

Rotating Benzyl Substituent in *ansa*-Bis(indenyl)zirconocenes Controls Propene Polymerization

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A series of benzyl-substituted, dual-site *ansa*-metallocenes were synthesized and characterized. Their isolated *rac*- and *meso*-diastereomers were studied in propene polymerization after methylaluminoxane or borate activation. Catalysts' polymerization behavior were investigated in various polymerization conditions, and produced polypropenes (PPs) were characterized with NMR, GPC, and DSC. The *rac*- and *meso*-diastereomers of these unsymmetric catalysts bearing a SiMe₂ bridge produced PP with similar activity, tacticity, and molar mass. According to quantum chemical calculations, the benzyl group in the catalysts can rotate, having significant energy minima. The reason that the diastereomers produce PP with similar molar mass is linked to these local energy minima and is further discussed.

Introduction

Since the discovery of methylaluminoxane (MAO) as an efficient activator of homogeneous metallocene catalysts in the mid 1970s^{1,2} and isospecific polymerization of propene in 1985, massive research efforts in both academia and the chemical industry were directed toward metallocene-based polymerization catalysts. During the last 20 years fundamental concepts concerning the influence of the chiral ligand framework on polymer tacticity, including enantiomorphic site control and chain back-skipping mechanisms, were developed.^{3–5} Because stereospecific propene polymerization requires by definition a chiral metal center, the ligand frameworks are designed to be rigid. Even a flexible ethylene bridge between the cyclopentadienyl moieties is often changed to a more rigid dimethylsilyl bridge. By tuning the catalyst structure, highly iso- and syndiotactic polypropenes

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(PPs) have been successfully produced. Topics concerning the influence of ligand structures on the polymer tacticities as well as the polymerization mechanisms are thoroughly reviewed.⁶

In the area of metallocene catalysts unsymmetric, dual-site metallocenes are especially intriguing, as they can be used for controlled stereoerror formation during the propene polymerization. With these catalysts structurally defined hemiisotactic polypropene and various syndio- and isotactic polypropenes with variable amounts of stereoerrors in their microstructure were introduced.^{4,7–9} When the molar mass and amount of stereoerrors are balanced, the polypropenes can possess significant elastic properties. It appears that in most unsymmetric, dual-site catalysts reported so far, the origin for the stereoselectivity is a consecutive chain back-skipping prior to the monomer coordination to the metal.^{10–12}

In general, the *meso*-isomers of bis(indenyl)zirconocene catalysts are known to produce atactic PP with low molar mass. We reported recently the catalytic properties of the

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Figure 1. Diastereomers of SiMe₂(3-benzylindenyl)(indenyl)ZrCl₂ (meso-1 and rac-1) produce isotactic polypropenes with similar microstructures and molar masses under equivalent polymerization conditions.

meso- and rac-diastereomers of benzyl-substituted metallocene SiMe₂(3-benzylindenyl)(indenyl)ZrCl₂ (1) in propene polymerization after MAO activation; unexpectedly these diastereomers produce polypropene with similar tacticities and molar masses under equivalent polymerization conditions (Figure 1).¹³ This previously unprecedented similarity in polymer characteristics indicates that the coordination sites of the unsymmetric diastereomers have equivalent steric surroundings caused by the ligand framework. Furthermore, the rotating benzyl substituent in the 3-position seems to provide an interesting and novel way to control the stereospecificity and especially molar mass of the polypropene. In this respect, we herein report on a set of new benzyl-substituted complexes and computational studies together with polymerization experiments to understand how the benzyl group influences the molar mass and selectivity in the enantiofacial coordination of propene.

Experimental Section

General Information and Materials. All syntheses and manipulations were performed under an inert argon atmosphere by using standard Schlenk techniques. All starting materials were standard reagent grade and used as received. Diethyl ether, pentane, hexane, and toluene were distilled over sodium, and benzophenone was used as an indicator, if not mentioned otherwise. Dichloromethane was distilled over calcium dihydride.

Instrumentation and Measurements. ¹H NMR spectra were recorded on a Varian Gemini 200 spectrometer operating at 200 MHz, and ¹³C NMR spectra of polypropenes were obtained on a Varian Gemini 2000XL (75 MHz, 10 mm probe in TCB/C₆D₆ (9:1) at 120 °C with 45° pulse angle, 7 s delay, and 2000 scans). The [mmmm] methyl signal of polypropene with chemical shift $\delta = 21.80$ ppm was used as an internal standard. GC/MS analysis was made with a Varian 3800 GC and a Varian Saturn 2000 GC/MS/MS. Mass spectra and high-resolution mass spectra were recorded on a JEOL JMS-SX102 mass spectrometer, operating at 70 eV.

Synthesis and Characterization. The addition of 2-methyl-4,5benzindene $(3b)^{14}$ to (benzylindenyl)chlorodimethylsilane^{13,15} (3a) gave the desired ligand precursor (3c) (Scheme 1). The yield was only 48% compared to nearly quantitative reaction with unsubstituted indene. Successful synthesis of the ethyl-bridged preligand analogue (2c) was achieved in a reaction between benzyl bromide (2b) and ethylbisindenyllithium (2a). Complexation of the silyl- and ethyl-bridged preligands in dichloromethane and toluene with ZrCl₄ gave the desired products, respectively.

1-Benzyl-3-[2-(1*H***-inden-1-yl)ethyl]-1***H***-indene (2c/2c*).** *n***-Butyllithium (22.5 mL, 35.8 mmol, 1.6 M in hexane) was added to** Scheme 1



3-[2-(1H-inden-1-yl)ethyl]-1H-indene (10.34 g, 35.8 mmol) (2a) in 200 mL of diethyl ether at 0 °C. The reaction mixture was stirred at room temperature for 4 h. Benzyl bromide (2b) (15.3 g, 89.5 mmol) in 40 mL of diethyl ether was added dropwise to the cooled (0 °C) Li salt solution. After overnight stirring at RT the reaction mixture was quenched with 150 mL of a saturated solution of NH₄Cl. Water and the organic layer were separated, and the water phase was extracted three times with 30 mL of diethyl ether. Combined organic layers were dried with NaSO₄(s) and evaporated to constant weight. The product (yellow viscous oil) was purified by column chromatography using a toluene/hexane (1:4) mixture as an eluent. Yield: 2.52 g (20%). ¹³C NMR could not be interpreted due to overlapping peaks of the diastereomers. ¹H NMR (CHCl₃): δ 7.39–7.04 (m, 13H, Ar, Cp_{Ind}), 6.75 (m, 1H, Cp_{Ind}), 6.42 (m, 1H, Cp_{Ind}), 6.03 (m, 1H, CpInd), 3.77 (d, 2H, CH₂), 3.32 (m, 2H, Cpaliphatic), 1.94-1.35 (m, 4H, Et_{bridge}). MS(EI+) *m*/*z* (%): 348 (47), 219 (53), 129 (100).

(3-Benzyl-1H-inden-1-yl)(2-methylbenz[e]-1H-inden-1-yl)dimethylsilane (3c/3c*). n-Butyllithium (31 mL, 50 mmol, 1.6 M in hexane) was added to 2-methylbenzindene (3b) (9.0 mL, 50 mmol) in 150 mL of diethyl ether at 0 °C. The reaction mixture was stirred at room temperature for 2 h. (3-Benzylindenyl)-(chloro)dimethylsilane (3a) (14.8 g, 50 mmol) in 40 mL of diethyl ether was added to the cooled, 0 °C, Li salt solution. After overnight stirring at RT the reaction mixture was quenched with 150 mL of a saturated solution of NH₄Cl. The organic layer was separated, dried with NaSO₄(s), and evaporated to constant weight. The product (yellow viscous oil) was purified by column chromatography using a toluene/hexane (1:4) mixture as an eluent. Yield: 10 g (48%). ¹³C NMR could not be interpreted due to overlapping peaks of the diastereomers. ¹H NMR (CHCl₃): δ 8.02 (d, 1H, Ar), 7.79 (d, 1H, Ar), 7.52-7.03 (m, 12H, Ar and 1H, Cp_{Ind}), 6.05/6.00 (s, 1H, Cp_{Ind}/s, 1H, Cp_{Ind}), 3.82 (d, 2H, CH₂), 3.67 (s, 1H, Cpaliphatic), 3.56/3.47 (s, 1H, Cpaliphatic/s, 1H, Cp_{aliphatic}), 2.28/2.22 (s, 3H, CH₃/s, 3H, CH₃), -0.21, -0.27, -0.49, -0.51 (s, 3H, SiCH₃ and s, 3H, SiCH₃/s, 3H, SiCH₃ and s, 3H, SiCH₃). MS(EI+) m/z (%): 442 (35), 263 (55), and 237 (100).

Ethyl(3-benzylindenyl)(2-methylbenz[*e*]indenyl)zirconium Dichloride (meso-2 and rac-2). *n*-Butyllithium (8.25 mL, 13.2 mmol, 1.6 M in hexane) was added dropwise to a precooled (0 °C) solution of 1-benzyl-3-[2-(1*H*-inden-1-yl)ethyl]-1*H*-indene (2c) (2.3 g, 6.6 mmol) in 150 mL of diethyl ether. Stirring was continued for 2 h at room temperature. Diethyl ether was removed. Precooled (-78 °C) precipitate and 150 mL (-78 °C) of dichloromethane were combined. When the temperature of the mixture had stabilized to -78 °C, zirconium tetrachloride (1.54 g, 6.6 mmol) was added and the reaction mixture was allowed to warm to room

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temperature. After stirring overnight at room temperature the reaction mixture was filtered and evaporated in vacuo. Diastereomers were separated by recrystallization from toluene/hexane mixtures. *Meso-* and *rac-*isomers were yellow powders, and yields were 1.1 g (30%) and 0.74 g (22%), respectively. **meso-2** ¹H NMR (CHCl₃): δ 7.56–6.99 (m, 13H) 6.76 (d, ²J_{HH} = 3.29 Hz, 1H) 6.41 (d, ²J_{HH} = 3.30 Hz, 1H) 6.20 (s, 1H), 4.18 (s, 2H) 3.98 (m, 2H) 3.59 (m, 2H). MS(EI+): *m/z* (%) 508 (90), 473 (45), 382 (100). HRMS-(EI+) *m/z* for C₂₇H₂₂Cl₂Zr: observed 506.0123; error -4.5 ppm. **rac-2** ¹H NMR (CHCl₃): δ 7.66–7.02 (m, 13H) 6.57 (d, ³J_{HH} = 3.3 Hz, 1H), 6.23 (d, ³J_{HH} = 3.3 Hz 1H), 5.95 (s, 1H), 4.03 (AB, ²J_{HH} = 21.62 Hz, 2H), 3.71 (m, 4H). MS(EI+) *m/z* (%): 508 (100), 473 (70), 382 (95). HRMS(EI+) *m/z* for C₂₇H₂₂Cl₂Zr: observed 506.0121; error -5.0 ppm.

Dimethylsilyl(3-benzylindenyl)(2-methylbenz[e]indenyl)zirconium Dichloride (meso-3 and rac-3). n-Butyllithium (15 mL, 23.9 mmol, 1.6 M in hexane) was added dropwise to a precooled (0 °C) solution of (3-benzylindenyl)(2-methylbenzindenyl)dimethylsilane (3c) (5.3 g, 12 mmol) in 150 mL of diethyl ether. Stirring was continued for 2 h at room temperature. Diethyl ether was removed. Precooled (-78 °C) precipitate and 150 mL (-78 °C) of dichloromethane were combined. When the temperature of the mixture had stabilized to -78 °C, zirconium tetrachloride (2.8 g, 12 mmol) was added and the reaction mixture was allowed to warm to room temperature. After stirring overnight at room temperature the reaction mixture was filtered and evaporated in vacuo. Diastereomers were separated by recrystallization from toluene/hexane mixtures. Meso- and rac-isomers were yellow powders, and yields were 1.1 g (15%) and 0.6 g (8%), respectively. meso-3 ¹H NMR (CHCl₃): δ 7.95 (d, ${}^{3}J_{HH} =$ 7.33 Hz, 1H), 7.59–7.23 (m, 7H), 7.16–7.01 (m, 7H), 6.80 (m, 1H), 5.76 (s, 1H), 4.12 (AB, ${}^{2}J_{HH} =$ 19.05 Hz, 2H), 2.26 (s, 3H), 1.34 (s, 3H,), 0.97 (s, 3H). MS(EI+): m/z (%) 602 (100), 567 (90), 237 (40). HRMS(EI+) m/z for $C_{32}H_{28}Cl_2SiZr$: observed 600.0370; error -2.4 ppm. rac-3 ¹H NMR (CHCl₃): δ 7.98 (m, 1H), 7.71 (m, 1H), 7.60-7.00 (m, 13H), 6.90 (m, 1H), 5.68 (s, 1H), 3.85 (AB, ${}^{2}J_{HH} = 16.12$ Hz, 2H), 2.26 (s, 3H), 1.21 (s, 3H), 1.08 (s, 3H). MS(EI+) m/z (%): 602 (90), 567 (100), 237 (45). HRMS(EI+) m/z for C₃₂H₂₈Cl₂SiZr: observed 600.0442; error +9.6 ppm.

Polymerization Studies. Propene polymerizations with **meso-3** and **rac-3** were carried out in a 1 L Büchi steel autoclave. The monomer consumption and pressure as well as the inside temperature were controlled by computerized real-time monitoring. First MAO (Al:Zr = 2000) and 280 mL of toluene (distilled over sodium after 1.5 h refluxing) were loaded into the autoclave, and the temperature was set. After the temperature was set the propene pressure was adjusted to the desired level and the zirconium dichloride complex (**meso-3** or **rac-3**) in 20 mL of toluene was injected into the autoclave. The polymerization reaction was quenched in 400 mL of acidic methanol. After stirring an hour the precipitate was washed carefully with methanol for 2 h and dried overnight at 60 °C.

Polymerizations with **meso-2** and **rac-2** were carried out in a 0.5 dm³ Büchi stainless steel autoclave equipped with a propeller-like stirrer. Toluene (300 mL, pro analysis, supplied by Merck) was used as solvent. Toluene and propene (3.5, Messer) were purified by passing through three columns containing molecular sieves, CuO, and Al₂O₃. MAO (10% solution in toluene, Crompton Corporation) and TIBA (Crompton Corporation) were used as delivered. Cocatalyst, [HNPhMe₂]-[B(C₆F₅)₄], was purchased from Akzo Nobel.

The progress of the polymerization was followed using a mass-flow meter to monitor the propene consumption. Weight average molecular weights (M_w) and molecular weight distributions (MWD) were measured at 140 °C with a Waters Alliance 2000 size exclusion chromatography instrument (SEC) equipped with Waters HT3, HT4, HT5, and HT6 columns. 1,2,4 -Trichlorobenzene was used as solvent, and the flow rate was 1.0 cm³/min. The columns were universally calibrated with narrow molecular weight polystyrene standards.

Solid-State Structure. A crystal suitable for X-ray measurements was selected and mounted on a glass fiber using the oil drop method,¹⁶ and the data were collected at 173 K using a Nonius KappaCCD diffractometer. The intensity data were corrected for Lorentz and polarization effects and for absorption by the multiscan method.¹⁷ The crystal structures were solved and refined with SHELX97.¹⁸ Graphics were done using the SHELXTL¹⁹ program package. The hydrogen atoms were introduced into their calculated positions and refined with fixed geometry with respect to their carrier atoms or were picked from the residual electron density map without further refinement.

Computational Studies. Cationic isobutyl-substituted complexes of **meso-3** and **rac-3** were used in the computational studies. Isobutyl was used to mimic a growing polymer chain. Benzyl rotation calculations were done while propene was coordinated on the benzyl side of the catalyst and isobutyl on the other side. Benzyl rotated in 20-degree steps around its bond to an indenyl group.

Calculations were performed by the hybrid density functional B3LYP method. Huzinaga's all-electron basis set (Zr, 433321/433/421)²⁰ was used for zirconium and the standard $6-31G^*$ basis set for other atoms. All complexes were verified as either a minimum or a transition state by vibrational frequency calculations. All calculations were carried out by Gaussian 03 quantum chemistry software.²¹

Results and Discussion

Ligands and Complexes. To gain more understanding about the influence of the benzyl group on the catalyst stereoselectivity and chain growth, the ligand framework in meso-1 and rac-1 was modified by attaching a methyl group to the $2(\alpha)$ -position and a benzo substituent to the 4- and 5-positions (meso-3 and rac-3 in Scheme 2). The former is supposed to increase the molar mass of the polymer, while the latter is known to improve metallocene catalysts' activity and stereoselectivity.²² In addition, ethyl-bridged analogues of 1 (meso-2 and rac-2) were prepared to increase the flexibility of the ligand framework. The selected ligands and complexes were prepared by using straightforward synthesis

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routes, and the *rac*- and *meso*-diastereomers were separated by fractional recrystallization. It should be noted that *meso* and *rac* abbreviations are used in this article intentionally to symbolize the orientation of the indenyl ligand in the complex, although both are actually racemic mixtures of two enantiomers.

A solid-state structure was measured for *meso-*[(3-benzyl- $1-\eta^5$ -indenyl)(2-methylbenz[*e*]- $1-\eta^5$ -indenyl)dimethylsilane]zirconium dichloride (**meso-3**) (Figure 2). A comparison of the solid-state structure of **meso-3** with the previously published structure of **meso-1**¹³ does not show any significant differences in angles or distances between zirconium and Cp rings. The angle of the Cp planes in the structure is nearly the same as in the unsubstituted **meso-1**, being 1.15 degrees smaller. In both crystal structures the benzyl group points away from the metal center. Accordingly, as the coordination spheres of **meso-1** and **meso-3** are similar, possible differences in propene polymerization arises from the α -methyl and 4,5-benzo substituents of **meso-3**.

Polymerization. Diastereomers of MAO-activated metallocene complexes 1-3 were studied in propene polymerization, and classical rac-Et(Ind)ZrCl₂ (EBI) was used for a comparison. Under similar polymerization conditions (50 °C and 0.71 M propene) EBI/MAO gave 6.6 times higher, benzo-substituted rac-3/MAO gave 4.1 times higher, and the ethyl-bridged rac-2/MAO gave 1.6 times higher activities than rac-1. When compared to rac-1, the influence of the α -methyl and the 4,5-benzo substituents in **rac-3** is clearly seen, besides in the higher activity, in improved isotacticity and molar mass of the PP (Table 1). As for rac-1 and meso-1, detailed pentad analysis reveals that also the diastereomer pair rac-3 and meso-3 produced nearly identical PP, even if the polymerization conditions were varied (Figure 3). Produced polypropenes have a pentad ratio of [mmmr]:[mmrr]: $[mrrm] \approx 2:2:1$, and this indicates the presence of enantiomorphic site control. Furthermore, the facts that catalysts lose their stereocontrol with increasing temperature and catalysts improve the stereocontrol with increasing monomer concentrations point to a chain migratory insertion mechanism rather than a chain back-skipping mechanism (Table 1 and Figure 3).²³



Figure 2. Solid-state structure of *meso*-dimethylsilyl(3-benzyl- η^{5} -indenyl)(2-methyl[4,5]benz- η^{5} -indenyl)zirconium dichloride (**meso-3**). Atoms are represented by anisotropic displacement ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (deg): Cp_{plane}-Cp_{plane}, 60.95; Cp_{center}-Zr-Cp_{center}, 128.46; Cp_{center}(lower)-Zr, 2.222; Cp_{center}(upper)-Zr, 2.250.

In general, the polymerization activities of the dimethylsilyl-bridged **rac-1**/MAO and the ethyl-bridged **rac-2**/MAO do not differ markedly from each other, but the latter produces PP with slightly lower isotacticity and molar mass (Table 1). As with **rac-3**/MAO, isospecificity of the catalysts reduces rapidly with the increasing reaction temperature, while decreasing monomer pressure has only a modest influence (Figure 3). At very low propene concentrations (here 0.48 M) the chain end epimerization strengthens and reduces significantly the activity as well as the isotacticity. This is typical for catalysts working under the enantiomorphic site control mechanism.²⁴

Opposite the diastereomers pairs of 1 and 3, rac-2/MAO turned out to be more active than meso-2/MAO, and more surprisingly the latter produces PP with 7% lower [mmmm] pentad content at 50 °C and 0.71 M propene. The change of MAO with borate cocatalyst did not introduce any significant differences in polymer pentad distribution, although a slight decrease in PP stereoselectivity and molar mass is observed. Also, the counterion does not influence the ratio of stereoselectivity between rac-2/MAO and meso-2/MAO diastereomer pairs (Table 1).

Due to the flexible ethylene bridge, the indenyl ligands have a chance to move between the forward and backward conformations. By blocking this fast flip between the conformers with a bridge substituent, Rieger et al. have shown that the conformers have a marked difference in stereoslectivity; the forward conformer has significantly higher stereocontrol than the backward conformer.²⁵ The presence of these conformers

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Table 1. Propene Polymerization Results of the MAO-Activated Complexes^a

catalyst run id	temp (°C)	[C ₃] (M)	$t_{\rm p}^{\ b}$ (min)	yield (g)	activity ^c	[mmmm] (%)	[mmmr] (%)	[mmrr] (%)	[mrrm] (%)	${M_{ m w}}^d$ (kg/mol)	PD^e	$T_{\rm m}^{f}$ (°C)
rac-1 ¹³	30	0.71	60	2.9	0.8	45.3	15.5	15.4	7.7	38	2.0	74
rac-1	50	0.48	33	0.9	1.4	37.1	16.1	16.2	8.3	16	2.0	62
rac-1	50	0.71	31	4.6	2.5	40.2	16.0	15.8	8.1	25	1.9	67
rac-1	50	1.16	44	11.3	2.7	41.9	15.9	15.5	8.0	29	1.9	69
rac-1	50	1.76	33	14.2	3.0	44.1	15.6	15.3	7.7	33	2.1	73
rac-1	50	3.38	34	24.4	2.6	45.0	15.4	15.1	7.6	38	2.0	76
rac-1	70	0.71	35	8.6	4.2	26.4	15.9	16.7	8.4	12	2.4	n.d.'
rac-1	85	0.71	41	14.2	5.9	15.9	13.2	14.8	7.7	4.8	2.2	n.d.
rac-2	30	0.71	30	2.5	1.4	52.3	14.7	13.7	6.8	30	2.0	92
rac-2	50	0.48	30	1.3	1.1	33.5	16.5	16.7	8.3	11	1.8	72
rac-2	50	0.71	30	7.3	4.1	45.9	15.6	15.1	7.5	18	1.8	80
rac-2	50	1.16	30	13.2	4.6	50.1	15.1	14.2	7.1	24	1.9	88
rac-2	50	1.76	30	25.6	5.8	53.5	14.4	13.6	6.8	29	2.0	94
rac-2	70	0.71	30	16.5	9.3	33.3	16.4	16.9	8.5	9.7	1.8	n.d.
rac-2	85	0.71	30	22.7	12.8	20.2	15.3	16.6	8.5	5.6	1.8	n.d.
rac-2 ^g	50	0.71	50	2.9	1.7	42.9				14	1.8	
meso-2	30	0.71	30	2.4	1.4	45.4	15.0	14.0	6.8	23	2.3	n.d.
meso-2	50	0.71	30	5.1	2.8	39.0	16.0	14.9	7.7	13	2.1	n.d.
meso-2	50	1.16	30	10.2	3.5	43.0	15.1	14.6	7.0	17	2.1	82
meso-2	50	1.76	30	14.8	3.4	45.7	15.0	14.0	7.0	21	2.2	89
meso-2	70	0.71	30	12.0	6.8	27.8	15.7	16.2	7.7	7.3	1.8	n.d.
meso-2	85	0.71	30	12.5	7.0	17.3	14.1	15.4	7.8	4.5	1.8	n.d.
meso-2 ^g	50	0.71	50	4.5	2.5	36.8				9.0	1.8	
rac-3	30	0.71	33	3.0	3.0	64.5	12.1	11.7	5.8	133	2.38	108
rac-3	50	0.48	31	4.7	7.6	53.5	14.5	14.2	7.0	26	2.13	91
rac-3	50	0.71	30	9.2	10.2	57.2	13.7	13.4	6.6	37	2.11	96
rac-3	50	1.16	30	16.5	11.2	60.3	13.1	12.8	6.3	41	2.09	100
rac-3	50	1.76	31	29.8	13.1	61.9	12.6	12.2	6.0	51	2.02	104
rac-3	50	3.38	31	52.7	12.2	62.5	12.5	12.1	5.9	68	1.99	106
rac-3	70	0.71	31	16.9	18.3	39.1	15.8	16.1	8.0	16	2.76	n.d.
rac-3	85	0.71	33	14.4	14.7	20.6	14.8	16.5	8.3	5.8	2.38	n.d.
meso-3	30	0.71	36	2.4	4.5	67.9	11.7	11.0	5.3	131	2.4	111
meso-3	50	0.48	30	3.7	12.4	51.4	15.0	15.1	7.3	41	2.05	84
meso-3	50	0.71	30	6.8	15.3	55.4	14.1	14.0	6.9	49	2.03	92
meso-3	50	1.16	31	10.8	14.2	59.8	13.2	12.8	6.3	54	2.06	100
meso-3	50	1.76	31	16.2	14.4	63.6	12.4	11.8	5.8	66	1.96	106
meso-3	50	3.38	31	18.4	8.51	65.5	11.8	11.3	5.5	79	2.07	110
meso-3	70	0.71	33	9.4	19.0	38.5	16.2	16.7	8.1	17	2.35	67
meso-3	85	0.71	32	7.9	16.9	21.3	15.2	17.0	8.3	6.8	2.34	n.d.

^{*a*}In toluene and Al:Zr = 2000 See Supporting Information for detailed pentad analysis. ^{*b*}Polymerization time. ^{*c*}Activity expressed as kg polymer/[(mmol Zr)[C₃] h]. ^{*d*}Weight average molar mass. ^{*e*}Polydispersity. ^{*f*}Polypropene melting temperature. ^{*g*}Borate cocatalyst. ^{*h*}Not detected.



Figure 3. Isotactic pentads as a function of polymerization temperature (left) and propene concentration (right).

in ethyl-bridged **2** explains in general the reduced stereoregularity as well as molar mass when compared those of **1**. Apparently, the different stereoselectivity of **rac-2**/MAO and **meso-2**/MAO is also connected to the presence of the bridge conformers and illustrates the different steric shielding caused by the rotating benzyl group and aromatic indenyl ring at the β -positions.

Computational studies were performed to understand in more detail the influence of the benzyl substituent on propene polymerization, especially on the origin of the stereospecificity and the high molar mass of the polymers produced by the *meso*-diastereomers. In **meso-3** one of the coordination sites is shielded only by the benzyl substituent (A-site), while the other (B-site) is heavily shielded by the indenyl and benz[*e*]indenyl groups (Figure 4). When the growing PP chain lies on the A-site, the $C(\alpha)-C(\beta)$ chain segment of the polymer tends to orientate down toward the benz-[*e*]indenyl ligand, and thus the propene coordinated on the B-site is *re*-coordinated; that is, the methyl group points toward the benzylindenyl (Figure 5). The B-site is clearly stereoselective for propene coordination. After insertion the



Figure 4. Structures of the complexes used in the calculations. The dimethylsilyl bridges between the Cp moieties and hydrogen atoms are omitted for clarity.



Figure 5. Optimized structures of meso- and rac-3 bearing a coordinated propene at the A-site and an isobutyl ligand as a model for the polymer chain at the B-site illustrate two important energy minima of the benzyl rotation. The dimethylsilyl bridges between the Cp moieties and the hydrogen atoms are omitted for clarity.

polymer chain moves to the B-site, and now propene can coordinate to the A-site next to the rotating benzyl group. As the B-site is shielded by indenyl and benz[*e*]indenyl groups, the growing chain slightly prefers the orientation toward the indenyl. The propene coordination on the A-site leads to random stereoerror formation. As a result, **meso-3** produces isotactic PP with variable amounts of stereoerrors.

In rac-3, the B-site is surrounded by the indenyl group, while the A-site is shielded by the benzyl substituent and the benz[*e*]indenyl ligand (Figure 4). When the polymer chain is located on the B-site, the $C(\alpha)-C(\beta)$ chain segment has a clear preference to point down to the benz[*e*]indenyl ligand and the propene coordination on the A-site occurs selectively from the *si*-side (i.e., the methyl group of propene points up toward the benzyl group) (Figure 5). The chain at the more shielded A-site has no clear preference for the orientation, and this causes the formation of stereoerrors. It is plausible that **rac-3** and **meso-3** produce PP with similar tacticity.

Cationic complexes of **meso-** and **rac-3** bearing a coordinated propene and an isobutyl ligand as a model for the polymer chain were selected for starting points to investigate the role of the benzyl substituent in the activated metallocene (Figure 5). Accordingly, when propene coordinates to the A-site and the polymer chain (isobutyl ligand) occupies the B-site, the benzyl substituent can rotate quite freely around its Cp–CH₂ bond. The energy barriers of the rotations are nearly independent of the used diastereomer and propene enantioface (Figure 6). In both diastereomers the Cp–CH₂–Ph angle varies between 111° and 123° during a 360-deg rotation.

The most stable rotamer for all of these complexes is achieved when the dihedral angle $(C_{Ph}-CH_2-C_{Cp}-C_{Cp})$ is 60°; that is, benzyl is pointing upward, away from the cationic metal center (compare to the orientation of the benzyl group in the solid state, Figure 2). Another significant minimum is located around 165°. Here the benzyl substituent is approximately in the plane of the indenyl ligand and occupies the place where a methyl substituent in α -position to the bridge head atom would be if present. These α -substituents are known to be important, as they diminish the rate for the chain termination via β -H elimination, and as a result, polymers with increased molar mass are obtained.^{3,23,26} This effect is also seen here when the molar mass of PPs from 1/MAO and 3/MAO are compared (Table 1). As benzyl-substituted meso-2 produces PP with clearly higher molar mass than the unsubstituted meso-Et(Ind)ZrCl₂, this rotamer seems to have, indeed, a role in polymerization (determining the molar mass). This mechanistic insight provides also an explanation for the dramatic influence of the reaction temperature on molar mass of the polymers. An increase in thermal energy allows benzyl to rotate more freely, thus increasing the tendency for β -H elimination and causes short-chain PP at high temperatures. This can be detected from Table 1.

As reported previously, a benzyl substituent in the cyclopentadienyl ligand has a tendency to coordinate with the cationic metal center.²⁷ Benzyl coordination is favored over propene coordination by 11-23 kJ/mol. The energy differences are not high enough to block the polymerization, but certainly reduce the catalytic activity in comparison to metallocenes without the benzyl group (activity of EBI is 6.6 times higher than with **rac-1**). It is worth noticing that the rotation energy required to substitute coordinated benzyl with propene (Figure 6). According to the modeling, the benzyl group may also turn away from the coordination site to give enough space for propene coordination with the metal center.

To provide an estimate of the overall capability of the benzyl substituent to block the active metal center, we have calculated the transition state for *si*-propene insertion to benzyl-coordinated **meso-3** complex. The height of the activation barrier is 53.4 kJ/mol, suggesting that the coordinated benzyl group is effective in blocking the active site, but the

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Figure 6. Energy curves of meso- and rac-3 bearing a coordinated propene at the A-site and an isobutyl ligand at the B-site during the benzyl rotation against the Cp–Bn dihedral angle. At 60° benzyl is pointing away from the zirconium, and at 165° the phenyl ring is residing in the position of the α -substituent of the indenyl ligand (see Figure 5).

energy is not that high that it prevents the withdrawal of the benzyl group to allow the propene coordination and chain propagation to initiate. Likely, the overall result is the loss of activity, also observed experimentally.

Conclusions

Unlike typical metallocene catalysts, the diastereomer pairs of the studied unsymmetric catalysts produce PP with similar activity, tacticity, and molar mass. While similar stereoselectivity in the diastereomer pairs is mainly explainable by β -substituents in the studied ligand frameworks, the intriguing similarity in molar mass of the polymers arises from the rotating benzyl group. Quantum chemical calculations show that the benzyl group in the diastereomeric pairs where both propene and polymer chain are coordinated on the zirconium has two preferable energy minima while it rotates around the CH_2 -Cp axis. In this case the phenyl ring tends to point away from the active center or to locate in the indenyl plane. The former rotamer has no direct influence on the chain growth, whereas in the latter rotamer the benzyl group acts as a 2-methyl substituent and therefore reduces the rate of chain terminations. Due to this rotamer, the indenyl ligand has two preferred energy minima and resembles occasionally a classical fluorenyl ligand and, therefore, causes the similarity in polypropene molar mass regardless of the applied diastereomer.

Polymerization conditions have a strong influence on catalytic activity, stereoselectivity, and polymer molar mass. At low polymerization temperature the benzyl group has limited mobility and it occupies the coordination place for an incoming monomer. This is the reason for the low activity. When occasionally replaced by propene, the benzyl group swings to the indenyl plane. This causes the high molar mass of the polymer. As the catalysts work under the enantiomorphic site control mechanism, a low temperature is needed for high stereospecificity. With increasing reaction temperature, the energy for the benzyl ring rotation increases and this causes a substantial decrease in stereospecificity and in PP molar mass, whereas benzyl spends less time around the active center and thus the activity substantially increases. The benzyl-substituted catalysts respond as classical C_2 -symmetric metallocenes toward changes in monomer concentration. The stereoselectivities of the catalysts and molar masses of the PPs increase steadily with elevated propene concentrations. At low propene concentrations (at 0.48 M) polymerization activity declines due to the chain end epimerization.

In general, this study underlines that a rotating substituent can indeed be applied in catalyst design and a catalyst with high response under the reaction conditions can be designed. It is an intriguing idea to apply similar concepts in different fields of homogeneous catalysis and to improve by this manner catalysts' response to changes in reaction conditions.

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Supporting Information Available: Crystallographic data for **meso-3** are available as a CIF file. Detailed pentad analysis of the PPs is provided. This material is available free of charge via the Internet at http://pubs.acs.org.