Program for Crystal Structure Determination; Universität Göttingen, Göttingen, Germany, 1997.

Table 2. Crystal Structure Determination of 11−13

	11	**12**	**13**
empirical formula	$C_{23}H_{21}AlO_2$	$C_{24}H_{23}AlO_2$	$C_{24}H_{22}AlClO_2 \cdot C_7H_8$
fw	356.38	370.40	496.98
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a (Å)	17.9530(2)	8.6445(4)	14.9719(8)
b (Å)	8.1396(2)	13.5215(6)	16.4856(8)
c (Å)	25.7938(5)	17.0360(8)	12.1561(6)
α (deg)	90	90	90
β (deg)	90	95.152(2)	112.932(2)
γ (deg)	90	90	90
V (Å^3)	3769.25(13)	1983.24(16)	2763.3(2)
Z	8	4	4
D(calcd) (g/cm^3)	1.256	1.241	1.195
μ(Mo Kα) (mm^{-1})	0.121	0.118	0.195
F(000)	1504	784	1048
cryst size (mm^3)	0.42 × 0.14 × 0.12	0.54 × 0.12 × 0.08	0.54 × 0.32 × 0.18
$\theta_{\min}$, $\theta_{\max}$ (deg)	1.58, 24.00	1.93, 26.00	1.93, 23.36
index ranges	$-20 \le h \le 20$ $-9 \le k \le 7$ $-29 \le l \le 29$	$-10 \le h \le 10$ $-16 \le k \le 15$ $-21 \le l \le 8$	$-10 \le h \le 16$ $-17 \le k \le 18$ $-13 \le l \le 13$
no. of rflns collected	19 404	6225	5779
no. of indep rflns	2957 ($R_{\text{int}} = 0.1313$)	3817 ($R_{\text{int}} = 0.1116$)	1976 ($R_{\text{int}} = 0.0944$)
max/min transmission	0.9781/0.7147	0.9563/0.4896	0.9766/0.5413
no. of data/restraints/params	2957/0/238	3817/0/247	1976/31/158
GOF on F^2	1.035	0.898	1.043
R indices ($I > 2\sigma(I)$)			
R1	0.0613	0.0746	0.0986
wR2	0.1250	0.1118	0.2651
R indices (all data)			
R1	0.1120	0.2119	0.1595
wR2	0.1459	0.1512	0.3168
residual electron density (e/Å^3)			
max	0.259	0.412	0.650
min	−0.257	−0.369	−0.815

of **6** are disordered about two positions, with occupancy factors of 0.69(2) and 0.31(2). All C−C distances of the disordered part were restrained to be equal. The asymmetric unit of **13** contains a toluene molecule which is disordered about a 2-fold rotation axis. All C−C distances of the phenyl ring and all C−C−C angles belonging to the phenyl group were restrained to be equal. The $C^{aryl}-CH_3$ bond length was restrained to 1.5 Å. The carbon atoms of the disordered parts were refined isotropically; all other non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. SADABS[13] was used to perform area-detector scaling and absorption corrections. Further details are part of the Supporting Information.

Polymerization Experiments. All procedures were carried out under an argon atmosphere using Schlenk techniques. Ethylene and hexane, purchased from Linde and Merck, respectively, were purified by passage through columns containing Cu catalysts (BASF R3-11) and through molecular sieves (10 Å). The aluminum alkyls were used as solutions in hexane. $TiCl_4$, supported on $MgCl_2$,[4d] was used as a suspension in hexane.

All polymerization reactions were carried out in a 1 L Büchi glass autoclave equipped with a cooling system. The addition of the gaseous monomer was achieved by a Broker 4850 massflow controller. For the standard experiment, the reactor was evacuated at 95 °C for 1 h, then cooled to 40 °C, and charged in an argon reverse flow with hexane and the required amount of the catalyst suspension up to an overall volume of 200 mL. After the reactor was heated to the polymerization temperature of 60 °C, ethylene was added up to a total pressure of 2.5 bar. The polymerization was started by injection of the hexane solution of the respective aluminum alkyl as the cocatalyst. During the reaction, the total pressure was kept constant by supplying ethylene. After a polymerization time of 1 h, the polymerization was quenched by addition of 5 mL of ethanol. The polymer solution was stirred overnight with diluted hydrochloric acid followed by neutralization with $NaHCO_3$, washing with water, evaporation of hexane, and drying.

The melting points of the polymers were determined by differential scanning calorimetry using a DSC-4 instrument from Perkin-Elmer. To eliminate any thermal history, the samples (5 mg) were heated to 200 °C, cooled to 0 °C (cooling rate 20 °C/min), and again heated to 200 °C. The values of the second run are reported. The molar masses M_η were determined using an Ubbelohde viscosimeter (capillary 530 0a, $K = 0.005$ mm^2/s^2). The samples were prepared by dissolving 50 mg of polymer in 50 mL of decahydronaphthalene stabilized with 1 g/L of 2,6-di-*tert*-butyl-4-methylphenol and measured at 135 °C.

Results and Discussion

Synthesis and Characterization. Intramolecularly oxygen-stabilized organoaluminum compounds have been synthesized either by hydroalumination of allylic ethers[14] or by reacting dialkylaluminum halides with salts of the appropriate oxygen-functionalized ligand.[15] The first derivatives of this kind, $^iBu_2Al(CH_2)_3OEt$ (**2**) and $^iBu_2Al(CH_2)_3OPr$, were prepared by Zakharkin et al.[14] in 1959 by hydroalumination of C_3H_5OEt and C_3H_5-OPr with $^iBu_2AlH$, but both compounds have been characterized only poorly. We repeated the synthesis of **2** under modified reaction conditions and additionally

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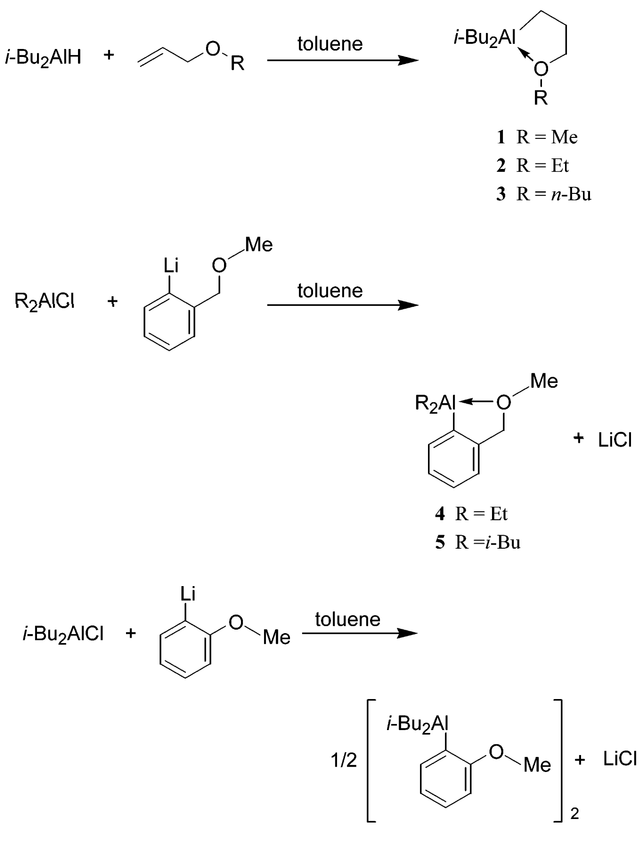
[14] Zakharkin, L. I.; Savina, L. A. *Izv. Akad Nauk SSSR, Otd. Khim. Nauk* **1959**, 444.

[15] Bähr, G.; Müller, G. E. *Chem. Ber.* **1955**, *88*, 251.

Scheme 1



1 R = Me
2 R = Et
3 R = *n*-Bu

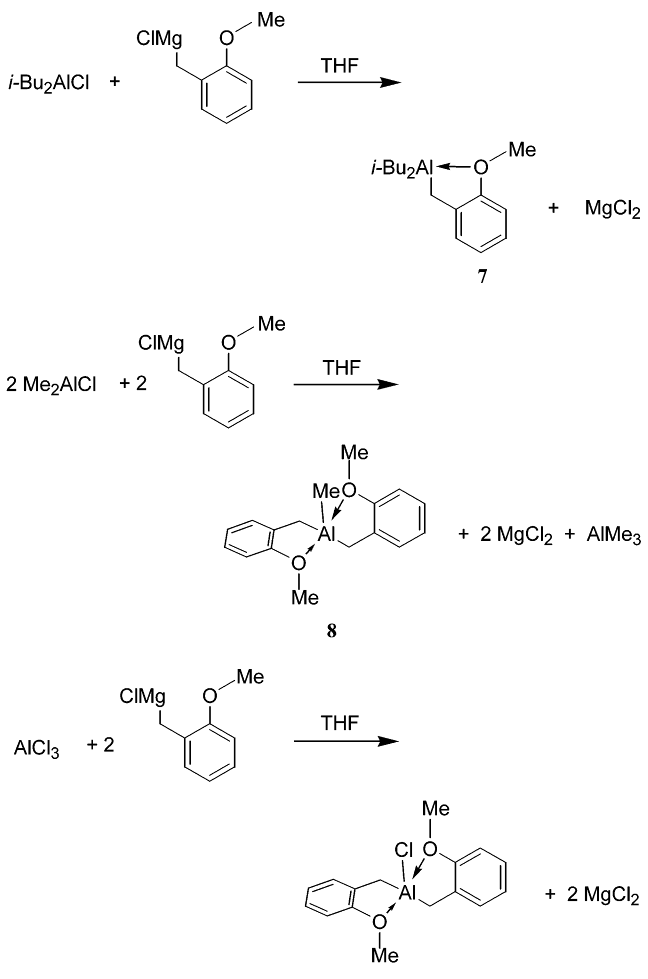
4 R = Et
5 R =*i*-Bu

6

characterized the compound by its NMR and mass spectra. C_3H_5OMe and C_3H_5OBu react in an analogous manner with $^iBu_2AlH$ to give the intramolecularly oxygen-stabilized complexes $^iBu_2Al(CH_2)_3OMe$ (**1**) and $^iBu_2Al(CH_2)_3OBu$ (**3**) (Scheme 1). In contrast, triorganoaluminum compounds containing oxygen-functionalized aryl ligands can be prepared only with difficulty by hydroalumination reactions but are far better accessible by metathetical reactions. Thus, the reactions of Et_2AlCl and $^iBu_2AlCl$ with (2-(methoxymethyl)phenyl)lithium or (2-methoxyphenyl)lithium, respectively, in toluene at −60 or −50 °C to 20 °C yield the oxygen-functionalized dialkylarylaluminum complexes $Et_2AlC_6H_4CH_2OMe$-2 (**4**), $^iBu_2AlC_6H_4CH_2OMe$-2 (**5**), and $^iBu_2AlC_6H_4OMe$-2 (**6**) as colorless, distillable oils (**4**, **5**) or colorless crystals (**6**) in yields of 50−60% (Scheme 1). Whereas **4** and **5** are monomers stabilized by intramolecular O→Al coordination and formation of five-membered-ring systems, compound **6** dimerizes, forming an eight-membered, intermolecularly O→Al stabilized ring system, thus avoiding the tension of a four-membered-ring system which would have to form in the case of intramolecular O→Al coordination.

According to the results described above, the reaction of equimolar amounts of $^iBu_2AlCl$ and 2-methoxybenzylmagnesium chloride in THF at 0−20 °C produces $^iBu_2AlCH_2C_6H_4OMe$-2 (**7**) as a colorless, distillable oil in a yield of 49% (Scheme 2). In contrast, the 1:1 molar reaction of Me_2AlCl and the same Grignard reagent did not afford the dimethylaluminum analogue of **7** but a mixture of solid products which could not be separated from each other. Only a few tiny crystals precipitated from the toluene extract of this mixture of solids at −30 °C, which proved to be bis(2-methoxybenzyl)methylaluminum (**8**) according to the result of an X-ray structure analysis. Obviously, the tendency of dimethylaluminum chloride to dismutate in solution[16−19] leads to a mixture of Me_3Al, Me_2AlCl, $MeAlCl_2$, $AlCl_3$, and their possible metathetical products. Also the reaction of equimolar amounts of $AlCl_3$ and (2-methoxybenzyl)magnesium chloride in THF at −30 to +20 °C did not produce the expected (2-methoxybenzyl)aluminum dichloride but bis(2-methoxybenzyl)aluminum chloride (**9**) in yields of 29% with respect to the amount of $AlCl_3$ used in the reaction.

Scheme 2



7

8

9

Ligand redistribution was also observed in the reactions of dimethyl- and diethylaluminum chloride with (8-methoxynaphthyl)- and (8-ethoxynaphthyl)lithium (Scheme 3). Though the reaction of Et_2AlCl with (8-ethoxynaphthyl)lithium results in the formation of 25% of the expected (8-ethoxynaphthyl)diethylaluminum (**10**), the isolation of $Et_3Al(Et_2O)$ as the first fraction in the course of the distillative workup of the reaction mixture clearly gives evidence for ligand re-

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(16) Thiyagarajan, B.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1999**, *18*, 5347.

(17) Klosin, J.; Roof, G. R.; Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 4684.

(18) Hair, G. S.; Battle, S. L.; Decken, A.; Cowley, A. H.; Jones, R. A. *Inorg. Chem.* **2000**, *39*, 27.

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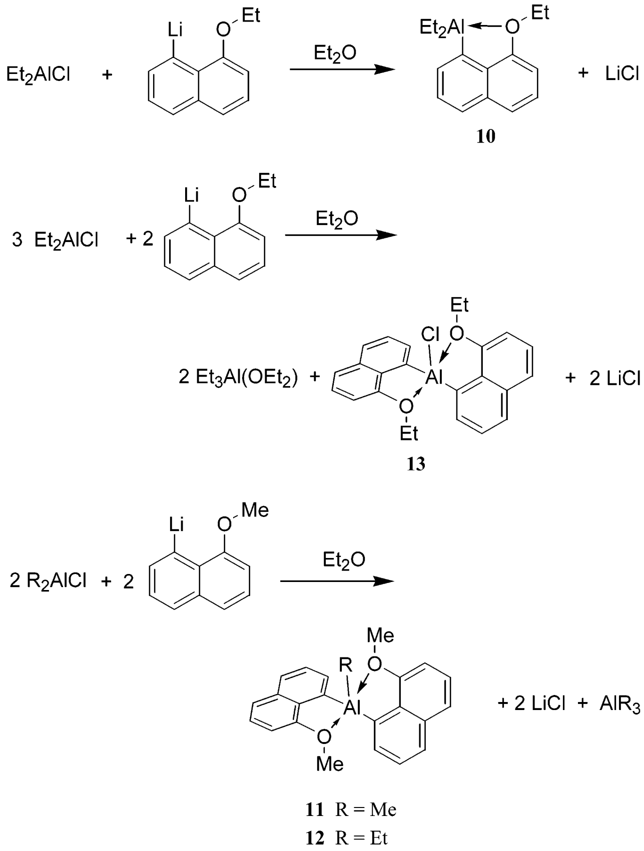
Scheme 3



distribution. Compound **10**, a light yellow oil, was isolated as the second fraction at 146 °C (0.01 mbar). A few crystals of bis(8-ethoxynaphthyl)aluminum chloride (**13**), a further redistribution product, crystallized from the solution obtained by dissolving the distillation residue in toluene. Also, Me_2AlCl and Et_2AlCl react with (8-methoxynaphthyl)lithium to give the redistribution products bis(8-methoxynaphthyl)methylaluminum (**11**) and bis(8-methoxynaphthyl)ethylaluminum (**12**) in low yields.

The above reactions suggest that the type of respective product depends on the Lewis basicity of the oxygen atom on one hand and on the bulkiness and the electronic properties of the alkylaluminum groups on the other hand. Due to the direct connection of the oxygen atom to the aromatic ring system of the methoxynaphthyl and the methoxybenzyl ligands, its donor strength will be weaker than the donor strength of the oxygen atom in the (methoxymethyl)phenyl ligand. For this reason, Et_2AlCl reacts with ((methoxymethyl)-phenyl)lithium to give mainly the monoaryldialkylaluminum complex **4**, whereas the reactions of Me_2AlCl, Et_2AlCl, and $AlCl_3$ with (2-methoxynaphthyl)lithium and (2-methoxybenzyl)lithium yield the diarylmonoalkylaluminum complexes **8**, **9**, **11**, and **12**. ${}^iBu_2AlCl$ with its bulky alkyl groups reacts more independently of the Lewis basicity of the oxygen atom, yielding always the desired diisobutyl(aryl/benzyl)aluminum complexes **5**−**7** in resonable yields. It appears that the dismutation reaction is slower, due to the size of the ^{i}Bu groups.

The colorless complexes are soluble in polar solvents such as diethyl ether and THF as well as in aromatic solvents such as toluene and benzene. Whereas the bis(aryl/benzyl)aluminum complexes **9**, **11**, and **12**, as well as complex **6**, are almost insoluble in nonpolar solvents such as *n*-hexane, the dialkylaluminum complexes **1**−**5**, **7**, and **10** are quite soluble in such solvents. All compounds are sensitive to air and moisture, but in comparison to the high sensitivity of commercially available Me_3Al and Et_3Al, only to a moderate degree.

All NMR resonance signals of the compounds appear in the expected areas. For the diisobutylaluminum complexes **2**, **3**, and **5**, as well as for the diethylaluminum complex **10**, signal splitting is observed at room temperature, which can be explained by a strong coordination of the oxygen atom to the metal aluminum center, causing hindered rotation of the alkyl groups and of the ligand containing the donor atom. A less strong coordination allows full rotation of the alkyl groups and the ligand around the aluminum−carbon bonds.[20a] Barron et al. reported that in the case of a dimeric quinoline compound containing five-coordinate aluminum centers, the anti conformation of the isobutyl groups and the hindered rotation leads to splitting of the NMR signals of those groups.[20c] Restricted rotation of isobutyl groups was also reported for compounds with four-coordinate aluminum.[20b] However, although the molecules **1**−**3** are not chiral, the isobutyl groups are located outside the plane of symmetry of the C_s-symmetric molecules, causing diastereotopic methylene protons regardless of the Al−C bond rotation rate. A similar situation occurs in **5** and **10**. Probably due to a coincidental overlap of resonances, corresponding splittings are not observed for **1**[21] and **7** or for the diastereotopic benzyl protons in **9**. The ^{27}Al NMR spectra of **1**−**5**, **7**, and **10** confirm the existence of four-coordinate aluminum centers.[22] The chemical shift values (δ(^{27}Al) 180−195 ppm) are comparable with those found for $Et_3Al·THF$ and ${}^iBu_3Al·THF$ (δ(^{27}Al) 180 ppm).[23] The ^{27}Al resonance of bis(methoxybenzyl)aluminum chloride (**9**) (δ(^{27}Al) 134 ppm) appears in the region expected for five-coordinate aluminum compounds,[22,23] whereas the spectra of the complexes **11** and **12** show very broad signals, the chemical shift values of which cannot be specified. However, the X-ray structure determination of both compounds proves the existence of five-coordinate aluminum centers. The ^{1}H and ^{13}C NMR spectra of **6** in benzene-d_6 are the only ones that are hard to interpret. Complex **6** exists in the solid state as a dimer, but in benzene solution it partially dissociates, as confirmed by cryoscopic molecular weight determinations (mol wt found 376; mol wt calcd 496.68) and also by ^{27}Al NMR spectroscopy. The ^{27}Al spectrum of **6** recorded in benzene-d_6 shows a resonance signal (δ(^{27}Al) 220 ppm) in the upper range of the shift values known for

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[20] (a) Schumann, H.; Hartmann, U.; Wassermann, W. *Polyhedron* **1990**, *9*, 353. (b) Gilbertson, R. D.; Haley, M. M.; Weakley, T. J. R.; Weiss, H.-C.; Boese, R. *Organometallics* **1998**, *17*, 3105. (c) Francis, J. A.; Bott, S. G.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1998**, 3305.

[21] The chemical shifts of the methylene protons of the ^{i}Bu groups and the methoxypropyl ligand (Al−CH_2−) are nearly equal, and doublet and triplet coupling patterns, respectively, cannot be separated; the whole range was therefore described as a multiplet structure in the Experimental Section.

[22] (a) Benn, R.; Rufinska, A. *Angew. Chem.* **1986**, *98*, 851; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861. (b) Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem.* **1983**, *95*, 808; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779.

[23] Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufinska, A. *J. Organomet. Chem.* **1987**, *333*, 155.

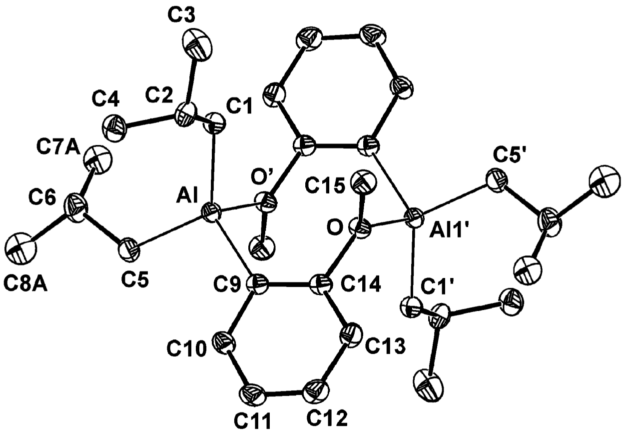

Figure 1. ORTEP plot[24] of the molecular structure and the numbering scheme of **6** with 30% probability thermal ellipsoids. For clarity, all hydrogen atoms and one part of the disorderd atoms are omitted. Selected bond lengths (Å) and bond angles (deg): Al−O′ = 1.9381(17), Al−C(1) = 1.977(2), Al−C(5) = 1.982(3), Al−C(9) = 2.012(2), Al−O = 3.2889(17), C(1)−C(2) = 1.534(3), C(5)−C(6) = 1.526(4); O′−Al−C(1) = 101.66(9), O′−Al−C(5) = 106.13(10), O′−Al−C(9) = 101.47(8), C(1)−Al−C(5) = 120.62(11), C(1)−Al−C(9) = 117.60(10), C(5)−Al−C(9) = 106.76(11), C(2)−C(1)−Al = 117.37(17), C(6)−C(5)−Al = 122.43(17). Symmetry transformation used to generate equivalent atoms: (′) $-x + 1, -y + 1, -z + 1$.

three-coordinate aluminum complexes,[22] whereas the spectrum of a solution of **6** in THF-d_8 proves the formation of a monomeric, four-coordinated THF adduct (δ(^{27}Al) 176 ppm). Such THF solutions also produce well-defined ^{1}H and ^{13}C NMR spectra.

The EI mass spectra of all complexes except the aluminum halide complex **9** show either no molecular ion peaks or molecular ion peaks of an intensity below 5%. The most intense metal-containing fragments correspond to the loss of one or two of the non-oxygen-containing aluminum-bonded alkyl groups. The loss of the second alkyl group of **1**−**7** and of **10** may occur via a β-H-elimination process, leading to the fragment $[MH - R_2]^+$. The complex **9** is comparatively stable under EI conditions. Its molecular ion peak $[C_{16}H_{18}Al^{35}ClO_2]^+$ (m/z 304) appears with 16% intensity. A peak with m/z 183 of 50% intensity marks the loss of one of the two 2-methoxybenzyl ligands.

Crystals of the complexes suitable for single-crystal X-ray diffraction analysis were obtained by recrystallization from toluene (**6**, **9**, **12**, **13)** or benzene (**11**). In the case of **8**, the crystals which separated directly from the reaction mixture were used for structure determination. The complexes **8**, **9**, and **13** crystallize in the monoclinic space group *C*2/*c*, with half of the molecules in the asymmetric unit. The Al−X (X = Me, Cl) atoms lie on a crystallographic 2-fold axis, in accord with the C_2 symmetry axis of the molecule running along this bond. Compound **6** crystallizes in the orthorhombic space group *Pbcn* and consists of oxygen-bridged dimers showing inversion symmetry. The asymmetric unit contains one monomeric, crystallographically independent molecule. The asymmetric units of orthorhombic **11** (space group *Pbca*) and monoclinic **12** (space group $P2_1/c$) consist of one crystallographically independent molecule. The solid-state structures of these molecules are shown in Figures 1−6.

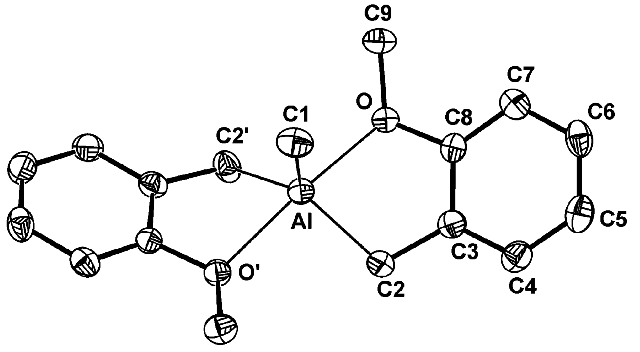

Figure 2. ORTEP plot[24] of the molecular structure and the numbering scheme of **8** with 50% probability thermal ellipsoids. For clarity, all hydrogen atoms are omitted. Selected bond lengths (Å) and bond angles (deg): Al−C(1) = 1.976(4), Al−C(2) = 1.991(2), Al−O = 2.1523(17); O−Al−O′ = 169.04(11), O−Al−C(1) = 95.48(5), O−Al−C(2) = 78.65(9), O−Al−C(2)′ = 95.90(9), C(1)−Al−O′ = 95.48(5), C(2)′-Al−O′ = 78.65(9), C(1)−Al−C(2) = 119.44(9), C(2)−Al−C(2)′ = 121.12(18). Symmetry transformation used to generate equivalent atoms: (′) $-x, y, -z + {}^1/_2$.

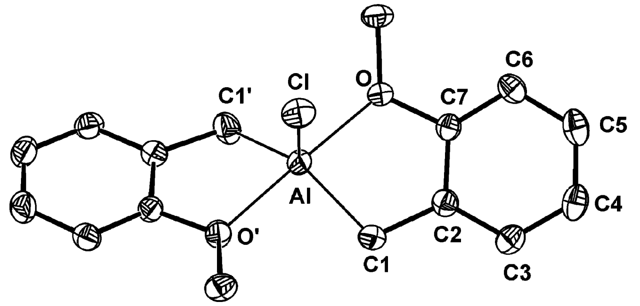

Figure 3. ORTEP plot[24] of the molecular structure and the numbering scheme of **9** with 50% probability thermal ellipsoids. For clarity, all hydrogen atoms are omitted. Selected bond lengths (Å) and bond angles (deg): Al−Cl = 2.1960(10), Al−C(1) = 1.9752(18), Al−O = 2.0700(11); O′−Al−O = 175.34(8), O−Al−Cl = 92.33(4), O−Al−C(1) = 81.76(6), O−Al−C(1)′ = 96.06(6), C(1)−Al−Cl = 117.65(7), C(1)′−Al−C(1) = 124.69(13). Symmetry transformation used to generate equivalent atoms: (′) $-x + 1, y, -z + {}^1/_2$.

The aluminum atoms in **8**, **9**, and **11**−**13** are five-coordinated. The coordination geometry corresponds to a distorted trigonal bipyramid with three carbon atoms (**8**, **11**, **12**) or two carbon atoms and one chlorine atom (**9**, **13**) in equatorial positions and two oxygen atoms in axial positions. Due to the crystallographic symmetry, the two Al−O distances are equal in **8** (2.15 Å), **9** (2.07 Å), and **13** (2.12 Å) and differ only slightly for **11** (2.11/2.14 Å) and **12** (around 2.14 Å). In comparison to the exclusively alkyl/aryl substituted complexes **8**, **11**, and **12**, the electron-withdrawing chlorine atom in **9** and **13** is expected to cause some decrease of the Al−O bond length. This is the case in **9**, whereas in **13** the rigid naphthyl ligand possibly prevents a further approach of the oxygen atom to the aluminum atom. The Al−N distances of the 8-(dimethylamino)naphthyl complexes $(Me_2N)C_{10}H_6AlMe_2$ (2.06 Å)[3a] and $(Me_2N)C_{10}H_6AlCl_2$ (2.02 Å)[18] confirm the above conclusion. The O−Al−O angles in **8** (169.0°), **9** (175.3°), **11** (171.7°), **12** (173.0°), and **13** (173.0°) are closer to 180° than in the known five-coordinate bidentate oxygen-stabilized aluminum alkoxides[22b,26] and are in good agreement with the

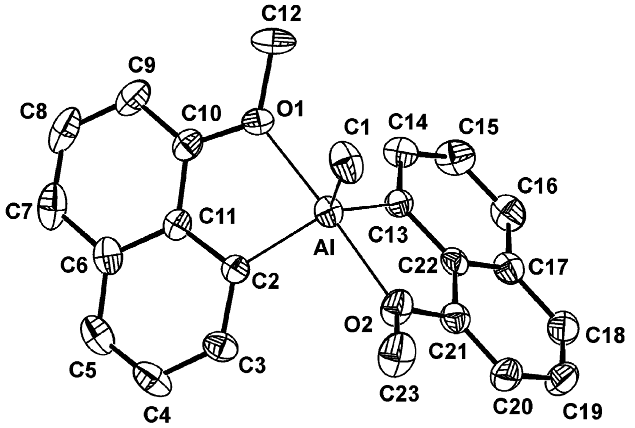

Figure 4. ORTEP plot[24] of the molecular structure and the numbering scheme of **11** with 50% probability thermal ellipsoids. For clarity, all hydrogen atoms are omitted. Selected bond lengths (Å) and bond angles (deg): Al−C(1) = 1.985(3), Al−C(2) = 1.979(3), Al−C(13) = 1.968(4), Al−O(1) = 2.135(3), Al−O(2) = 2.111(3); O(1)−Al−O(2) = 171.72(11), C(2)−Al−C(13) = 115.32(14), C(1)−Al−O(1) = 93.01(14), C(1)−Al−O(2) = 95.24(15), C(2)−Al−O(1) = 79.77(12), C(2)−Al−O(2) = 96.47(13), C(13)−Al−O(1) = 94.36(13), C(13)−Al−O(2) = 80.52(13), C(1)−Al−C(2) = 121.51(15), C(1)−Al−C(13) = 123.11(16).

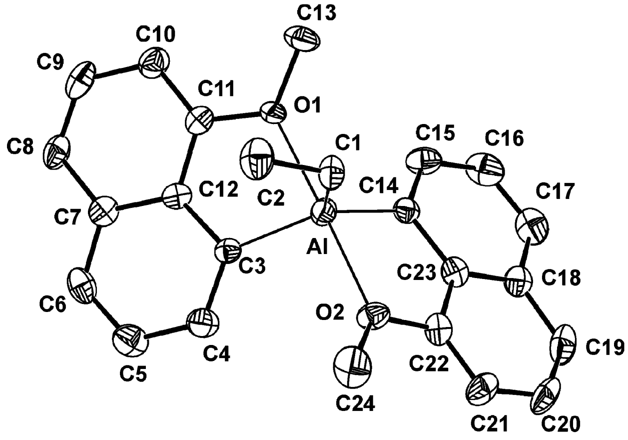

Figure 5. ORTEP plot[24] of the molecular structure and the numbering scheme of **12** with 50% probability thermal ellipsoids. For clarity, all hydrogen atoms are omitted. Selected bond lengths (Å) and bond angles (deg): Al−C(1) = 1.977(5), Al−C(3) = 1.978(5), Al−C(14) = 1.981(5), Al−O(1) = 2.137(3), Al−O(2) = 2.140(3), C(1)−C(2) = 1.535(6); O(1)−Al−O(2) = 172.97(15), C(3)−Al−C(14) = 119.99(19), C(1)−Al−O(1) = 91.98(18), C(1)−Al−O(2) = 95.05(17), C(3)−Al−O(1) = 79.52(16), C(3)−Al−O(2) = 97.25(17), C(14)−Al−O(1) = 96.62(16), C(14)−Al−O(2) = 79.51(16), C(1)−Al−C(3) = 117.39(18), C(1)−Al−C(14) = 122.6(2), C(2)−C(1)−Al = 113.0(3).

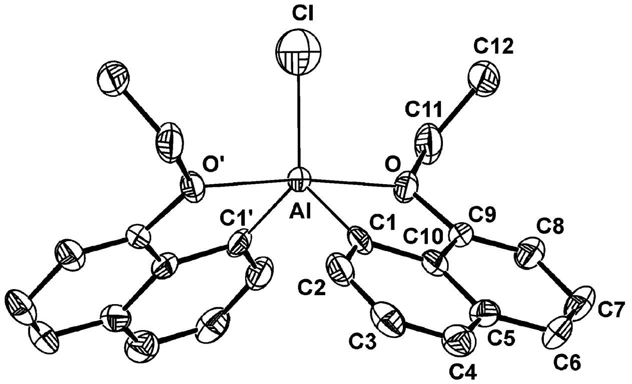

Figure 6. ORTEP plot[24] of the molecular structure and the numbering scheme of **13** with 30% probability thermal ellipsoids. For clarity, all hydrogen atoms are omitted. Selected bond lengths (Å) and bond angles (deg): Al−Cl = 2.169(5), Al−C(1) = 1.989(7), Al−O = 2.120(4); Cl−Al−O = 93.50(12), Cl−Al−C(1) = 122.28(16), O−Al−O′ = 173.0(2), O−Al−C(1) = 80.5(2), O−Al−C(1)′ = 95.8(2), C(1)′−Al−C(1) = 115.4(3). Symmetry transformation used to generate equivalent atoms: (′) $-x, y, -z + {}^{3}/_{2}$.

values estimated for the N−Al−N angles in $[(Me_2NCH(CH_3))C_6H_4]_2AlBr$ (177.0°)[27] and $[(Me_2NCH_2)C_6H_4]_2AlMe$ (173.0°).[28] Compound **6** exists in the solid state as a centrosymmetric dimer in which the two monomeric units are connected by intermolecular Al−O coordination, yielding an eight-membered $Al_2O_2C_4$ ring. The geometry of the ring is comparable with the geometry of other eight-membered-ring compounds containing two dialkylaluminum moieties such as $[{}^tBu_2Al(\mu\text{-}OC_5H_4N\text{-}2)]_2$[20c] and $[Me_2Al(\mu\text{-}N_3C_7H_{13})]_2$.[29] In **6** each aluminum atom is in the center of a distorted tetrahedron formed by the CH_2 carbon atoms of the two isobutyl groups, one phenyl carbon atom, and the respective coordinating oxygen atom. The Al−O distance (1.94 Å) is in the range expected for oxygen-containing Lewis base adducts of organoaluminum compounds[30] and agrees well with the longer Al−O distance (1.94 Å) in the four-membered Al_2O_2 ring system of $[Me_2Al(\mu\text{-}OC_6H_4OMe)]_2$ (1.94 Å)[25] and of similar aluminum phenoxides.[31]

Polymerization of Ethylene. The intramolecularly oxygen-stabilized aluminum alkyls **3**−**5**, **7**, **10**, and **12** were tested as cocatalysts for the polymerization of ethylene in the presence of the well-known $TiCl_4/MgCl_2$ catalyst system. In general, triethylaluminum is used as the cocatalyst in the industrial production of polyolefins. In comparison to triethylaluminum, the advantage of heteroatom-stabilized cocatalysts is their considerably higher stability to moisture and oxygen, thus allowing far easier handling in smaller plants.

All tested oxygen-stabilized aluminum alkyls are active as cocatalysts. Table 3 shows the polymerization conditions, the activities of the catalyst/cocatalyst systems used, and the yields and properties of the polymers obtained. Whereas compounds **7** and **10** are even more active than Et_3Al (∼6500 (**7**, **10**), ∼4500 $kg_{PE}/(mol_{Ti}$ h M) (Et_3Al)) and complex **4** shows an activity value approximately equal to that of Et_3Al (∼4000 $kg_{PE}/$

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(29) (a) Aeilts, S. L.; Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 3265. (b) Ashenhurst, J.; Brancaleon, L.; Hassan, A.; Liu, W.; Schmider, H.; Wang, S.; Wu, Q. *Organometallics* **1998**, *17*, 3186. (c) Chang, C.-C.; Srinivas, B.; Wu, M.-L.; Chiang, W.-H.; Chiang, M. Y.; Hsiung, C.-S. *Organometallics* **1995**, *14*, 5150.

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Table 3. Polymerization Conditions, Activity of the Catalyst/Cocatalyst Systems Used, and Yield and Properties of the Polymers[a]

cocat.	amt of cocat. (10^{-4} M)	amt of $TiCl_4/MgCl_2$ (10^{-5} M)	Al/Ti ratio	yield of PE (g)	activity ($kg_{PE}/(mol_{Ti}$ h M))	T_m (°C)	M_η (kg/mol)
7	3.1	1.5	20	4.5	6500	136	1600
10	3.1	1.5	20	4.3	6370	141	2200
Et_3Al	3.1	1.5	20	3.1	4500	138	1400
4	3.1	1.5	20	2.9	4290	142	1700
5	6	3	20	2.1	1500	140	1800
12	6	3	20	1.8	1325	139	1500
3	6	3	20	0.9	900	141	1300

[a] Conditions: $T_p = 60$ °C; $t_p = 1$ H; solvent, 200 mL of hexane; ethene pressure, 2 bar.

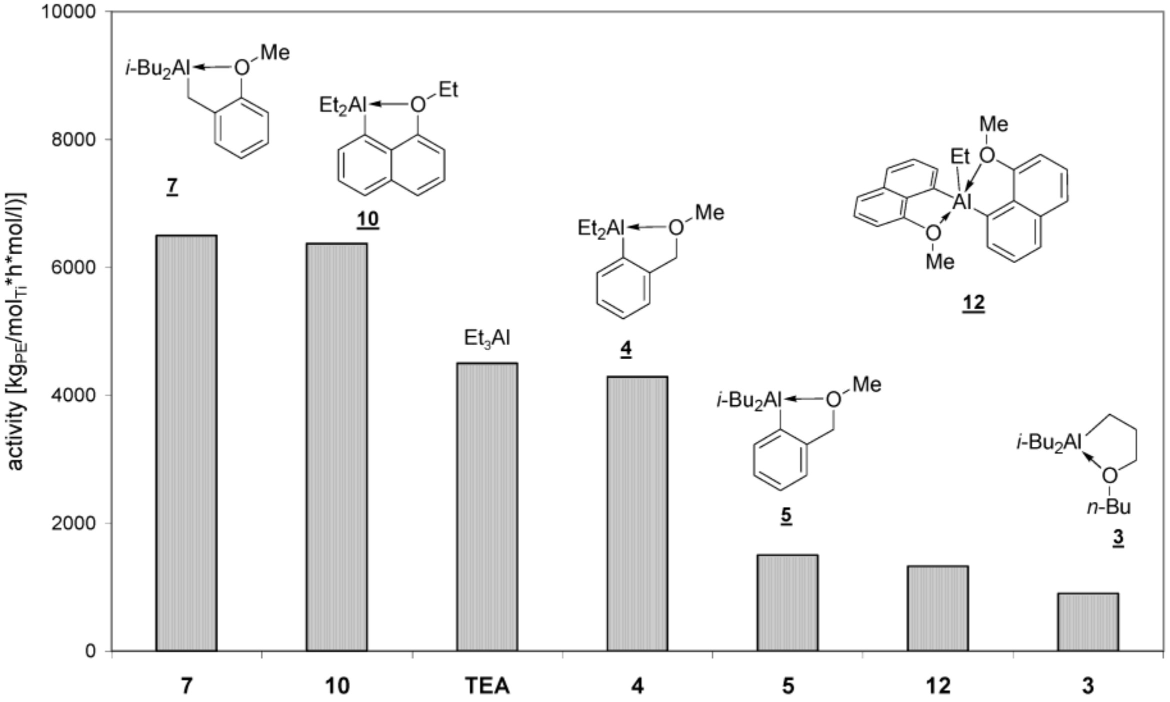

Figure 7. Comparison of the cocatalytic activities of the compounds **3**, **4**, **5**, **7**, **10**, and **12** with the activity of the cocatalyst triethylaluminum (TEA) for the polymerization of ethylene. Conditions: catalyst, $TiCl_4$ supported on $MgCl_2$; polymerization temperature T_p, 60 °C; polymerization time t_p, 1 h; Al/Ti ratio, 20.

(mol_{Ti} h M)), the activity values of **5**, **12**, and **3** are below the value of Et_3Al and decrease in the cited order (Figure 7).

Figure 7 clearly demonstrates that **7** and **10**, in which the oxygen atom is directly bonded to an aromatic ring system, are not only the most active cocatalysts but also show nearly the same activity values. Additionally, the comparison of the activities of compounds **4** and **5** indicates that bulky substituents at the aluminum lower the catalytic activity dramatically. The nonaromatic aluminum compound **3** shows the lowest activity of all tested aluminum alkyls, demonstrating that the aromatic ring system plays an important role in the activity of cocatalysts.

Table 4. Polymerization Conditions, Activity of the Catalyst/Cocatalyst 7 Systems Used, and Yield of the Polymers[a]

Al/Ti ratio	amt of **7** (10^{-4} M)	amt of $TiCl_4/MgCl_2$ (10^{-5} M)	yield of PE (g)	activity ($kg_{PE}/(mol_{Ti}$ h M))
3	3.1	1.5	1.8	2600
5	3.1	1.5	2.4	3400
10	3.1	1.5	3.3	4700
20	3.1	1.5	4.5	6500
50	3.1	3	3.6	5200
75	3.1	3	2.7	3900

[a] Conditions: $T_p = 60$ °C; $t_p = 1$ h; solvent, 200 mL of hexane; ethene pressure, 2 bar.

Polymerizations of ethylene were also carried out with varying Al/Ti ratios. Table 4 gives the polymerization conditions, the activity of the catalyst/cocatalyst systems used, and the yield of the polymers obtained. The influence of the Al/Ti ratio on the polymerization activity of **7**, the aluminum compound with the highest activity, is presented in Figure 8. In the experiments, the catalyst concentration is kept constant while the amount of aluminum alkyl varies. The highest activity of **7** is found for an Al/Ti ratio of 20. With both lower and higher Al/Ti ratios the activity decreases but still remains on a satisfying level of 3000−5500 $kg_{PE}/(mol_{Ti}$ h M).

The resulting polymers were compared with regard to their thermal properties, their crystallinity, their molar masses, and their short- and long-chain branches. Although the polymerization activity values cover a wide range and depend strongly on the kind of aluminum alkyl used, the properties of the polymers formed do not differ significantly. Further details of the polymerization results and the properties of the polymers will be published elsewhere.

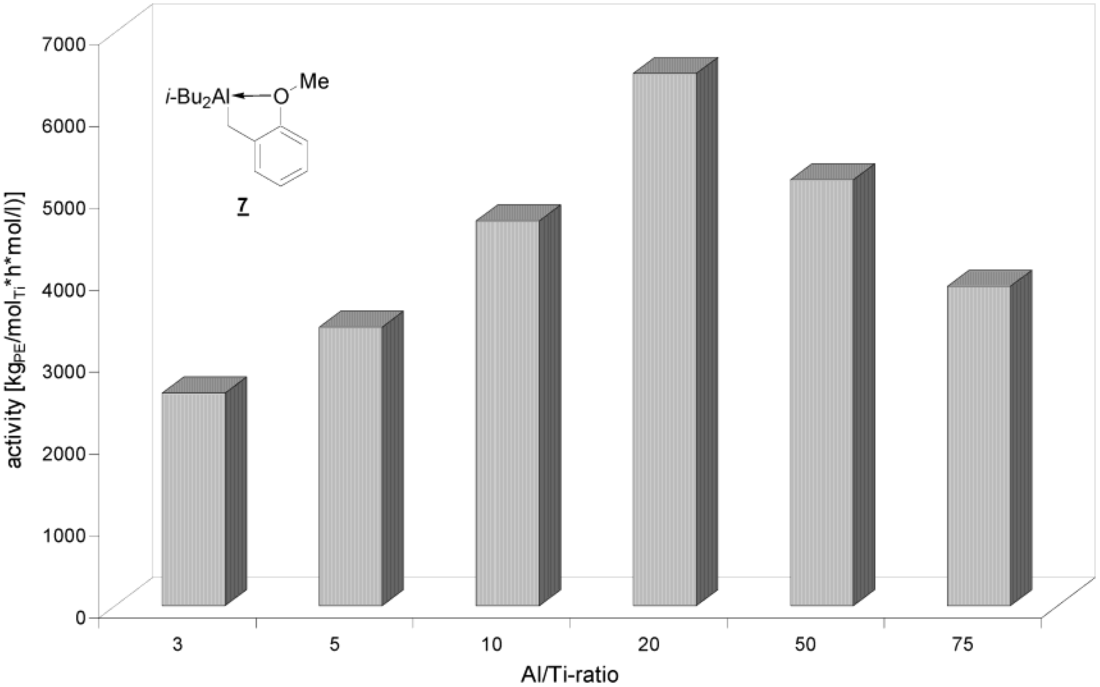

Figure 8. Activities of the cocatalyst **7** for the polymerization of ethylene estimated in dependence on the catalyst/cocatalyst ratio. Conditions: catalyst, $TiCl_4$ supported on $MgCl_2$; polymerization temperature T_p, 60 °C; polymerization time t_p, 1 h.

Conclusion

The intramolecularly oxygen-stabilized triorganoaluminum compounds $^iBu_2Al(CH_2)_3OR$ (R = Me, Et, *n*-Bu), $R_2AlC_6H_4CH_2OMe$ (R = Et, ^iBu), $^iBu_2AlC_6H_4OMe$, $^iBu_2AlCH_2C_6H_4OMe$, $Et_2AlC_{10}H_6OEt$, and $RAl(C_{10}H_6OMe)_2$ (R = Me, Et), as well as the diorganoaluminum chlorides $(MeOC_6H_4CH_2)_2AlCl$ and $(EtOC_{10}H_6)_2AlCl$, were prepared by hydroalumination or metathetical reactions. In general, the compounds are monomeric, with the aluminum atom being four-coordinated. With the exception of $Et_2AlC_{10}H_6OEt$-8 and $^iBu_2AlCH_2C_6H_4OMe$, intramolecularly oxygen-stabilized dialkylaluminum benzyl or naphthyl ethers could not be isolated. Instead, redistribution products containing five-coordinate aluminum are formed. For steric reasons, only $^iBu_2AlC_6H_4OMe$ dimerizes, yielding an eight-membered intramolecularly stabilized Al−C$_2$−O−Al−C$_2$−O ring system.

The new intramolecularly oxygen-stabilized aluminum alkyls are very active cocatalysts for the $TiCl_4$-catalyzed ethylene polymerization. $^iBu_2AlCH_2C_6H_4OMe$ and $Et_2AlC_{10}H_6OEt$ even exceed the activity of triethylaluminum, the common cocatalyst in industry. The activities of oxygen-stabilized aluminum alkyls as cocatalysts strongly depend on their structure and are furthermore influenced by the Al/Ti ratio.

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Supporting Information Available: Full details of the X-ray structural analyses of the complexes **6**, **8**, **9**, and **11**−**13**, including complete tables of crystal data, atomic coordinates, bond lengths and angles, and positional and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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