Zirconocene Complexes with Cyclopenta[/]phenanthrene Ligands: Syntheses, Structural Dynamics, and **Properties as Olefin Polymerization Catalysts**

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(2-Methylcyclopenta[/]phenanthryl)₂ZrCl₂ and (2-phenylcyclopenta[/]phenanthryl)₂ZrCl₂ were synthesized and used, after activation with MAO, as catalysts for the polymerization of propene. The resulting polymers had low isotacticities (8-18% [mmmm]). Ligand rotation barriers for the corresponding Zr-dibenzyl derivatives were determined by dynamic NMR spectroscopy. Pathways and transition states for ligand rotation in this series of complexes were studied by molecular-mechanics calculations and are discussed in relation to the microstructure of the respective polymer products.

Introduction

Thermoplastic elastomers with an isotactic-atactic block structure were reported in 1995 by Hauptmann and Waymouth to arise from the polymerization of propene with (2-phenylindenyl)₂ZrCl₂ (1)/MAO.¹ This zirconocene catalyst is thought to interconvert between two isomers with different stereospecificities by rotation of the ligands, the rac-like chiral isomer producing isotactic, crystalline blocks and the achiral meso-like isomer being responsible for atactic, amorphous blocks (Scheme 1). Under these premises, a nonrandom block structure with distinct isotactic and atactic blocks will form provided that the rate of olefin insertion is greater than that of the mutual rotation of the ligand moieties. A more recent comparison of polymers generated by the unbridged complex 1 with reactor blends obtained with mixtures of the rac- and meso-isomers of the corresponding dimethylsilyl-bridged complex supports this view.²

Since annelation of the indenyl ligands in bridged zirconocene complexes with additional aromatic rings was found to enhance catalyst activities and polymer isotacticities,^{3,4} we have now prepared complexes similar to 1 with further rings annelated to the indenyl ligands and studied their properties as propene polymerization



catalysts to characterize the factors that control the formation of thermoplastic elastomeric polyolefin materials.

Results

Preparation and Characterization of Cyclopenta-[/]phenanthrene Zirconium Complexes. Complexes 2 and 3 were synthesized by deprotonation of the respective ligand precursors, 4 and 5,⁴ with *n*-butyllithium and subsequent reaction with ZrCl₄ in toluene according to Scheme 2. Their ¹H NMR spectra in CDCl₃ solution (see Experimental Section) are consistent with an apparent C_{2v} symmetry, which indicates that ligand rotation is fast on the ¹H NMR time scale at room temperature.

Crystals suitable for an X-ray structure analysis were obtained from a concentrated solution of 3 in methylene chloride. Unlike catalyst 1, the unit cell of which contains both a rac-like and a meso-like isomer,1c zirconocene **3** crystallizes, in space group $P\overline{1}$, as its *rac*like isomer only, with the phenyl substituents oriented away from the chloride ligands. The phenyl rings are bent by 4-5° out of the plane of the adjacent cyclopenta-

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^{(3) (}a) Spaleck, W.; Kuber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* 1994, *13*, 954.
(b) Stehling, U.; Diebold, J.; Kirsten, R.; Röll, W.; Brintzinger, H. H.; Jüngling, S.; Mülhaupt, R.; Langhauser, F. *Organometallics* 1994, *13*, 001 964.

^{(4) (}a) Schneider, N.; Huttenloch, M. E.; Stehling, U.; Kirsten, R.; Schaper, F.; Brintzinger, H. H. *Organometallics* **1997**, *16*, 3413. (b) Schneider, N.; Prosenc, M. H.; Brintzinger, H. H. *J. Organomet. Chem.* 1997, 7213.



Table 1. Selected Distances (Å) and Angles (deg)for Complexes 3 and 3B

com	plex 3	complex 3B		
Zr-Cl(1)	2.410(2)	Zr-C(47)	2.322(7)	
Zr-Cl(2)	2.415(2)	Zr-C(54)	2.263(7)	
Zr-Cpc ^a	2.241, 2.234	Zr- Cp _c	2.268, 2.259	
Zr-C _{Cp}	2.475(7)-2.598(6)	$Zr-C_{Cp}$	2.500(7) - 2.644(6)	
Cl(1)– Zr – $Cl(2)$	97.04(8)	C(47) - Zr - C(54)	95.5(3)	
Cp _{c,1} -Zr-Cp _{c,2}	131.9	Cp _{c,1} -Zr-Cp _{c,2}	131.6	
Cp _c -Zr-Cl(1)	105.6, 105.6	$Cp_c-Zr-C(47)$	106.8, 101.7	
$Cp_c - Zr - Cl(2)$	104.8, 106.7	$Cp_c - Zr - C(54)$	107.5, 107.7	

^a Cp_c is the centroid of the cyclopentadienyl ring.



Figure 1. Crystal structure of complex **3** (thermal parameters are drawn at 50% probability; hydrogen atoms are omitted for clarity).

dienyl rings; they are rotated out of this plane by $6-20^{\circ}$. The phenanthrene moiety is likewise bent by $3-5^{\circ}$ out of the cyclopentadienyl plane (Figure 1, Table 1).

The corresponding dibenzyl complexes **2B** and **3B** were obtained by treating the zirconocene dichloride complexes **2** and **3** with benzylmagnesium chloride in toluene. Crystals of **3B** suitable for X-ray structural analysis were obtained by slow evaporation of a benzene solution.

3B crystallized, as yellow prisms, in the chiral space group $P2_12_12_1$. The benzyl ligands are η^1 -bonded

Table 2. MAO-Activated Propene Polymerization, $[Zr] = 55 \ \mu M$, Al:Zr = 1000:1

			activity			
			[10 ⁵ gPP/			%
catalyst	$T[^{\circ}C]$	<i>p</i> [bar]	(mol Žr∙h)]	TOF [s ⁻¹]	$M_{ m w}$	mmmm
1 ^a	0	1.7	6.2	4.1	395 000	13.2
1	0	2	6.8	4.5	580 000	22
2	0	2	10.7	7.1	802 800	8
3	0	2	0.2	0.13	94 300	18

^a See ref 1.



Figure 2. Crystal structure of complex **3B** (thermal parameters are drawn at 50% probability; hydrogen atoms are omitted for clarity).

with $Zr-CH_2-C_6H_5$ angles of 126–133°, similar to those reported for other benzyl zirconocene complexes (Figure 2).⁵ In comparison with **3**, the benzyl groups appear to be more sterically demanding than chloride ligands; they cause an elongation of the $Zr-C_{Cp}$ distances and a more pronounced bending of the phenanthrene framework by 5–10° out of the cyclopentadienyl plane (Table 1).

Propene Polymerizations. Complexes **2** and **3** were studied with regard to their properties as catalysts for the polymerization of propene. The reaction systems contained the respective complexes in a concentration of 55 μ M, together with MAO (Al:Zr = 1000:1) in toluene solution at 0 °C under a constant propene pressure of 2 bar (Table 2).

⁽⁵⁾ Jordan, R. F.; LaPointe, R. E.; Baenzinger, N.; Hinch, G. H. Organometallics **1990**, *9*, 1539.

For comparison, complex **1** was resynthesized and used under the same conditions. The activity of **3**/MAO was significantly less than that of **1**/MAO. While the molecular weight of the polymer obtained was also far lower, the isotacticity was about the same as for **1**/MAO. Nevertheless, no melting transition was detected for the polymer obtained with **3**/MAO.⁶ Complex **2**/MAO, on the other hand, was more active than **1**/MAO and generated a polymer with much higher molecular weight. In this case, however, the polymer was nearly atactic and thus did not give rise to any melting transition either.

Possible reasons for the loss of thermoplastic properties of the polymer obtained with **2** and **3** could be either a lower rate of propene insertion or a faster rotational isomerization in comparison with **1**. Both cases would lead to a diminished isotactic block length and, hence, to the absence of a melting transition. To ascertain to which degree the polymer microstructure depends on variations in the rates of ligand rotation, the latter were investigated by variable-temperature NMR studies.

Dynamic NMR Investigations on Ligand Rotation Rates. Room-temperature ¹H NMR spectra of 2 and **3** in CDCl₃ solution indicate an apparent C_{2v} symmetry, i.e., fast ligand rotations. Some signal broadening from conformational exchange was detected for complex 3, but even at a temperature of -75 °C the internal rotation was not frozen out. Apparently, the rotational activation barrier in 3 is too small for lineshape analysis or EXSY spectroscopy to be feasible. Instead, temperature-dependent NOE measurements were used to determine the rotational barrier. Cross relaxation rates detected in NOESY spectra depend both on the proton-proton distances and on the rate of molecular tumbling. In the temperature region of sign inversion of the NOE, tumbling rates can be quantified and internal energy barriers can be estimated.⁷ By determining NOE intensities for 3 at seven temperatures between 198 and 300 K, the activation energy of the internal rotation was estimated to be $E_{\rm A} = 4.5 \pm 2$ kcal/mol in CDCl₃ solution.⁸

Since a substantially higher isomerization barrier of ca. 12 kcal/mol had been reported for the dibenzyl derivative of **1** (**1B**) by NMR line-shape analysis at temperatures of -72 to 20 °C,⁹ we have studied isomerization rates also of the dibenzyl derivatives **2B** and **3B** by NMR techniques.



Figure 3. Variable-temperature ¹H NMR spectra of complex 3B.

 Table 3. Ligand Rotation Rates and Activation

 Barriers for Complexes 1B-3B

	1 B ^a			2B			3B	
<i>T</i> [K]	$k \left[\mathbf{s}^{-1} \right]$	ΔG^{\sharp}	$T[\mathbf{K}]$	$k \left[\mathbf{s}^{-1} ight]$	ΔG^{\sharp}	$T[\mathbf{K}]$	<i>k</i> [s ⁻¹]	ΔG^{\sharp}
203.1	13	10.7	191.5	50	9.6	222.5	7.5	12.0
213.7	18	11.1	198.5	100	9.6	231.5	20	12.1
222.3	32	11.3	208.0	400	9.6	245.5	90	12.1
232.8	75	11.5	220.0	900	9.8	256.0	300	12.0
243.4	150	11.7				267.0	750	12.1
255.0	400	11.8				281.0	2000	12.2
264.9	775	11.9				306.5	12000	12.2
274.7	1600	12.0				314.5	22000	12.2
285.6	3300	12.0						
292.1	6700	12.0						

^a Taken from ref 9.

While the room-temperature NMR spectra of 2B and **3B** in toluene- d_8 indicate, again, an apparent C_{2v} symmetry, i.e., fast rotation of the ring ligands, two signal sets were detected for the cyclopenta[/]phenanthrene protons at ca. 200 K (Figure 3). The NMR spectra at this temperature correspond to the C_2 symmetry of the *rac*-like X-ray structure of **3B**, where the two halves of each phenanthrene ring have different chemical environments and the protons at each benzyl methylene group are diastereotopic. Signal separations of 56 Hz for H₁, 124 Hz for H₂, 49 Hz for H₃, 669 Hz for H₄, and 615 Hz for H_5 (cf. Figure 3) at 210 K led to wellseparated individual coalescence temperatures. Total band-shape analysis¹⁰ was performed for **3B** over a range of more than 100 K, and ΔG^{\ddagger} was found to be 12.1 ± 0.2 kcal/mol at 0 °C (Table 3). The temperature dependence indicates a slightly negative ΔS^{\dagger} . The diastereotopic methylene protons of the benzyl groups split into an AB spin system below 230 K. An isomerization barrier of 12.0 \pm 0.5 kcal/mol was found for the coupled two-site exchange of these protons, in good agreement with the isomerization barrier of the cyclopenta[/]phenanthrene protons. We can thus conclude that the racemization process of **3B** is associated with an internal energy barrier of 12.1 kcal/mol at 0 °C, which is quite close to that of 12.0 kcal/mol reported for complex 1B.9

⁽⁶⁾ Mansel, S.; Pérez, E.; Benavente, R.; Pereña, J. M.; Bello, A.; Röll, W.; Kirsten, R.; Beck, S.; Brintzinger, H. H. *Macromol. Chem. Phys.* **1999**, *200*, 1292.

⁽⁷⁾ Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH Publishers: New York, 1989.

⁽⁸⁾ Measurements and calculations were performed as described in: Poppe, L.; v. Halbeek, H. J. Am. Chem. Soc. 1992, 114, 1092. Cross relaxation rates (o) were calculated from the relative intensity of cross (I_c) and diagonal (I_d) signals in NOESY spectra with the mixing time t_{m} : $\sigma = -I_c/(I_d t_m)$; according to: Macura, S.; Farmer, B. T., II; Brown, L. R. *J. Magn. Reson.* **1986**, *70*, 493. Overall and internal motions are assumed to be thermally induced: $t_c = A \exp(E_a/RT)$. The NOE H₁ -H₂ was chosen as representative for the overall tumbling rate of 3. The cross relaxation becomes positive above 215 K in toluene, and the activation energy of the overall molecular tumbling was determined to be 1.8 kcal/mol. The NOE $H_5 \rightarrow H_6$ has contributions from the H_5 and H_6 protons of the same phenanthrene ring and additionally it is influenced by the short H_5 to H_6 distance (2.3 Å, estimated from the X-ray structure) between the two phenanthrene rings of 3. This cross relaxation rate is also influenced by the internal motion, and it becomes positive above 225 K. We estimated the correlation time for the internal dynamics according to the spectral density function of Lipari and Szabo (Lipari, G.; Szabo, A. *J. Am. Chem. Soc.* **1982**, *104*, 4546), which assumes two independent tumbling rates.

⁽⁹⁾ Bruce, R. W.; Coates, G. W.; Hauptmann, E.; Waymouth, R. M.; Ziller, J. W. J. Am. Chem. Soc. **1997**, *119*, 11174.

⁽¹⁰⁾ Sandström, J. *Dynamic NMR Spectroscopy*, Academic Press: New York, 1982.

The methyl-substituted complex 2B shows signal separations of only 58 Hz for H₄ and 152 Hz for H₅. Lineshape analysis, in the temperature range of 191-220 K (Table 3), gave $\Delta G^{\ddagger} = 9.6 \pm 0.3$ kcal/mol. To corroborate this estimate, we recorded an EXSY spectrum at 191.5 K with a very short mixing time of 10 ms. Since no assumptions about T_2 relaxation are necessary, EXSY spectroscopy is in general associated with small experimental errors, but was not feasible for complex **3B** due to signal overlap. For **2B**, an exchange rate of 55 s⁻¹ determined from the intensity of the cross signals between the H_5 signals¹¹ corresponds, again, to an isomerization barrier of $\Delta G^{\ddagger} = 9.5 \pm 0.1$ kcal/mol at this temperature. A significantly lowered rotational barrier thus results when the 2-phenyl substituent is replaced by a 2-methyl group. As for complex **1B**,⁹ meso-like isomers of **2B** and **3B** are not detectable by NMR. The question thus arises whether the interconversion between the two enantiomeric *rac*-like forms proceeds by way of a meso-like intermediate.

Force-Field Calculations. To characterize the reaction paths of these isomerizations, we have studied this ligand rotation process by a molecular-mechanics investigation. For this purpose, the Amber94 force field was used to model the organic parts of the complexes.¹² For the coordination geometry around the metal center, we used optimized force-field parameters based on those published by Doman et al.^{13a} and Höweler et al.^{13b} (see Supporting Information). Comparison of calculated and experimentally determined structures for several substituted bisindenyl zirconium dichloride and dibenzyl complexes (Figure 4)¹⁴ documents close agreement with crystallographically determined bond parameters and, in particular, with Cp–Cp torsion angles.¹⁵

In a first step, we investigated the isomerization of the dichloride complexes **2** and **3** and, for comparison, also that of complex **1**, for which molecular-mechanics calculations of ligand rotation have been published by Cavallo et al.¹⁶ and Pietsch et al.¹⁷ Ligand rotation was modeled by changes of the dihedral angles Φ_1 and Φ_2 in steps of 5° (Figure 5), followed by relaxation of all other geometry parameters. The resulting energy surface is shown in Figure 6; relative energies of stationary points are shown in Table 4.

The relative energies obtained for the rotamers of complex 1, while slightly higher than those obtained in the previous force-field studies, show the same energy ordering and similar geometries. The energy surface contains four distinct minima and resembles that obtained by Cavallo et al.¹⁶ The minima **B** and **C** (see Figure 7) correspond to the *rac*-like and *meso*-like rotamers found in the crystal structure of complex 1.

c-,meso-(2-phenylindenyl)2ZrCl2,	1'	observed	calculated
\sim	Zr-Cpc	2 24 Å	2 24 Å
	Zr-Cl	2.42 Å	2.42 Å
	Ø 7r-C	2.55 Å	2.54 Å
	Cpc-Zr-Cpc	131°	130°
	torsion angle θ	171°	178°
\sim	Zr-Cp₀	2.23/2.25 Å	2.23/2.24 Å
	Zr-Cl	2.42/2.43 Å	2.42/2.42 Å
	Ø Zr-Cop	2.54 Å	2.54 Å
	Cp⊶Zr-Cp₀	131°	130°
Q.	torsion angle $\boldsymbol{\theta}$	34°	32°
-(2-phenylcyclopenta[/]phenanth	nryl)2ZrCl2, 3		
\Box	Zr-Cp.	2.23/2.24 Å	2.24 Å
	Zr-Cl	2.41 Å	2.42 Å
9	Ø Zr-Co	2.54 Å	2.54 Å
	Cpc-Zr-Cpc	132°	132°
A B	torsion angle θ	108°	110°
c-(2-phenylcyclopenta[/]phenanth	nryl)2Zr(benzyl)2. 3B	<u>.</u>	
	Zr-Cp₀	2.26/2.27 Å	2.26 Å
	Zr-Cbenzyl	2.26/2.32 Å	2.29 Å
	Ø Zr-C _{op}	2.56 Å	2.56 Å
O ST	Cp₀-Zr-Cp₀	132°	131°
	torsion angle $\boldsymbol{\theta}$	110°	116°
eso-(1-methyl-2-phenylindenyl)2Z	IrCl2, 6 ²		
	Zr-Cp₀	2.24 Å	2.26 Å
St.	Zr-Cl	2.43 Å	2.42 Å
	Ø Zr-Cop	2.55 Å	2.55 Å
	Cp₀-Zr-Cp₀	134°	132°
\bigcirc	torsion angle θ	30°	31°
c-(1-methyl-2-phenylindenyl)₂ZrC	l ₂ , 7 ²		
	Zr-Cp₀	2.24 Å	2.26 Å
a v	Zr-Cl	2.42 Å	2.42 Å
	Ø Zr-C cp	2.55 Å	2.55 Å
$\sim \Rightarrow$	Cp₀-Zr-Cp₀	132°	132°
U T	torsion angle θ	148°	144°

1

1

Figure 4. Observed and calculated structures for substituted bis(indenyl)zirconium complexes.



Figure 5. Definition of torsion angles Φ and θ .

As noted before,^{16,17} the minimum of lowest energy (**A**) corresponds to another *rac*-like rotamer with a smaller torsion angle θ of about 120° between the two ligand moieties. The fourth minimum (**D**), which represents a rotamer with the phenyl substituent of one ligand lying between the two chloride ligands, is rather insignificant due to its high energy.

For the interconversion between enantiomeric *rac*isomers (**A** and **A**') two pathways are possible. The first of these involves rotation of one ligand with the annelated ring passing over the two chloride ligands (transition state **E**). The other one corresponds to the rotation

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⁽¹²⁾ Cornell, W. D.; Cieplak P.; Bayly C. I.; Gould I. R.; Merz K. M., Jr.; Ferguson D. M.; Spellmeyer D. C.; Fox T.; Caldwell J. W.; Kollman P. A. *J. Am. Chem. Soc.* **1995**, *117*, 5179.

^{(13) (}a) Doman, T. N.; Hollis, T. K.; Bosnich, B. J. Am. Chem. Soc. **1995**, 117, 1352. (b) Höweler, U.; Mohr, R.; Knickmeier, M.; Erker, G. Organometallics **1994**, 13, 2380.
(14) Complexes **6** and **7** have not been used in the optimization of

⁽¹⁴⁾ Complexes **6** and **7** have not been used in the optimization of the force field and can thus serve as a check on its accuracy.

⁽¹⁵⁾ Deviations between calculated and crystallographically determined Cp–Cp torsion angles arise when strongly electron-withdrawing substituents, such as fluorine or trifluoromethyl, are present in the aromatic rings.

⁽¹⁶⁾ Cavallo, L.; Guerra, G.; Corradini, P. *Gazz. Chim. Ital.* **1996**, *126*, 463.



Figure 6. Energy surface of ligand rotations of complex **1** with isoenergetic lines at a distance of 1 kcal/mol (redundant data for $\Phi > 180^{\circ}$ given for clarity), with alternative isomerization paths via transition states **E** (dashed line) and **F** (solid line).



Figure 7. Geometries of minima and transition states on the rotational energy surface of complex **1**.

 Table 4. Relative Energies and Torsion Angles^a

 Calculated for Complex 1

	relative energies [kcal/mol]			torsion angles θ^a [deg]		
rotamer	this work	ref 16	ref 17	this work	ref 16	ref 17
A (rac)	0	0	0	128	≈ 105	118
B (<i>rac</i>)	2.7	1.4	n.m.	179	$\approx \! 180$	n.m.
C (meso)	1.6	1.0	0.6	32	${\approx}40$	23
D	3.6	n.m.	n.m.	102	n.m.	n.m.
Е	7.3	<10	5	84	n.m.	47
F	5.5	<8	n.m.	119	n.m.	n.m.

 a Definition of torsion angle θ see Figure 5; n.m.: not mentioned or not calculated.

with the substituent in 2-position passing over the chloride ligands (transition state \mathbf{F}).¹⁸

Analogous calculations for complexes **2** and **3** yield similar energy surfaces, with results as summarized in Table 5. For the three complexes calculated, the isomerization between the two enantiomeric *rac*-like isomers is possible only with the *meso*-like form as an intermediate. On these isomerization paths the highest activation barrier is always the one between the *rac*and *meso*-like rotamers, which differ by less than 2 kcal/ mol in their relative energies (Figure 8). We can thus



Figure 8. Energy profile for the racemization of complex **1** along the isomerization paths indicated in Figure 6.

Table 5. Relative Energies Calculated for the Dichloride Complexes 1–3 and for the Dibenzyl Complexes 1B–3B [kcal/mol]

	-					
rotamer	1	3	2	1B	3 B	2B
A (<i>rac</i>)	0	0	0.8	0	0	2.3
B (<i>rac</i>)	2.7	2.8	0	4.3	2.7	0
C (meso)	1.6	1.6	0.4	1.6	1.5	2.0
D	3.6	3.2	0.4	5.0	2.5	1.1
Ε	7.3	7.8	5.5	7.7	8.3	6.2
F	5.5	4.9	3.7	8.8	11.2	8.6

conclude that the activation barrier of the rac-rac isomerization determined by NMR spectroscopy is identical with the barrier for the rac-meso isomerization, proposed to be crucial for the mechanism of the polymerization reaction.

In all three complexes, rotation via transition state **F** is favored. For complex **3**, the activation barrier of 4.9 kcal/mol, calculated for the rotation over transition state **F**, is in good agreement with the value of 4.5 ± 2 kcal/mol, determined by dynamical NMR. Among complexes **1**–**3**, the highest activation barrier of 5.5 kcal/mol is observed for complex **1**, while a value of only 3.7 kcal/mol is obtained for the methyl-substituted complex **2**.

Determination of the energy surfaces for the dibenzyl complexes 1B-3B is complicated by the rotational freedom of the benzyl ligands, which results in additional minima and transition states. The values in Table 5 represent the minima of lowest energy and the lowest activation barriers for the interconversion between *rac*- and *meso*-like isomers. As for the dichlorides 1-3, racemization proceeds also for the dibenzyl complexes 1B-3B by way of a transition state located between a *rac*- and a *meso*-like isomer.

In contrast with the dichloride complexes 1-3, rotation over transition state **E** is favored however for the benzyl derivatives 1B-3B. The activation barriers thus obtained follow similar trends as the experimental values determined by dynamic NMR (Table 6): The same values are found for complexes 1B and 3B, while the value for 2B is smaller by 2 kcal/mol. The difference of 4 kcal/mol between the calculated values of ΔH^{\ddagger} and the measured values of ΔG^{\ddagger} can be attributed to entropic factors. In the transition state for this rotation the phenyl ring of one of the benzyl ligands is sandwiched between both indenyl ligands (Figure 9). For complex $1B^9$ as for 3B slightly negative values of ΔS^{\ddagger} , derived

⁽¹⁸⁾ In contrast with a previous report, 17 our calculations show no evidence of π -stacking interactions during ligand rotation. This is in line with a recent experimental study on hydrogenated analogues of complex $1.^{\rm 1d}$



Figure 9. Transition state E for the ligand rotation of complex 1B.

 Table 6. Comparison of Observed and Calculated Activation Barriers [kcal/mol]

	1B	3B	2B
ΔH^{\ddagger} (calculated)	8	8	6
ΔG^{\ddagger} (observed)	12	12	10

from the experimental data, are in agreement with a loss of rotational freedom in the transition state.

To decide which rotational transition state (E as observed for the dibenzyl derivatives or F as for the dichlorides) is favored by the active species in polymerization, the latter was modeled for 1 and 3 in a manner similar to that proposed by Pietsch et al. for complex 1,¹⁷ i.e., by using a 2-methyl-1-butyl ligand to model the growing polymer chain, while keeping the second coordination site occupied by a methyl group. Due to the reduced symmetry of these complexes and the high number of possible rotamers of the 2-methyl-1-butyl ligand, several additional minima and transition states were found on the energy surfaces. Interconversion between all minima proceeds most easily by rotation via transition state F. For the phenyl-substituted indenyl and cyclopenta[/]phenanthrene complexes, 1C and **3C**, we find rotational barriers of approximately 4–6 kcal/mol. Apparently, the transition to a *meso*-like rotation intermediate occurs more easily in the presence of one relatively large (2-methyl-1-butyl) and one small (methyl) ligand than in the presence of the two mediumsized benzyl ligands. With regard to the height of the rotation barrier as well as to their rotation via transition state **F**, these model complexes thus resemble more closely their dichloride precursors than the dibenzyl derivatives.

Discussion

Our molecular-mechanics calculations allow us to delineate in detail the reaction paths for the racemization of a number of unbridged zirconocene dichloride and dibenzyl complexes; they reproduce, furthermore, the rotational barriers derived from dynamic NMR methods with reasonable accuracy. The results of these calculations thus support the assumption that, for each of the complexes studied, the experimentally determined racemization barrier corresponds directly to that of the conversion between its *rac*-like and *meso*-like isomers, i.e., for the isomerization process thought to be responsible for the switch in stereoselectivity typical for these catalyst systems.¹⁹

Based on experimental data for the dibenzyl complexes 1B and 3B, and on calculations for 1 and 3, 1B and **3B**, and **1C** and **3C**, we have to assume similar ligand rotation barriers for the 2-phenyl-substituted catalysts 1/MAO and 3/MAO. The observation that polymers produced with 3/MAO appear to containunlike the stereoblock polymers produced with 1/MAOonly short isotactic sequences can be explained by the unexpectedly low rate of olefin insertion in 3/MAO, which is indicated by an activity 1-2 orders of magnitude lower than that of 1/MAO. For the 2-methylsubstituted catalyst 2/MAO, on the other hand, which has an even higher activity than 1/MAO, the substantially reduced ligand rotation barrier is likely to cause the lack of crystallizable isotactic stereoblocks in its polypropene products.

While the relative rates of ligand rotation and the polymerization activities estimated for catalysts 1-3/ MAO are thus qualitatively in line with the microstructures of their respective polypropene products, a disturbing but probably significant quantitative discrepancy remains to be explained:⁹ The ligand rotation barrier of $\Delta G^{\ddagger} \approx 5$ kcal/mol, experimentally determined for the dichloride complex 3 and calculated for this complex as well as for the catalyst models 1C and 3C, corresponds to rates of ligand rotation of ca. 10⁸ s⁻¹. These rotational frequencies, and even the reduced ligand rotation rates of $1000-1500 \text{ s}^{-1}$ found for the dibenzyl complexes **1B** and **3B**, exceed the average insertion rate of 0.1-10 olefins/s in these catalyst systems by several orders of magnitude. This is not in line with the mechanism proposed for stereoblock formation with these catalysts.

As an explanation for this apparent discrepancy, we propose that olefin insertion rates during actual chain growth are much higher than the apparent turnover frequencies given in Table 2, which are derived from time-averaged activities: Consideration of ligand displacement equilibria and kinetics indicates that each Zr-polymeryl cation is converted from the preponderant, presumably inactive contact-ion pair to a reactive outer-sphere cation-anion pair only for minute fractions of its total lifetime.²⁰ During these short periods, uninterrupted chain growth would have to occur with an actual rate much higher than that derived from time-averaged activities.

Control of stereoblock polymer formation by ligand rotation would then require that the periods of active chain growth of a Zr–polymeryl species are shorter than its average lifetime by a factor of at least 10^3 and possibly of as much as 10^8 , such that the actual rate of olefin insertion during these growth periods exceeds that of ligand rotation. While these relations appear conceivable in light of energy differences of roughly 8 kcal/mol associated with anion displacement from alkylmetallocene cations,²¹ substantial further studies, e.g., with regard to the dependence of isotactic block lengths

⁽¹⁹⁾ The assumption that the *rac*-like isomers of these complexes are isoselective is supported by the observation that the rac isomer of the Me₂Si-bridged analogue of **2** produces highly isotactic polypropene.^{4a}

^{(20) (}a) Fink, G.; Zoller, W. *Makromol. Chem.* **1981**, *182*, 3265, and references therein. (b) Reichert, K. H. *Angew. Makromol. Chem.* **1981**, *94*, 1. (c) Beck, S.; Prosenc, M.-H.; Brintzinger, H. H. *J. Mol. Catal. A: Chem.* **1998**, *128*, 41.

⁽²¹⁾ Chan, M. S. W.; Vanka, K.; Pye, C. C.; Ziegler, T. Organometallics 1999, 18, 4624.

on monomer concentrations,²² are clearly required to corroborate this view.

Experimental Section

General Comments. Moisture- and air-sensitive compounds were handled under an argon atmosphere using Schlenk or drybox techniques. THF and toluene were distilled from sodium, pentane was distilled from Na-K-alloy, and CH2-Cl₂ was distilled from CaH₂. ZrCl₄ (Fluka) was sublimed prior to use. Cyclopenta[]phenanthrenes 4 and 5 were synthesized as described earlier.⁴ Benzylmagnesium chloride was synthesized according to the literature.²³ ¹H and ¹³C NMR spectra were obtained with a Bruker DRX 600 spectrometer at a proton resonance frequency of 600.13 MHz. Chemical shifts are referenced to the solvent, and temperatures are determined from the signal separation in a MeOH sample. ¹H spin systems were identified from TOCSY and DQF-COSY spectra, and ¹³C resonances were assigned from inverse ¹³C-¹H shift correlations (HMQC).²⁴ Mixing times in NOESY (EXSY) spectra were chosen short enough to prevent spin diffusion. Exchangebroadened spectra were simulated with the program DNMR-SIM.²⁵ ΔG^{\ddagger} values were calculated from the two-site exchange rates with the Eyring equation.²⁶

General Method for Syntheses of Bis(cyclopenta[1]phenanthrene)zirconium Dichlorides. A solution of 2.2 mmol of the respective cyclopenta[/]phenanthrene in 10 mL of THF was treated with 1.44 mL of a 1.6 M solution of *n*-butyllithium in hexane at -78 °C. After stirring overnight the reaction mixture was evaporated to dryness, washed with 30 mL of pentane, and treated with a suspension of 415 mg of zirconium tetrachloride (1.09 mmol) in 50 mL of toluene. The mixture was stirred for 3 h at 90 °C, cooled to room temperature, stirred overnight, and filtered. The yellow residue was washed with 20 mL of pentane and THF.

Bis(2-methylcyclopenta[]phenanthrene)zirconium Dichloride (2). The yield was 390 mg (58%). ¹H NMR (600 MHz, CDCl₃): δ 8.53–8.49 (m, 4 H), 8.94–7.97 (m, 4 H), 7.61-7.58 (m, 8 H), 6.64 (s, 4 H), 1.53 (s, 3 H). MS (EI): m/z 620 (28%, M⁺), 391 (100%, M⁺ – 4), 230 (85%, 4-H), 215 (28%, 4 – Me). Anal. Calcd for $C_{36}H_{26}ZrCl_2$: C, 69.66; H, 4.22. Found: C, 69.50; H, 4.52.

Bis(2-phenylcyclopenta[]phenanthrene)zirconium Dichloride (3). The yield was 90 mg (11%). ¹H NMR (600 MHz, CD₂Cl₂): δ 8.44 (d, J = 8.2 Hz, 4 H₁), 7.55 (t, J = 8.2Hz, 4 H₂), 7.41 (t, J = 7.8 Hz, 4 H₃), 7.38 (d, J = 7.8 Hz, 4 H₄), 7.06 (s, 4 H₅), 7.63–7.57 (m, 10 H_{Ph}). MS (EI): m/z 744 $(12\%, M^+)$, 453 (41%, $M^+ - 5$), 415 (18%, $M^+ - 5 - Cl$), 291 (85%, 5 – H). Anal. Calcd for C₄₆H₃₀ZrCl₂·CH₂Cl₂: C, 68.03; H, 3.89. Found: C, 68.14; H, 4.00.

Bis(2-methylcyclopenta[1]phenanthrene)zirconium Dibenzyl (2B). A 77 mg sample of 3 (0.12 mmol) in 10 mL of toluene was treated with 0.23 mL of a 1.1 M solution of benzylmagnesium chloride (0.25 mmol) in ether. The reaction mixture was stirred for 2 days at room temperature, evaporated to dryness, washed with 10 mL of pentane, and extracted with 20 mL of toluene. The toluene extract was evaporated to dryness to yield a yellow powder. ¹H NMR (600 MHz, C₆D₅CD₃): δ 8.26 (d, J = 7.5 Hz, 4 H₁), 7.33–7.28 (m, 8 H_{2.3}),

(25) DNMR-SIM (Hägele, G., Heidelberg, Germany) is available via http://www.uni-duesseldorf.de/WWW/MathNat/AC1/forschung/nmr/ dnmr-sim.htm. The program is based on DNMR 3 (Binsch, G.; Kessler, H. Angew. Chem., Int. Ed. Engl. 1980, 19, 445).
(26) Kessler, H. Angew. Chem. 1970, 82, 237.

Table 7. Crystallographic and Experimental Data^a for Complexes 3 and 3B

	3	3B
formula	C46H30Cl2Zr·CH2Cl2	C ₆₀ H ₄₄ Zr
cryst color and form	yellow needle	yellow orthogonal
		prism
cryst syst	triclinic	orthorhombic
space group	$P\overline{1}$	$P2_{1}2_{1}2_{1}$
a [Å]	10.218(5)	12.801(4)
<i>b</i> [Å]	10.993(6)	17.842(5)
c [Å]	16.430(9)	18.223(6)
α [deg]	100.16(3)	90
β [deg]	97.03(3)	90
γ [deg]	93.71(3)	90
$Z; V[Å^3]$	2; 1796(2)	4; 4162(2)
cryst size [mm]	0.1 imes 0.3 imes 0.4	0.3 imes 0.3 imes 0.4
$T[K]; d_{calcd} [g/cm^3]$	243; 1.534	243; 1.366
μ [mm ⁻¹], <i>F</i> (000)	0.640, 844	0.306, 1776
scan mode; θ range	adaptive ω ;	adaptive ω ;
[deg]	1.9 - 24.0	2.3 - 27.0
no. of reflns collcd	5299	10 021
no. of ind reflns	4810	8970
obsd reflns	3920	5004
$(I > 2\sigma(I))$		
solution ^b	direct methods	direct methods
no. of params; GOF	470; 0.988	550; 1.037
$R(F), \hat{R}_{w}(F^{2})^{c}$	0.0627, 0.1514	0.0660, 0.1244
largest diff peak	1.020	0.829
[e Å ³]		
Flack <i>x</i> -param		-0.10(8)

a Conditions: Siemens P4 four-circle diffractometer, Mo Ka radiation, graphite monochromator. All non-hydrogen atoms were refined anisotropically. Hydrogens were refined on the calculated positions with fixed isotropic U, using riding model techniques. SHELXS-86, SHELXL-93 (G. Sheldrick, University of Göttingen, 1990 and 1993). ^{*c*} Weighting scheme: **3**: $w^{-1} = \sigma^2(F_0^2) + (0.0697P)^2$ + 12.2662*P*. **3B**: $W^{-1} = \sigma^2(F_0^2) + (0.0467P)^2 + 2.3585P$, with P = $(F_0^2 + 2F_c^2)/3.$

7.54 (d, J = 7.4 Hz, 4 H₄), 6.06 (s, 4 H₅), 6.64 (d, J = 7.4 Hz, 4 H_{0-Ph}), 7.07 (t, J = 7.6 Hz, 4 H_{m-Ph}), 6.82 (t, J = 7.2 Hz, 2 H_{p-Ph}), 1,33 (s, 6 H_{Me}), 0,63 (s, 4 $H_{methylene}$).

Bis(2-phenylcyclopenta[]phenanthrene)zirconium Dibenzyl (3B). A 20 mg sample of 4 (0.03 mmol) in 5 mL of toluene was treated with 0.05 mL of a 1.1 M solution of benzylmagnesium chloride (0.06 mmol) in ether. The reaction mixture was kept for 2 days at room temperature and evaporated to dryness to yield a yellow powder. ¹H NMR (600 MHz, C₆D₅CD₃): δ 8.08 (d, J = 8.1 Hz, 4 H₁), 7.21 (t, J = 7.4Hz, 4 H₂), 7.07 (t, J = 7.3 Hz, 4 H₃), 6.6 (bs, 4 H₄), 6.8 (bs, 4 H₅), 7.50 (d, J = 7.4 Hz, 4 H_{o-Ph-Phe}), 7.34 (t, J = 7.4 Hz, 4 $H_{m-Ph-Phe}$), 7.26 (t, J = 7.3 Hz, 2 $H_{p-Ph-Phe}$), 6.30 (d, J = 7.5Hz, 4 H_{0-Ph-Bn}), 6.98–6.96 (m, 4 H_{m-Ph-Bn}), 6.82 (t, J = 7.3Hz, 2 H_{p-Ph-Bn}), 0,52 (s, 4 H_{methylene}).

Polymerizations and Polymer Analysis. Into a Büchi 1 L autoclave (previously cleaned by stirring with a 0.5% solution of AlⁱBu₃ in toluene and subsequently dried in vacuo at 50 °C) were added, in the following order, 350 mL of toluene, 4.50 g of methylaluminoxane MAO (5.21 mass % Al, molar mass ca. 800, Witco AG) in 10 mL of toluene, and 10 mL of a toluene solution of the zirconocene complex (Table 2). After the reaction mixture was stirred for 30 min at 0 °C under an argon atmosphere of 1 bar, the autoclave was pressurized with a propene pressure of 2 bar (i.e., to a total pressure of 3 bar). During the polymerization reaction, the total pressure of 3 bar was kept constant by further addition of propene. Finally, the autoclave was vented and the reaction mixture drained into 1 L of methanol acidified with 10 mL of concentrated aqueous HCl. The precipitated polymer was collected by filtration, washed with methanol, and dried at 50 °C to constant weight. Molecular weight distributions were determined by GPC, melting points by DSC (Kunststoff-Labor, BASF AG). Polymer ¹³C NMR spectra were measured in $C_2D_2Cl_4$ (δ 74.1 ppm) at

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⁽²³⁾ Organikum; Becker, H. G. O., et al. VEB Deutscher Verlag der Wissenschaften: Berlin, 1977; p 623.

⁽²⁴⁾ General NMR procedures for biopolymer characterization are described by: Kessler, H.; Schmitt, W. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; Wiley: Chichester, 1996.

analyzed by methods described in the literature.^{27,28}

120 °C on a 250 MHz spectrometer operated at 62.9 MHz and publica

Force-Field Calculations. Calculations were carried out using the Hyperchem 5.0 program on a conventional PC (Pentium 200) in the manner described above. In the case of complexes **1B**–**3B**, **1C**, and **3C** care was taken to find the overall minimum for each point with respect to the rotational freedom of the ligands. Minima on the obtained energy surface were optimized without restraints. Transition states were located as points of highest energy on rotation paths with one torsion angle restrained with an accuracy of $\pm 1^\circ$.

Crystal Structure Determinations. Space group determinations, diffraction data collection, and solution and refinement of the structures were conducted as summarized in Table 7. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary

publication no. CSD 408120 and CSD 408121. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: 2D plots of the energy surfaces calculated, force-field parameters involving metal coordination, and tables of the X-ray crystallographic data for complexes **3** and **3B**. This material is available free of charge via the Internet at http://pubs.acs.org.

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