Dual-Side *ansa*-Zirconocene Dichlorides for High Molecular Weight Isotactic Polypropene Elastomers

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The four new asymmetric *ansa*-zirconocene dichlorides *rac*-[1-(9-η^5-fluorenyl)-2-(2-phenyl-1-η^5-indenyl)ethane]zirconium dichloride (**4c**), *rac*-[(9-η^5-fluorenyl)(5,6-cyclopenta-2-methyl-1-η^5-indenyl)dimethylsilane]zirconium dichloride (**4d**), *rac*-[(9-η^5-fluorenyl)(2-methyl-1-η^5-indenyl)dimethylsilane]zirconium dichloride (**4e**), and *rac*-[(9-η^5-fluorenyl)(2-phenyl-1-η^5-indenyl)dimethylsilane]zirconium dichloride (**4f**) have been prepared, and their polymerization behavior was compared to the recently published *rac*-[1-(9-η^5-fluorenyl)-2-(5,6-cyclopenta-2-methyl-1-η^5-indenyl)ethane]zirconium dichloride (**4a**) and *rac*-[1-(9-η^5-fluorenyl)-2-(2-methyl-1-η^5-indenyl)ethane]zirconium dichloride (**4b**). The Si-bridged ligands are easily accessible by the reaction of fluorenyllithium with dimethyldichlorosilane and the subsequent addition of indenyllithium. A similar route using 1-(9-fluorenyl)-2-bromoethane was applied for the synthesis of the ethylene-bridged ligands. The Zr(IV) complexes of all ligands are highly active catalysts for the propene polymerization reaction after activation with MAO. The influence of the bridge and the particular substitution pattern of the indenyl fragments has been studied with respect to monomer concentration and polymerization temperature. The exchange of the ethylene bridge by a dimethylsilane unit results in a strong increase of the molecular weights but also in a decreased polymerization activity deriving from a fast decomposition of the active catalyst species. Interestingly, significantly higher polymer molecular weights could be found for the complexes that contain the 5,6-cyclopentyl substituent on the indenyl moiety. All catalysts showed the effect of a declining stereoselectivity with increasing monomer concentration, leading to the formation of homopolypropene elastomers. The mechanism of stereoerror formation of these C_1-symmetric species was investigated by deuterium labeling studies on the propene monomers and by comparison with C_2-symmetric complexes.

Introduction

Since the first introduction of homogeneous *ansa*-metallocene catalysts for the stereoregular polymerization of propene,[1] attempts to find new insights into the stereochemical control of propene polymerization reactions have rapidly increased.[2] The observation by Chien et al.[3] that elastic polypropene of narrow molecular weight distribution could be obtained with the asymmetric homogeneous titanocene catalyst [MeHC(Me$_4$-Cp)(Ind)]TiCl$_2$ resulted in a variety of research activities on suitable catalysts for the production of elastic polypropene. Collins et al.[4,5] reported the modification of Chien's basic catalyst structure toward a dimethylsilane bridge and hafnium as the transition metal. The elastic properties were ascribed to arise from blocklike structures of isotactic and atactic sequences, in analogy with Chien's work.[3] Recently, we reported on the use of the highly active zirconocene dichloride **4a**/MAO (Scheme 1) for the production of the first high molecular weight, isotactic polypropene with controllable amounts of isolated stereoerrors for achieving and adjusting elastic properties.[6] It was found that the 2-methyl group and the 5,6-substitution are necessary requirements to obtain a high enough molecular weight and a sufficient amount of stereoerrors for the formation of elastic, isotactic polypropenes. Contrary, the 4,5-front substitution resulted only in partly isotactic polymers of relatively low molecular weight.[6−8]

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[4] (4) (a) Gauthier, W. J.; Corrigan, J. F.; Nicholas, N. J.; Collins, S. *Macromolecules* **1995**, *28*, 3771. (b) Gauthier, W. J.; Collins, S. *Macromolecules* **1995**, *28*, 3778.

[5] (5) Bravakis, A. M.; Bailey, L. E.; Pigeon, M.; Collins, S. *Macromolecules* **1998**, *31*, 1000.

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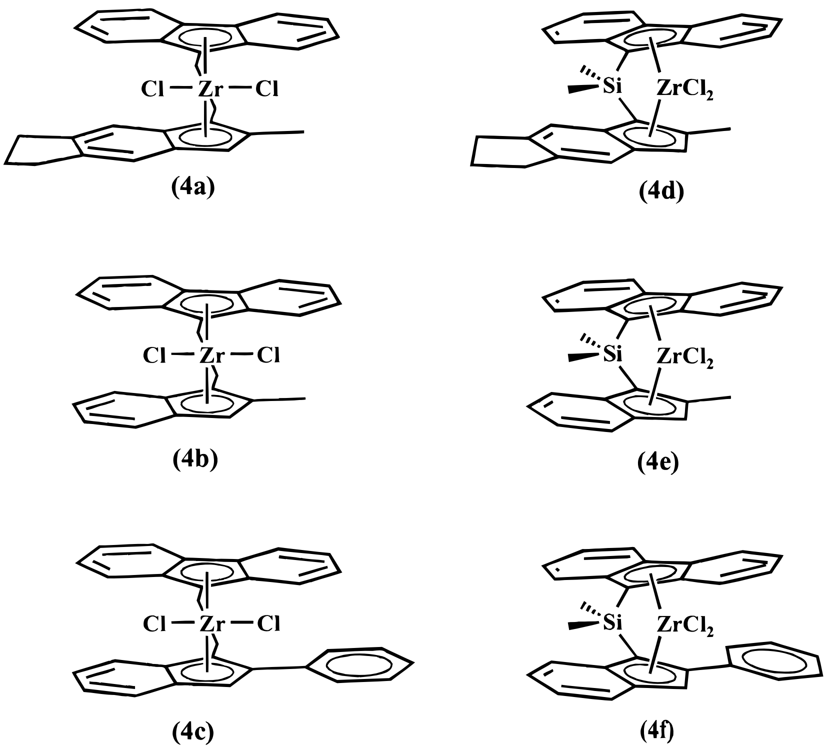
Scheme 1



In our present work we prepared and investigated the asymmetric complexes **4c**−**f** in comparison with the recently published zirconocenes **4a**[6] and **4b**[8] to gain more information on the influence of the 5,6-substitution on the polymerization behavior. By exchanging the ethylene bridge with a dimethylsilane unit, we intended to increase the molecular weight and the catalyst activity to make the polymers even more interesting for industrial application. Furthermore, we continued our investigations on the mechanism of stereoerror formation of the C_1-symmetric metallocenes by applying deuterium-labeled monomers and compared the results with the mechanism of some representative C_2-symmetric complexes.

Results and Discussion

Ligand and Complex Synthesis. The Si-bridged ligands are easily accessible by the addition of Me_2Cl_2-Si to an ether solution of the fluorenyl anion. The resulting (9-fluorenyl)dimethylchorosilane (Scheme 2, path A, Sp = Me_2Si) can be used without further purification after removing the solvent and excessive Me_2Cl_2Si. The separately prepared indenyllithium is subsequently added to an ether solution of (9-fluorenyl)-dimethylchorosilane (**1b**) at room temperature.[9] Stirring overnight and recrystallization from hexane gave yields up to 80%.

The synthesis of ethylene-bridged asymmetric zirconocenes can be realized in two different ways. In 1994 a new route to asymmetric zirconocenes containing indenyl and fluorenyl fragments was developed in our group.[10] By nucleophilic ring-opening of substituted epoxides with fluorenyllithium, a wide variety of substituents can easily be introduced, and even more, a stereogenic center is introduced into the ethylene bridge. The resulting chiral ligands are obtained after functionalization of the alcohols with trifluoromethane sulfonic acid anhydride and further reaction with a second indenyl moiety. Another route[8,11] similar to the procedure leading to the Si-bridged ligands was used for the synthesis of the C_2H_4-bridged ligands **3a**−**c** (Scheme 2, path A, Sp = C_2H_4). The 1-(9-fluorenyl)-2-bromoethane (**1a**) can be prepared by the addition of 1,2-dibromoethane to fluorenyllithium. This stable intermediate was employed in subsequent reactions with indenyllithium compounds **2a**−**c** without purification, leading to the ethylene bridged ligands **3a**−**c** in up to 65% yield.

The ligands **3a**−**c** were converted into their corresponding zirconocenes by deprotonation with *n*-BuLi in diethyl ether at −78 °C, stirring for 2 h at ambient temperature, and subsequent addition of $ZrCl_4$ to a toluene solution of the dianion. The reaction was stirred at room temperature overnight. The Zr(IV) complexes were isolated in up to 90% yield after separation from LiCl.[12] A similar approach was used for the Si analogues **3d**−**f**. The precipitated orange complexes were separated from the toluene solution and rapidly extracted with cold toluene. The toluene was immediately removed, and the orange powder was washed several times with dry Et_2O and pentane. The Si-bridged zirconocenes are only slightly soluble in organic solvents. They are quite unstable in solution and show an

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[7] Nippon Chemicals, EP 0707016A1.

[8] Thomas, E. J.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1999**, *18*, 1439.

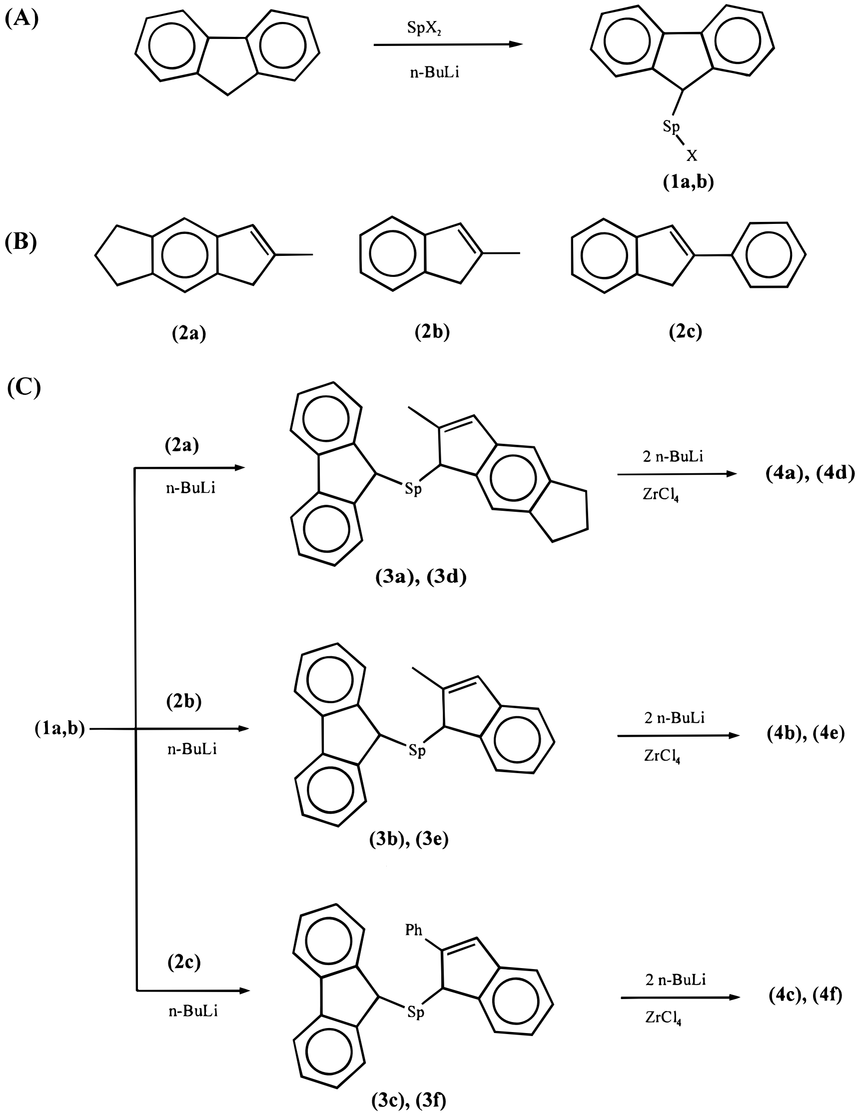
[9] (a) Ewen, J. A.; Elder, M. J. *Ziegler Catalysts*; Springer-Verlag: Berlin, 1995. (b) Chen, Y.-X.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem*. **1995**, *497*, 1. (c) Patsidis, K.; Alt, G. H.; Milius, W.; Palackal, S. J. *J. Organomet. Chem*. **1996**, *509*, 63.

[10] Fawzi, R.; Steinmann, M.; Jany, G.; Rieger, B. *Organometallics* **1994**, *13*, 647.

[11] Alt, H. G. U.S. Patent 5191132, 1993.

[12] The ethylene-bridged complexes were obtained with the following yields. **4a**: 92%; **4b**: 85%, **4c**: 56%.

Scheme 2



$SpX_2 = C_2H_4Br_2$ or $(CH_3)_2Cl_2Si$
(1a), (3a), (3b), (3c): $Sp = C_2H_4$
(1b), (3d), (3e), (3f): $Sp = (CH_3)_2Si$

extreme sensitivity to moisture.[13] However, they can be stored under dry argon. Resconi et al.[14] reported on a similar behavior for $Me_2Si(9\text{-}Flu)_2ZrCl_2$. The high instability of this molecule was attributed to the decreasing ligand hapticity resulting from repulsive interactions of the phenyl hydrogens in the rear fluorenyl positions α-standing to the Me_2Si unit. The same destabilizing effect is assumed to be responsible for the low stability of our Si-bridged zirconocene catalysts[15] and leads to significantly reduced catalytic activities in propene polymerization experiments (see below).

Propene Polymerizations. Monomer concentration and temperature dependency of the different catalysts were investigated in propene polymerizations in order to obtain polypropenes with tailored isotacticities (Table 1).

Surprisingly, large differences were observed in the polymerization behavior of the examined catalysts. The highest polymer yields could be obtained with the ethylene-bridged metallocenes **4a**/MAO and **4b**/MAO (at $T_p = 30$ °C up to 2.5×10^3 and at $T_p = 50$ °C up to 4.6×10^3 kg of PP (mol of Zr $[C_3]$ h)$^{-1}$). Exchange of the ethylene bridge by a dimethylsilane unit (**4d**−**f**/MAO) resulted in a rapid decline of the propene consumption curve during the course of the polymerization reaction. The activated species decompose quickly, especially at elevated temperatures, so that already after the first 15 min only about 20% of the starting activity is left (Figure 1, **4d**/MAO). In contrast, the propene consumption of the ethylene-bridged complexes increases within the first 15−30 min of the polymerization experiment (Figure 1, **4a**/MAO), indicating a slow activation reaction with MAO, resulting presumably from the sterically demanding substituents around the zirconium center.

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[13] Thomas, E. J.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **2000**, *33*, 1546.

[14] Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998.

[15] Intensive trials to grow crystals suitable for X-ray structure analysis remained unsuccessful due to the low stability of the Me_2Si-bridged complexes in solution.

Table 1. Polymerization Results of Propene with Asymmetric Complexes 4a–f/MAO

run	cat.	amount[a]	T_p[b]	$[\mathrm{C}_3]$[c]	t_p[d]	yield[e]	activity[f]	n_iso[g]	M_w[h]	$M_\mathrm{w}/M_\mathrm{n}$
1	**4a**	6	30	1.2	73	17.3	2000	8.9	55	1.8
2	**4a**	3.8	30	3.0	39	18.0	2400	7.4	89	1.8
3	**4a**	2.7	30	5.1	30	17.6	2600	7.1	125	1.9
4	**4a**	3.8	50	3.0	21	18.3	4600	10.3	46	1.9
5	**4d**	10	30	1.2	120	12.5	n.d.[i]	12.2	103	1.8
6	**4d**	10	30	3.0	61	15.2	n.d.	10.5	132	1.9
7	**4d**	10	30	5.1	30	17.4	n.d.	9.4	158	1.9
8	**4d**	10	50	3.0	25	13.2	n.d.	14.7	85	1.9
9	**4b**	5	30	1.2	72	15.6	2100	6.1	62	1.8
10	**4b**	5	30	3.0	39	16.7	1700	5.7	81	1.9
11	**4b**	5	30	5.1	25	16.6	1600	4.7	83	1.9
12	**4e**	20	30	1.2	106	16.1	n.d.	9.3	73	1.8
13	**4e**	10	30	3.0	69	15.7	n.d.	8.5	81	2.0
14	**4e**	10	30	5.1	33	16.4	n.d.	8.0	92	2.0
15	**4e**	10	50	3.0	65	12.6	n.d.	10.8	64	1.9
16	**4c**	10	30	3.0	27	18.4	1400	100.0	62	2.3
17	**4c**	10	30	5.1	29	20.3	800	35.8	86	2.5
18	**4f**	50	30	1.2	193	8.5	n.d.	15.9	32	1.9
19	**4f**	30	30	3.0	118	8.9	n.d.	13.6	74	1.8
20	**4f**	30	30	5.1	125	16.2	n.d.	12.3	99	1.8
21	**4f**	30	50	3.0	101	5.2	n.d.	16.3	31	1.9

[a] μmol (Al/Zr = 2000). [b] °C. [c] mol L^{-1}. [d] min. [e] g. [f] kg of PP (mol of Zr [C$_3$] h)$^{-1}$. [g] Average isotactic block length n_iso=4+2[mmmm]/[mmmr]. [h] kg mol^{-1}. [i] n.d. = not determined, because of rapid deactivation of the catalyst active species.

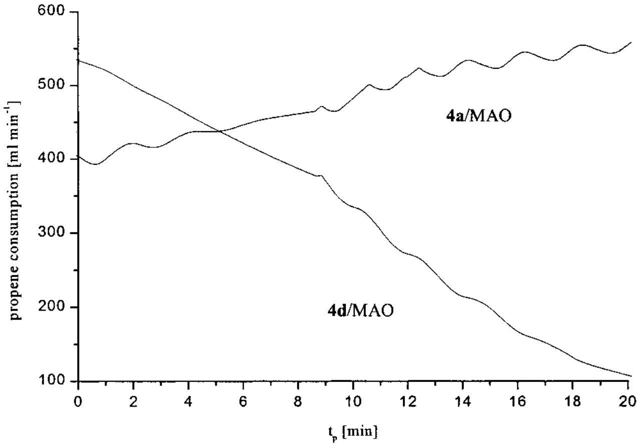

Figure 1. Propene consumption curves obtained with **4a**/MAO and **4d**/MAO under the following polymerization conditions. **4a**/MAO: T_p = 50 °C, $[\mathrm{C}_3]$ = 3.0 mol L^{-1}, n_Zr = 3.8 μmol; **4d**/MAO: T_p = 50 °C, $[\mathrm{C}_3]$ = 3.0 mol L^{-1}, n_Zr = 10 μmol

This behavior is significantly different compared with C_2-symmetric *ansa*-metallocenes that show higher activities for the Si-bridged species due to the enlarged bite angle of the Cp ligands in such complexes.[16]

The highest molecular weights were obtained for polymers produced with the Si-bridged, 5,6-cyclopentyl-substituted complex **4d**/MAO (Table 1, entries 6, 7). Interestingly, the 5,6-cyclopentyl group seems to have generally a beneficial influence on the molecular weight, despite its remote position within the complex relative to the active Zr(IV) center (Table 1, entry 3). We have no genuine explanation for this surprising effect. However, experiments with deuterated propene monomers (see below) show that the 5,6-alkyl substituents suppress effectively a chain end epimerization process (found to be responsible for the formation of stereoerrors in C_2-symmetric catalysts)[17,18] and hinder at the same time a subsequent chain termination reaction, leading to higher molecular weight products.

The [mmmm]-pentad concentration of the polymers produced with the different C_1-symmetric metallocene catalysts varies over a broad range (10%–98%, cf. Table 2). The most conspicuous effect of the Si-bridged *ansa*-metallocenes **4d**/MAO and **4e**/MAO is the distinct ascent of the isotacticity compared with their ethylene-bridged counterparts **4a**/MAO and **4b**/MAO. With 5,6-cyclopentyl substitution of the indenyl fragment (**4a**,**d**) an increase of the isotacticity is observed. This effect can be explained by a favored back-skip of the growing polymer chain before a new monomer inserts on the aspecific side of the complexes, induced by the additional steric hindrance of the 5,6-cycloaliphatic substituent (Scheme 3).[6]

The series of propene polymerizations applying the 2-phenyl-substituted complexes **4c**/MAO has produced polymers with the highest isotacticities (e.g., **4c**: mmmm = 98%, Table 2, entry 16). Exchange of the C_2H_4 bridge by a Me_2Si unit (**4f**) results in a strong decrease of the isotacticity of the polypropene products (e.g., Table 2, entry 20), while for both complexes the same influence of the monomer concentration on the stereoselectivity is observed (Table 2, **4c**: entries 16, 17; **4f**: entries 19, 20), suggesting that a mechanism like the one depicted in Scheme 3 might still be active. Generally, 2-phenyl substitution leads to a strong decrease in polymerization activity, while the molecular weight is not essentially altered.

Mechanisms of Stereoerror Formation. C_2-Symmetric Catalysts. Brintzinger et al.[17] and Busico et al.[18] have demonstrated by using deuterated propene monomers that formation of the [mrrm]-stereoerror pentad at low monomer concentrations is, to a large extent, a consequence of an isomerization ("chain end epimerization") of the Zr–alkyl bond[19] in C_2-symmetric

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(16) Cf.: Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem.* **1995**, *107*, 1255, and references therein.

(17) (a) Leclerc, M. K.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1996**, *118*, 9024. (b) Leclerc, M. K.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 1651.

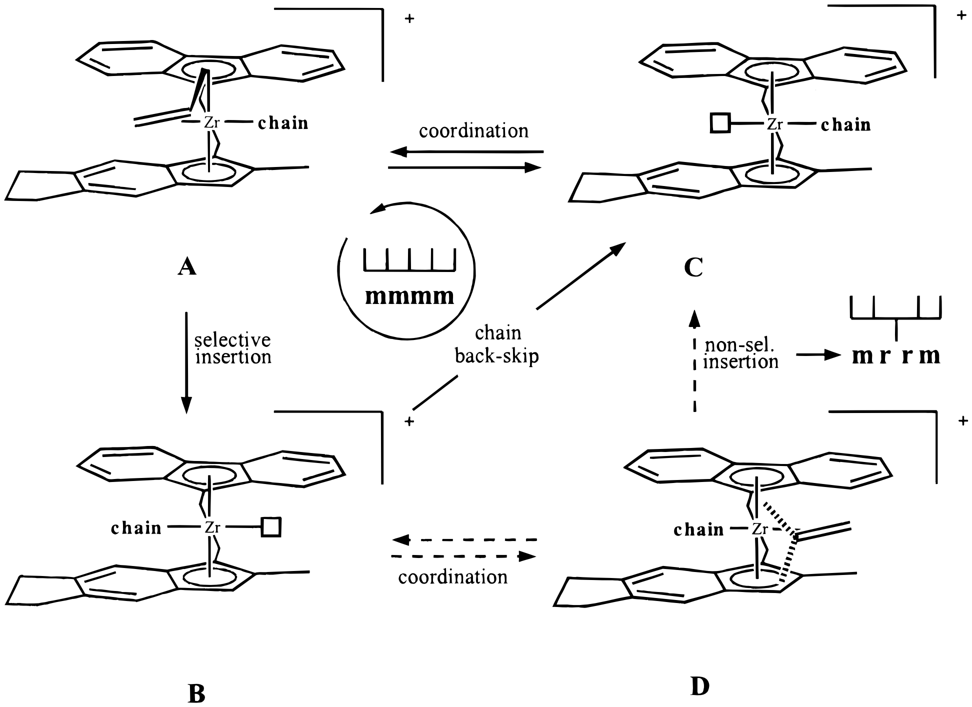
(18) (a) Busico, V.; Caporaso, L.; Cipullo, R.; Landriani, L.; Angelini, G.; Margonelli, A.; Segre, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 2105. (b) Busico, V.; Brita, D.; Caporaso, L.; Cipullo, R.; Vacatello, M. *Macromolecules* **1997**, *30*, 3971. (c) Busico, V.; Cipullo, R.; Caporaso, L.; Angelini, G.; Segre, A. L. *J. Mol. Catal. A* **1998**, *128*, 53.

Table 2. Polypropene Pentad Distribution[a] (in %)

run	cat.	[mmmm]	[mmmr]	[rmmr]	[mmrr]	[mmrm]+[rrmr]	[rrrr]	[rrrm]	[mrrm]
1	**4a**	42.5	17.5	2.1	19.9	3.4	1.6	2.8	10.2
2	**4a**	30.3	17.7	2.7	21.3	5.9	4.6	6.6	10.9
3	**4a**	27.8	17.7	2.7	22.0	6.6	5.3	7.4	10.5
4	**4a**	49.1	15.7	1.5	17.7	3.1	2.4	1.8	8.7
5	**4d**	61.6	15.0		16.3				7.1
6	**4d**	50.6	15.6	1.4	16.8	3.1	1.7	2.5	8.2
7	**4d**	44.0	16.3	1.8	17.8	4.1	3.0	3.9	9.1
8	**4d**	67.4	12.6		13.0	0.9		0.5	5.5
9	**4b**	17.6	16.5	3.8	21.6	20.8	8.9	10.4	11.4
10	**4b**	13.4	15.6	5.4	22.5	10.3	14.0	11.8	7.0
11	**4b**	9.7	13.7	5.5	18.5	10.7	15.7	14.8	11.4
12	**4e**	44.1	16.7	1.8	18.5	4.0	3.1	3.5	8.3
13	**4e**	39.3	17.5	2.3	20.6	3.8	3.7	4.8	8.0
14	**4e**	35.3	17.6	2.4	21.2	4.2	5.4	6.1	7.9
15	**4e**	56.2	16.4		18.0	2.1		1.6	5.8
16	**4c**	98.0	2.0						
17	**4c**	86.0	5.4		6.3				2.3
18	**4f**	70.5	11.8		12.6				5.1
19	**4f**	62.2	12.9	1.1	12.0	2.5	0.9	1.7	5.9
20	**4f**	57.9	13.9	1.4	12.8	3.2	1.2	2.1	6.2
21	**4f**	71.7	11.7		11.9				4.7

[a] [mrmr] ≤ 1% (ref 24).

Scheme 3



catalysts (e.g., **EBTHI**).[20] Such deuterium labeling studies enable differentiation between intrinsic errors that are formed by a wrong enantiofacial discrimination of the prochiral monomer and isomerization-induced errors, which result from an intramolecular rearrangement of the Zr-bound chain.[17,18] In the methyl region of the ^{13}C NMR spectrum of polypropene produced with 1-d-propene, the [mrrm]-pentad due to intrinsic errors can be identified at 19.6 ppm, while a deuterium-containing methyl group—resulting from an isomerization of the Zr−alkyl bond—appears upfield as a triplet ($J(^{13}C, ^{2}H) = 19$ Hz) centered at 19.3 ppm (Figure 2 A).

Table 3[21] summarizes data on the stereoselectivity of **EBI**/MAO[22] depending on the monomer concentration at constant polymerization temperature (50 °C). These results are in good agreement with literature values.[23] The amount of [mrrm]-error pentads increases from

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(19) For isomerization via an allyl mechanism, see: (a) Resconi, L.; Camurati, I.; Sudmeijer, O. *Topics Catal.* **1999**, *7*, 145. (b) Resconi, L. *J. Mol. Catal. A* **1999**, *146*, 167.

(20) **EBTHI** = *rac*-ethylenbis(4,5,6,7-tetrahydro-1-η^5-indenyl)zirconium dichloride.

(21) To obtain sufficient polymer yields with the deuterated monomer, which obviously contained traces of catalyst-poisoning impurities, the applied catalyst and cocatalyst concentrations were high. As a consequence, the start of the polymerizations was retarded and chain termination occurred mainly by chain transfer to aluminum. Polymerizations with undeuterated propene at different MAO concentrations up to 0.5 mol L^{-1} showed that the amount of stereoerrors was not influenced by the MAO concentration.

(22) **EBI** = *rac*-ethylenebis(1-η^5-indenyl)zirconium dichloride.

(23) Resconi et al. (*Macromolecules* **1995**, *28*, 6667) reported under comparable polymerization conditions [mmmm]-pentad values of 86% at 4.4 and 2.8 mol/L, 82% at 0.85 mol/L, 80% at 0.5 mol/L, and 55−68% at ≤0.4 mol/L (diffusion controlled). Busico et al. (*J. Am. Chem. Soc.* **1994**, *116*, 9329) reported correspondingly [m]-diads ranging from 82% at 0.4 mol/L to a maximum value of 92% in bulk.

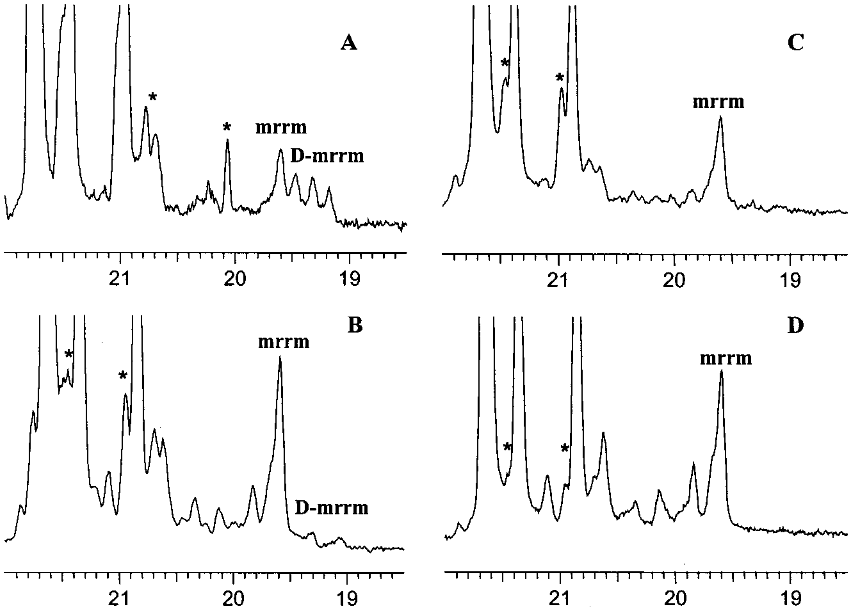

Figure 2. ^{13}C NMR spectra of the methyl region of deuterated polypropenes obtained at 50 °C with **EBI**/MAO and 0.4 mol L^{-1} 1-d-propene (A), with **4b**/MAO and 0.4 mol L^{-1} 1-d-propene (B), with **4a**/MAO and 0.4 mol L^{-1} 1-d-propene (C), and 3.0 mol L^{-1} 1-d-propene (D). Asterisks denote signals arising from *n*-propyl end groups and 3,1-misinsertions for A, and from isobutyl end groups for B, C, and D.

Table 3. Polypropene Pentad Distribution (in %) for C_2-Symmetric Catalysts EBI/MAO and EBTHI/MAO (T_p = 50 °C)

cat.[a]	mon.[b]	[mon.][c]	Al/Zr	[mmmm]	[mmrr]	[mrrm]	d-[mrrm]
EBI	C_3	0.4	3000	74	8.6	4.0	
EBI	C_3	0.85	3000	80	5.6	2.9	
EBI	C_3	1.9	3000	84	5.7	2.3	
EBI	C_3	3.3	3000	85	4.7	1.9	
EBI	d-C_3	0.4	1500	69	9.5	1.9	2.6
EBI	d-C_3	0.85	1500	79	6.4	2.0	1.3
EBI	d-C_3	1.3	1500	82	5.5	2.0	<0.2
EBTHI	d-C_3	0.4	200	50	16.4	3.3	6.7

[a] [Zr] = (1−2) × 10^{-5} mol L^{-1} for C_3 polymerizations, [Zr] = 3.3 × 10^{-4} mol L^{-1} for d-C_3 polymerizations (ref 19). [b] Monomers: C_3 = propene, d-C_3 = 1-d-propene. [c] mol L^{-1}.

1.9% to 4.0% with a decline of the monomer concentration from 3.3 to 0.4 mol L^{-1}. Results obtained with the deuterated monomer under the same conditions demonstrate that the amount of intrinsic errors [mrrm] is nearly constant (1.9% to 2.0%, respectively) and is essentially independent of the monomer concentration, as expected. Isomerization-induced errors d-[mrrm][24] start to play a significant role at propene concentrations below 1 mol L^{-1}. Hydrogenation of the indenyl ligand increases the amount of intrinsic [mrrm]-error pentads from 1.9% to 3.3% at 50 °C. The amount of isomerization-induced errors is nearly 3-fold for the hydrogenated catalyst at a monomer concentration of 0.4 mol L^{-1}. The experimentally verified higher probability of the **EBTHI** catalyst to produce stereoerrors by chain end isomerization indicates that it must have a lower k_{ins}/k_{iso} ratio than **EBI**. This is in agreement with results obtained by Busico et al.[18b] by fitting data from propene polymerizations to a model accounting for chain growth and chain epimerization. We found further that at this temperature the amount of intrinsic errors is higher for the hydrogenated catalyst, which may (beyond lower enantioselectivity) be a consequence of an increased probability for error formation by a reaction path involving β-H abstraction.[25] An increased probability of the hydrogenated catalyst to undergo reactions via β-H elimination and Zr−H bond formation is reflected in its higher sensitivity toward chain termination by hydrogen and after insertion of a comonomer.[26]

For C_2-symmetric catalysts the origin of stereoerrors is thus based on two mechanisms: (1) their structure-dependent ability for the enantioselective discrimination of the prochiral propene monomer and (2) the monomer insertion rate, which is slow enough to allow kinetic competition of error-inducing side reactions, from which the step of Zr−H bond formation might play a decisive role.

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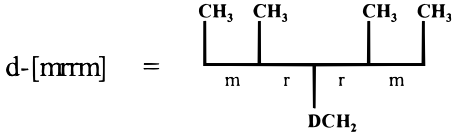
(24) For the mechanism of d-[mrrm] formation see refs 17−19.



(25) Busico et al. (ref 18) observed that the amount of nondeuterated stereoirregular [mrrm]-units decreases when using 2-deuterated propene instead of 1-deuterated propene, which indicates that the [mrrm]-pentad also represents errors formed by a mechanism involving β-H/D abstraction, being slower for the 2-deuterated monomer because of an isotope effect.

(26) (a) Malmberg, A.; Kokko, E.; Lehmus, P.; Löfgren, B.; Seppälä, J. V. *Macromolecules* **1998**, *31*, 8448. (b) Kokko, E.; Malmberg, A.; Lehmus, P.; Löfgren, B.; Seppälä, J. V. *J. Polym. Sci., Part A* **2000**, 38, 376.

Table 4. Pentad Distribution (in %) for C_1-Symmetric Catalysts 4a/MAO, 4b/MAO, and 4d/MAO

cat.[a]	T_p[b]	[d-C_3][c]	Al/Zr	[mmmm]	[mmrr]	[mrrm]	d-[mrrm]
1	50	0.4	1000	66	12.6	5.3	n.o.
1	50	1.9	750	56	14.1	6.7	n.o.
1	50	3.0	500	49	15.1	7.5	n.o.
2	50	0.4	375	51	14.3	6.6	0.8
2	50	1.9	375	32	17.2	8.7	n.o.
4	30	0.6	500	48	16.8	7.6	n.o.
4	30	3.0	500	46	16.9	7.8	n.o.

[a] $[Zr] = (3-10) \times 10^{-4}$ mol L^{-1}. [b] °C. [c] mol L^{-1}.

C_1-Symmetric Catalysts. For catalysts such as those applied in the present study the mechanism of stereoerror formation is different compared with C_2-symmetric species, which is already indicated by their tendency to produce less stereoregular polypropenes with increasing monomer concentration. We have previously presented a possible explanation for the observed polymerization behavior of asymmetric dual-side catalysts such as **4a**/MAO.[6] Isotactic sequences are formed by a reaction path that involves repeated migratory insertion of the chain to the monomer coordinated between the sterically demanding fluorenyl—indenyl moieties (Scheme 3, A → B) and a consecutive back-skip of the chain to the sterically less encumbered side (B → C). Increasing the monomer concentration leads to a higher probability for monomer coordination at the less hindered side before a back-skip of the growing polymer chain can occur.[27] Migratory insertion of the chain to the free side results in a nonselective insertion of the monomer (D → C). The next insertion from A → B is again stereoselective,[28] leading—after a back-skip of the polymer chain—to an isolated [mrrm]-error pentad. For these catalysts the ratio of the rate of back-skip of the chain to the rate of monomer coordination at the free side can be understood to determine to a large extent the amount of isolated stereoerrors formed during the polymerization reaction. The amount of stereoerrors increases with the monomer concentration (cf. Table 2, 4), because the rate of monomer coordination at the free side (B → D) depends on monomer concentration, while the rate of back-skip of the chain (B → C) is an intramolecular reaction. To elucidate the role of kinetically feasible isomerization reactions possibly contributing to stereoerror formation for these asymmetric dual-side catalysts, we performed a series of experiments using 1-d-propene and analyzed the deuterium distribution in the resulting polymers (Table 4). The most important result is the fact that for the 5,6-cyclopentyl-containing complexes **4a**/MAO and **4d**/MAO the methyl d-[mrrm]-pentad is entirely missing. This indicates that isomerization reactions such as those observed for C_2-symmetric species do not play any significant role in stereoerror formation for the complexes of this type.[29] Interestingly, for **4b/**MAO, which does not bear the 5,6-cycloalkyl substitution, the d-[mrrm]-pentad is observable, however only in reduced quantities. The observation that the 5,6-cycloalkyl substituent suppresses the isomerization reaction might be a preliminary explanation of the higher molecular weights of polypropenes prepared with **4a**/MAO and **4d**/MAO.[30] This hypothesis is supported by Brintzinger et al., who recently reported that the epimerization process seems to be linked to chain termination via hydride abstraction.[17] Further work on the influence of 5,6-substituents on the polymerization behavior of indenyl-containing asymmetric complexes is underway.

Conclusion

The asymmetric, dual-side catalysts presented in the present study open the access to a broad range of isotactic polypropene microstructures. A controlled tailoring of the properties of the polymer products from highly elastic to crystalline thermoplastic is enabled by varying the catalyst structure and the polymerization conditions. Introduction of a Si-bridge into the ligand frame results in a further increase of the molecular weight, unfortunately combined with a strong decline of the polymerization activity due to decomposition of the active species. Interestingly, the 5,6-substitution on the indenyl moiety of the ethylene-bridged species was found to play an important role in obtaining a good balance between optimized activity, increased molecular weight, and a sufficient amount of stereoerrors for the design of thermoplastic elastomers. In C_2-symmetric complexes the stereoerrors are formed at low monomer concentrations to a large extent by kinetically competitive side reactions, like Brintzinger's and Busico's chain end epimerization processes. For the C_1-symmetric catalysts of the present study, the stereoerror formation originates predominantly from the kinetic competition between chain back-skip and monomer coordination at the aspecific side of the catalyst structure.

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. Indane, fluorene, benzene, 1,2-dibromoethane, 2-phenylindene, $ZrCl_4$, $HfCl_4$, $AlCl_3$, *cis/trans*-1-bromo-1-propene (98%), and methanol-d_1 (99.5%) were used as received from Merck and Aldrich. 2-Methylindene was prepared according to literature procedures.[31] The syntheses of the ethylene-bridged ligands **3a**,**b** have been previously described in the literature.[6,8] The corresponding complexes **4a**,**b** and the zirconocenes **EBI** and **EBTHI** were prepared according to literature recipes.[6] Methylaluminoxane and triisobutylaluminum were purchased from Witco, and toluene for the polymerization reactions was purchased from Merck.

All compounds were analyzed by ^1H NMR on a Bruker AC 200 or AMX 500 at ambient temperatures and referenced to TMS. Mass spectra were aquired with Finnigan (SSQ 7000)

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(27) For theoretical calculations on the occurrence of back-skip of the growing chain in the case of asymmetric metallocenes, see: Guerra, G.; Cavallo, L.; Moscardi, G.; Vacatello, M.; Corradini, P. *Macromolecules* **1996**, *29*, 4834.

(28) Monomer misinsertion from A → B after D → C will result in [mrmr]-error pentads, the concentration of which is however close to zero in polypropenes obtained with asymmetric catalysts of the type studied here.

(29) Brintzinger et al. reported a similar observation for C_2-symmetric metallocenes bearing bulky ligand frameworks (ref 17a).

(30) The hypothesis that epimerization reaction leads to a higher chance for chain termination finds further support by end-group analysis. ^1H NMR spectra indicate that the deuterated polypropenes obtained with **4b**/MAO contain vinylidenic protons that are shifted downfield by ca. 0.02 ppm. This shift is caused (ref 17) by a neighboring methyl group that contains deuterium, resulting from isomerization. For **4a**/MAO such vinylidenic protons were not observed, as expected.

and Varian (MAT-711) instruments. Elemental analyses were determined in the microanalytical laboratory of the University of Ulm.

1-d-Propene. A mixture of *cis/trans*-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 evaporated to dryness. The resulting white solid lithium compounds were suspended in 200 mL of toluene. At 0 °C methanol-d_1 (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 ^{1}H NMR spectrum ($CDCl_3$ ($\delta = 7.24$ ppm), 500 MHz) showed that the product contained 41% of *cis*-1-d-propene $HDC{=}CHCH_3$ (dq, $\delta = 4.91$ ppm, $^3J = 10$ Hz, $^4J = 1.5$ Hz, 1H) and 59% of *trans*-1-d-propene (dq, $\delta = 5.00$ ppm, $^3J = 17$ Hz, $^4J = 1.8$ Hz, 1H).

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 a 10 min 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 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 propene 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 propene were monitored and recorded online. The polymerization reactions were stopped and treated as described above.

Polymer Analysis. ^{13}C NMR spectra were recorded on a Varian GEMINI 2000 spectrometer ($C_2D_2Cl_4$, 100 °C, 75 MHz, 10 mm probe) or on 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.[32] Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC, Waters 150 C ALC, 140 °C in 1,2,4-trichlorobenzene) relative to polystyrene and polypropene standards.

Preparation of 1-(9-Fluorenyl)-2-(2-phenylindenyl)ethane (3c). A portion of 4.8 g (28.9 mmol) of fluorene was diluted in 100 mL of Et_2O and cooled to −78 °C. Addition of a 1.6 M solution of *n*-BuLi in hexane (18.1 mL, 28.9 mmol) and stirring for an additional 2 h afforded the formation of fluorenyllithium. Subsequent cooling to −78 °C and further treatment with an excess of 1,2-dibromoethane (14.9 mL, 173 mmol) formed the substituted fluorenyl compound **1a**. The remaining mixture was allowed to attain room temperature and stirred for an additional 2 h. Removal of the solvent and excess of 1,2-dibromoethane yielded **1a** as a beige solid. A solution of **1a** in 80 mL of Et_2O was added at room temperature to the separately prepared lithium salt of 2-phenylindene **2c** (5.5 g, 28.9 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 over Na_2SO_4. Evaporation of the solvent and recrystallization from *n*-hexane yielded **3c** as a white solid (7.7 g, 20.2 mmol, 69%).

3c: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.2−2.65 (m, 4H, CH_2 bridge), 3.7 (s, 2H, CH_2 indene), 4.2 (t, 1H, CH 9-*H*-fluorene), 6.8−7.9 (m, 18H, indene olefinic, aromatic protons indene system, aromatic fluorene); MS (FD) *m/z* 384 (M^+, 100%). Anal. Calcd C, 93.71; H, 6.29. Found: C, 93.53; H, 6.37.

Preparation of 1-(9-Fluorenyl)-1-(5,6-cyclopenta-2-methylindenyl)dimethylsilane (3d). A portion of 5 g (30.1 mmol) of fluorene was diluted in 100 mL of Et_2O and cooled to −78 °C. Addition of a 1.6 M solution of *n*-BuLi in hexane (18.8 mL, 30.1 mmol) and stirring for an additional 2 h resulted in the formation of fluorenyllithium. Subsequent cooling to −78 °C and further treatment with an excess of dimethyldichlorosilane (14.6 mL, 120 mmol) afforded the substituted fluorenyl compound **1b**. The remaining mixture was allowed to attain room temperature and stirred for an additional 2 h. Removal of the solvent and excess of dimethyldichlorosilane in vacuo gave **1b** as a beige powder. This solution was added after dilution with 100 mL of Et_2O at ambient temperature to the separately prepared lithium salt of the 5,6-cyclopenta-2-methylindene **2a** (5.1 g, 30.1 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 over Na_2SO_4. Evaporation of the solvent and recrystallization from *n*-hexane yielded **3d** as a white solid (8.9 g, 22.7 mmol, 75%).

3d: ^{1}H NMR (200 MHz, $CDCl_3$) δ −0.46, −0.51 (2 s, 6H, CH_3 bridge), 2.01 (m, 2H, CH_2 five-membered aliphatic ring), 2.11 (s, 3H, CH_3) 2.83 (pseudo-q, 4H, CH_2 five-membered aliphatic ring), 3.58 (s, 1H, CH indene), 4.18 (s, 1H, CH 9-*H*-fluorene), 6.5 (s, 1H, indene olefinic), 7.08−7.87 (m, 10H, aromatic protons indene system, aromatic fluorene); MS (FD) *m/z* 392 (M^+, 100%). Anal. Calcd C, 85.66; H, 7.19. Found: C, 85.69; H, 7.14.

Preparation of 1-(9-Fluorenyl)-1-(2-methylindenyl)dimethylsilane (3e). Following the procedure described for **3d**, fluorene (4.5 g, 27.2 mmol), dimethyldichlorosilane (13.5 mL, 114 mmol), and 2-methylindene **2b** (3.5 g, 27.2 mmol) gave **3e** as a white solid (7.1 g, 20.1 mmol, 74%).

3e: ^{1}H NMR (200 MHz, $CDCl_3$) δ −0.49, 0.53 (2 s, 6H, CH_3 bridge), 2.11 (s, 3H, CH_3), 3.65 (s, 1H, CH indene), 4.15 (s, 1H, CH 9-*H*-fluorene), 6.54 (s, 1H, indene olefinic), 6.92−7.89 (m, 10H, aromatic protons indene system, aromatic fluorene); MS (FD) *m/z* 352 (M^+, 100%). Anal. Calcd C, 85.17; H, 6.86. Found: C, 85.45; H, 6.82.

Preparation of 1-(9-Fluorenyl)-1-(2-phenylindenyl)dimethylsilane (3f). Following the procedure described for **3d**, fluorene (4.3 g, 26.0 mmol), dimethyldichlorosilane (12.5 mL, 104 mmol), and 2-phenylindene **2c** (5.0 g, 26.0 mmol) gave **3f** as a white solid (8.4 g, 20.2 mmol, 78%).

3f: ^{1}H NMR (200 MHz, $CDCl_3$) δ −0.89, −0.61 (2 s, 6H, CH_3 bridge), 3.97 (s, 1H, CH indene), 4.30 (s, 1H, CH 9-*H*-fluorene), 6.95−7.86 (m, 18H, indene olefinic, aromatic protons indene system, aromatic fluorene); MS (FD) *m/z* 414 (M^+, 100%). Anal. Calcd C, 86.91; H, 6.32. Found: C, 86.62; H, 6.32.

Preparation of *rac*-[1-(9-η^5-Fluorenyl)-2-(2-phenyl-1-η^5-indenyl)ethane]zirconium Dichloride (4c). A 1.5 g portion (4.9 mmol) of 1-(9-fluorenyl)-2-(2-phenylindenyl)ethane, **3c**, was diluted in 60 mL of Et_2O and cooled to −78 °C. After treatment of the ligand precursor with 4.9 mL of *n*-BuLi at −78 °C the reaction mixture was warmed to room temperature and stirred for 2 h. Subsequently, the solvent was removed in

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(31) Chang, Y. H.; Ford, W. T. *J. Org. Chem.* **1981**, *46*, 3758

(32) Busico, V.; Cipullo, R.; Corradini, P.; Landriani, L.; Vacatello, M.; Segre, A. L. *Macromolecules* **1995**, *28*, 1887

vacuo and the resulting lithium salt was diluted with 60 mL of toluene. Cooling to −78 °C and addition of solid $ZrCl_4$ (0.91 g, 3.9 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 **4c** (1.2 g, 2.3 mmol, 56%) could be obtained by recrystallization from toluene solution.

4c: ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.9−4.65 (m, 4H, CH_2 bridge), 6.65 (s, 1H, indene), 6.8−7.9 (m, 17H, aromatic); MS (EI) *m/z* 544, peak distribution of isotopes according to expected contents. Anal. Calcd C, 66.16; H, 4.07. Found: C, 65.88; H, 4.23.

Preparation of *rac*-[Dimethylsilanediyl-(9-η^5-fluorenyl)(5,6-cyclopenta-2-methyl-1-η^5-indenyl)]zirconium Dichloride (4d). 1-(9-Fluorenyl)-1-(5,6-cyclopenta-2-methylindenyl)dimethylsilane, **3d** (1.4 g, 3.56 mmol), was diluted in 60 mL of Et_2O and cooled to −78 °C. After treatment of the ligand precursor with 4.45 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 60 mL of toluene. Cooling to −78 °C and addition of solid $ZrCl_4$ (0.83 g, 3.56 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 **4d** (0.65 g, 1.18 mmol, 33%) could be purified by washing with Et_2O and pentane.

4d: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33, 1.46 (2 s, 6H, CH_3 bridge), 1.74−1.99 (m, 2H, CH_2 cyclopentane ring), 2.17 (s, 3H, CH_3), 2.45−2.99 (m, 4H, CH_2 cyclopentane ring), 6.49 (s, 1H, indene), 6.85−7.98 (m, 10H, aromatic); MS (EI) *m/z* 552, peak distribution of isotopes according to expected contents. Anal. Calcd C, 60.84; H, 4.74. Found: C, 60.58; H, 4.91.

Preparation of *rac*-[Dimethylsilanediyl-(9-η^5-fluorenyl)(2-methyl-1-η^5-indenyl)]zirconium Dichloride (4e). Following the procedure described for **4d**, 1-(9-fluorenyl)-1-(2-methylindenyl)dimethylsilane, **3e** (1.43 g, 4.06 mmol), 1.6 M *n*-BuLi in *n*-hexane (5.07 mL, 8.12 mmol), and $ZrCl_4$ (0.94 g, 4.06 mmol) gave **4e** as a orange solid (0.59 g, 1.15 mmol, 28%).

4e: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.35, 1.48 (2 s, 6H, CH_3 bridge), 2.21 (s, 3H, CH_3), 6.60 (s, 1H, indene), 6.90−8.04 (m, 10H, aromatic); MS (EI) *m/z* 512, peak distribution of isotopes according to expected contents. Anal. Calcd C, 58.57; H, 4.33. Found: C, 58.28; H, 4.48.

Preparation of *rac*-[Dimethylsilanediyl-(9-η^5-fluorenyl)(2-phenyl-1-η^5-indenyl)]zirconium Dichloride (4f). Following the procedure described for **4d**, 1-(9-fluorenyl)-1-(2-phenylindenyl)dimethylsilane, **3f** (1.53 g, 3.68 mmol), 1.6 M *n*-BuLi in *n*-hexane (4.6 mL, 7.36 mmol), and $ZrCl_4$ (0.86 g, 3.68 mmol) gave **4f** as a orange solid (0.59 g, 1.03 mmol, 28%).

4f: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.9, 1.53 (2 s, 6H, CH_3 bridge), 6.97−7.98 (m, 18H, indene, aromatic); MS (EI) *m/z* 574, peak distribution of isotopes according to expected contents. Anal. Calcd C, 62.69; H, 4.21. Found: C, 62.31; H, 4.43.

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