Asymmetric Metallocene Catalysts Based on Dibenzothiophene: A New Approach to High Molecular Weight Polypropylene Plastomers

Sandra Deisenhofer,† Tanja Feifel,† Jürgen Kukral,† Martti Klinga,‡
Markku Leskelä,‡ and Bernhard Rieger*,†

Department for Materials and Catalysis, University of Ulm, D-89069 Ulm, Germany, and
Department of Inorganic Chemistry, University of Helsinki, FIN-00014 Helsinki, Finland

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Synthesis and polymerization data of a series of new sulfur-containing C_1-symmetric metallocenes,*rac*-[1-(9-η^5-fluorenyl)-2-(2-methylbenzo[*b*]indeno[4,5-*d*]thiophen-1-η^5-yl)ethane]-zirconium dichloride (**7a**), *rac*-[1-(9-η^5-fluorenyl)-2-(2-methylbenzo[*b*]indeno[4,5-*d*]thiophen-1-η^5-yl)ethane]hafnium dichloride (**7b**), *rac*-[1-(9-η^5-fluorenyl)-2-(2-methylbenzo[*b*]indeno[4,5-*d*]thiophen-1-η^5-yl)ethane]hafnium dimethyl (**7c**), and *rac*-[1-(9-η^5-fluorenyl)-2-(2-methylbenzo[*b*]indeno[4,5-*d*]thiophen-3-η^5-yl)ethane]zirconium dichloride (**8**), are reported. The characteristic structural feature of these complexes is the 2-methyl-1*H*-benzo[*b*]indeno[4,5-*d*]thiophene moiety (**3**: MBIT), which was derived from dibenzothiophene. In the case of **7a**−**c** the MBIT unit shows a “back” orientation, whereas in **8** it is directed to the “front” of the tetrahedral metallocene dichloride species, which was unambiguously illustrated by X-ray structure analysis. Propylene polymerization experiments revealed higher activity and stereoselectivity for **7a**/MAO compared to **8**/MAO. The catalysts **7a**,**8**/MAO were found to operate under different polymerization mechanisms indicated by a diverse correlation of tacticity and polymerization temperature. Crystalline, flexible polypropylenes with tacticities ranging from 65 ≤ [mmmm] ≤ 90 and molecular weights up to 2×10^5 g mol^{-1} were obtained for **7a**/MAO, whereas experiments using **8**/MAO produced low tacticity, waxy materials. To achieve ultrahigh molecular weight isotactic polypropylene plastomers (M_w up to 1.5×10^6 g mol^{-1}), further investigations on the hafnium dimethyl complex **7c**/[$(C_6H_5)_3C^+$][$(C_6F_5)_4B^-$] in liquid propylene were performed.

Introduction

One major challenge in polymerization catalysis of olefins is the precision control of polymer microstructures, which allows the designing of material properties.[1] In recent times, tailor-made C_1-symmetric metallocene catalysts gave access to polymers of varying microstructures depending on the nature of the active metal center and on the particular ligand substitution.[2−4] In 1999, we presented a new family of highly active zirconocene dichlorides that allowed the programming of single stereoerrors along an isotactic chain, depending on the monomer concentration.[5] These asymmetric “dual-side” catalysts (e.g., **6a**,**b**, Scheme 1) possess alkyl[6] or alkoxy[7] substituents in the 5,6-position of the indenyl moieties that suppress chain-end epimerization reactions[8−10] and lead to improved activities and to

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† University of Ulm.

‡ University of Helsinki.

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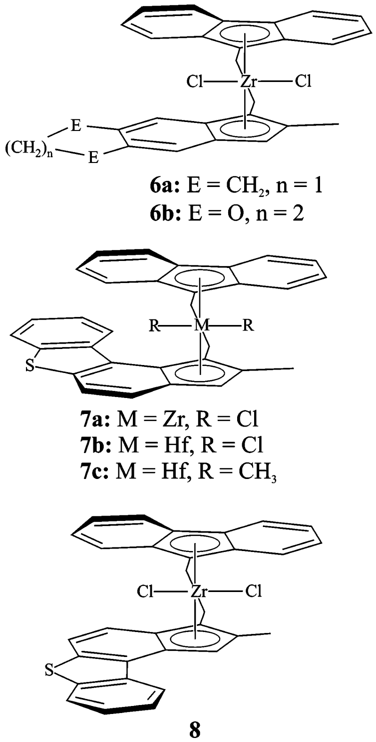
Scheme 1



6a: E = CH_2, n = 1
6b: E = O, n = 2

7a: M = Zr, R = Cl
7b: M = Hf, R = Cl
7c: M = Hf, R = CH_3

8

ultrahigh molecular weights.[11] However, these 5,6-substituted metallocene catalysts afford high concentrations of isolated stereoerrors, leading to “soft” polypropylenes of low crystallinity, although with excellent elastomeric properties.

To extend the portfolio of material properties toward isotactic plastomers[12] (higher stiffness materials), we intended to look for other structural motifs that should maintain the excellent performance of our asymmetric catalysts but might afford higher tacticity values. We focused on rigid substituents in the 6,7-position of the 2-methylinden-1-yl fragment to create a situation with a similar enantiofacial discrimination of the prochiral propene monomer on either complex side in the migratory polyinsertion reaction. We report here on synthesis, characterization, and polymerization performance of the novel asymmetric, heteroatom-containing zirconocene and hafnocene catalysts **7a**−**c** and **8** (Scheme 1)[13] bearing a substituted indenyl fragment derived from dibenzothiophene. This indene unit points backward in the complexes **7a**−**c**, whereas in **8** the same fragment adopts a forward orientation.

Results and Discussion

Ligand and Complex Synthesis. 2-Methyl-1*H*-benzo[*b*]indeno[4,5-*d*]thiophene (**3**: MBIT) was prepared by a recently published three-step procedure describing a facile route to 2-methylindenes in up to 80% overall yield (Scheme 2).[5] Starting from methacrylic acid chloride (MAC) and dibenzothiophene (**1**), the corresponding ketone (**2**) was obtained in a one-pot reaction by Friedel−Crafts acylation and subsequent Nazarov cyclization. Reduction of the ketone, followed by water elimination, afforded MBIT (**3**) as a crystalline solid. Interestingly, deprotonation with *n*-BuLi leads to a further proton abstraction of the acid protons in α-position to the sulfur atom.[14] Therefore MBIT was deprotonated with *p*-anisyllithium, which was prepared separately by the reaction of *p*-bromoanisole and *n*-BuLi.[15,16] A 1:1 mixture of the isomeric, ethylene-bridged ligands **5a**,**b** was prepared by treatment of 2-(9-fluorenyl)ethyl trifluoromethanesulfonate (**4**)[17] with Li-MBIT. Trials to separate **5a**,**b** by crystallization or chromatography over silica remained unsuccessful. The orange zirconocene complexes **7a**,**8** (1:1 ratio) were synthesized by reaction of the dilithio salts of **5a**,**b** with $ZrCl_4$ in toluene. Pure **7a** was obtained by crystallization from toluene. Repeated fractionation of the mother liquor afforded the isomer **8** also in crystalline form. Analogous reaction conditions were required for synthesis and separation of the hafnocene dichloride species **7b**.[18] Treatment of the dichloro compound **7b** with an excess of methyllithium in ether and extraction of the crude product with toluene yielded the dimethyl complex **7c**.

Solid State Structure. A single-crystal X-ray structure investigation was performed on complex **7a** (Figure 1, Table 1), which crystallizes in the triclinic space group $P\bar{1}$.[19] Suitable crystals were obtained by diffusion of pentane in a toluene solution of **7a**. The front view of complex **7a** (Figure 1A) reveals that the position of the ethylene bridge at C3 of the MBIT unit and the connection of the benzothiophene fragment to C8 and C15 of the basic indenyl ring lead to a back orientation of this moiety with the sulfur atom pointing outward. Due to the distant position of the sulfur atom, unfavorable intramolecular interactions with the zirconium center are excluded.

The side view of complex **7a** (Figure 1B) indicates some peculiarities of the complex architecture. The

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(10) Yoder, J. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 2548.

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(12) In contrast to conventional isotactic polypropylene (95 ≤ [mmmm] ≤ 100) with high stiffness and homopolypropylene elastomers (25 ≤ [mmmm] ≤ 60) showing rubber elastic behavior nonelastic but flexible polymers in the range of 60−95% tacticity are named “plastomers”. Compared to highly isotactic thermoplastic materials, plastomers display lower stiffness and show therefore increased flexibility.

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(15) BuLi as a strong base deprotonates the Cp ring as well as the aromatic proton in α-position to the sulfur atom. By use of the weaker base *p*-anisyllithium only the desired deprotonation of the Cp ring could be achieved.

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(18) The corresponding “forward-isomer” of the hafnocene complexes was formed in a 1:1 mixture with **7b**. However, it was not separated due to the poor polymerization performance of the isostructural Zr analogue.

(19) Trials to grow crystals from **8** for determination of the overall structure have been successful. Complex **8** crystallizes in the monoclinic space group $P2_1/n$ with a = 11.518(4) Å, b = 14.572(4) Å, c = 18.145(4) Å, β = 101.69(3)°, V = 2982.3(15) Å^3, and Z = 4. The results show clearly the general connectivity and the “front-orientation” of the MBIT unit as suggested in Scheme 1. However, due to poor quality of data and statistical indicators, the results are not suitable for publication.

Scheme 2

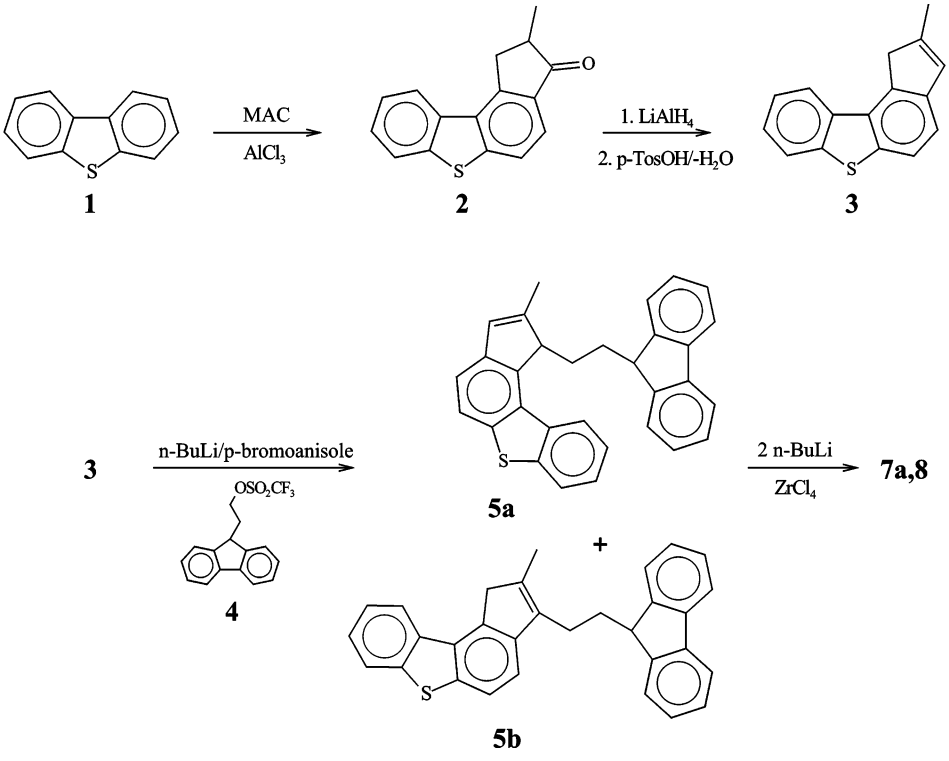

Table 1. Summary of Crystal Data and Structure Refinement Parameters for 7a

chemical formula	$C_{31}H_{22}Cl_2SZr$
fw	588.67
cryst color and form	orange plate
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	9.789(4)
b (Å)	14.815(6)
c (Å)	8.821(4)
α (deg)	102.51(4)
β (deg)	96.51(3)
γ (deg)	100.18(3)
V (Å^3)	1213.8(9)
Z	2
D_C (Mg/m^3)	1.611
abs coeff μ (mm^{-1})	0.779
F(000)	596
cryst size (mm)	0.35 × 0.25 × 0.15
scan mode	$2\theta/\omega$
$\theta_{\max}$ (deg)	25.04
index ranges	$0 \le h \le 11$ $-17 \le k \le 17$ $-10 \le l \le 10$
no. of unique/all reflns	4279/4551
no. of obsd reflns [$I > 2\sigma(I)$]	3364
no. of params	316
goodness-of-fit on $S(F^2)^a$	1.019
final R indices [$I > 2\sigma(I)$]^b	$R_1 = 0.0486$, $wR_2 = 0.1121$
R indices (all data)^b	$R_1 = 0.0725$, $wR_2 = 0.1191$
largest differential peak and hole (e/Å^3)	0.738 and −0.613

[a] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters. [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

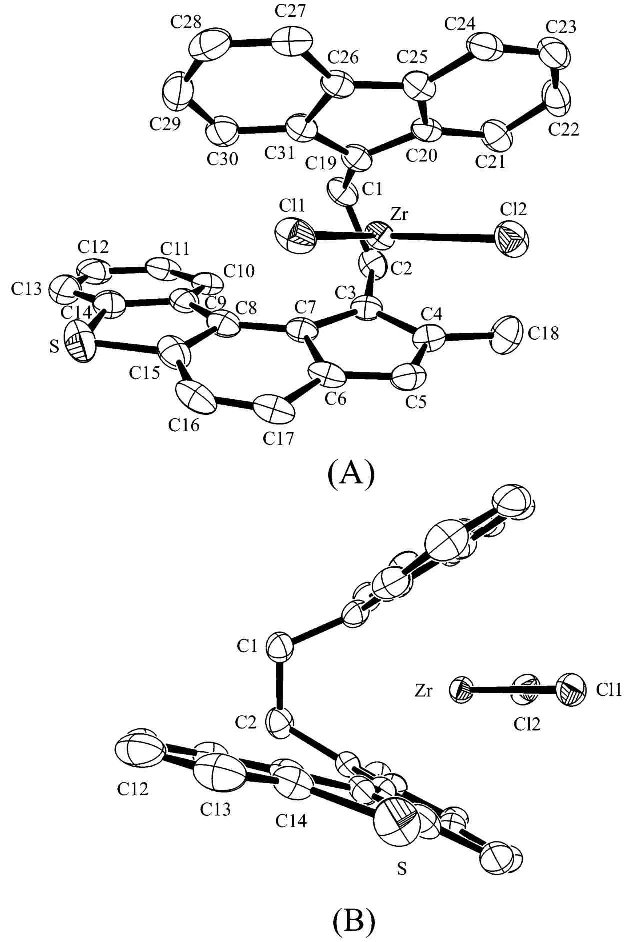

Figure 1. X-ray crystal structure of complex **7a**: (A) front view, (B) side view.

Cp^{Flu}–Zr–Cp^{MBIT} angle δ (Table 2:[20] 128.04(5)°) and ϕ (Table 2: 62.89(5)°), the bite angle between the least-squares planes of the two Cp ligands, are between those of the Zr complexes EBI[21] (δ: 126.9°[22], ϕ: 62.1) and EBF[23] (δ: 129.0°[24], ϕ: 64.3). The angle γ^{Flu} (Table 2:

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[20] Definitions of the *ansa*-metallocene angles: β = deviation from perpendicularity of the Zr–centroid vector. γ = distortion of the bridge atom from the Cp plane. δ = angle formed by the metal center and the ring centroid vectors. ϕ = bite angle between the least-squares planes of the two Cp ligands.

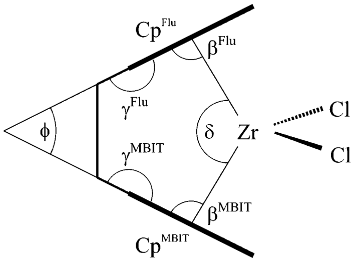

Figure 2. Schematic representation of bond angles listed in Table 2.

Table 2. Relevant Geometrical Parameters for 7a

β^{Flu} (deg)	80.74(5)
β^{MBIT} (deg)	88.33(5)
γFlu (deg)	189.47(5)
γMBIT (deg)	175.19(5)
ϕ (deg)	62.89(5)
δ (deg)	128.04(5)
Cl−Zr−Cl (deg)	96.80(6)
Zr−Cl(1) (Å)	2.4116(15)
Zr−Cl(2) (Å)	2.4238(17)
av Zr−centroid($\mathrm{Cp}^{\mathrm{MBIT}}$) (Å)	2.530(4)
av Zr−centroid($\mathrm{Cp}^{\mathrm{Flu}}$) (Å)	2.574(4)
Zr−centroid($\mathrm{Cp}^{\mathrm{MBIT}}$) (Å)	2.222(4)
Zr−centroid($\mathrm{Cp}^{\mathrm{Flu}}$) (Å)	2.271(4)
Zr1−C3 ($\mathrm{Cp}^{\mathrm{MBIT}}$) (Å)	2.504(4)
Zr1−C4 ($\mathrm{Cp}^{\mathrm{MBIT}}$) (Å)	2.497(5)
Zr1−C5 ($\mathrm{Cp}^{\mathrm{MBIT}}$) (Å)	2.507(5)
Zr1−C6 ($\mathrm{Cp}^{\mathrm{MBIT}}$) (Å)	2.571(4)
Zr1−C7 ($\mathrm{Cp}^{\mathrm{MBIT}}$) (Å)	2.570(4)
Zr1−C19 ($\mathrm{Cp}^{\mathrm{Flu}}$) (Å)	2.404(4)
Zr1−C20 ($\mathrm{Cp}^{\mathrm{Flu}}$) (Å)	2.535(4)
Zr1−C25 ($\mathrm{Cp}^{\mathrm{Flu}}$) (Å)	2.678(4)
Zr1−C26 ($\mathrm{Cp}^{\mathrm{Flu}}$) (Å)	2.696(4)
Zr1−C31 ($\mathrm{Cp}^{\mathrm{Flu}}$) (Å)	2.559(5)

189.47(5)°) differs from results previously reported for other bridged indenyl and fluorenyl complexes, for which typically values less than 180° were observed.[24] However, the resulting increased accessibility of the zirconium center is obviously one reason for the higher activity of complex **7a**.[25] Furthermore, we observed that the back orientation of the angular MBIT fragment possibly establishes an intramolecular repulsive interaction of the phenyl hydrogens in the rear position of the fluorenyl unit and the backward-orientated MBIT system. To avoid this unfavorable steric strain, the benzothiophene part of the ligand bends away from these hydrogens, resulting in deviation of the aromatic planarity.

The mean Zr(IV)−fluorenyl carbon distance of **7a** (2.574(4) Å) is distinctly longer than the distance between Zr(IV) and the carbon atoms of MBIT (2.530(4) Å), leading to a nonsymmetric positioning of the Zr(IV) center between the two Cp planes. The value of β^{Flu} close to 80° (Table 2: 80.74(5)°) and the corresponding Zr−C distances ranging from 2.404(4) to 2.696(4) Å point to a reduced hapticity of the fluorenyl fragment toward η^3 bonding.[26] In contrast, a β^{MBIT} value of 88.33(5)° indicates a nearly ideal η^5 coordination of the aromatic five-membered Cp ring of the MBIT moiety to Zr(IV).

Polymerization Studies. After activation with MAO the zirconocenes **7a**,**8**/MAO were shown to be suitable catalysts for the polymerization of propylene. To elucidate the mechanistic aspects, monomer and temperature dependencies of these new heterocenes were investigated (Table 3).

The polymerization activities of both catalysts increased with raising polymerization temperature and monomer concentration. The highest values in the case of MAO activation were obtained with **7a**/MAO (entry 3: $T_{\mathrm{p}} = 60$ °C, 13.5×10^3 kg PP (mol of Zr [C_3] h)$^{-1}$), whereas **8**/MAO produced polypropylenes with significantly reduced activity (entry 11: $T_{\mathrm{p}} = 60$ °C, 4.9×10^3 kg PP (mol of Zr [C_3] h)$^{-1}$). On the basis of the fact that carbon (2.55) and sulfur (2.58)[27] hardly differ in their electronegativities and due to the remote position of the sulfur atom, we do not contribute any activity values to electronic effects of the heteroatom.

In polymerization experiments with **7a**/MAO we obtained isotactic polypropylenes with [mmmm] pentad concentrations ranging from 65 to 85% and molecular weights up to 2×10^5 g mol^{-1}. Although a change in monomer concentration had no significant influence on tacticity, we observed the effect of linearly decreasing stereoselectivity with increasing polymerization temperature, which is in contrast to the expected chain back-skip mechanism of other asymmetric zirconocenes based on indenyl and fluorenyl units.[5] On the contrary, complex **8**/MAO produced low-tacticity polypropylenes with decreased molecular weights (entry 15: $T_{\mathrm{p}} = 30$ °C, [mmmm] = 17%, $M_{\mathrm{w}} = 5.9 \times 10^4$ g mol^{-1}).

Investigations on the hafnium dimethyl complex **7c**/[$(\mathrm{C}_6\mathrm{H}_5)_3\mathrm{C}^+$][$(\mathrm{C}_6\mathrm{F}_5)_4\mathrm{B}^-$] were performed to achieve a further molecular weight enhancement of the plastomers obtained with the isostructural complex **7a**/MAO (Table 3).[28] Polymerization experiments in liquid propylene showed that the molecular weight could be increased up to 1.5×10^6 g mol^{-1} at 0 °C accompanied by a slight drop in stereoselectivity.[29] These results are in accordance with our recent findings that significantly higher molecular masses could be obtained for borate-activated dimethyl complexes deriving from the absence of chain transfer to aluminum.[11]

Mechanistic Considerations. As demonstrated, the catalysts **7a**,**8**/MAO differ significantly in their polymerization behavior, indicating diverse mechanisms. The stereoselectivity of **8**/MAO declined with increasing monomer concentration and temperature, pointing to a reaction path that involves repeated migratory insertion of the chain to the monomer coordinated between the sterically demanding fluorenyl-indenyl moieties and a consecutive back-skip of the chain to the less hindered

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(21) Ethylene(bisindenyl)zirconium dichloride.

(22) Dang, V. A.; Yu, L.-C.; Balboni, D.; Dall'Occo, T.; Resconi, L.; Mercandelli, P.; Moret, M.; Sironi, A. *Organometallics* **1999**, *18*, 3781.

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(29) The broad molecular weight distribution results mostly from the insolubility of the ultrahigh molecular weight products in liquid propylene at lower temperatures.

Table 3. Polymerization Results of Propylene with Complexes 7a,8/MAO[a] and 7c/$[(C_6H_5)_3C^+][(C_6F_5)_4B^-]$[b]

entry	cat.	amount[c]	T_p[d]	$[C_3]$[e]	activity[f,g]	[mmmm][h]	M_w[i]	M_w/M_n
1	**7a**	4.0	60	0.7	5.4	64.8	7	2.2
2	**7a**	3.0	60	1.6	10.4	70.2	12	2.2
3	**7a**	1.9	60	2.6	13.5	70.4	16	2.3
4	**7a**	3.0	50	1.6	9.3	77.6	22	1.9
5	**7a**	5.0	30	1.6	1.6	86.3	148	1.8
6	**7a**	2.4	30	3.0	3.6	84.9	182	2.1
7	**7a**	2.5	30	5.1	8.6	82.2	200	1.9
8	**7c**	3.7	30	C_3H_6 (l)	15.9	77.7	254	2.6
9	**7c**	8.5	0	C_3H_6 (l)	5.3	75.4	1524	3.8
10	**8**	6.0	60	1.6	2.3	42.1	13	2.5
11	**8**	5.0	60	2.6	4.9	38.2	22	2.1
12	**8**	8.0	50	1.6	1.1	35.7	17	2.1
13	**8**	16.0	30	1.6	0.3	18.3	33	2.2
14	**8**	16.0	30	3.0	0.3	18.2	49	2.3
15	**8**	12.0	30	5.1	0.5	17.3	59	1.9

[a] Performed in toluene, Al/Zr = 2000. [b] Performed in liquid propylene, borate/Hf = 5. [c] [μmol]. [d] [°C]. [e] [mol L^{-1}]. [f] Entries 1−7, 10−15 in toluene: [10^3 kg of PP (mol of Zr $[C_3]$ h)$^{-1}$]. [g] Entries 8 and 9 in liquid propylene: [10^3 kg of PP (mol of Zr h)$^{-1}$]. [h] [%]. [i] [kg mol^{-1}].

Table 4. Pentad Distribution (in %) for Polypropylenes with 7a,8/MAO[a]

entry	cat.	[mmmm]	[mmmr]	[rmmr]	[mmrr]	[mmrm] + [rrmr]	[rrrr]	[rrrm]	[mrrm]
1	**7a**	64.8	14.5	n.o.[b]	15.4	≤1%	n.o.	≤1%	5.3
2	**7a**	70.2	12.3	n.o.	12.6	≤1%	n.o.	≤1%	4.9
3	**7a**	70.4	12.7	n.o.	12.2	≤1%	n.o.	≤1%	4.7
4	**7a**	77.6	9.9	n.o.	9.5	n.o.	n.o.	n.o.	3.0
5	**7a**	86.3	6.0	n.o.	6.0	n.o.	n.o.	n.o.	1.8
6	**7a**	84.9	6.4	n.o.	6.8	n.o.	n.o.	n.o.	1.8
7	**7a**	82.2	7.0	n.o.	7.4	n.o.	n.o.	n.o.	3.4
10	**8**	42.1	16.3	1.6	16.7	6.3	3.0	5.0	7.8
11	**8**	38.2	16.0	1.8	18.0	6.9	3.9	5.8	8.3
12	**8**	35.7	16.9	1.7	18.4	7.1	4.3	6.3	8.8
13	**8**	18.3	15.1	3.1	20.1	9.0	13.7	10.2	10.5
14	**8**	18.2	16.3	1.6	23.0	4.6	21.4	12.3	4.2
15	**8**	17.3	16.3	5.9	18.2	6.6	19.1	11.2	2.6

[a] [rmrm]: entries 1−7: not observed, entries 10−15: ≤1%. [b] n.o.: pentads not observed.

side.[5] At higher pressure isolated stereoerrors are formed because monomer coordination at the sterically less crowded side is faster than the chain back-skip. This is supported by the fact that the [mrmr] pentad is absent in the polymer samples (Table 4).

In polymerization reactions with catalyst **7a**/MAO the effect of increasing stereoselectivity with decreasing temperature could be observed, leading to isotactic homopolypropylenes with [mmmm] pentad concentrations in the range 65−85%. This is expected for a mechanism that is characteristic for C_2-symmetric metallocenes. Chien et al. reported a similar behavior for *rac*-[1-(9-η^5-fluorenyl)-2-(2,4,7-trimethyl-1-η^5-indenyl)ethane]zirconium dichloride and attributed this difference in the stereoerror formation to the fact that both sides of the catalyst are stereoselective; that is, isotactic polypropylene results in the same manner as for C_2-symmetric catalysts.[30] We assume for complex **7a**/MAO a similar polymerization mechanism where chain backskip plays only a minor role and stereoerror formation is mostly due to wrong enantiofacial insertion on both sides. The pentad ratio of [mmmr]:[mmrr]:[mrrm] ≈ 2:2:1, which is typical for isospecific metallocenes operating under enantiomorphic site control, supports this "C_2-symmetric-like" polymerization behavior (Table 4).

Conclusion

In the present study we focused on the synthesis and polymerization behavior of novel asymmetric, heteroatom-containing zirconocene and hafnocene catalysts bearing a substituted indenyl fragment ("MBIT") derived from dibenzothiophene. The structural characteristic of these catalyst architectures is the orientation of the MBIT moiety, either to the front (**8**) or to the back (**7**) of the complex. The direction of this fragment causes the resulting metallocenes to operate under different polymerization mechanisms indicated by a diverse correlation of tacticity and polymerization temperature. **7a**/MAO followed the trend observed for C_2-symmetric catalysts leading to the formation of isotactic, crystalline polypropylenes with [mmmm] pentad concentrations in the range 65−85%. In contrast, **8**/MAO produced reduced tacticity polypropylenes of lower molecular weight, pointing to an involvement of chain back-skip processes.

Asymmetric, 5,6-substituted metallocene species (e.g., **6a**,**b**; Scheme 1) afford high-performance homopolypropylene elastomers with low [mmmm]-pentad concentrations. Most importantly, the hafnium catalyst **7c**/$[(C_6H_5)_3C^+][(C_6F_5)_4B^-]$ of the present study opens access to a novel family of flexible polypropylene plastomers with isotacticities above 60% and ultrahigh molecular weights (up to 1.5×10^6 g mol^{-1}). This fills nicely the gap between the "soft" thermoplastic elastomers and the stiff polypropylene materials consisting of a nearly perfect isotactic microstructure. The precise correlation

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of microstructure, crystallization behavior, and material properties will be the subject of future investigations.

Experimental Section

General Procedures. All reactions were performed under dry argon atmosphere using standard Schlenk techniques. Hydrocarbon and ether solvents were dried by distillation from $LiAlH_4$, and methylene chloride was distilled from CaH_2. Dibenzothiophene, methacrylic acid chloride, *n*-BuLi, MeLi, $AlCl_3$, $ZrCl_4$, and $HfCl_4$ were used as received from Merck and Aldrich. $[(C_6H_5)_3C^+][(C_6F_5)_4B^-]$,[31] 2-(9-fluorenyl)ethanol,[17] and *p*-anisyllithium[15] were prepared according to literature recipes. Methylaluminoxane and triisobutylaluminum were purchased from Witco, and toluene for the polymerization reactions was from Merck.

All compounds were analyzed by ^1H NMR on a Bruker DRX 400 or AMX 500 at ambient temperatures and referenced to TMS. Mass spectra were aquired with Finnigan (SSQ 7000) and Varian (MAT-711) instruments. Elemental analyses were determined in the Microanalytical Laboratory of the University of Ulm.

Propylene Polymerization Reactions. The polymerization reactions in toluene were performed in a 1 L Büchi steel reactor at constant pressure and temperature. The autoclave was charged with 300 mL of toluene and with the desired amount of MAO. Subsequently, the polymerization temperature was adjusted, the reactor was charged with propylene up to the desired partial pressure, and the preactivated catalyst solution (Al:Zr = 100:1) was injected into the autoclave via a pressure buret. 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 propylene were monitored and recorded online.

For polymerization reactions in liquid propylene a 0.5 L steel reactor was used. At 0 °C the desired amount of propylene was condensed in the autoclave and thermostated to polymerization temperature. A mixture of the catalyst in 2 mL of toluene and 0.5 mL of triisobutylaluminum as a scavenger was added, followed by the injection of $[(C_6H_5)_3C^+][(C_6F_5)_4B^-]$ in toluene.

The polymerization reactions were stopped by pouring the reaction mixture into acidified methanol or, with liquid monomer, by injection of methanol. The polymer products were washed with methanol, filtered, and dried in vacuo at 60 °C.

Polymer Analysis. ^{13}C NMR spectra were recorded on a Bruker AMX 500 spectrometer ($C_2D_2Cl_4$, 80 °C, 2.2 s delay time) and analyzed by known methods.[32] Molecular weights and molecular weight distributions were determined by gel permeation chromatography (Waters, alliance GPC 2000, 145 °C in 1,2,4-trichlorobenzene) relative to polystyrene and polypropene standards.

Preparation of 2-Methyl-1*H*-benzo[*b*]indeno[4,5-*d*]thiophene (3). Dibenzothiophene **1** (20 g, 108.7 mmol) was added slowly at −78 °C to a stirred solution of 10.6 mL of methacryloyl chloride (108.7 mmol) and 15.3 g of $AlCl_3$ (114.8 mmol) in 250 mL of methylene chloride and allowed to attain room temperature overnight. The solution was carefully hydrolyzed at 0 °C, and the organic phase was separated, washed with an aqueous solution of K_2CO_3, and dried over Na_2SO_4. After removing the solvent and crystallization in toluene/pentane ≈ 10:1 2-methyl-1,2-dihydrobenzo[*b*]indeno[4,5-*d*]thiophen-3-one (**2**) was obtained as a crystalline solid (21.6 g, 85.9 mmol, 79%).

A 16.8 g (66.7 mmol) portion of **2** was diluted in 50 mL of THF and added at 0 °C to a suspension of 0.9 g of $LiAlH_4$ in 100 mL of THF. The reaction was stirred overnight and carefully hydrolyzed with ice and aqueous HCl. After separating the organic phase, the solution was neutralized with an aqueous solution of K_2CO_3 and dried over Na_2SO_4. Evaporation of the solvent and washing with Et_2O afforded the diastereomeric alcohols **2a** as a crystalline solid (16.6 g, 65.4 mmol, 98%).

The diastereomeric alcohols (16.6 g, 65.4 mmol) were dissolved in 100 mL of toluene, and 1.0 g of *p*-toluene sulfonic 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 dried over Na_2SO_4. After evaporation of the solvent 2-methyl-1*H*-benzo[*b*]indeno[4,5-*d*]thiophene (**3**) was obtained as a crystalline solid (14.9 g, 63.1 mmol, 97%).

2: ^1H NMR (400 MHz, $CDCl_3$) δ 1.37 (d, 3H, CH_3), 2.84, 3.22 (2m, 2H, CH_2, indanone ring), 3.94 (m, 1H, CH, indanone system), 7.45, 7.80, 8.22 (3m, 6H, aromatic); MS (GC−MS) *m/z* 252 (M^+, 100%). Anal. Calcd: C, 76.19; H, 4.76. Found: C, 76.05; H, 4.72.

2a: ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (d, 3H, CH_3), 1.75 (br, 1H, OH group), 2.43, 2.88 (2m, 2H, CH_2, indanol ring), 3.72 (m, 1H, CH, indanol ring), 4.85 (d, 1H, CH, indanol ring), 7.67 (d, 1H, aromatic), 7.40, 7.80, 8.13 (3m, 5H, aromatic); MS (GC−MS) *m/z* 254 (M^+, 100%). Anal. Calcd: C, 75.59; H, 5.51. Found: C, 75.45; H, 5.56.

3: ^1H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 3H, CH_3), 3.74 (s, 2H, CH_2, indene ring), 6.66 (s, 1H, CH olefinic), 7.74 (d, 1H, aromatic), 7.48, 7.85, 8.27 (3m, 5H, aromatic); MS (GC−MS) *m/z* 236 (M^+, 100%). Anal. Calcd: C, 81.36; H, 5.08. Found: C, 81.49; H, 5.23.

Preparation of 1-(9-Fluorenyl)-2-(2-methyl-1*H*-benzo[*b*]indeno[4,5-*d*]thiophen-1-yl)ethane (5a) and 1-(9-Fluorenyl)-2-(2-methyl-1*H*-benzo[*b*]indeno[4,5-*d*]thiophen-3-yl)ethane (5b). A 2.67 g (12.7 mmol) sample of 2-(9-fluorenyl)ethanol was diluted in 100 mL of CH_2Cl_2, and 1.8 mL of triethylamine was added. The solution was cooled to 0 °C, and $(CF_3SO_2)_2O$ (2.1 mL, 12,7 mmol) in 30 mL of CH_2Cl_2 was added slowly. The reaction mixture was stirred for 1 h at 0 °C, washed twice with ice water, and dried over Na_2SO_4. The solvent was removed in vacuo, and the resulting triflate **4** was diluted in 50 mL of THF. The lithium salt of **3** was prepared separately at −78 °C from 3.00 g of **3** (12.7 mmol) and *p*-anisyllithium (12.7 mmol) in toluene/dioxane = 10:1 and isolated as a yellow solid after stirring for 2 h at room temperature. Subsequently, the diluted triflate **4** was added at −78 °C to a solution of the lithium salt of **3** in 50 mL of THF and allowed to attain room temperature overnight. 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 over Na_2SO_4, and the solvent was evaporated. Chromatographic purification over silica with CH_2Cl_2 yielded a 1:1 mixture of two structure isomers **5a**,**b** as a crystalline material (3.81 g, 8.9 mmol, 70%).

5a: ^1H NMR (400 MHz, $CDCl_3$) δ 1.85 (s, 3H, CH_3), 1.01−1.27 (m, 1H, CH_2 bridge), 1.42−1.68 (m, 2H, CH_2 bridge), 1.80−1.85 (m, 1H, CH_2 bridge), 3.53 (t, 1H, CH indene), 3.64 (t, 1H, CH 9-*H*-fluorene), 6.45 (s, 1H, indene olefinic), 6.42, 6.56, 6.89−7.73 (m, 14H, aromatic protons indene system, aromatic fluorene).

5b: ^1H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 3H, CH_3), 2.07−2.13 (m, 2H, CH_2 bridge), 2.26−2.30 (m, 2H, CH_2 bridge), 3.44 (s, 2H, CH_2 indene), 4.00 (t, 1H, CH 9-*H*-fluorene), 7.06−7.97 (m, 14H, aromatic protons indene system, aromatic fluorene); MS (CI) *m/z* 428 (M^+, 100%). Anal. Calcd: C, 86.92; H, 5.61. Found: C, 86.86; H, 5.73.

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Preparation of *rac*-[1-(9-η^5-Fluorenyl)-2-(2-methylbenzo[*b*]indeno[4,5-*d*]thiophen-1-η^5-yl)ethane]zirconium Dichloride (7a) and *rac*-[1-(9-η^5-Fluorenyl)-2-(2-methylbenzo[*b*]indeno[4,5-*d*]thiophen-3-η^5-yl)ethane]zirconium Dichloride (8). A 0.96 g sample of an isomeric mixture of **5a**,**b** (2.24 mmol) was diluted in 100 mL of toluene/dioxane = 10:1 and cooled to −78 °C. After addition of 1.6 M *n*-BuLi in *n*-hexane (2.80 mL, 4.48 mmol) the reaction mixture was stirred for 4 h at room temperature. Subsequently, the resulting lithium salt was isolated and diluted with 100 mL of toluene. Cooling to −78 °C and addition of solid ZrCl$_4$ (0.52 g, 2.24 mmol) afforded the formation of an orange suspension. The mixture was stirred overnight and filtered, and the remaining solid was extracted several times with toluene. By fractionated crystallization from toluene **7a** (0.34 g, 0.58 mmol, 52%) and **8** (0.12 g, 0.20 mmol, 18%) could be obtained in pure form as orange solids.

7a: ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.35 (s, 3H, CH$_3$), 3.88−3.94 (m, 1H, CH$_2$ bridge), 4.16−4.23 (m, 1H, CH$_2$ bridge), 4.55−4.71 (m, 2H, CH$_2$ bridge), 6.47 (s, 1H, indene), 5.94 (d, 1H, aromatic), 6.56 (t, 1H, aromatic), 7.13−7.92 (m, 10H, aromatic), 8.08 (d, 1H, aromatic), 8.82 (d, 1H, aromatic). MS (EI) *m*/*z* 588, peak distribution of isotopes according to expected contents. Anal. Calcd: C, 63.27; H, 3.74. Found: C, 63.39; H, 3.80.

8: ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.32 (s, 3H, CH$_3$), 3.85−3.96 (m, 1H, CH$_2$ bridge), 4.04−4.12 (m, 1H, CH$_2$ bridge), 4.13−4.26 (m, 1H, CH$_2$ bridge), 4.56−4.68 (m, 1H, CH$_2$ bridge), 6.82 (s, 1H, indene), 7.05−8.10 (m, 14H, aromatic); MS (EI) *m*/*z* 588, peak distribution of isotopes according to expected contents. Anal. Calcd: C, 63.27; H, 3.74. Found: C, 63.41; H, 3.85.

Preparation of *rac*-[1-(9-η^5-Fluorenyl)-2-(2-methylbenzo[*b*]indeno[4,5-*d*]thiophen-1-η^5-yl)ethane]hafnium Dichloride (7b). Following the procedure described for **7a** 0.83 g of an isomeric mixture of **5a**,**b** (1.93 mmol), 2.41 mL of 1.6 M *n*-BuLi in *n*-hexane (3.86 mmol), and 0.62 g of HfCl$_4$ (1.93 mmol) gave **7b** as a yellow solid (0.22 g, 0.33 mmol, 34%).

7b: ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.44 (s, 3H, CH$_3$), 4.05−4.13 (m, 1H, CH$_2$ bridge), 4.27−4.36 (m, 1H, CH$_2$ bridge), 4.47−4.62 (m, 2H, CH$_2$ bridge), 6.38 (s, 1H, indene), 5.90 (d, 1H, aromatic), 6.53 (t, 1H, aromatic), 7.09−7.89 (m, 10H, aromatic), 8.08 (d, 1H, aromatic), 8.82 (d, 1H, aromatic); MS (EI) *m*/*z* 676, peak distribution of isotopes according to expected contents. Anal. Calcd: C, 55.07; H, 3.26. Found: C, 55.21; H, 3.29.

Preparation of *rac*-[1-(9-η^5-Fluorenyl)-2-(2-methylbenzo[*b*]indeno[4,5-*d*]thiophen-1-η^5-yl)ethane]hafnium Dimethyl (7c). A 0.15 g portion (0.22 mmol) of *rac*-[1-(9-η^5-fluorenyl)-2-(2-methylbenzo[*b*]indeno[4,5-*d*]thiophen-1-η^5-yl)ethane]hafnium dichloride (**7b**) was diluted in 50 mL of Et$_2$O and cooled to 0 °C. Treatment with an excess of 1.6 M MeLi in Et$_2$O (5.55 mL, 8.88 mmol) afforded the formation of a yellow suspension, which was stirred for 1 h at room temperature. The remaining mixture was cooled to 0 °C again, and 0.8 mL of dibromoethane was added to destroy unreacted MeLi. After stirring for an additional hour at room temperature the solvent was removed in vacuo and the residual solid fraction was extracted with toluene. Subsequent removal of the toluene afforded **7c** as a yellow solid (0.11 g, 0.17 mmol, 78%).

7c: ^{1}H NMR (400 MHz, CDCl$_3$) δ −2.47, −1.50 (2s, 6H, CH$_3$), 2.20 (s, 3H, CH$_3$), 3.65−3.77 (m, 1H, CH$_2$ bridge), 3.94−4.06 (m, 1H, CH$_2$ bridge), 4.08−4.19 (m, 2H, CH$_2$ bridge), 6.39 (s, 1H, indene), 5.81 (d, 1H, aromatic), 6.42 (t, 1H, aromatic), 6.99−8.07 (m, 11H, aromatic), 8.78 (d, 1H, aromatic). Anal. Calcd: C, 62.40; H, 4.41. Found: C, 62.49; H, 4.43.

X-ray Crystallography. Crystal data of the compounds **7a** and **8** were collected with a Rigaku AFC7S single-crystal diffractometer at 193(2) K using Mo Kα radiation (graphite monochromator), 0.71073 Å (ω/2θ scans). Intensities were corrected for Lorentz and polarization effects.[33] A ψ-scan absorption correction was performed.[34] Solution and refinement: SHELX-97 (Sheldrick, 1997); figures with the labeling scheme: ORTEP3 (Farrugia, 1997).[35] The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on calculated positions. The displacement factor of the H atoms was 1.2× (or 1.5× for methyl hydrogens) that of the host atom.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 184338 for compound **7a**. Copies of these data may be obtained on application to Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Supporting Information Available: Tables of crystallographic data, atomic coordinates, bond lengths, bond angles, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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