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Communications

rac and *meso* Diastereomers of an Unsymmetric Zirconocene Dichloride Produce Polypropenes with Similar Tacticities and Molar Masses

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Summary: The dual-site zirconocene dichlorides rac- and meso-$SiMe_2$(3-benzylindenyl)(indenyl)$ZrCl_2$ have been synthesized and used, after a methylaluminoxane activation, in propene polymerization. These diastereomers produce isotactic polypropenes with similar microstructures and molar masses under equivalent polymerization conditions.

Methylaluminoxane (MAO) activated zirconocene dichlorides are excellent catalysts in propene polymerization.[1,2] These single-center catalysts have high activity, have excellent copolymerization properties, and produce polypropene with a uniform microstructure and narrow polydispersity. During the last 20 years, a significant amount of effort in catalyst design has been concentrated on the bridged C_2-symmetric complexes aimed at the preparation of commercially valuable isotactic polypropene.[3] Nowadays the influence of the catalyst's symmetry on stereoselectivity as well as the mechanism for stereoselective polymerization, i.e. enantiomorphic site control, is rather well established. However, the controlled diastereospecific synthesis of racemic (C_2 symmetric) metallocenes is still problematic, and depending on the synthetic route, various amounts of mesomeric (C_s symmetric) complex is simultaneously formed.[4,5] From the application point of view, these C_s-symmetric *meso* diastereomers must be separated from *rac* ones, because they lack stereospecificity and produce atactic polypropene with low molar mass,[6] which significantly reduce material properties of the *i*-PP.

In addition to the preparation of isotactic polypropene by C_2-symmetric catalysts, metallocenes have a huge potential to further modify the stereostructure of polypropene by altering the substituent pattern on the cyclopentadienyl rings.[2] Depending on the substituents and, therefore, catalyst symmetry, various types of stereoregular polypropenes such as syndiotactic (C_s symmetric)[7] and hemi-isotactic (C_1 symmetric)[8] have been reported. There has been also specific interest in C_1-symmetric dual-site zirconocenes aimed at an elastic polypropene preparation by introducing a controlled amount of stereoerrors into otherwise stereoregular

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(1) Busico, V.; Cipullo, R. *Prog. Polym. Sci.* **2001**, *26*, 443.

(2) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253.

(3) Spaleck, W.; Küber, F,; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954.

(4) To enhance the rac/meso ratio, various synthetic methods have been applied. See: Zhang, X.; Zhu, Q.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 8093 and references therein.

(5) For the classification of the metallocenes according to their symmetry, see: Farina, M.; Di Silvestro, G.; Terragni, A. *Macromol. Chem. Phys.* **1995**, *196*, 353. Di Silvestro, G.; Sozzani, P.; Terragni, A. *Macromol. Chem. Phys.* **1996**, *197*, 3209. Farina, M. *Trends Polym. Sci.* **1994**, *2*, 80.

(6) Resconi, L.; Jones, R. L.; Rheingold, A. L.; Yap, G. P. A. *Organometallics* **1996**, *15*, 998.

(7) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. *J. Am. Chem. Soc.* **1988**, *110*, 6255.

(8) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48*−*9*, 253.

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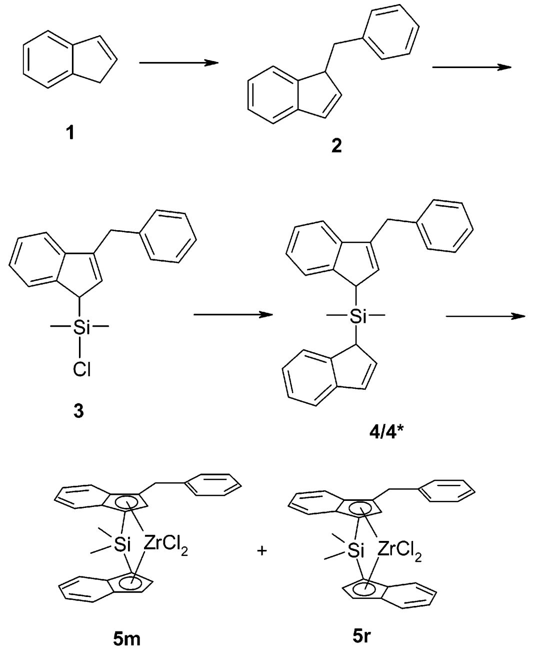
Scheme 1



polypropene.[9] Due to the two different coordination sites, the stereocontrol of the polymerization is more complicated than in the case of C_2-symmetric ones and a mechanism based on the consecutive back-skipping of the growing polymer chain has been demonstrated.[2] In this work, we have modified the structure of classical C_2-symmetric $Me_2Si(Ind)_2ZrCl_2$ by attaching a benzyl group to one of the indenyl ligands. The *rac* and *meso* diastereomers of the obtained C_1-symmetric zirconocene were separated and activated by MAO in order to elucidate their catalytic properties and mechanism in the propene polymerization.

Unsymmetric dimethylsilyl-bridged benzylindenyl ligand precursors are easily accessible via the synthetic route described here (Scheme 1).[10] Benzylindene (**2**) was synthesized from indenyllithium and benzyl bromide.[11,12] (3-Benzyl-1*H*-indenyl)chlorodimethylsilane (**3**) was also synthesized according to the procedure outlined in the literature.[13] The addition of indenyllithium to **3** in diethyl ether produced (3-benzyl-1*H*-indenyl)(1*H*-indenyl)dimethylsilane (**4/4***).[14] The syntheses of **2**, **3**, and **4/4*** occur nearly quantitatively, and therefore, no additional purification steps are required. The corresponding zirconocene dichloride was formed in the reaction between zirconium tetrachloride and dilithium salts of **4/4***. The *rac* and *meso* isomers were then separated by fractional recrystallization, and a crystal structure of *meso*-dimethylsilyl(3-benzylindenyl)(indenyl)zirconium dichloride (**5m**) has been determined (Figure 1).[15]

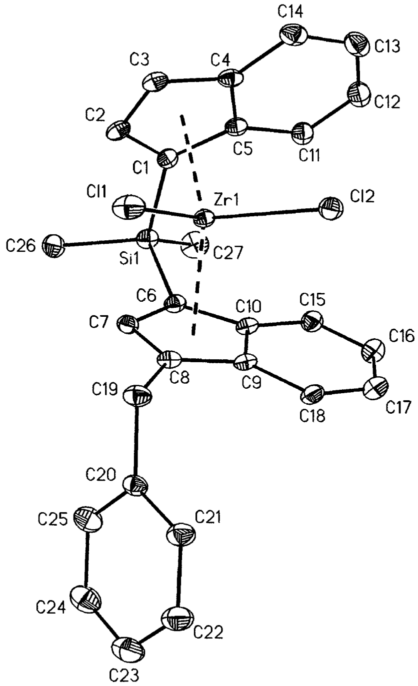


Figure 1. Drawing of the complex *meso*-dimethylsilyl(3-benzyl-η^5-indenyl)(η^5-indenyl)zirconium dichloride (**5m**), with one CH_2Cl_2 molecule omitted. Atoms are represented by anisotropic displacement ellipsoids at the 30% probability level. Bond distances (Å) and angles (deg) include the following: $Cp_{plane}-Cp_{plane}$, 62.1°; $Cp_{center}-Zr-Cp_{center}$, 128.2°; $Cp_{center}(1)-Zr$, 2.229; $Cp_{center}(2)-Zr$, 2.247.

The catalytic activities of the **5m**/MAO and **5r**/MAO are moderate, varying from 0.8 to 11.2 kg of polymer/((mmol of Zr) [C_3] h) being 4 and 7 times less than the values obtained with EBI[16] under similar conditions. After activation, propene consumption was found to increase toward the end of the polymerization run. Regardless of the polymerization conditions used, **5m**/MAO always showed higher activity (2-fold) than the *rac* diastereomer (Table 1). This kind of contradictory outcome was unexpected, as *meso*-$Me_2SiInd(3\text{-}Me\text{-}Ind)ZrCl_2$/MAO, having a symmetry similar to that of **5m**, is 7 times less active than its *rac* isomer.[17] Both **5m**/MAO and **5r**/MAO increase their activity at an increased temperature with a constant propene concentration (0.71 M), while at a constant polymerization temperature (50 °C), different propene concentrations do not significantly affect the polymerization activity of the catalysts. Only at a low propene concentration (0.48 M) does a strong decline in activity take place.

Chain termination is known to be dominating among *meso*-metallocenes, leading to oligomeric PP. In the case of **5m**/MAO and **5r**/MAO, the chain termination rates are, however, rather similar, as reflected in the obtained molar masses (Table 1); only at low temperature (30 °C)

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(9) Rieger, B.; Troll, C. *Macromolecules* **2002**, *35*, 5742.

(10) See the Supporting Information for detailed synthesis and analyses.

(11) Jany, G.; Gustafsson, M.; Repo, T.; Aitola, E.; Dobado, J. A.; Klinga, M.; Leskelä, M. *J. Organomet. Chem.* **1998**, *553*, 173.

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(13) Alt, H. G.; Reb, A.; Kundu, K. *J. Organomet. Chem.* **2001**, *628*, 211. See the Supporting Information for corrected ^1H NMR analysis.

(14) The designation **4/4*** denotes that the product is a mixture of diastereomers.

(15) Compound **5m** ($C_{27}H_{24}Cl_2SiZr$) crystallized from dichloromethane in the triclinic space group $P\bar{1}$ with $a = 10.665(2)$ Å, $b = 13.839(3)$ Å, $c = 9.635(2)$ Å, $\alpha = 108.77(3)°$, $\beta = 90.55(3)°$, $\gamma = 77.99(3)°$, $V = 1314.4(5)$ Å^3, and $D_{calcd} = 1.576$ g/cm^3 for $Z = 2$. Data were collected at 193(2) K on a Rigaku AFC-7S diffractometer. Least-squares refinement of the model based on 4450 unique reflections converged to a final R1 = 3.24% ($I > 2\sigma(I)$) and wR2 = 7.56%. The SHELX97 program was used in refinement (Sheldrick, G. M. University of Göttingen, Göttingen, Germany).

(16) EBI = *rac*-ethylenebis(1-η^5-indenyl)$ZrCl_2$. The polymerization temperature was 50 °C and the propene concentration 0.71 M.

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

Table 1. Propene Polymerization[a] Results of the Catalysts 5m/MAO and 5r/MAO

catalyst	temp (°C)	$[C_3]$ (M)	t_p[b] (min)	yield (g)	activity[c]	[*mmmm*] (%)	[*mmmr*] (%)	[*mmrr*] (%)	[*mrrm*] (%)	M_w[d] (kg mol^{-1})	PD[e]	T_m[f] (°C)
5r	30	0.71	60	2.9	0.83	45.3	15.5	15.4	7.7	38.2	2.03	73.9
5r	50	0.48	33	0.9	1.37	37.1	16.1	16.2	8.3	16.2	2.03	61.6
5r	50	0.71	31	4.6	2.51	40.2	16.0	15.8	8.1	24.5	1.93	66.8
5r	50	1.16	44	11.3	2.66	41.9	15.9	15.5	8.0	29.2	1.88	68.6
5r	50	1.76	33	14.2	2.96	44.1	15.6	15.3	7.7	32.9	2.10	72.7
5r	50	3.38	34	24.4	2.56	45.0	15.4	15.1	7.6	38.0	1.96	75.9
5r	70	0.71	35	8.6	4.15	26.4	15.9	16.7	8.4	11.6	2.39	n.d.
5r	85	0.71	41	14.2	5.87	15.9	13.2	14.8	7.7	4.8	2.21	n.d.
5m	30	0.71	59	3.5	1.00	46.7	16.0	15.3	7.6	19.1	2.89	74.3
5m	50	0.48	37	6.5	4.42	36.0	16.3	16.6	8.2	16.7	2.36	61.8
5m	50	0.71	43	11.8	4.66	39.6	16.2	16.1	7.8	19.5	2.17	64.3
5m	50	1.16	32	16.0	5.10	44.8	15.7	15.6	7.7	22.0	2.19	69.2
5m	50	1.76	41	38.4	6.38	45.8	15.4	15.0	7.5	29.1	1.91	75.7
5m	50	3.38	32	38.4	4.31	47.2	15.2	14.8	7.4	35.7	1.89	80.7
5m	70	0.71	35	22.9	11.19	26.7	16.1	16.7	8.4	12.0	2.65	n.d.
5m	85	0.71	34	19.2	9.60	16.6	14.3	16.0	7.8	6.6	2.33	n.d.

[a] In toluene. [b] Polymerization time. [c] Activity expressed as kg of polymer/((mmol of Zr) $[C_3]$ h). [d] Weight average molar mass. [e] Polydispersity. [f] Polypropene melting temperature.

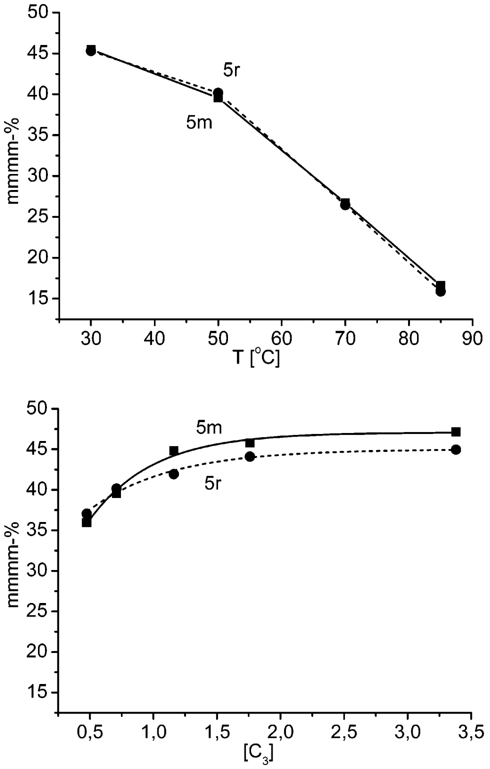

Figure 2. Isotactic pentads versus (a, top) polymerization temperature and (b, bottom) propene concentration.

do polymerizations with **5r**/MAO produce substantially higher molar mass than the *meso* diastereomer.

The ^{13}C NMR spectroscopic characterization of the polypropenes revealed very interesting features. The isotactic pentad sequences in polypropenes are nearly identical when the polypropenes of the catalysts **5m**/MAO and **5r**/MAO are compared (parts a and b of Figure 2).[18] The temperature has a significant effect on stereocontrol in both catalysts; isotacticity decreases quite linearly as a function of the polymerization temperature at a constant propene concentration, and the loss of stereoselectivity is observed at high temperatures. It is notable that the isotacticity vanishes at the same rate with both catalysts (Figure 2a). The stereoselectivity of **5r**/MAO and **5m**/MAO gradually increases with increasing monomer concentration, the latter species being slightly more stereoselective (Figure 2b).

Metallocene structure, especially the presence or absence of β-substituents, determines the catalyst symmetry and the ability to control the stereochemistry of each monomer insertion. **5m** has a benzyl group located on the open side of the zirconocene and two sterically equal aromatic β-substituents on the hindered side (Figure 1), while in **5r** the hindered side consists of two different β-substituents. This ligand arrangement creates two distinct coordination sites, which are diastereotopically related to each other. According to the concept of enantiomorphic site control, the propene coordination to the sterically hindered side of **5m** or **5r** is stereoselective, whereas the open site is aspecific. The modest isotacticity of the obtained polymers is in accordance with this dual-site nature of the catalysts.

Stereochemical control in dual-site metallocene catalysts, even among those with similar molecular symmetries, has been shown to be sensitive to variations in the bridge structure and especially to changes in the ligand substitution pattern.[19] The influence of the sterically bulky benzyl substituent is nicely illustrated when the polymerization behaviors of **5m**/MAO and **5r**/MAO are compared with the those of the *rac* and *meso* diastereomers of $Me_2SiInd(3\text{-}Me\text{-}Ind)ZrCl_2$/MAO; the structure-related symmetries caused by 3-Me and 3-benzyl substituents in Ind−M fragments resemble each

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[18] To further investigate the homogeneity of the polymers, they were subjects of fractionation. As an example, Soxhlet extractions for two polymers made at 50 °C with [prop] = 1.76 M with **5m**/MAO and **5r**/MAO are described. After 3 h of refluxing the diethyl ether fraction was collected (containing approximately 50% of the polymer) and the solvent was changed to hexane, in which all polymers were fully soluble. Diethyl ether and hexane soluble fractions of both polymers were analyzed with ^{13}C NMR, giving identical spectra.

[19] (a) Thomas, E. J.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **2000**, *33*, 1546. (b) Chen, Y.-X.; Rausch, M. D.; Chien, J. W. C. *J. Organomet. Chem.* **1995**, *497*, 1. (c) Thomas, E. J.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **2000**, *19*, 4077. (d) Deisenhofer, S.; Feifel, T.; Kukral, J.; Klinga, M.; Leskelä, M.; Rieger, B. *Organometallics* **2003**, *22*, 3495. (e) Kukral, J.; Lehmus, P.; Feifel, T.; Troll, K.; Rieger, B. *Organometallics* **2000**, *19*, 3767. (f) Dietrich, U.; Hackmann, M.; Rieger, B.; Klinga, M.; Leskelä, M. *J. Am. Chem. Soc.* **1999**, *121*, 4348. (g) Rieger, B.; Jany, G.; Fwazi, R.; Steimann, M. *Organometallics* **1994**, *13*, 647. (h) Gauthier, W. J.; Collins, S. *Macromolecules* **1995**, *28*, 3779. (i) Gauthier, W. J.; Corrigan, J. F.; Taylor, N. J.; Collins, S. *Macromolecules* **1995**, *28*, 3771.

other, but their influences on the polymerization properties are significantly distinct.[20] While *rac*-Me_2SiInd-(3-Me-Ind)$ZrCl_2$/MAO produces isotactic polypropene, its *meso* isomer yields only oligomers, although with similar stereoselectivity.[17] In addition, the diastereomers of the $Me_2SiInd(3\text{-}Me\text{-}Ind)ZrCl_2$ catalyst increase in stereoselectivity at an increased polymerization temperature as well as at decreased monomer concentration, both of which indicate the existence of the chain back-skip mechanism.

In the polymerization reactions with **5r**/MAO and **5m**/MAO, the increase in [*mmmm*] pentad as well as the decrease in [*mrrm*] pentad contents with an increase of propene concentration indicates the presence of a mechanism for the stereocontrol similar to that in the case of C_2-symmetric metallocenes, e.g. EBI and *rac*-[ethylenebis(4,5,6,7-tetrahydro-1-η^5-indenyl)]$ZrCl_2$ (EBTHI). The observed loss of isotacticity at an elevated temperature with **5r**/MAO and **5m**/MAO further supports the above statement, as the stereoerror formation in C_2-symmetric metallocene is to a large extent caused by the wrong enantiofacial insertion at the isospecific site.[21] If the back-skipping mechanism would be prevailing, as it is in the case of some C_1-symmetric metallocenes, catalyst selectivity should increase with the decreasing monomer concentration as well as with increasing polymerization temperature. Further support for the chain migratory insertion mechanism can be found from the pentad ratio of [*mmmr*]:[*mmrr*]:[*mrrm*] $\approx$ 2:2:1, which is typical for the catalysts working under the enantiomorphic site control (Table 1). A similar mechanism for the stereocontrol has been reported also for C_1-symmetric metallocenes *rac*-[1-(9-η^5-fluorenyl)-2-(2,4,7-trimethyl-η^5-1-indenyl)ethane]$ZrCl_2$[19a,c] and *rac*-[1-(9-η^5-fluorenyl)-2-(2-methylbenzo[*b*]indeno[4,5-*d*]thiophen-1-η^5-yl)ethane]$ZrCl_2$.[19d]

It has been shown that the benzyl group attached to a cyclopentadienyl ring in the cationic unbridged [(η^5-cyclopentadienyl)(benzyl-η^5-cyclopentadienyl)]$ZrMe^+$ complex can coordinate with the cationic Zr center via agostic η^1-bonding from an ortho carbon of the phenyl ring.[22] Because of the decent activity of **5r**/MAO and **5m**/MAO, the interaction does not seem to have a significant role here.[23]

These two complexes are to our knowledge the first *rac*/*meso* diastereomer pair that produce polypropene with similar tacticities and molar masses under equivalent polymerization conditions. This similarity indicates that the coordination sites of the diastereomers have equivalent steric surroundings caused by the ligand framework. The diastereomers have a type of polymerization behavior similar to that known for C_2-symmetric metallocenes, and the polypropenes produced can be best characterized as elastomeric isotactic polymers with variable amounts of stereoerrors in their microstructure. Future work will be focused on the enhancement of the catalytic performance of these leading structures as well as on a detailed mechanistic understanding.

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Supporting Information Available: Text describing the synthesis and characterization of the new compounds and the polymerization procedure and tables of crystallographic data for **5m**; the crystallographic data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] Grimmer, N. E.; Coville, N. J.; Koning, C. B. *J. Organomet. Chem.* **2002**, *642*, 195.

[21] Another error-inducing side reaction is kinetic epimerization of the polymer chain end, which might be significant at low monomer concentrations (below 1 mol L^{-1}). See: (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. (c) Busico, V.; Caporaso, L.; Cipullo, R.; Landriani, L.; Angelini, G.; Margonelli, A.; Segre, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 2105. (d) Busico V.; Brita, D.; Caporaso, L.; Cipullo, R.; Vacatello, M. *Macromolecules* **1997**, *30*, 3971. (e) Busico, V.; Cipullo, R.; Caporaso, L.; Angelini, G.; Segre, A. L. *J. Mol. Catal. A* **1998**, *128*, 53.

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[23] The activities of **5m** and **5r** resemble those reported for Et(Ind)Flu$ZrCl_2$ under comparable polymerization conditions,[19f] while in unbridged (1-benzylindenyl)$_2ZrCl_2$ complexes the benzyl substitution prevents propene polymerization and reduces significantly the catalytic activity also in ethene polymerization.[11]