Oxygen-Containing, Asymmetric "Dual-Side" Zirconocenes: Investigations on a Reversible Chain Transfer to Aluminum

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A series of new oxygen-substituted, asymmetric zirconocene dichlorides (*rac*-{1-[5,6-(ethylenedioxy)-2-methyl-1-η^5-indenyl]-2-(9-η^5-fluorenyl)ethane}zirconium dichloride (**3a**), *rac*-{1-[5,6-(ethylenedioxy)-2-methyl-1-η^5-indenyl]-2-(9-η^5-fluorenyl)ethane}dimethylzirconium (**3b**) and *rac*-{[5,6-ethylenedioxy)-2-methyl-1-η^5-indenyl](9-η^5-fluorenyl)dimethylsilane}zirconium dichloride (**3c**)} have been prepared and their polymerization behavior was investigated in dependence of monomer concentration, temperature and catalyst activation. The presence of oxygen substituents on the indenyl ring results in a strong increase of polymerization activities and also of polymer molecular weights with decreasing Al/Zr ratio. Significantly higher molecular masses and activities were found for the dimethyl complex **3b** after activation with $[(C_6H_5)_3C^+][(C_6F_5)_4B^-]$ deriving from the absence of chain transfer to aluminum and higher concentration of active catalyst species. The mechanism of stereoerror formation of the oxygen-containing C_1-symmetric catalyst was investigated by deuterium labeling studies on propene monomers. The results are discussed on the basis of a reversible chain transfer to aluminum.

Introduction

We reported recently on a new family of asymmetric Zr^{IV} complexes that allows to achieve and adjust elastic polymer properties by a controlled placement of isolated stereoerrors along isotactic polypropene chains.[1] A widely disregarded issue in the development of metallocene chemistry was the incorporation of heteroatoms into the ligand framework, but it found growing interest in the last years.[2,3] First investigations were mainly restricted to methoxy groups as π-donors substituents. A negative influence on the catalyst activity and the polymer molecular weights was observed and explained by the interaction between the donor substituents and methylalumoxane (MAO) resulting in electron withdrawal instead of electron donation.[4] The introduction of amino groups in 2-position of indenyl ligands[5,6] was found by Brintzinger et al.[5] to give modest activities after an induction time of several hours. On the other hand, the investigation of sterically shielded 2-siloxy-substituted bis(indenyl) complexes by Leino et al.[2] and Lehmus et al.[3] evidenced these complexes not to suffer from induction periods and to give a considerable increase in ethene polymerization activities compared to their unsubstituted analogues. Recently, Ewen et al.[7] reported on heteroatom-containing aromatic ligands with a polymerization performance rivaling that of the corresponding unsubstituted complexes.

In the present work a matter of particular interest was to combine both, the unique polymerization properties of our C_1-symmetric metallocene catalysts and the high potential for extending the concept of ligand design by introducing heteroatoms into the ligand framework. Therefore, the oxygen-substituted complexes **3a−c** (Scheme 1) were synthesized and tested in propene polymerization experiments using MAO and $[(C_6H_5)_3C^+][(C_6F_5)_4B^-]$ as cocatalysts. By imbedding the heteroatoms into a dioxane ring, we aimed at a protection of the heterocycle against C−O splitting reactions with MAO and thus to improve the catalyst stability.[8] Polymerization studies using deuterated propene were performed to elucidate the role of the aluminum cocatalyst in the mechanism of stereoerror formation of **3a**/MAO.[1b]

Results and Discussion

Ligand and Complex Synthesis

The ethylene-bridged ligand **2a**H$_2$ (Scheme 2, top) was synthesized via the 1-bromo-2-(9-fluorenyl)ethane intermediate. Analogously, the dimethylsilane-bridged ligand **2b** was prepared by addition of excess $(CH_3)_2SiCl_2$ to a vigor-

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[‡] X-ray structure analysis

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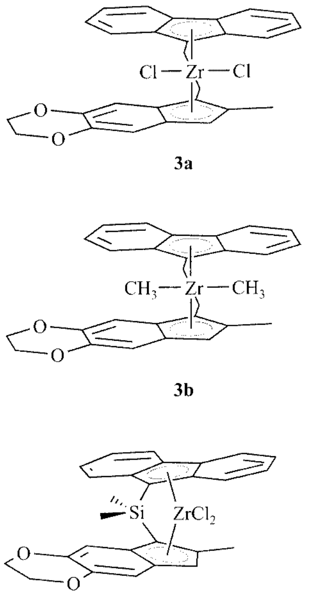
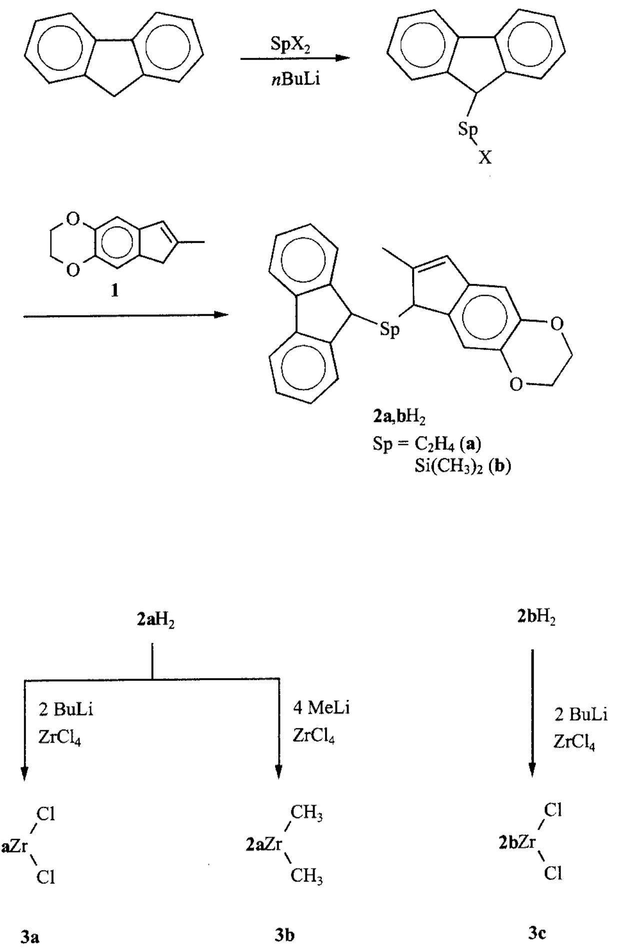


Scheme 1



Scheme 2

ously stirred suspension of fluorenyllithium. Treatment of the ethylene- and silane-substituted fluorenyl intermediates with indenyllithium afforded the corresponding ligands **2a**,**b**H_2.[9] The zirconocene complexes **3a**−**c** (Scheme 2, bottom) were synthesized in moderate to high yields after reaction of the dilithium salt of the ligands **2a**,**b**H_2 with solid $ZrCl_4$ and purified by crystallization from toluene. Compounds **3a**,**b** are stable products and even the Si-bridged complex **3c** is, in contrast to related difluorenyl- or fluorenyl/indenylzirconium dichlorides,[1b,10] relatively stable in solution. The dimethyl derivative **3b** was obtained by a straightforward one-pot reaction of 4 equiv. of methyllithium with **2a**H_2, followed by the addition of $ZrCl_4$.[11] This simplified synthesis of the dimethylmetallocene evades separate preparation and isolation of the dichloro compounds and their subsequent reaction with methylmagnesium bromide or methyllithium.

Crystal and Molecular Structure

A single-crystal X-ray structure investigation was performed on complex **3a** (Figure 1, Table 4) which crystallizes in the monoclinic space group $P2_1/n$. The $Cp^{Flu}-Zr-Cp^{Ind}$ angle δ (Figure 2[12], Table 1, 128.1°) and φ (63.8°), the bite angle between the least-squares planes of the two Cp ligands, are in between those of the Zr complexes **EBI**[13] ($\delta = 126.9°$[14], $\varphi = 62.1°$) and **EBF**[15] ($\delta = 129.0°$[16], $\varphi = 64.3°$). In contrast, γ angles slightly larger than 180° ($\gamma^{Flu} = 186.98°$, $\gamma^{Ind} = 182.82°$) differ from results previously reported for other bridged indenyl and fluorenyl complexes for which typically values smaller than 180° were observed.[16] A genuine explanation of this effect cannot be given, yet. However, the resulting increased accessibility of the zirconium center is obviously one reason for the high activities of our asymmetric catalysts.[17]

The Zr−fluorenyl centroid bond of **3a** (2.59 Å) is distinctly longer than the distance between Zr^{IV} and the indenyl centroid (2.52 Å) leading to a nonsymmetric positioning of the Zr^{IV} center between the two Cp planes. A β^{Ind} value of 86.52° points toward a nearly ideal η^5-coordination of the indenyl ring to Zr^{IV}. This is different for the fluorenyl fragment. The value of β^{Flu} close to 80° (81.68°) and the corresponding Zr−C distances (ranging from 2.435 to 2.688 Å) clearly indicate a reduced hapticity of the fluorenyl fragment toward η^3-coordination.[18]

Propene Polymerization Experiments

Polymerization Activity

The experimental data (Table 2) indicate that all zirconocene compounds of the series **3a**−**c** are suitable catalysts for the polymerization of propene after MAO or $[(C_6H_5)_3C^+][(C_6F_5)_4B^-]$ activation.

The polymerization activities of the oxygen-containing complexes **3a**,**c**/MAO correlate tightly with the total amount of MAO. A distinct increase in catalyst activity could be observed with decreasing MAO concentration ($100 \leq Al/Zr \leq 2000$). The maximum activity is reached at Al/Zr ratios of around 300:1.[3] Seemingly, the polar oxygen substituents promote the approach of the Lewis acidic alu-

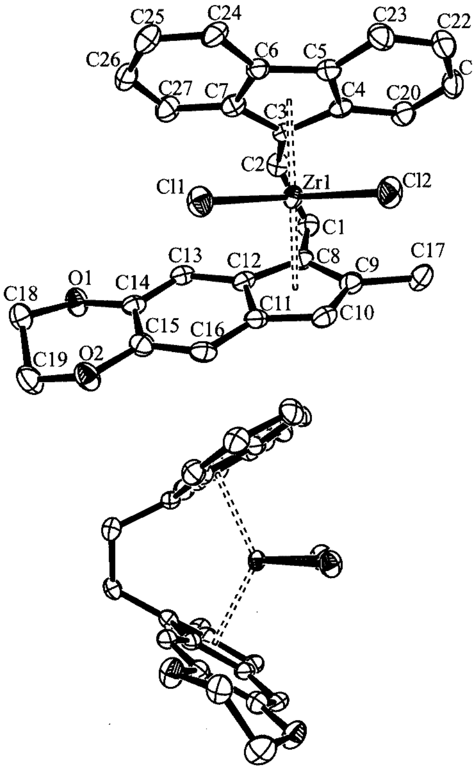


Figure 1. Two projections of the molecular structure and labeling scheme of complex **3a**

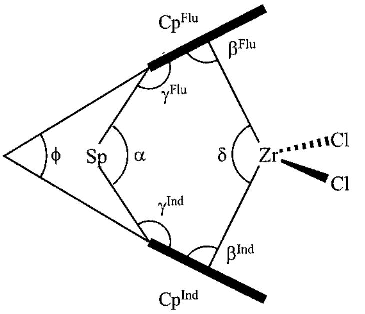


Figure 2. Schematic illustration of relevant band angles

Table 1. Selected bonding parameters of complex **3a**

	3a[a]
α	–
β^{Flu}	81.7(5)
β^{Ind}	86.5(5)
γ^{Flu}	187.0(5)
γ^{Ind}	182.8(5)
φ	63.8(5)
δ	128.1(5)
Cl−Zr−Cl	98.00(4)
Zr−Cl(1)	2.4214(12)
Zr−Cl(2)	2.4264(13)
av. Zr−centroid(Cp^{Flu})[b]	2.588(4)
av. Zr−centroid(Cp^{Ind})[b]	2.519(4)
Zr−centroid(Cp^{Flu})	2.285(4)
Zr−centroid(Cp^{Ind})	2.211(4)
Zr1−C3 (Cp^{Flu})	2.435(4)
Zr1−C4 (Cp^{Flu})	2.554(4)
Zr1−C5 (Cp^{Flu})	2.676(4)
Zr1−C6 (Cp^{Flu})	2.688(4)
Zr1−C7 (Cp^{Flu})	2.589(4)
Zr1−C8 (Cp^{Ind})	2.459(4)
Zr1−C9 (Cp^{Ind})	2.496(4)
Zr1−C10 (Cp^{Ind})	2.512(4)
Zr1−C11 (Cp^{Ind})	2.603(4)
Zr1−C12 (Cp^{Ind})	2.526(4)

[a] Bond lengths are given in Å and angles in °. [b] av. Zr−centroid (Cp^{Flu},Cp^{Ind}) is the mean value of the 5 bonds of the carbon atom of the Cp plane to the Zr atom.

minum cocatalyst to the zirconium center and accelerate the activation reaction in the apolar polymerization medium toluene. At higher cocatalyst concentrations excessive MAO operates as an polymerization-inhibiting agent. The incorporation of the heteroatoms into a ring system protects the oxygen groups sufficiently against MAO-induced C−O splitting and consequently inhibits catalyst decomposition.[19] A further significant activity increase up to a factor of 10 {at T_P = 30 °C up to 5100 kg PP (mol of Zr [C_3] h)$^{-1}$} could be observed for complex **3b**/[$(C_6H_5)_3C^+$][$(C_6F_5)_4B^-$] indicating that this cocatalyst provides a maximized concentration of active Zr^{IV} centers.[20]

The exchange of the ethylene bridge by a dimethylsilane unit results in slightly declined polymerization activities at T_P = 30 °C which, however, distinctly increases up to 3800 kg PP (mol of Zr [C_3] h)$^{-1}$ at 50 °C; **3c**/MAO is the first dimethylsilane-bridged system we investigated that shows not a rapid decomposition during the first minutes of the polymerization reaction,[1b] but rather leads to a constant propene consumption.

Molecular Weights

The molecular weights of the polypropenes obtained with **3a−c** decrease at higher Al/Zr ratios (Figure 3). The polydispersities of the polymer products are within the narrow range of 1.7 to 2.0 indicating homogeneous polymerization conditions. This decline shows again that chain transfer to aluminum plays a decisive role,[4,21] in line with the above discussion of catalyst activities. As a result of this facile chain termination reaction isopropyl end groups are observed after acidic workup (Figure 4)[5] instead of vinylic chain ends resulting from spontaneous β-H abstraction. After borate activation of **3b**, excluding the possibility of transfer to aluminum, the molecular weights improved from 3.0 × 10^4 up to 16.0 × 10^4 g mol^{-1} (Table 2, Entries 4, 8).

Stereoregularity

The [mmmm] pentad concentration of the polymers products resulting from **3a−c** varies over a broad range (34−65%, cf. Table 3) depending on temperature, monomer concentration and bridging unit. These results are in accordance with our recently published chain back-skip mechanism based on fluorenyl and indenyl units and with the slightly increased tacticity found for dimethylsilane-bridged zirconocenes.[1,22] Interestingly, the isotacticities of the polymers prepared with **3a**,**c**/MAO are independent of the Al/Zr

Table 2. Polymerization results of propene with the asymmetric complexes **3a**,**c**/MAO and **3b**/$[(C_6H_5)_3C^+][(C_6F_5)_4B^-]$

Run	Cat.	Amount [μmol]	T_p [°C]	$[C_3]$ [mol L^{-1}]	Al/Zr	t_p [min]	Yield [g]	Activity[a]	M_w [b]	M_w/M_n	[mmmm] [%]
1	**3a**	25	30	3.0	100	7	8.5	1000	65	1.8	35.2
2	**3a**	10	30	3.0	300	15	9.0	1200	60	1.7	34.1
3	**3a**	10	30	3.0	1000	25	8.8	700	45	1.7	35.2
4	**3a**	20	30	3.0	2000	17	8.0	500	30	1.9	36.1
5	**3a**	5	30	5.1	300	24	15.0	1500	115	1.8	35.8
6	**3b**	6	30	1.2	–	13	8.0	5100	135	2.0	55.6
7	**3b**	3	30	3.0	–	20	8.7	2900	150	1.9	42.5
8	**3b**	2	30	5.1	–	16	8.3	3100	160	1.8	36.8
9	**3c**	10	30	3.0	100	–	–	–[c]	–	–	–
10	**3c**	10	30	3.0	200	28	8.2	600	90	1.9	54.1
11	**3c**	15	30	3.0	500	25	8.8	500	75	1.7	53.3
12	**3c**	30	30	3.0	1000	40	6.7	100	50	1.7	53.0
13	**3c**	20	30	3.0	2000	45	7.6	150	55	1.8	51.5
14	**3c**	10	50	3.0	500	5	9.4	3800	70	1.8	65.1

[a] [kg of PP (mol of Zr $[C_3]$ h)$^{-1}$]. [b] [10^{-3} g mol^{-1}]. [c] No activity observed.

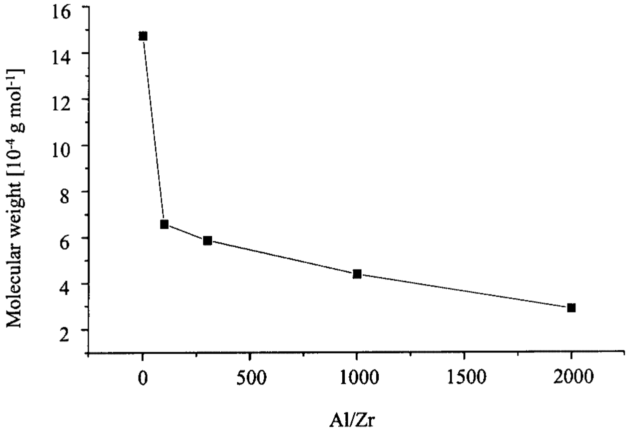


Figure 3. Plot of molecular weight versus Al/Zr ratio

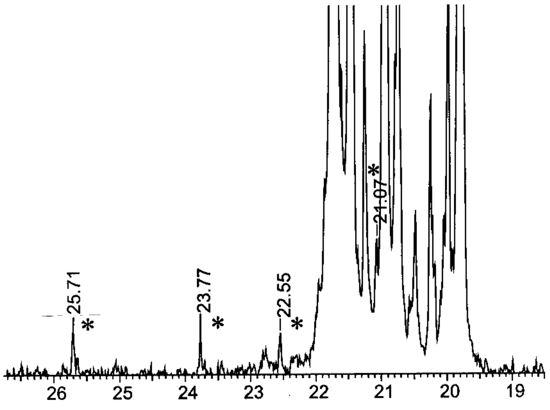


Figure 4. ^{13}C NMR spectra of the methyl region of a polypropene sample (**3a**/MAO; T_p = 30 °C; 1.2 mol L^{-1} 1-[D]-propene); the marked peaks denote signals arising from isobutyl end groups

ratio. This is a surprising finding because reduced activities and molecular weights indicate a direct interaction of MAO and Zr^{IV} centers which we expected to affect also the stereoselectivity of the insertion reaction. Moreover, borate activation (**3b**/$[(C_6H_5)_3C^+][(C_6F_5)_4B^-]$) leads to increased isotacticities (Table 3, Entries 1–4, 6, 7) proving that MAO does contribute to the overall stereoselectivity of the polymerization reaction. One possible explanation of this striking role of MAO in the error formation process might be a reversible chain transfer reaction. The reduced molecular weights of the polymer products at higher Al/Zr ratios proved the unidirectional transfer of polymer chains from Zr^{IV} to aluminum. Relocation from aluminum to the other enantiomer of the C_1-symmetric catalyst species would lead to the formation of a single stereoerror and could – at enhanced frequencies – account for the observed reduction of isotacticities in case of MAO-activated complexes.[23]

Besides electronics effects,[4,24] for which we assume that they are not relevant for our type of asymmetric catalysts and different side selectivity (back-skip), chain end epimerization[25] could be responsible for stereoerror formation. In order to rule out this mechanism, we performed deuterium labeling experiments on stereoerror distributions of the asymmetric zirconocene **3a** and referenced the results to **EBI**/MAO as a representative, C_2-symmetric catalyst typically undergoing chain end epimerization at low monomer concentrations.

For **3a**/MAO we could not detect isomerization-induced stereoerrors at any of the applied monomer concentrations,[26] while for **EBI**/MAO a decrease in the monomer concentration raised the amount of [D]-[mrrm] stereoerror pentads, as expected (Figure 5, Table 3). These findings reflect a significant difference in the mechanism of stereoerror formation for these two catalyst systems. For **EBI**/MAO [mrrm] stereoerrors result to a large extent from kinetically competitive chain end isomerization reactions. The decisive factor causing stereoerrors in **3a**/MAO at high monomer concentrations is the kinetic competition between chain back-skip and monomer coordination to the aspecific side of the catalyst structure. At low C_3 pressure, a significant fraction of stereoerrors can be most likely ascribed to the above discussed reversible transfer to aluminum.

Table 3. Polypropene pentad distribution for C_2-symmetric **EBI**/MAO and C_1-symmetric **3a**/MAO (T_p = 50 °C)

Entry	Cat.[a]	Mon.[b]	[Mon.] [mol L^{-1}]	Al/Zr	[mmmm] [%]	[mmrr]	[mrrm]	[D]-[mrrm]
1	**EBI**	C_3	0.4	3000	74	8.6	4.0	–
2	**EBI**	C_3	0.85	3000	80	5.6	2.9	–
3	**EBI**	C_3	1.9	3000	84	5.7	2.3	–
4	**EBI**	C_3	3.3	3000	85	4.7	1.9	–
5	**EBI**	[D]-C_3	0.4	1500	69	9.5	1.9	2.6
6	**EBI**	[D]-C_3	0.85	1500	79	6.4	2.0	1.3
7	**EBI**	[D]-C_3	1.3	1500	82	5.5	2.0	< 0.2
8	**3a**	C_3	1.9	1000	55	14.1	6.9	–
9	**3a**	C_3	1.9	2000	53	14.2	7.1	–
10	**3a**	C_3	1.9	5000	53	14.0	7.1	–
11	**3a**	C_3	0.4	1000	60	11.7	6.0	–
12	**3a**	[D]-C_3	1.9	300	57	14.1	6.5	n. o.
13	**3a**	[D]-C_3	0.4	300	65	12.6	5.1	n. o.

[a] [Zr] = $1-2 \times 10^{-5}$ mol L^{-1} for C_3 polymerizations, [Zr] = 3.3×10^{-4} mol L^{-1} for [D]-C_3 polymerizations. [b] Monomers: C_3 = propene, [D]-C_3 = 1-[D]-propene.

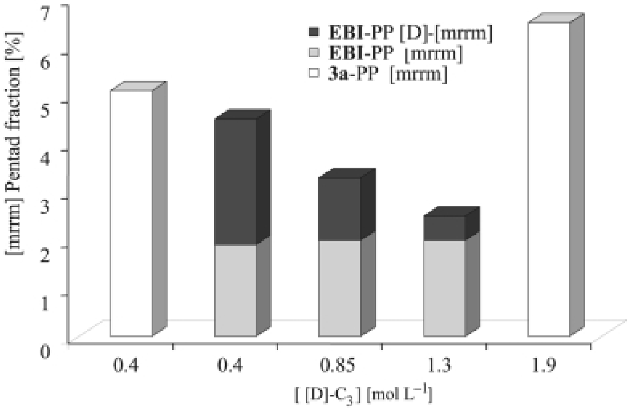


Figure 5. Amount of [mrrm] stereoerror pentads and fraction of isomerization induced [D]-[mrrm] stereoerrors as function of monomer concentration (**3a**,**EBI**/MAO; T_p = 50 °C)

Conclusion

The asymmetric, dual-side catalysts presented in the current study combine both, the excellent capability of C_1-symmeteric metallocenes to produce tailor-made polypropenes and the potential to incorporate functionalities into highly active metallocene catalysts. The introduction of the heteroatoms into a benzodioxane ring enhances the catalyst stability during the polymerization process. The oxygen substitution obviously promotes MAO approach to the catalyst center resulting in high rates of catalyst activation at low cocatalyst concentrations (high cocatalyst efficiency). On the other side, facile chain transfer to aluminum is already observed at lower Al/Zr ratios again pointing toward the close proximity of Zr^{IV} and Al^{MAO} ions. The observed catalyst stereoselectivities are discussed by chain back-skip and by a mechanism for which MAO operates as a transporting agent of polymer chains between zirconium centers. Thereby, relocation of a chain from one enantiomer to the other leads to stereoerrors which afford the formation of lower isotactic polypropenes.

Experimental Section

General Remarks: All reactions were performed under dry argon using standard Schlenk techniques. Hydrocarbon and ether solvents were dried by distillation from $LiAlH_4$, dichloromethane was distilled from CaH_2. Fluorene, 1,2-(ethylenedioxy)benzene, 1,2-dibromoethane, methacryloyl chloride, *n*BuLi, MeLi, $ZrCl_4$, $AlCl_3$ and (*Z*)/(*E*)-1-bromo-1-propene (98%) and [D_1]methanol (99.5%) were used as received from Merck and Aldrich. The complex **EBI**[1b] and the trityl borate $[(C_6H_5)_3C^+][(C_6F_5)_4B^-]$[27] were prepared according to literature procedures. Methylaluminoxane and triisobutylaluminum were purchased from Witco and toluene for the polymerization reactions from Merck. All compounds were analyzed by ^1H NMR with a Bruker AC 200 or AMX 500 at ambient temperatures and referenced to TMS. Mass spectra were acquired with Finnigan (SSQ 7000) and Varian (MAT-711) instruments. Elemental analyses were determined in the Microanalytical Laboratory of the University of Ulm.

1-[D]-Propene: A mixture of (*Z*)/(*E*)-1-bromo-1-propene (72 g, 0.6 mol) was added to freshly cut lithium (12.5 g, 1.8 mol) in 300 mL of ether at 0 °C. After stirring overnight, the mixture was filtered and the filtrate concentrated to dryness. The resulting white solid lithium compounds were suspended in 200 mL of toluene. At 0 °C [D_1]methanol (24 g, 0.73 mol) was added and the evolving gas was condensed through a cold trap at −50 °C into a steel vessel at −196 °C. The gas was further purified by passing it through molecular sieves and bubbling it through triisobutylaluminum, resulting in a yield of 20.5 g of 1-[D]-propene (80%). The ^1H NMR spectrum [$CDCl_3$ (δ = 7.24), 500 MHz] showed that the product contained 41% of (*E*)-1-[D]-propene (*H*DC=CHCH$_3$) [δ = 4.91 (dq, ^3J = 10.0, ^4J = 1.5 Hz, 1 H)] and 59% of (*E*)-1-[D]-propene [δ = 5.00 (dq, ^3J = 17.0, ^4J = 1.8 Hz, 1 H)].

Polymerization Reactions with 1-[D]-Propene: Polymerizations with deuterated propene were performed in a 50-mL steel autoclave. The solvent toluene, cocatalyst MAO and the catalyst were fed under argon and allowed to reach the desired polymerization temperature.

After 10 min of contact time, monomer was added, and temperature (±1 °C) and pressure (±100 mbar) were kept constant. The polymerization was stopped by pouring the reaction mixture into acidified methanol. The polymer product was washed with a methanol/HCl solution and with methanol. The product was filtered and dried in vacuo at 60 °C overnight. The yields of deuterated polypropene were between 0.2 and 0.8 g.

Propene Polymerization Reactions: The polymerization reactions were performed in a 0.5-L or a 1-L Büchi steel reactor at constant pressure and temperature. The autoclave was charged with 200 or 300 mL of toluene, respectively, and with the desired amount of MAO. Subsequently, the polymerization temperature was adjusted, the reactor was charged with propene up to the desired partial pressure, and the preactivated catalyst solution (Al/Zr = 100:1) was injected into the autoclave via a pressure burette. The monomer consumption was measured by the use of 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 stopped and treated as described above.

Polymer Analysis: ^{13}C NMR spectra were recorded with a Varian GEMINI 2000 spectrometer ($C_2D_2Cl_4$, 100 °C, 75 MHz, 10 mm probe) or a Bruker AMX 500 spectrometer ($C_2D_2Cl_4$, 80 °C, 125 MHz, 5 mm probe) in the inverse gated decoupling mode with a 3-s pulse delay and a 45° pulse to attain conditions close to the maximum signal-to-noise ratio. The number of transients accumulated was between 5 and 15 K. The spectra were analyzed by known methods.[28] Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC, Waters 2000, 140 °C in 1,2,4-trichlorobenzene) relative to polystyrene and polypropene standards.

5,6-(Ethylenedioxy)-2-methylindene (1): 42.7 mL (367.2 mmol) of 1,2-(ethylenedioxy)benzene was added slowly at −78 °C to a stirred solution of 51.4 g of $AlCl_3$ (385.6 mmol) and 35.7 mL (367.2 mmol) of methacryloyl chloride in 300 mL of dichloromethane and allowed to attain room temperature overnight. The solution was carefully hydrolyzed with ice, and the organic phases were separated, washed with an aqueous solution of K_2CO_3 and dried with Na_2SO_4. After removing the solvent and crystallization in pentane, 5,6-(ethylenedioxy)-2-methylindan-1-one was obtained as a solid (62.7 g, 306.9 mmol, 84%). 40.0 g (195.9 mmol) of 5,6-(ethylenedioxy)-2-methylindan-1-one was diluted in 100 mL of Et_2O and added at −78 °C to a suspension of 5.0 g of $LiAlH_4$ (131.7 mmol) in 100 mL of Et_2O. The reaction mixture was stirred overnight and carefully hydrolyzed with ice and aqueous HCl. After separating the organic phases, the solution was neutralized with an aqueous solution of K_2CO_3 and dried with Na_2SO_4. After evaporation of the solvent and crystallization from toluene/hexane (ca. 3:2) the diastereomeric alcohols were obtained as a crystalline solid (27.3 g, 132.3 mmol, 68%). The alcohol (15.0 g, 72.73 mmol) was dissolved in 100 mL of toluene and 1.0 g of *p*-toluenesulfonic acid was added. The solution was heated under reflux using a water separation funnel until no further water was produced. The reaction mixture was neutralized by washing with aqueous KOH and was subsequently dried with Na_2SO_4. The solvent was evaporated, and the indene **1** was obtained as a crystalline solid (7.8 g, 41.46 mmol, 57%). Data of the ketone: ^1H NMR (200 MHz, $CDCl_3$): δ = 1.27 (d, 3 H, CH_3), 2.63 (m, 2 H, CH_2, indanone ring), 3.27 (m, 1 H, CH, indanone system), 4.29 (m, 4 H, CH_2, dioxane ring), 6.68, 7.25 (2 s, 2 H, aromatic). MS (GC-MS): *m*/*z* (%) = 204 (100) [M^+]. $C_{12}H_{12}O_3$ (204.2): calcd. C 70.58, H 5.92; found C 70.96, H 5.92. Data of the Alcohol: ^1H NMR (200 MHz, $CDCl_3$): δ = 1.11 (d, 3 H, CH_3), 1.79 (broad, 1 H, OH group), 2.33 (d, 2 H, CH_2, indanol ring), 2.95 (m, 1 H, CH, indanol ring), 4.13 (m, 4 H, CH_2, dioxane ring), 4.55 (d, 1 H, CH, indanol ring), 6.61, 6.80 (2 s, 2 H, aromatic). MS (GC-MS): *m*/*z* (%) = 206 (100) [M^+]. $C_{12}H_{14}O_3$ (206.2): calcd. C 69.88, H 6.84; found C 69.66, H 6.79. Data of **1**: ^1H NMR (200 MHz, $CDCl_3$): δ = 2.15 (s, 3 H, CH_3), 3.20 (s, 2 H, CH_2, indene ring), 4.21 (m, 4 H, CH_2 dioxane ring), 6.31 (s, 1 H, CH olefinic), 6.80, 7.30 (2 s, 2 H, aromatic). MS (GC-MS): *m*/*z* (%) = 188 (100) [M^+]. $C_{12}H_{12}O_2$ (188.2): calcd. C 76.57, H 6.43; found C 76.16, H 6.59.

1-[5,6-(Ethylenedioxy)-2-methylindenyl]-2-(9-η^5-fluorenyl)ethane (2aH$_2$): 4.35 g (26.16 mmol) of fluorene was dissolved in 100 mL of Et_2O and cooled to −78 °C. Addition of a 1.6 M solution of *n*BuLi in hexane (16.4 mL, 26.16 mmol) and stirring for additional 2 h afforded the formation of fluorenyllithium. Subsequent cooling to −78 °C and further treatment with an excess of 1,2-dibromoethane (13.6 mL, 160 mmol) formed the substituted fluorenyl compound. The remaining mixture was allowed to attain room temperature and stirred for additional 4 h. Removal of the solvent and excess of 1,2-dibromoethane yielded the fluorenyl intermediate as a beige solid. This solid was added after dilution with 100 mL of Et_2O at ambient temperature to the separately prepared lithium salt of the 5,6-(ethylenedioxy)-2-methylindene (**1**) (4.92 g, 26.16 mmol). The reaction mixture was stirred overnight and refluxed for 2 h. The crude product was treated with a saturated aqueous solution of NH_4Cl and washed several times with water. The organic phase was separated and dried with Na_2SO_4. Evaporation of the solvent and crystallization from *n*-hexane yielded **2a**H$_2$ as a white solid (4.45 g, 11.7 mmol, 45%). Data of **2a**H$_2$: ^1H NMR (200 MHz, $CDCl_3$): δ = 1.25−1.69 (m, 4 H, CH_2 bridge), 1.78 (s, 3 H, CH_3), 2.97 (t, 1 H, CH, indene), 3.8 (t, 1 H, CH, 9*H*-fluorene), 4.17 (m, 4 H, CH_2, dioxane ring), 6.23 (s, 1 H, olefinic indene), 6.60, 6.63 (2 s, 2 H, aromatic indene), 7.16−7.70 (m, 8H, aromatic fluorene). MS (EI): *m*/*z* (%) = 380 (100) [M^+]. $C_{27}H_{24}O_2$ (380.5): calcd. C 85.23, H 6.36; found C 85.15, H 6.48.

(5,6-Ethylenedioxy-2-methylindenyl)(9-η^5-fluorenyl)dimethylsilane (2bH$_2$): 4.09 g (24.62 mmol) of fluorene was dissolved in 150 mL of Et_2O and cooled to −78 °C. Addition of a 1.6 M solution of *n*BuLi in hexane (15.4 mL, 24.62 mmol) and stirring for additional 4 h resulted in the formation of fluorenyllithium. Subsequent cooling to −78 °C and further treatment with an excess of dichlorodimethylsilane (13.6 mL, 98.5 mmol) afforded the substituted fluorenyl compound. The remaining mixture was allowed to attain room temperature and stirred for additional 2 h. Removal of the solvent and excess of dichlorodimethylsilane in vacuo gave the fluorenyl intermediate as a beige powder. This solid was added after dilution with 100 mL of Et_2O at ambient temperature to the separately prepared lithium salt of 5,6-(ethylenedioxy)-2-methylindene (**1**) (4.63 g, 24.62 mmol). The reaction mixture was stirred overnight and refluxed for 2 h. The crude product was treated with a saturated aqueous solution of NH_4Cl and washed several times with water. The organic phase was separated and dried with Na_2SO_4. Evaporation of the solvent and recrystallization from *n*-hexane yielded **2b**H$_2$ as a white solid (7.2 g, 17.8 mmol, 72%). Data of **2b**H$_2$: ^1H NMR (200 MHz, $CDCl_3$): δ = −1.64, −1.57 − (2 s, 6 H, CH_3 bridge), 0.94 (s, 3 H, CH_3), 3.03 (m, 4 H, CH_2, dioxane ring), 5.26 (s, 1 H, CH, olefinic), 5.63, 5.77 (2 s, 2 H, aromatic indene), 6.02−6.74 (m, 8 H, aromatic fluorene). MS (EI): *m*/*z* (%) = 410 (100) [M^+]. $C_{27}H_{26}O_2Si$ (410.6): calcd. C 78.98, H 6.38; found C 78.65, H 6.41.

***rac*-{1-[5,6-(Ethylenedioxy)-2-methyl-1-η^5-indenyl]-2-(9-η^5-fluorenyl)-ethane}zirconium Dichloride (3a):** 1.7 g (4.47 mmol) of 1-[5,6-(ethylenedioxy)-2-methyl-1-η^5-indenyl]-2-(9-η^5-fluorenyl)-ethane (**2a**H_2) was dilssolved in 150 mL of Et_2O and cooled to −78 °C. After treatment of the ligand precursor with 5.6 mL of *n*BuLi at −78 °C, the reaction mixture was warmed to room temperature and stirred for 4 h. Subsequently, the solvent was removed in vacuo and the resulting lithium salt was diluted with 60 mL of toluene. Cooling to −78 °C and addition of solid $ZrCl_4$ (1.04 g, 4.47 mmol) afforded the formation of an orange suspension which was warmed to room temperature and stirred overnight. The mixture was filtered, and the remaining solid fraction was extracted with toluene until the organic phase remained colorless. Removal of the solvent gave an orange powder from which pure **3a** (2.05 g, 3.79 mmol, 91%) could be obtained by crystallization from toluene solution. Data of **3a**: ^1H NMR (500 MHz, $CDCl_3$): δ = 2.14 (s, 3 H, CH_3), 3.72−4.58 (m, 4 H, CH_2, bridge), 6.01, 6.75 (s, 1 H, aromatic indene), 7.14−7.95 (m, 9 H, aromatic indene, aromatic fluorene). MS (EI): *m*/*z* = 538 (peak distribution of isotopes according to expected contents). $C_{27}H_{22}Cl_2O_2Zr$ (540.6): calcd. C 59.99, H 4.10; found C 59.56, H 4.17.

***rac*-{1-[5,6-(Ethylenedioxy)-2-methyl-1-η^5-indenyl]-2-(9-η^5-fluorenyl)ethane}dimethylzirconium (3b):** 0.75 g (1.97 mmol) of 1-[5,6-(ethylenedioxy)-2-methyl-1-η^5-indenyl]-2-(9-η^5-fluorenyl)ethane (**2a**H_2) was dissolved in 50 mL of Et_2O and cooled to −78 °C. After treatment of the ligand precursor with 4.94 mL (7.90 mmol) of MeLi at −78 °C, the reaction mixture was warmed to room temperature and stirred for 4 h. Solid $ZrCl_4$ (0.46 g, 1.97 mmol) was added to the stirred suspension of the lithium salt of **2a**H_2 at room temperature and the reaction mixture was stirred for 24 h with a final formation of a light-brown suspension. The solvent was removed in vacuo and replaced with toluene. The suspension was filtered and the residual solid fraction was extracted with toluene until the organic phase remained colorless. Removal of the solvent gave a yellow powder from which pure **3b** (0.66 g, 1.32 mmol, 67%) could be obtained by crystallization from toluene. Data of **3b**: ^1H NMR (200 MHz, $CDCl_3$): δ = −2.34, −1.36, (2 s, 6 H, CH_3), 1.94 (s, 3 H, CH_3), 3.37−4.21 (m, 4 H, CH_2 bridge), 5.97 (s, 1 H, indene), 6.65, 6.89 (2 s, 2 H, aromatic indene), 6.99−7.94 (m, 8 H, aromatic fluorene). $C_{29}H_{28}O_2Zr$ (499.8): calcd. C 69.70, H 5.65; found C 69.43, H 5.88.

***rac*-{[5,6-(Ethylenedioxy)-2-methyl-1-η^5-indenyl](9-η^5-fluorenyl)dimethylsilane}zirconium Dichloride (3c):** 1-[5,6-(Ethylenedioxy)-2-methyl-1-η^5-indenyl]-2-(9-η^5-fluorenyl)dimethylsilane (**2b**H_2) (1.80 g, 4.38 mmol) was dissolved in 50 mL of Et_2O and cooled to −78 °C. After treatment of the ligand precursor with 5.5 mL of *n*BuLi at −78 °C, the reaction mixture was warmed to ambient temperature and stirred for 2 h. Subsequently, the solvent was removed in vacuo and the resulting lithium salt was diluted with 50 mL of toluene. Cooling to −78 °C and addition of solid $ZrCl_4$ (1.02 g, 4.38 mmol) afforded the formation of an orange suspension which was warmed to room temperature and stirred overnight. The mixture was filtered, and the remaining solid fraction was extracted with toluene until the organic phase remained colorless. Removal of the solvent gave an orange powder. The zirconocene **3c** (1.37 g, 2.41 mmol, 55%) could be purified by washing with Et_2O and pentane. Data of **3c**: ^1H NMR (200 MHz, $CDCl_3$): δ = −0.44, −0.37 (2 s, 6 H, CH_3, bridge), 2.13 (s, 3 H, CH_3), 4.22 (m, 4 H, CH_2, dioxane ring), 6.46 (s, 1 H, indene), 6.82, 6.96 (2 s, 2 H, aromatic indene), 7.14−7.88 (m, 8 H, aromatic fluorene). MS (EI): *m*/*z* = 568 (peak distribution of isotopes according to expected contents). $C_{27}H_{24}Cl_2O_2SiZr$ (570.7): calcd. C 56.82, H 4.24; found C 56.58, H 4.54.

X-ray Crystallography: The unit cell parameters were determined and the crystal data of **3a** was collected with a Rigaku AFC7S single-crystal diffractometer at 193(2) K using Mo-K_α radiation (graphite monochromator, 0.71073 Å); 2-θ/ω scans. Intensities were corrected for Lorentz and polarization effects; TEXSAN (Molecular Structure Corporation, **1993**).[29] A ψ-scan absorption correction was made, $0.89 < T < 1.00$ (North et al., **1968**).[30] Solution and refinement: SHELX97 (Sheldrick, **1997**),[31] direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on calculated positions. The displacement factors of the H atoms were 1.2× or 1.5× to that of the host atom. One disordered toluene molecule is occupying the centre of symmetry. Graphics: SHELXTL/PC (Sheldrick, **1990**).[32] Deatils are listed in Table 4. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-164853. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 4. Crystal data, data collection and structure refinement parameters of complex **3a**

Empirical formula	$C_{30.50}H_{26}Cl_2O_2Zr$
Formula mass	586.63
Crystal color and form	orange prism
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	12.500(3)
b [Å]	15.671(3)
c [Å]	12.678(4)
β [°]	96.07(2)
V [Å^3]	2469.5(11)
Z	4
D_C [Mg/m^3]	1.578
μ [mm^{-1}]	0.690
F(000)	1196
Crystal size [mm]	0.38 × 0.25 × 0.16
Scan mode	2θ/ω
$θ_{max}$ [°]	25.25
Index ranges	$0 \le h \le 15$ $0 \le k \le 18$ $-15 \le l \le 15$
No. of unique reflections	4446
No. of observed reflections [$I > 2σ(I)$]	3319
No. of parameters	352
Goodness of fit on $S(F^2)$[a]	1.039
Final R indices [$I > 2σ(I)$][b]	$R_1 = 0.0479$, $wR_2 = 0.1015$
R indices (all data)[b]	$R_1 = 0.0809$, $wR_2 = 0.1099$
Largest differential peak/hole [e/Å^3]	0.518/−0.399

$R(F) = ||F_o| - |F_c||/|F_o|$; $wR(F^2) = [w(F_o^2 - F_c^2)^2/wF_o^4]^{1/2}$.

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