Dialkoxy-Substituted, C_1-Symmetric Metallocenes: Synthesis and Catalytic Behavior in the Propylene Polymerization Reaction

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The synthesis of a series of C_1-symmetric metallocene complexes *rac*-[1-(5,6-dialkoxy-2-methyl-1-η^5-indenyl)-2-(9-η^5-fluorenyl)ethane]zirconium dichlorides (alkyl: *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl) is described. These complexes are versatile catalysts in the polymerization of propylene after *in situ* activation with triisobutylaluminum (TIBA) and $Ph_3C[B(C_6F_5)_4]$ in toluene and heptane solution. All catalysts show higher solubility and improved polymerization properties in industrially used hydrocarbon solvents (*e.g.* heptane). However, the molecular weights and isotacticity values of the resulting polypropylene materials are decreased compared to the ethoxy-bridged analogue *rac*-[1-(5,6-ethylenedioxy-2-methyl-η^5-indenyl)-2-(9-η^5-fluorenyl)ethane]zirconium dichloride. A possible explanation is based on enhanced interaction of the active catalyst centers with Al(III) scavenger molecules even at low Al : Zr ratios, leading to reversible chain transfer.

Key words: Metallocene Catalysis, Dialkoxy Substitution, Propylene Polymerization

Introduction

One significant advantage in metallocene polymerization catalysis [1] is the easy possibility to design polymer microstructures and the corresponding material properties by variation of the catalyst structure. This can be performed by various methods. The nature of the cocatalyst [2] certainly plays a decisive role as well as the variation of the ligand framework [3]. Recently, we published a series of papers on asymmetric, "dual-side", catalysts that produce high performance polypropylene elastomers [4]. Here, a substitution in 5,6-position of the indenyl moiety has a major influence on the polymerization properties concerning a shift to higher molecular weight PP materials. However, the partially reduced solubility of these compounds in hydrocarbon solvents, like hexane or heptane, hinders a broader application [5, 6]. In this context we synthesized a series of zirconocene derivatives containing 5,6-di(*n*-alkoxy)indenyl ligands [7, 8] and tested their catalytic behavior in the polymerization of propylene in toluene and heptane solution revealing significant changes compared to their non-alkoxy-substituted counterparts and to an ethoxy-bridged analogue.

Results and Discussion

Ligand synthesis

The 1,2-ethylidene-bridged, fluorenyl-indenyl ligands **7a – d** are built up from the 5,6-dialkoxyindene anions and an equimolar amount of 9-(2-bromoethyl)-fluorene **6** *via* a convergent route (Scheme 1). The fluorene derivative **6** is obtained by a modified literature procedure from fluorene after deprotonation with *n*-BuLi and treatment with excess 1,2-dibromoethane. The indene derivatives are formed within several steps: The etherification of **1** with the corresponding *n*-alkyl bromide (10 mol-% excess) using K_2CO_3 in DMF gives the dialkoxybenzenes. A subsequent Friedel-Crafts cycloacylation with methacroyl chloride at -78 °C leads to the indanones **3a – d** using $AlCl_3$ as Lewis acid in 10 mol-% excess. Lower quantities result in non-cyclic side products, whereas higher amounts of aluminum chloride cause partially cleavage of the ether functionalities. The synthesis of the diastereomeric indanoles **4a – d** is performed quantitatively by reduction with $NaBH_4$. These are transformed directly to the desired indene precursors **5a – d** by dehydration with *p*-toluenesulfonic acid at 70 °C.

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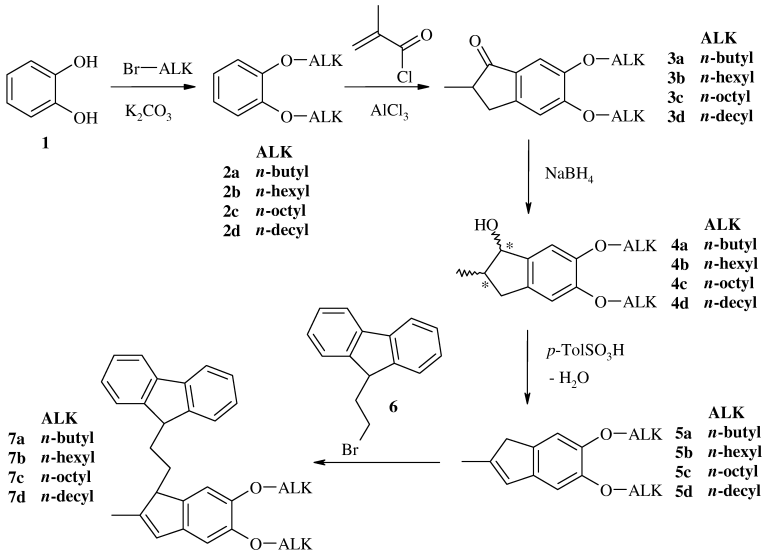
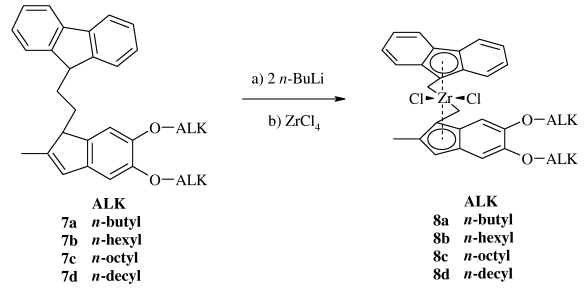


Scheme 1. Ligand synthesis.

Synthesis of zirconium complexes

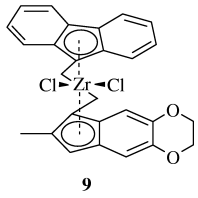
The synthesis of the *rac*-[1-(5,6-dialkoxy-2-methyl-1-η^5-indenyl)-2-(9-η^5-fluorenyl)ethane] zirconocene dichlorides **8a – d** is performed by deprotonation of compounds **7a – d** and treatment with an equimolar amount of $ZrCl_4$ (Scheme 2). Re-crystallization from toluene or toluene/hexane mixtures give the orange, solid products in good to moderate yield [9].



Scheme 2. Catalyst synthesis.

Polymerization reactions

The propylene polymerization behavior of complexes **8a – d** is tested at various temperatures and monomer concentrations in toluene and heptane solution. The results are compared to an analogous set of experiments using a similar catalyst structure containing an ethylene dioxid group at the 5,6-position of the indenyl moiety **9** (Formula 3). Activation is performed by *in situ* treatment with triisobutylaluminum (TIBA; ratio 100:1) and subsequent addition of $Ph_3C[B(C_6F_5)_4]$ (ratio 10:1). Complete alkylation with TIBA proceeds only after heating for one hour at 50 °C, which nearly doubles polymerization activities, compared to experiments without preliminary heating. The polymerizations were repeated several times with reproducible results [10].



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Formula 3.

The polymerization behavior of catalysts **8a – d** in toluene solution (Table 1: Run 1 – 18) comprises moderate catalyst activities at 30 °C with no significant variation concerning the monomer pressure, but can be enhanced by a factor of 2 by raising the polymerization temperature to 50 °C. The isotacticity values are at both temperatures in the range of 10 – 15% revealing atactic material. The obtained molecular weights are between 20000 and 70000 g/mol and show no significant dependency on the monomer pressure, temperature and variation of the alkoxy-chain length. The results are compared to an analogue set of polymerization reactions in toluene using structure **9** (Fig. 3). This catalyst is known to polymerize α-olefins according to

Table 1. Polymerization results with **8a – d** and **9** / TIBA / $Ph_3C[B(C_6F_5)_4]$ in toluene.

Run	Cat.	Amount [μmol]	Temp. [°C]	Pressure [bar]	[C_3] [g/mol]	Yield [g]	t_p [h]	M_w[a]	PD	Activity[b]	[mmmm][c]
1	**8a**	5	30	3.0	1.3	2.63	0.52	20000	1.7	800	11.3
2	**8a**	5	30	5.0	3.0	7.89	0.75	50000	4.7	700	10.0
3	**8a**	10	30	7.0	5.0	8.43	0.43	30000	3.6	800	11.6
4	**8a**	5	50	6.5	3.0	7.69	0.30	40000	3.5	1700	12.0
5	**8b**	10	30	3.0	1.3	10.13	0.91	30000	4.2	900	11.2
6	**8b**	10	30	5.0	3.0	7.50	0.50	30000	4.6	500	12.2
7	**8b**	10	30	7.0	5.0	7.50	0.51	30000	3.6	300	10.4
8	**8b**	5	50	6.5	3.0	7.50	0.30	40000	5.9	1700	12.6
9	**8c**	10	30	3.0	1.3	8.44	1.00	40000	2.9	700	10.3
10	**8c**	10	30	5.0	3.0	11.25	0.67	40000	2.8	600	10.6
11	**8c**	10	30	7.0	5.0	11.25	0.58	40000	2.7	900	10.9
12	**8c**	5	40	5.7	3.0	11.25	0.50	40000	3.1	1500	11.8
13	**8c**	5	50	6.5	3.0	11.25	0.30	50000	4.8	2500	14.9
14	**8d**	10	30	3.0	1.3	7.50	0.83	40000	2.7	600	10.8
15	**8d**	10	30	5.0	3.0	7.50	0.70	40000	3.5	400	11.2
16	**8d**	10	30	7.0	5.0	7.50	0.55	40000	3.3	300	13.4
17	**8d**	5	40	5.7	3.0	11.25	0.55	50000	3.7	1400	12.6
18	**8d**	5	50	6.5	3.0	11.25	0.28	70000	4.3	2700	15.3
19	**9**	2	30	3.0	1.3	2.70	0.50	120000	2.0	2100	50.7
20	**9**	2	30	5.0	3.0	4.50	0.50	130000	3.2	1500	43.9
21	**9**	2	30	7.0	5.0	9.00	1.00	160000	3.5	1000	43.3
22	**9**	2	50	6.5	3.0	8.70	0.50	100000	2.9	2900	63.3

[a] Relative against PP standards; [b] kg PP/[molZr]*[C_3]*h; [c] isotacticity [%].

Table 2. Polymerization results with **8d** / TIBA / $Ph_3C[B(C_6F_5)_4]$ in heptane.

Run	Cat.	Amount [μmol]	Temp. [°C]	Pressure [bar]	[C_3] [g/mol]	Yield [g]	t_p [h]	M_w[a]	PD	Activity[b]	[mmmm][c]
23	**8d**	10	30	3.0	0.7	6.19	0.88	30000	4.0	1000	9.7
24	**8d**	10	30	5.0	1.7	9.38	0.35	50000	3.4	1600	9.6
25	**8d**	5	30	7.0	3.0	9.38	0.27	70000	2.4	2300	8.1
26	**8d**	10	50	4.0	0.7	9.38	0.33	30000	6.1	4100	12.7

[a] Relative against PP standards; [b] kg PP/[molZr]*[C_3]*h; [c] isotacticity [%].

the earlier proposed "back-skip" mechanism. Here, the polymerizations expose results expected for this catalyst family (Table 1: Run 19 – 22). Molecular weights are enhanced by approximately a factor of 2 compared to **8a – d** and higher M_W values are obtained at lower temperatures. The most explicit differences occur at the PP isotacticities: Complex **9** produces PP comprising [mmmm] sequences from 50% to 65% and the isotacticities increase at the higher temperatures, as expected [4]. Also the declining [mmmm] values with higher monomer concentration at polymerization temperatures of 30 °C are typical for the "back-skip" polymerization mechanism.

The *n*-alkoxy substituted metallocenes **8a – d** reveal a significantly increased solubility in hydrocarbon solvents (hexane, heptane) compared to **9**. Solubility tests of **8a – d** in heptan gave clear solutions within concentrations of 1 – 10 μm/ml. Experiments with **9** showed only insufficient catalyst solubility under these conditions and therefore, no catalyst activity in propylene polymerizations occurred. Exemplary polymerization experiments of **8d** in heptane solution (Table 2) were performed under conditions similar to run 1 – 22 (Table 1). The resulting molecular weights (M_W: 30000 – 70000 g/mol) and isotacticity values ([mmmm]: approx. 10%) are completely in the same range compared to polymerization experiments in toluene. However, there are significantly increased polymer yields (up to factor 8) relative to experiments in toluene.

A probable explanation for these unexpected experimental results might be seen in an enhanced interaction of active sites with aluminum scavenger molecules [11]. In MAO activated polymerization reactions with **9** [4b] in toluene a reversible chain transfer to Al cen-

ters is supported by deuterium labeling experiments. Such a reversible transport process results in lower M_W and [mmmm] values, due to the existence of the two enantiomeric zirconocene species with opposite enantiofacial discrimination of prochiral propene monomer molecules [12]. Reduced Al : catalyst ratios within *in situ* TIBA/borate activation method of **9** suppress this transfer effect and lead again to higher tacticities and molecular weights. Apparently, different circumstances exist in polymerizations using **8a – d** and TIBA/$Ph_3C[B(C_6F_5)_4]$: Here, molecular weights and isotacticities of the obtained polymer materials are low, even after MAO-free activation processes. A possible explanation for this effect might be found in the amphiphilic nature of the catalyst sites, bearing polar "Zr-head functions" and apolar *n*-alkoxy substituents. In apolar media, in our case especially in heptane, this might lead to a close contact of oxygen-substituted zirconocenium centers and Al(III)-activator molecules *via* formation of (*e.g.* inverse micellar) aggregates. This assumption proposal cannot be supported experimentally (light scattering, *etc.*) yet, due to the high sensitivity of the cationic catalyst sites.

Conclusion

Here we present a series of new, C_1-symmetric metallocene complexes containing diverse 5,6-di(*n*-alkoxy)indenyl ligands. These structures are versatile catalysts for the polymerization of propylene in toluene and heptane solution using *in situ* TIBA/$Ph_3C[B(C_6F_5)_4]$ activation. The introduction of apolar alkyl segments into the ligand structure leads to a good solubility in hydrocarbon solvents compared to non-alkyl substituted counterparts. Additionally, the resulting polymerization activities of **8a – d** in heptane can be enhanced compared to experiments in toluene. This is an advantageous fact as hydrocarbons like heptane can be used as solvents in industrial polymerization processes. However, the obtained polypropylenes reveal significant changes in the catalyst properties compared to similar non-substituted structures resulting in reduced polymer molecular weights and isotacticities. A hypothetical explanation is based on an extended interaction between Lewis acidic Al centers of the TIBA co-activator and the active catalyst. This would lead to a reversible chain transfer, which is accepted for analogue systems and results in reduced M_W- and [mmmm] values. The synthesis of analogous catalyst structures bearing *n*-alkyl-substituted indenyl moieties is underway to suppress the influences of Al-coordination at oxygen containing ligand fragments.

Experimental Section

General remarks

The *rac*-[1-(5,6-ethylenedioxy-2-methyl-η^5-indenyl)-2-(9-η^5- fluorenyl)ethane]zirconium dichloride **9** [4b] and $Ph_3C[B(C_6F_5)_4]$ [13] were synthesized according to literature procedures, 9-(2-bromoethyl)-fluorene **6** [14] and the 1,2-dialkoxybenzenes **2a – d** [15] according to modified literature methods. All synthetical work (except the synthesis of **2a – d**) was done using standard Schlenk techniques under argon atmosphere. The 1-bromoalkanes, 1,2-dihydroxybenzene, methacroyl chloride, *p*-toluenesulfonic acid, fluorene, 1,2-dibromoethane, *n*-BuLi (1.6 molar in hexane), K_2CO_3, Na_2SO_4, $NaBH_4$, $AlCl_3$ and $ZrCl_4$ were purchased from Aldrich. Triisobutylaluminum (1 molar in hexane) was purchased from Crompton, solvents for synthesis and polymerizations were purchased from Merck and dried *via* distillation over $LiAlH_4$.

NMR analysis of the prepared compounds was performed on a Bruker DRX 400 spectrometer at ambient temperatures and referenced to the $CDCl_3$ solvent signal. Elemental analysis (Vario EL Elementar) and mass spectra (Finnigan MAT SSQ 7000) were determined by the Microanalytical Laboratory of the University of Ulm. PP analysis: ^{13}C NMR spectra were recorded on a Bruker AMX 500 spectrometer ($C_2D_2Cl_4$, 90 °C, 125 MHz, 5 mm probe) in the invers gated decoupling mode with a 3 s pulse delay and a 45 °C pulse to attain conditions close to the maximum signal-to-noise ratio. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC, Waters 2000, 140 °C in 1,2,4-trichlorobenzene) relative to polypropylene standards.

Synthesis

1,2-Dialkoxybenzenes **2a – d**

A suspension of 750.0 mmol (*M*: 138.21 g/mol; 103.66 g) of K_2CO_3, 250.0 mmol (M:110.11 g/mol; 27.53 g) of 1,2-dihydroxybenzene **1** and 600.0 mmol of 1-bromoalkane in 500 ml of DMF was stirred for 12 h at 80 °C in a 2 l round-bottom flask with reflux condenser. After cooling to room temperature 500 ml of H_2O und 800 ml of Et_2O was added. After separation of remaining inorganic salts the H_2O / DMF phase was washed with 200 ml of water. The combined ether phases were extracted with 2×200 ml of H_2O and distilled to dryness.

2a: Yield: 48.20 g (*M*: 222.33 g/mol; 217.1 mmol; 86.9%) red oil. – ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.02$ (t, 6H, CH_3), 1.54 (m, 4H, $-CH_2CH_3$), 1.83 (m, 4H, $-OCH_2CH_2-$), 4.03 (q, 4H, $-OCH_2$), 6.91 (s, 4H, *H*ar). – ^{13}C NMR

(400 MHz, $CDCl_3$): δ = 14.4, 19.8; 32.0, 69.5, 114.8, 114.8, 121.6, 149.9. – MS (GC-MS): m/z = 222 [M^+]. – $C_{14}H_{22}O_2$: calcd. C 75.63, H 9.97; found C 75.49, H 9.81.

2b: Yield: 62.91 g (*M*: 278.44 g/mol; 226.3 mmol; 90.5%) red liquid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, 6H, CH_3), 1.36 (m, 8H, -$CH_2CH_2CH_3$), 1.51 (m, 4H, -$OCH_2CH_2CH_2$-), 1.83 (m, 4H, -OCH_2CH_2-), 4.00 (t, 4H, -OCH_2), 6.89 (s, 4H, *H*ar). – MS (GC-MS): m/z = 278 [M^+]. – $C_{18}H_{30}O_2$: calcd. C 77.65, H 10.86; found C 77.62, H 10.79.

2c: Yield: 52.28 g (*M*: 334.55 g/mol; 157.4 mmol; 62.9%) red oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, 6H, CH_3), 1.30 (m, 16H, -$(CH_2)_4CH_3$), 1.48 (m, 4H, -$OCH_2CH_2CH_2$-), 1.81 (m, 4H, -OCH_2CH_2-), 3.99 (t, 4H, -OCH_2), 6.88 (s, 4H *H*ar). – ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13.9, 22.4, 22.5, 22.6, 26.0, 28.1, 28.7, 69.2, 114.1, 114.4, 120.9, 149.2. – MS (GC-MS): m/z = 334 [M^+]. – $C_{22}H_{38}O_2$: calcd. C 78.99, H 11.45; found C 78.91 H, 11.30.

2d: Yield: 12.18 g (*M*: 390.66 g/mol; 187.3 mmol; 74.9%) white needles after re-crystallization in 100 ml of EtOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, 6H, CH_3), 1.20 – 1.55 (m, 28H, CH_2), 1.71 – 1.90 (m, 4H, -O-CH_2CH_2-), 3.98 (t, 4H, -OCH_2-), 6.89 (s, 4H, *H*ar). – ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.2, 22.8, 26.2, 29.4, 29.5, 29.6, 29.7, 29.7, 32.0, 69.4, 114.3, 114.3, 121.1, 149.4. – $C_{26}H_{46}O_2$: calcd. C 79.94 H 11.87; found C 80.02 H 11.41.

5,6-Dialkoxy-2-methylindan-1-ones **3a – d**

14.67 g of $AlCl_3$ (*M*: 133.34 g/mol; 110 mmol) were suspended in 100 ml of dichloromethane in a 500 ml Schlenk flask, the mixture was cooled to −78 °C and 100 mmol of methacroyl chloride was added. A solution of 100 mmol of 1,2-dialkoxybenzene in 100 ml of CH_2Cl_2 was added over 1 h. After stirring 12 h at room temperature the suspension was cooled to −78 °C and hydrolyzed with 100 ml of H_2O. The organic phase was washed with 2 × 100 ml of water, dried with Na_2SO_4 and evaporated to dryness.

3a: Yield: 13.13 g (*M*: 290.41 g/mol; 45.2 mmol; 45,2%) white solid after re-crystallization from 50 ml of EtOH and washing with 20 ml of MeOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, 6H, CH_3 "chain"), 1.26 (s, 3H, CH_3-indenyl), 1.48 (m, 4H, -$OCH_2CH_2CH_2$-), 1.80 (m, 4H, -OCH_2-CH_2), 2.60 (m, 2H, CH_2-indenyl), 3.21 (m, 1H, CH-indenyl), 4.00 (t, 4H, −OCH_2-), 6.80 (s, 1H, *H*ar), 7.13 (s, 1H, *H*ar). – ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.5, 17.3 19.9, 31.6, 35.4, 42.9, 69.5, 106.8, 109.2, 129.4, 149.1, 149.9, 156.3, 208.9. – MS (GC-MS): m/z = 291 [M^+]. – $C_{18}H_{26}O_3$: calcd. C 74.45, H 9.02; found C 74.41, H 8.99.

3b: Yield: 11.89 g (*M*: 346.51 g/mol; 34.36 mmol; 34.4%) white solid after re-crystallization in 50 ml of EtOH and washing with 20 ml of MeOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, 6H, CH_3 "chain"), 1.23 (s, 3H, CH_3-indenyl), 1.35 – 1.55 (m, 12H, -$OCH_2CH_2(CH_2)_3$-), 1.90 (m, 4H, −OCH_2CH_2-), 2.66 (m, 2H, CH_2-indenyl), 3.29 (m, 1H, CH-indenyl), 4.01 (dt, 4H, -OCH_2-), 6.75 (s, 1H, *H*ar), 7.10 (s, 1H, *H*ar). – ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.3, 17.0, 22.9, 22.9, 25.9, 26.0, 29.2, 29.3, 31.8, 31.8, 35.1, 42.6, 69.4, 69.5 106.5, 108.9, 129.1, 148.8, 149.1, 149.9, 156.0, 208.6. – MS (GC-MS): m/z = 347 [M^+]. – $C_{22}H_{34}O_3$: calcd. C 76.26, H 9.89; found C 76.13, H 9.80.

3c: Yield: 15.17 g (*M*: 402.62 g/mol; 37.67 mmol; 37.7%) white solid after re-crystallization in 50 ml of MeOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, 6H, CH_3 "chain"), 1.23 (s, 3H, CH_3-indenyl), 1.25 – 1.35 (m, 20H, -$OCH_2CH_2(CH_2)_5$-), 1.46 (m, 4H, -OCH_2CH_2-), 2.52 (m, 2H, CH_2-indenyl), 3.20 (m, 1H, CH-indenyl), 4.01 (dt, 4H, -OCH_2-), 6.83 (s, 1H, *H*ar), 7.13 (s, 1H, *H*ar). – ^{13}C NMR (400 MHz, $CDCl_3$): δ = 12.3, 14.9, 20.8, 24.2, 24.2, 10 signals at 27.2 – 30.0, 40.4, 67.3, 67.5, 104.4, 106.7, 112.7, 127.0, 146.7, 147.4, 153.9, 206.4. – MS (GC-MS): m/z = 403 [MH^+]. – $C_{26}H_{42}O_3$: calcd. C 77.56, H 10.51; found C 77.85, H 10.30.

3d: Yield: 19.28 g (*M*: 458.73 g/mol; 42.02 mmol; 42.0%) white solid after re-crystallization in 50 ml of MeOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81 (t, 6H, CH_3 "chain"), 1.23 (s, 3H, CH_3-indenyl), 1.15 – 1.51 (m, 28H, -$OCH_2CH_2(CH_2)_7$-), 1.78 (m, 4H, -OCH_2CH_2-), 2.56 (m, 2H, CH_2-indenyl), 3.20 (m, 1H, CH-indenyl), 3.98 (dt, 4H, −OCH_2-), 6.76 (s, 1H, *H*ar), 7.10 (s, 1H, *H*ar). – MS (GC-MS): m/z = 460 [MH^+]. – $C_{30}H_{50}O_3$: calcd. C 78.55, H 10.99; found C 78.40, H 10.91.

5,6-Dialkoxy-2-methylindan-1-oles **4a-d**

30.0 mmol of **3a – d** and 30 mmol of $NaBH_4$ (*M*: 37.80 g/mol; 1.13 g) in 100 ml of EtOH were stirred for 24 h at room temperature in a 500 ml Schlenk flask. After neutralization with HCl, 100 ml of H_2O and 100 ml of Et_2O were added. The organic phase was separated and washed with 2 × 100 ml of water. Drying with Na_2SO_4 and evaporating to dryness lead to white solids which were converted directly to the corresponding indenes **5a – d** without purification.

5,6-Dialkoxy-2-methylind-1-enes **5a – d**

The indanoles **4a – d** were dissolved in 100 ml of toluene, 0.57 g of *p*-toluenesulfonic acid (*M*: 190.22; 3.0 mmol) was added and the mixture was stirred for 1 h at 70 °C. After washing with 2 × 100 ml of H_2O and drying with Na_2SO_4 the solvent was removed *via* distillation.

5a: Yield: 3.98 g (*M*: 274.41 g/mol; 14.5 mmol; 48.3% regarding to **3a**) white crystals after re-crystallization in 30 ml of EtOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, 6H, CH_3 "chain"), 1.49 (m, 4H, -$OCH_2CH_2CH_2$-) 1.78 (m, 4H, -OCH_2CH_2-), 2.09 (s, 3H, CH_3-indenyl), 3.19 (s, 2H, CH_2-indenyl), 3.97 (t, 4H, -OCH_2-), 6.36 (s, 1H, CH-indenyl), 6.81 (s, 1H, *H*ar), 6.97 (s, 1H, *H*ar). – ^{13}C NMR (400 MHz, $CDCl_3$): δ = 14.6, 17.3, 19.9, 32.2, 43.3, 70.2, 70.7, 107.5,

112.3, 127.3, 136.6, 140.0, 145.4, 147.1, 149.3. – MS (GC-MS): $m/z = 274$ [M^+]. – $C_{18}H_{26}O_2$: calcd. C 78.79, H 9.55; found C 78.74, H 9.56.

5b: Yield: 6.75 g (*M*: 330.52 g/mol; 20.4 mmol; 68.1% regarding to **3b**) white solid after re-crystallization in 20 ml of EtOH. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.89$ (t, 6H, CH_3 "chain"), 1.33 (m, 8H, -$OCH_2CH_2CH_2(CH_2)_3$-), 1.47 (m, 4H, -$OCH_2CH_2CH_2$-), 1.79 (m, 4H, -OCH_2CH_2-), 2.10 (s, 3H, CH_3-indenyl), 3.19 (s, 2H, CH_2-indenyl), 3.97 (t, 4H, -OCH_2-), 6.35 (s, 1H, CH-indenyl), 6.81 (s, 1H, *H*ar), 6.97 (s, 1H, *H*ar). – ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 14.7$, 17.3, 23.3, 26.4, 30.2, 32.2, 42.3, 70.5, 71.0, 107.4, 112.3, 127.4, 136.6, 140.0, 145.4, 147.1, 149.2. – MS (GC-MS): $m/z = 331$ [M^+]. – $C_{22}H_{34}O_2$: calcd. C 79.95, H 10.37; found C 79.88, H 10.32.

5c: Yield: 7.61 g (*M*: 386.62 g/mol; 19.7 mmol; 65.6% regarding to **3c**) white needles after re-crystallization in 30 ml of MeOH. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.83$ (t, 6H, CH_3 "chain"), 1.29 (m, 16H, -$OCH_2CH_2CH_2(CH_2)_4$-), 1.41 (m, 4H, -$OCH_2CH_2CH_2$-), 1.75 (m, 4H, -OCH_2CH_2-), 2.01 (s, 3H, CH_3-indenyl), 3.10 (s, 2H, CH_2-indenyl), 3.95 (t, 4H, -OCH_2-), 6.30 (s, 1H, CH-indenyl), 6.78 (s, 1H, *H*ar), 6.90 (s, 1H, *H*ar). – ^{13}C NMR (400 MHz, $CDCl_3$): $\delta = 14.0$, 16.6, 22.6, 29.2, 29.3, 29.4, 29.5, 31.7, 42.5, 69.7, 70.2, 104.4, 106.7, 111.5, 126.6, 125.8, 139.2, 144.6, 146.4, 148.5. – MS (GC-MS): $m/z = 386$ [MH^+]. – $C_{26}H_{42}O_2$: calcd. C 80.77, H 10.95; found C 80.61, H 10.84.

5d: Yield: 7.78 g (*M*: 442.73 g/mol; 17.6 mmol; 58.6% regarding to **3d**) white solid after re-crystallization in 50 ml EtOH. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.91$ (t, 6H, CH_3 "chain"), 1.20 – 1.54 (m, 28H, -$OCH_2CH_2(CH_2)_7$-), 1.80 (m, 4H, -OCH_2CH_2-), 2.11 (s, 3H, CH_3-indenyl), 3.22 (s, 2H, CH_2-Indenyl), 4.00 (m, 4H, -OCH_2-), 6.36 (s, 1H, CH-indenyl), 6.82 (s, 1H, *H*ar), 6.99 (s, 1H, *H*ar). – MS (GC-MS): $m/z = 443$ [MH^+]. – $C_{30}H_{50}O_2$: calcd. C 81.39, H 11.38; found C 81.21, H 11.29.

9-(2-Bromoethyl)-fluorene **6**

10.00 g of fluorene (*M*: 166.22 g/mol; 60.2 mmol) were degassed in a 500 ml Schlenk flask with a dropping funnel and dissolved in 300 ml of Et_2O. After cooling to −78 °C 37.6 ml of *n*-BuLi (1.6 molar in hexane; 60.2 mmol) were added over 0.5 h. After stirring for 2 h at room temperature the mixture was cooled again to −78 °C and 20.7 ml of 1,2-dibromoethane (*M*: 187.9 g/mol; 240.8 mmol; δ: 2.18) were added rapidly. Stirring for 12 h at room temperature lead to a yellow suspension, which was washed twice with 100 ml of H_2O. Evaporation to dryness gave a brown solid, which was re-crystallized from 50 ml of pentane.

Yield: 13.14 g (*M*: 273.17; 48.1 mmol; 74.9%) yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.53$ (m, 2H, FluHCH_2CH_2-), 3.31 (t, 2H, -CH_2Br), 4.17 (t, 1H, Flu*H*); 7.37, 7.42 and 7.78 (m, 8H, *H*ar). – ^{13}C NMR (400 MHz, $CDCl_3$): δ = 30.5, 36.6, 46.4, 120.1, 124.4, 127.2, 127.5, 141.1, 145.8. – MS (GC-MS): $m/z = 273$ [MH^+]. – $C_{15}H_{13}Br$: calcd. C 65.95, H 4.80; found C 65.89, H 4.77.

[1-(5,6-Dialkoxy-2-methylinden-1-yl)-2-(9-fluorenyl)]ethanes **7a – d**

20,0 mmol of **5a – d** were degassed and dissolved in 70 ml of a mixture of toluene/dioxane (10:1) in a 250 ml Schlenk flask. After cooling to −78 °C 12.5 ml of *n*-BuLi (1.6 molar in hexane; 20.0 mmol) were added. The obtained suspension was stirred for 2 h at room temperature, transferred to a dropping funnel and added to a solution of 9-(2-bromoethyl)fluorene **6** in 50 ml of toluene (250 ml Schlenk flask) *via* 2 h. The mixture was stirred at room temperature for 12 h and washed with 2 × 100 ml of water. The organic phase was dried with Na_2SO_4 and a yellow solid was obtained after removing the solvent.

7a: Yield: 5.74 g (*M*: 466.67 g/mol; 12.3 mmol; 61.55%) white powder after washing with 300 ml of isopropanol. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.99$ (m, 6H, CH_3-"chain"), 1.42 (m, 2H, CH_2-bridge), 1.52 (m, 4H, −$O(CH_2)_2CH_2$-), 1.69 (m, 2H, CH_2-bridge), 1.80 (m, 4H, −OCH_2CH_2-), 1.87 (s, 3H, CH_3-indenyl), 3.03 (t, 1H, CH-indenyl), 3.86 (t, 1H, FluH), 4.00 (m 4H −OCH_2-), 6.32 (s, 1H, olefinic CH-indenyl), 6.70 (s, 1H, *H*ar indenyl), 6.80 (s, 1H, *H*ar indenyl), 7.25 – 7.75 (m, 8H, *H*ar fluorenyl). – MS (GC-MS): $m/z = 466$ [M^+]. – $C_{33}H_{38}O_2$: calcd. C 84.94, H 8.21; found C 84.81, H 8.20.

7b: Yield: 7.97 g (*M*: 522.78 g/mol; 15.2 mmol; 76.4%) white solid after re-crystallization in 50 ml of isopropanol. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.92$ (m, 6H, CH_3-"chain"), 1.35 (m, 2H, CH_2-bridge), 1.41 (m, 12H, -$O(CH_2)_2(CH_2)_3$-), 1.70 (m, 2H, CH_2-bridge), 1.80 (m, 4H, -OCH_2CH_2-), 1.88 (s, 3H, CH_3-indenyl), 3.03 (t, 1H, CH-indenyl), 3.86 (t, 1H, FluH), 4.00 (m, 4H, -OCH_2-), 6.33 (s, 1H, olefinic CH-indenyl), 6.70 (s, 1H, *H*ar indenyl), 6.80 (s, 1H, *H*ar indenyl), 7.25 – 7.73 (m, 8H, *H*ar fluorenyl). – MS (GC-MS): $m/z = 523$ [M^+]. – $C_{37}H_{46}O_2$: calcd. C 85.01, H 8.87; found C 84.85, H 8.92.

7c: Yield: 7.92 g (*M*: 578.89 g/mol; 13.7 mmol; 68.4%) white solid after re-crystallization in 50 ml of ethanol. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.82$ (m, 6H, CH_3-"chain"), 1.22 (m, 20H, −$O(CH_2)_2(CH_2)_5$-), 1,25 (m, 2H, CH_2-bridge), 1.40 (m, 4H, −OCH_2CH_2-), 1.60 (m, 2H, CH_2-bridge), 1.81 (s, 3H, CH_3-indenyl), 2.96 (t, 1H, CH-indenyl), 3.79 (t, 1H, FluH), 3.92 (m, 4H, −OCH_2-), 6.26 (s, 1H, olefinic CH-indenyl), 6.63 (s, 1H, *H*ar Indenyl), 6.73 (s, 1H, *H*ar indenyl), 7.20 – 7.69 (m, 8H, *H*ar fluorenyl). – MS (GC-MS): $m/z = 579$ [M^+]. – $C_{41}H_{54}O_2$: calcd. C 85.07, H 9.40; found C 84.80, H 9.08.

7d: Yield: 6.53 g (*M*: 634.99 g/mol; 10.3 mmol; 51.4%) white solid after re-crystallization in 80 ml of ethanol. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.89$ (m, 6H, CH_3

"chain"), 1.28 (m, 28H, $-O(CH_2)_2(CH_2)_7$-), 1.48 (m, 2H, CH_2-bridge), 1.60 (m, 2H, CH_2-bridge), 1.75 (m, 4H, $-OCH_2CH_2$-), 1.88 (s, 3H, CH_3-indenyl), 3.03 (t, 1H, CH-indenyl), 3.86 (t, 1H, FluH), 4.00 (m, 4H, $-OCH_2$-), 6.34 (s, 1H, olefinic CH-indenyl), 6.70 (s, 1H, *H*ar indenyl), 6.80 (s, 1H, *H*ar indenyl), 7.21 – 7.78 (m, 8H, *H*ar fluorenyl). – MS (GC-MS): $m/z = 634$ [M^+]. – $C_{45}H_{62}O_2$: calcd. C 85.12, H 9.84; found C 85.02, H 9.87.

rac-[1-(5,6-Dialkoxy-2-methyl-1-η^5-indenyl)-2-(9-η^5-fluorenyl)ethane]zirconium dichlorides **8a – d**

5.0 mmol of **7 a – d** were degassed and dissolved in 80 ml of toluene/dioxane (10:1) in a 250 ml Schlenk flask. After cooling to −78 °C 10.0 mmol of *n*-BuLi (1.6 molar in hexane; 6.3 ml) was added. The mixture was stirred for 2 h at room temperature and re-cooled to −78 °C. Adding of 5.0 mmol solid $ZrCl_4$, stirring at room temperature for 12 h and subsequent evaporation of the solvent lead to the rough product. The purification was performed according to following procedures:

8a: Washing with 2 × 50 ml of hot toluene resulted in a clear solution which was concentrated to a volume of 20 ml. Cooling at −20 °C over night gave an orange precipitate. Yield: 0.93 g (*M*: 626.89 g/mol; 1.5 mmol; 29.56%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.91$ and 1,06 (t, each 3H, CH_3-"chain"), 1.43 and 1.59 (m, each 2H, -$O(CH_2)_2CH_2$-), 1.75 and 1.90 (m, each 2H, -OCH_2CH_2-), 2.14 (s, 3H, CH_3-indenyl), 3.76 and 4.44 (m, each 1H, CH_2-bridge to indenyl; diastereotope), 3.87 (t, 2H, CH_2-bridge to fluorenyl), 4.07 (m, 4H, -OCH_2-), 5.99 (s, 1H, olefinic CH-indenyl), 6.51 (s, 1H, *H*ar indenyl), 7.07 (s, 1H, *H*ar indenyl), 7.08 – 7.88 (m, 8H, *H*ar fluorenyl). – $C_{33}H_{36}Cl_2O_2Zr$: calcd. C 63.26, H 5.75; found C 63.87, H 5.86.

8b: After washing with 50 ml of toluene the clear solution was evaporated to dryness. Re-crystallization from 20 ml of toluene/hexane (1:1) gave an orange solid. Yield: 0.82 g (*M*: 682.90 g/mol; 1.2 mmol; 23.33%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ and 0.95 (t, each 3H, CH_3-"chain"), 1.28, 1.41 and 1.56 (m, together 12H, -$O(CH_2)_2(CH_2)_3$-), 1.75 and 1.91 (m, each 2H, -OCH_2CH_2-), 2.14 (s, 3H, CH_3-indenyl), 3.76 and 4.54 (m, each 1H, CH_2-bridge to indenyl; diastereotope), 3.86 (t, 2H, CH_2-bridge to fluorenyl), 4.06 (m, 4H, -OCH_2-), 5.99 (s, 1H, olefinic CH-indenyl), 6.51 (s, 1H, *H*ar indenyl), 7.07 (s, 1H, *H*ar indenyl), 7.08 – 7.89 (m, 8H, *H*ar fluorenyl). – $C_{37}H_{44}Cl_2O_2Zr$: calcd. C 67.07, H 6.65; found: C 67.24, H 6.56.

8c: After washing with 50 ml of toluene the clear solution was evaporated to dryness. Re-crystallization from 20 ml of toluene gave an orange solid. Yield: 2.22 g (*M*: 739.01 g/mol; 3.0 mmol; 60.12%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.86$ (m, 6H, CH_3-"chain"), 1.15 – 1.50 and 1.56 (m, together 20H, -$O(CH_2)_2(CH_2)_5$-), 1.76 and 1.89 (m, each 2H, -OCH_2CH_2-), 2.14 (s, 3H, CH_3-indenyl), 3.76 and 4.54 (m, each 1H, CH_2-bridge to indenyl; diastereotope), 3.86 (t, 2H, CH_2-bridge to fluorenyl), 4.06 (m, 4H, -OCH_2-), 5.99 (s, 1H, olefinic CH-indenyl), 6.51 (s, 1H, *H*ar indenyl), 7.07 (s, 1H, *H*ar indenyl), 7.08 – 7.89 (m, 8H, *H*ar fluorenyl). – $C_{41}H_{52}Cl_2O_2Zr$: calcd. C 66.58, H 7.04; found C 66.18, H 7.07.

8d: After washing with 50 ml of toluene the clear solution was evaporated to dryness. Re-crystallization from 20 ml of toluene gave an orange solid. Yield: 1.70 g (*M*: 795.11 g/mol; 2.1 mmol; 42.86%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.86$ (m, 6H, CH_3-"chain"), 1.15 – 1.50 and 1.55 (m, together 28H, -$O(CH_2)_2(CH_2)_7$-), 1.76 und 1.89 (m, each 2H, -OCH_2CH_2-), 2.14 (s, 3H, CH_3-indenyl), 3.76 and 4.52 (m, each 1H, CH_2-bridge to indenyl; diastereotope), 3.85 (t, 2H, CH_2-bridge to fluorenyl), 4.05 (m, 4H, -OCH_2-), 5.99 (s, 1H, olefinic CH-indenyl), 6.51 (s, 1H, *H*ar indenyl), 7.07 (s, 1H, *H*ar indenyl), 7.08 – 7.89 (m, 8H, *H*ar fluorenyl). – $C_{45}H_{60}Cl_2O_2Zr$: calcd. C 67.92, H 7.55; found C 68.02, H 7.66.

Propylene polymerizations

All reactions were performed in a 0.5 l Büchi steel reactor at constant pressure (±0.1 bar) and temperature (±1 °C). First the desired amount of dichloro-zirconocene precursor was dissolved in 10 ml of dry solvent under argon atmosphere in a Schlenk flask and 100 equivalents of TIBA were added. This solution was injected into the autoclave, which had been charged with 200 ml of the corresponding solvent. After stirring at 50 °C for one hour, the polymerization temperature was adjusted and the reactor was floated with propene up to the desired partial pressure. The polymerizations were started by injecting the appropriate amount of $PhC_3^+[B(C_6F_5)_4]^-$ (10 mmol/ml in toluene) *via* a pressure burette. The monomer consumption was measured by a calibrated gas flow meter (Bronkhorst F-111C-HA-33P), and the pressure was kept constant during the entire polymerization period (Bronkhorst pressure controller P-602C-EA-33P). Pressure, temperature and consumption of propene were monitored and recorded online. The polymerization reactions were quenched by injecting 1 ml methanol. Reaction mixtures were poured into acidified methanol (500 ml) and the polymer precipitated. The product was filtered, washed with excess methanol and dried in vacuum at 50 °C overnight.

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[8] Asymmetric complexes are easily accessible, also in larger quantities, relative to their C_2-symmetric analogues: There is no material- and time-consuming separation of *rac*- and *meso*-species, which might be especially difficult or even impossible for alkyl-substituted *rac*-derivatives.

[9] Purification of corresponding complexes with shorter alkoxy substituents at 5,6-position (*e.g.*: ALK = ethyl) failed due to insufficient solubility in apolar solvents.

[10] Activity values and molecular weight averages: $\pm$15%; isotacticities: $\pm$5%.

[11] A second hypothesis might be seen in a change of the polymerization mechanism by this 5,6-dialkoxy substitution. The long, flexible *n*-alkyl substituents might cause an increased interaction with the growing polymer chain. However, this assumption cannot explain the reduced isotacticity values with **8a – d** as well as the lack of influence of the polymerization temperature and the length of the *n*-alkyl substituents on the polymer properties.

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