Photoinduced *rac/meso* interconversions of bridged bis(indenyl) zirconium dichlorides [1]

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Abstract

Upon irradiation of a C_2-symmetric *rac*-isomer of an *ansa*-zirconocene dichloride, an interconversion into the C_S-symmetric *meso*-form is observed until a photostationary state between the two diastereomers is reached. The final *rac/meso*-proportion and the interconversion rate depend on the structure of the different metallocenes. Results of α-olefin polymerization catalyzed by [Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$ *rac* and *meso*, respectively, and methylalumoxane (MAO) as cocatalyst are reported. In propene polymerization the *rac*-diastereomer shows the higher activity whereas in pentene, hexene, and octene polymerization the *meso*-isomer is significantly more active. For all polymers a lower molecular weight is found using the *meso*-diastereomer as catalyst.

Keywords: Metallocenes; Stability; Photoconversion; Olefin polymerization

1. Introduction

The C_2 symmetric *rac*-isomers of bridged bis(indenyl) zirconium dichlorides combined with MAO [1] catalyze the isospecific polymerization of α-olefins very efficiently [2]. Since this discovery [3], many variations of the basic catalyst structure [En(H$_4$-Ind)$_2$]ZrCl$_2$ have been developed in order to produce a broad variety of poly-α-olefins with various chemical and physical properties [4,5]. For propene polymerization substitution at the indenyl ring system resulted in major improvements in activity

and molecular weight which led to commercial use of these metallocenes.

We found that depending on their age, toluenic solutions of some of the substituted bis(indenyl) zirconocenes gradually changed their polymerization properties when exposed to daylight. On the other hand, similarly prepared solutions that had been kept in the dark for several weeks produced polymers with identical properties to polymers synthesized with a freshly prepared zirconocene solution. The photoinstability of group IVB *ansa*-metallocenes has mostly been observed and examined for titanium compounds [6–10]. Brintzinger converted (R,S)-[En(H$_4$-Ind)$_2$]TiCl$_2$ (*meso*) completely and selectively into the *rac*-diastereomers (R,R) and (S,S) on exposure to either sunlight or light of a high pressure mercury lamp [11]. Racem-

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[1] This publication is dedicated to Prof.Dr. Erwin Weiß on the occasion of his 70th birthday.

ization of the (R,R)-enantiomer was observed by Collins et al., who also examined the behavior of several mono- or disubstituted ethylene-bridged biscyclopentadienyl titanocenes under irradiation conditions [12]. All titanocenes showed preference of the *rac-* over the *meso-*isomer. For zirconocenes so far only (S,S)-2,3-butylene-1,1'-bis(tetrahydroindenyl) zirconium dichloride was found to photoisomerize, but also showed extensive decomposition upon irradiation in THF solution [13]. We examined *rac/meso*-interconversion of several zirconocenes and one hafnocene when irradiated in aromatic hydrocarbons.

2. Experimental

All procedures were carried out in an argon atmosphere. Toluene and benzene were dried over sodium/potassium, liquid olefins (Merck) over $Al(Et)_3$ before use.

Rac/meso-interconversions were examined using a 366 nm Desaga mercury lamp (75 W) and dry toluene-d_8 or benzene-d_6 as solvents in sealed glass NMR-tubes. *Rac/meso* proportions were investigated by ^{1}H-NMR spectroscopy. Spectra were recorded on an AC 360 Bruker spectrometer.

Propene was purchased from Gerling, Holz and Co. and purified by passage through columns with Cu catalyst (BASF R3-11) and a molecular sieve of 10 Å. Zirconocenes were synthesized in our group or placed at our disposal by Hoechst. MAO was purchased from Witco. Polymerizations were performed in a 1 L Büchi glass autoclave which was charged successively with toluene, cocatalyst solution and monomer. They were initiated by injecting a zirconocene/MAO solution which had been allowed to prereact for 15 min and terminated by addition of ethanol. The products were washed with ethanol/HCl, neutralized, and dried in vacuum. Viscosimetry was carried out with an Ubbelohde capillary 0a ($K = 0.005$). Measuring conditions were 135°C/decahydronaphthalene

for PP, 30°C/toluene for PPe, 25°C/cyclohexane for PHex, 30°C/cyclohexane for PO. The Mark–Houwink constants ($k = 0.0238$ mL g^{-1}, $a = 0.725$, PP; 0.0323, 0.66, PPe; 0.0205, 0.72, PHex; $5.75 * 10^{-3}$, 0.78, PO) have been reported before [14–17]. Molecular weight distributions were determined by gel permeation chromatography on a Waters 150-C instrument (trichlorobenzene, 135°C). Differential scanning calorimetry analyses were performed on a Perkin-Elmer DSC-4 instrument (heating rate 20°C min^{-1}). The minima of the second scan are reported. Polymer ^{13}C-NMR spectra were recorded at 100°C on a 300 MHz Bruker MSL 300 spectrometer. NMR assignments for the higher poly(α-olefins) are reported in literature [18].

3. Results

Comparison of the ^{1}H-NMR spectra of a freshly prepared solution of *rac*-[Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$ and the same sample after exposure to daylight reveals a strong increase of the signals belonging to the *meso*-isomer (Fig. 1) [2]. No decomposition is observed if the irradiation is carried out in benzene-d_6 or toluene-d_8 [3].

The *meso:rac* ratio increases continually with the time the NMR tube is kept in daylight until a final ratio is reached that is not exceeded, even upon prolonged exposure to light. This can

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[2] The starting material had a *rac:meso* ratio of 13:1. ^{1}H NMR(toluene-d_8, 360 MHz, rt): *rac*-[Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$, δ 7.23 (s, 2H), 7.06 (s, 2H), 6.75 (s, 2H),2.99 (hpt, $^3J = 6.9$ Hz, 2H), 2.69 (hpt, $^3J = 6.8$ Hz, 2H), 2.12 (s, 6H), 1.35 (d, $^3J = 6.9$ Hz, 6H), 1.20 (d, $^3J = 6.9$ Hz, 6H), 1.17 (d, $^3J = 6.8$ Hz, 12H), 0.95 (s, 6H); *meso*-[Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$ δ 7.18 (s, 2H), 6.89 (s, 2H), 6.68 (s, 2H), 2.98 (hpt, $^3J = 6.9$ Hz, 2H), 2.66 (hpt, $^3J = 6.9$ Hz, 2H), 2.24 (s, 6H), 1.30 (d, $^3J = 6.9$ Hz, 6H), 1.15 (d, $^3J = 6.9$ Hz, 6H), 1.145 (d, $^3J = 6.9$ Hz, 6H), 1.08 (d, $^3J = 6.9$ Hz, 6H), 1.09 (s, 3H), 0.77 (s, 3H).

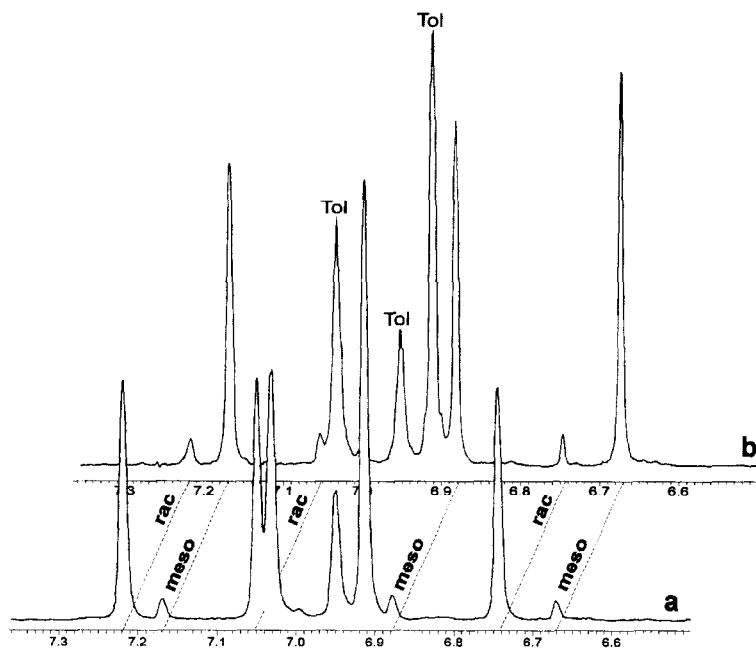[3] The integrals of the undeuterated toluene signals in the solvent were taken as internal standard.

Fig. 1. ^{1}H-NMR of [Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$: front – rac:meso = 13:1; back – rac:meso = 1:9.

be explained assuming that a dynamic equilibrium exists in the photostationary state for the interconversion of the two isomers (Fig. 2). Depending on the structure of the metallocene the photostationary state is reached after several weeks but this time can be shortened to hours or days if a 366 nm mercury lamp is used for irradiation. The value of the meso:rac-ratio in the photostationary state is identical for each

rac-[Me$_2$Si(Ind)$_2$]ZrCl$_2$ meso-[Me$_2$Si(Ind)$_2$]ZrCl$_2$

Fig. 2. Mechanism of rac / meso interconversion according to Bosnich [13].

metallocene, whether the solution has been exposed to an ultraviolet lamp or sunlight.

The conversion of rac-isomer into meso-isomer is observed for silylene bridged bis(indenyl)zirconocenes as well as for ethylene bridged compounds. It is evident that bond cleavage must take place in order for this transformation of configuration to occur. The mechanism of the photoisomerization of group IVB metallocenes has already been studied extensively by Harrigan et al. [6], Vitz et al. [7,8], Tsai [9] and Brindley [10] et al., who homolytically cleaved a Ti-(η^5-cyclopentadienyl) bond and detected recombination products in crossover experiments [7,8]. The reductive elimination of a cyclopentadienyl radical was also found for zirconium by the groups of Davies and Lappert [19]. It is conceivable that a Zr-(η^5-indenyl) bond of a bridged metallocene is similarly broken (Fig. 2). The indenyl radical that is still attached to the complex via the bridge is able to rotate around the Si-C^1-σ-bond (H$_2$C-C^1-σ-bond). Recombination with the metal could occur on both enantiotopic sides of the indenyl ring. This would lead either to the original metallocene or to the corresponding diastereomer.
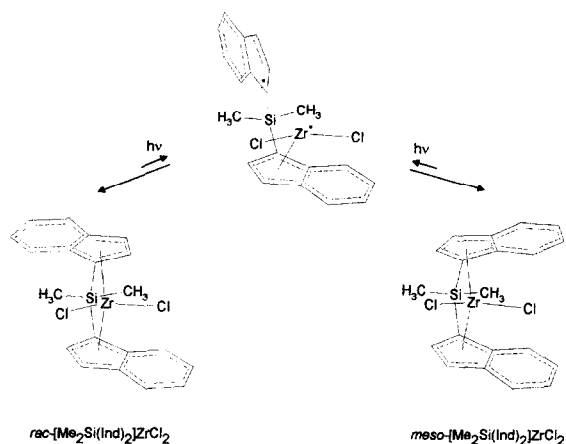
Table 1

Rac-meso ratios of several zirconocenes after 4 weeks of irradiation

Zirconocene	Rac:meso
[Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$	0.11
[Me$_2$Si(2-Me-4-PhInd)$_2$]ZrCl$_2$	0.25
[Me$_2$Si(2-Me-4,5-BzoInd)$_2$]ZrCl$_2$	0.35
[Me$_2$Si(Ind)$_2$]ZrCl$_2$	1.2
[Me$_2$Si(H$_4$-Ind)$_2$]ZrCl$_2$	1.6
[En(Ind)$_2$]ZrCl$_2$	1.7
[En(Ind)$_2$]HfCl$_2$	5.1
[En(H$_4$-Ind)$_2$]ZrCl$_2$	∞
[En(S-H$_4$-Ind)$_2$]Zr[OOC-R-C*(H)(Ph)OCOCH$_3$]$_2$	∞

For highly substituted zirconocenes that are most useful for the production of isotactic polypropene the photostationary state is unfortunately in favor of the *meso*-form while the unsubstituted ones yield an approximately statistic mixture of the two isomers (Table 1). Of the examined metallocenes only [En(H$_4$-Ind)$_2$]ZrCl$_2$ and its derivative [En(S-H$_4$-Ind)$_2$]Zr[OOC-R-C*(H)(Ph)OCOCH$_3$]$_2$ [20] do not show any *meso*-signals after irradiation.

The rate of the interconversion decreases as follows: [Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$ > [Me$_2$Si(2-Me-4,5-BzoInd)$_2$]ZrCl$_2$ > [Me$_2$Si(2-Me-4-PhInd)$_2$]ZrCl$_2$ > [Me$_2$Si(Ind)$_2$]ZrCl$_2$ ≫ [Me$_2$Si(H$_4$-Ind)$_2$]ZrCl$_2$ > [En(Ind)$_2$]ZrCl$_2$ > [En(Ind)$_2$]HfCl$_2$.

To determine the heat stability of the toluenic zirconocene solutions, we brought a sealed NMR tube into an NMR spectrometer at −30°C without exposure to light. Every 20 min a ^{1}H-NMR spectrum was recorded and every hour the temperature was raised by 20°C. We observed neither *rac*/*meso*-interconversion nor decomposition of the catalyst, even at 90°C.

Polymerizations of different α-olefins were carried out using [Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$/MAO as catalytic system. Propene, 1-pentene, 1-hexene, and 1-octene were homopolymerized using (a) freshly prepared toluenic solutions of the metallocene and (b) solutions that had reached the final *rac*/*meso* ratio of 1:9 (Table 2).

Propene polymerization shows a lower activ-

Table 2

Polymerization results obtained with [Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$ for propene, pentene, hexene and octene

Run [a]	Polymer	Act. [b]	M_η [c]	Q [d]	I [e]	T_m [f]	T_g [f]
1a	PP	8160	382	2.0	98	154	
1b		1380	166	3.9	64	153	
2a	PPe	132	88	2.3	33		−18
2b		421	51	1.8	12		−16
3a	PHex	171	107	2.1	33		−34
3b		662	63	1.7	9		−30
4a	PO	145	141	1.7	28		−57
4b		583	78	1.7	8		n.d.

Conditions: T_{Pol} = 30°C; Al/Zr = 7800; t_{Pol} = 1 h for all monomers; 2 bar propene, [Zr] = 1 ∗ 10^{-6} mol/L toluene and c_{Pe} = c_{Hex} = c_O = 1 mol/L toluene, [Zr] = 1 ∗ 10^{-5} mol/L toluene, respectively.
[1] Rac:meso = 13:1 for runs 1a, 2a, 3a, 4a, rac:meso = 1:9 for runs 1b, 2b, 3b, 4b.
[2] In kgPol/(mol Zr*h*c_{Mon}).
[3] In kg/mol.
[4] $Q = M_W/M_N$.
[5] In %mmmm.
[6] In °C.

ity and lower molecular weight for the irradiated solutions. The increase of atactic pentads in propene polymerization of a metallocene solution left to stand without foil-wrapping is depicted in Fig. 3.

The polymerization activities of the higher α-olefins pentene, hexene and octene are generally lower than those of propene polymeriza-
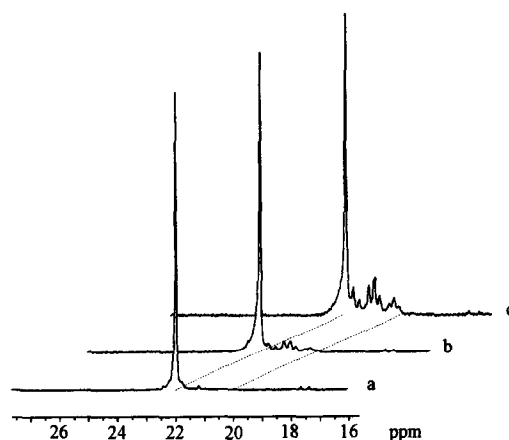

Fig. 3. ^{13}C-NMR of three PP samples prepared with toluenic solutions of [Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$ of different age: a – freshly prepared metallocene solution; b – metallocene solution after 13 days in daylight; c – metallocene solution after 33 days in daylight (near to photostationary state).

tions. It is interesting to note, though, that while in propene polymerization the *rac*-isomer is by far more active than the *meso*-isomer, it is vice versa for the higher α-olefins. The difference in polymerization behavior between the two isomers becomes clear if the activities for pure *rac*- and *meso*-[Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$/MAO, respectively, are calculated (Table 3).

The polymer obtained in run 1b (Table 2) was extracted with boiling heptane to yield an isotactic fraction of 62% and an atactic fraction of 38%. From these values the activities of the *rac*- and *meso*-diastereomer are determined as 8540 and 583 kg Pol/(mol Zr*h*c$_{Mon}$), respectively, in good agreement with the calculations (Table 3). A similar ratio was found by Collins et al. for *rac*- and *meso*-[En(H$_4$-Ind)$_2$]TiCl$_2$ [21].

The isotacticities of the higher poly(α-olefins) are much lower compared to PP. In the polymerizations with the irradiated solutions nearly statistical values are found for the pentads. Since the *meso*-isomer is more active for the higher α-olefins than the *rac*-isomer nearly all of the polymer is produced by the non-stereospecific diastereomer.

The molecular weight decreases with increasing *meso*-content for all monomers. The greatest difference is found in the propene polymerizations resulting in a distinctively bimodal gel permeation chromatogram for the polymer obtained in run 1b (Fig. 4). The atactic heptane-soluble material produced by the *meso*-diastereomer has a molecular weight of 67
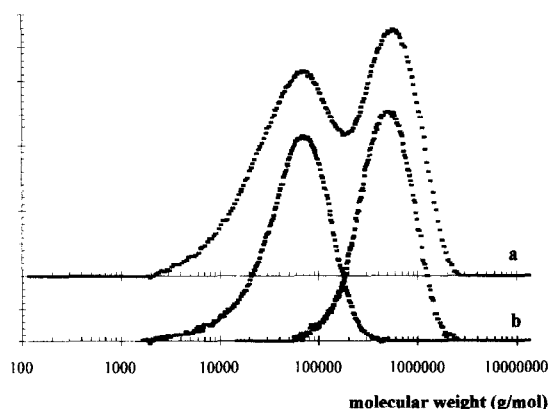

Fig. 4. Gel permeation chromatograms of run 1b (a) and the heptane-soluble and -insoluble fractions obtained from run 1b (b).

kg/mol; for the heptane-insoluble fraction a value of 403 kg/mol is found. The polydispersities are near to two for both fractions. In the case of higher α-olefin polymerizations the difference in molecular weight is less pronounced.

Sample 1a and 1b have nearly identical melting points. The difference in isotacticity is reflected in a reduced heat of fusion (ΔH_f(1b) $\approx$ 0.6ΔH_f(1a)).

4. Conclusions

The results emphasize the necessity to use *ansa*-zirconocene solutions either prepared immediately before polymerization or rigorously excluded from light to prevent isomerization. Highly substituted bridged bis(indenyl) metallocenes prefer the *meso*-configuration under irradiation conditions. *Meso*-[Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$ polymerizes propene with lower activity than its chiral isomer while the situation is vice versa for the higher α-olefins.

Table 3
Calculated activities of diastereomerically pure [Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$

Polymer	Activity [a] rac	Activity [a] meso	Activity ratio rac / meso
PP	8740	562	15.6
PPe	107	456	0.23
PHex	129	721	0.18
PO	107	636	0.17

[a] In kg Pol/(mol Zr*h*c$_{Mon}$).

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