

Propylene Polymerization with Chiral and Achiral Unbridged 2-Arylindene Metallocenes

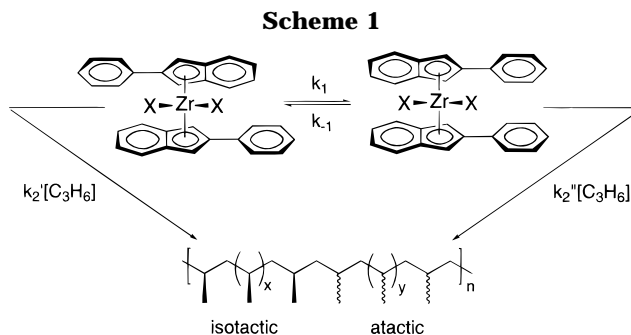
Raisa Kravchenko, Athar Masood, and Robert M. Waymouth*

Department of Chemistry, Stanford University, Stanford, California 94305

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Unbridged 2-arylindenyl metallocene complexes, such as bis(2-phenylindenyl)zirconium dichloride, in the presence of methylaluminoxane (MAO) are catalyst precursors for the synthesis of elastomeric polypropylenes. The effects of 1-methyl substitution on the polymerization behavior of these unbridged 2-arylindene complexes have been studied. The reaction of the lithium salt of 1-methyl-2-phenylindene with $ZrCl_4$ leads to the formation of two diastereomers of bis(1-methyl-2-phenylindenyl)zirconium dichloride: *rac*- and *meso*-(1-Me-2-PhInd) $_2ZrCl_2$. The two isomers have been separated by fractional crystallization and identified by X-ray crystallography. X-ray crystallographic analysis reveals that the dihedral angles between the planes of the phenyl and the indenyl rings have significantly increased upon 1-methyl substitution (28–34° compared to 10–12° for unsubstituted (2-PhInd) $_2ZrCl_2$), which suggests strong steric repulsion between the 1-methyl and 2-phenyl groups. In ethylene polymerization, the productivity of the catalyst derived from the *meso*-isomer is similar to that of the catalyst derived from (2-PhInd) $_2ZrCl_2$; higher productivity is observed for the catalyst derived from the *rac*-isomer. In polymerization of propylene, both substituted catalysts have a significantly lower productivity than the catalyst derived from unsubstituted (2-PhInd) $_2ZrCl_2$ and generate amorphous polypropylene with a low molecular weight and isotacticity.

The physical properties of polyolefins are strongly influenced by the microstructure of the polymer. Stereoregular isotactic polypropylene is a high-melting thermoplastic material, while stereorandom atactic polypropylene is amorphous. Polypropylene consisting of isotactic and atactic blocks is a thermoplastic elastomer. Natta was the first to produce rubbery polypropylene and to interpret its properties in terms of a stereoblock microstructure.^{1,2} Subsequent studies,^{3–5} particularly those by Collette and co-workers led to improved heterogeneous catalysts for the production of elastomeric polypropylene.^{6,7} The first homogeneous bridged titanocene-based system that generated elastomeric polypropylene was described by Chien and co-workers.^{8–10} Chien proposed a mechanism where the monomer insertion occurred sequentially at aspecific and isospecific coordination sites of the C_2 -symmetric metallocene. Collins has investigated a closely related system and proposed a different mechanism to account



for the stereoblock structure.^{11,12} We have recently reported a strategy for the production of stereoblock polypropylene with a nonbridged metallocene, bis(2-phenylindenyl)zirconium dichloride, (2-PhInd) $_2ZrCl_2$ (**1**).^{13–15} This catalyst was designed to switch its coordination geometry from aspecific to isospecific during the course of polymerization in order to generate atactic and isotactic blocks (Scheme 1). An advantage of this system is the ability to influence the structure and properties of the polymers by manipulation of the catalyst structure or polymerization conditions.^{13–15} For example, we have shown that catalyst modification through ligand substitution in 3,5-positions on the phenyl ring has a dramatic effect on its productivity and stereospecificity.¹⁴ Thus, by changes in catalyst or

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polymerization conditions, we have prepared materials ranging in properties from amorphous to elastomeric to tough plastics.¹⁵

As part of our continuing studies of ligand effects on the polymerization behavior of bis(2-aryindenyl) metallocenes, we now report the synthesis and study of zirconocenes with 1-methyl-substituted 2-phenylindenyl ligands, 1-Me-2-PhInd (**2**). In contrast to the previously studied 3,5-substitution on the phenyl ring, unsymmetric substitution in the 1-position on the indenyl reduces the overall symmetry of the ligand. As a result, two diastereomers: *rac*- and *meso*-(1-Me-2-PhInd)₂ZrCl₂ (**3-*rac*** and **3-*meso***) are expected. The ligand rotation in **3-*rac*** and **3-*meso*** can generate additional rotamers with a type of symmetry not accessible in the case of the previously studied bis(2-aryindenyl) complexes. Furthermore, these complexes provide insight on the effect of the 1-methyl substituent on the structure and polymerization behavior of 2-arylidene metallocene catalysts.

Experimental Section

General Considerations. All organometallic reactions were conducted using standard Schlenk and drybox techniques. Elemental analyses were conducted by Desert Analytics. Unless otherwise specified, all reagents were purchased from commercial suppliers and used without further purification. Bis(2-phenylindenyl)zirconium dichloride (**1**) was prepared according to the literature procedure.¹⁶ Pentane and methylene chloride used in organometallic synthesis were distilled from calcium hydride under nitrogen. Tetrahydrofuran was distilled from sodium/benzophenone under nitrogen. Toluene was passed through two purification columns packed with activated alumina and supported copper catalyst.¹⁷ Chloroform-*d*₃ and methylene chloride-*d*₂ were distilled from calcium hydride.

1-Methyl-2-phenylindene (2). Butyllithium (2.5 M in hexanes, 3.0 mL, 7.6 mmol) was added dropwise to a suspension of 2-phenylindene (1.382 g, 7.2 mmol) in THF (50 mL) at -78 °C to yield a dark orange solution. The solution was allowed to warm to room temperature and stirred for 30 min. Methyl iodide (1.3 mL, 22 mmol) was added to this solution dropwise, and the light brown reaction mixture was heated to 40 °C and stirred for 24 h. After that the solvents were removed *in vacuo*, and the resulting light brown solid was recrystallized from EtOH (25 mL) at room temperature affording white needles (1.075 g, 75% yield). ¹H NMR (CDCl₃, 20 °C, 300 MHz): δ 7.52–7.19 (overlapping signals from aromatic protons, 9H), 3.74 (q, *J* = 1.0 Hz, 2H), 2.31 (t, *J* = 1.1 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 20 °C, 75 MHz): δ 147.49 (C), 142.42 (C), 140.31 (C), 137.56 (C), 134.70 (C), 128.37 (CH), 128.24 (CH), 126.63 (CH), 126.40 (CH), 124.74 (CH), 123.32 (CH), 119.11 (CH), 40.96 (CH₂), 11.94 (CH₃).¹⁸

***rac*- and *meso*-Bis(1-methyl-2-phenylindenyl)zirconium Dichloride (3-*rac* and 3-*meso*, Respectively).** Butyllithium (2.5 M in hexanes, 6.7 mL, 17 mmol) was added dropwise to a colorless solution of 1-methyl-2-phenylindene (3.447 g, 17 mmol) in THF (50 mL) at -78 °C to give a dark yellow solution. The solution was slowly warmed to room temperature, stirred for 30 min, and then evaporated to dryness. Toluene (50 mL) was added to the resulting yellow solid. The resulting suspension was combined with ZrCl₄ (1.974 g, 8.4 mmol) suspended in toluene (70 mL). The

reaction mixture was stirred at 40 °C for 24 h. The turbid lemon yellow solution was cooled to room temperature and filtered through a frit packed with Celite. The Celite layer was washed with toluene (3 × 30 mL). The filtrates were evaporated to dryness. The resulting yellow solid (3.536 g, 65% yield) contained **3-*rac*** and **3-*meso*** in a 60:40 ratio. Repeated crystallization from CH₂Cl₂ afforded orange cubes of **3-*meso*** (554 mg, 10%). Repeated crystallization from THF/pentane (4:1) gave **3-*rac*** as yellow rods (610 mg, 11%). Spectroscopic data for **3-*rac***: ¹H NMR (20 °C, CDCl₃, 300 MHz): δ 7.56 (t, *J* = 7.2 Hz, 4H), 7.45 (m, 8H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.06 (s, 2H), 2.52 (s, 6H); ¹³C{¹H} NMR (CDCl₃, 20 °C, 75 MHz) δ 134.03 (C), 130.68 (C), 129.05 (CH), 128.70 (CH), 128.35 (C), 128.22 (CH), 126.64 (CH), 126.17 (CH), 125.17 (C), 124.74 (CH), 123.67 (CH), 120.91 (C), 98.64 (CH), 12.75 (CH₃).¹⁸ Anal. Found (Calcd): C, 67.26 (67.11); H, 4.86 (4.58). Spectroscopic data for **3-*meso***: ¹H NMR (20 °C, CDCl₃, 300 MHz) δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.34 (m, 11H), 7.19 (m, 5H), 6.07 (s, 2H), 2.57 (s, 6H); ¹³C{¹H} NMR (CDCl₃, 20 °C, 75 MHz) δ 133.61 (C), 133.51 (C), 129.31 (C), 128.12 (CH), 128.24 (CH), 127.85 (CH), 125.90 (CH), 125.43 (CH), 124.39 (CH), 123.88 (C), 123.84 (CH), 119.24 (C), 97.87 (CH), 12.64 (CH₃).¹⁸ Anal. Found (Calcd): C, 66.81 (67.11); H, 4.66 (4.58).

X-ray Structure Determination of 3-*meso*. A single crystal of *meso*-(1-Me-2-PhInd)₂ZrCl₂ was mounted in paratone oil on a glass fiber and placed in a cold stream of nitrogen on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K α radiation. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 centered reflections (22 in the range 35 < 2 θ < 37° and 3 in the range 20 < 2 θ < 21°) corresponded to a face-centered orthorhombic cell. The data were collected at -75 °C using the ω scan technique to a maximum 2 θ value of 50°.

A total of 2624 reflections were collected of which 2529 were unique. Over the course of data collection, the intensity standards decreased by an average of 0.2%. No decay correction was applied.

The structure was solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by difference Fourier maps but included initially at idealized positions 0.95 Å from their parent atoms before the last cycle of refinement. The final cycle of full-matrix least-squares refinement was based on 2325 observed reflections and 330 variable parameters and converged with *R* (*R*_w) = 2.6 (2.8).

X-ray Structure Determination of 3-*rac*. The crystal mounting procedure and conversion of the raw intensity data were the same as those described above. The complex was found to crystallize in a primitive monoclinic cell. Over the course of the data collection, the intensity standards decreased by an average of 2.2%. No decay correction was applied.

The structure was solved by the methods described above. The final cycle of full-matrix least-squares refinement was based on 3681 observed reflections and 316 variable parameters and converged with *R* (*R*_w) = 4.5 (6.5).

Tables of the anisotropic thermal coefficients, bond lengths, bond angles, torsion angles, and H-atom coordinates for both complexes are available as Supporting Information.

Ethylene and Propylene Polymerizations. Polymerization grade ethylene and propylene from Matheson and liquid propylene from Amoco were used. Both monomers were further purified by passage through two columns packed with activated alumina and supported copper catalyst. Methylaluminoxane (MAO), type 3A, from Akzo, was dried *in vacuo* prior to use.

Polymerizations in Toluene Solution. A 300 mL stainless steel Parr reactor equipped with a mechanical stirrer was charged with dry methylaluminoxane and toluene (80 mL). A 50 mL pressure tube was charged with the zirconocene solution in toluene (20 mL). The reactor was purged with the corre-

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sponding monomer 3–4 times by pressurizing and venting. The monomer was then equilibrated with the toluene in the reactor for 30 min at the polymerization temperature and pressure with constant stirring. The pressure tube with the metallocene solution was pressurized to 200 psig with argon, and the solution was injected into the reactor. After 1 h, the reaction was quenched by injecting methanol (20 mL). In the case of polypropylene, the polymer was precipitated by pouring its toluene solution into acidified MeOH (5% HCl), filtered, washed with MeOH, and dried in a vacuum oven at 40 °C to constant weight. In the case of polyethylene, the polymer was collected by filtration and dried in a vacuum oven at 40 °C to constant weight.

Polymerizations in Liquid Propylene. A 300 mL stainless steel Parr reactor equipped with a mechanical stirrer was evacuated, purged 4–5 times with gaseous propylene by pressurizing and venting, and charged with liquid propylene (100 mL). The monomer was equilibrated at the reaction temperature, and the reaction was initiated by injecting the zirconocene/MAO solution in toluene (20 mL) under Ar pressure (250 psig \times 30 mL). After 60 min, the reaction was quenched by injecting MeOH (20 mL). The polymer was precipitated in acidified MeOH (5% HCl), filtered, washed with methanol, and dried in a vacuum oven at 40 °C to constant weight.

Polymer Analyses. Molecular weights were determined by high-temperature gel permeation chromatography using polypropylene and polyethylene as GPC calibration standards. ^{13}C NMR measurements were performed on Varian XL 400 and Varian UI 300 instruments at 100 °C in 1,1,2,2-tetrachloroethane- d_2 using the acquisition time of 1 s with no additional delays between pulses and continuous proton decoupling. All spectra were referenced using the solvent peak. It was assumed that spin–lattice relaxation times and NOEs of all methyl groups were the same.^{19–23} The areas of the nine peaks in the methyl region determined from spectral integrations were used to characterize the sample microstructure.

Results

Literature procedures for the synthesis of 1-methyl-2-phenylindene starting from commercially available reagents gave this compound in less than 55% yield.^{24–26} We developed a higher yield synthesis of **2** from 2-phenylindene. A 75% yield was achieved when the lithium salt of 2-phenylindene was reacted with a 3-fold molar excess of methyl iodide at 40 °C in THF for 24 h. This procedure gave the isomer with a tetrasubstituted double bond (1-methyl-2-phenylindene), which in its ^1H NMR spectrum showed a characteristic methyl triplet at 2.31 ppm and a methylene quartet at 3.74 ppm, in agreement with the literature.^{25,27} The structure of **2** was confirmed by its successful use in zirconocene synthesis and subsequent X-ray analysis.

The reaction of 2 equiv of the lithium salt of **2** with ZrCl_4 in toluene gave **3-rac** and **3-meso** diastereomers

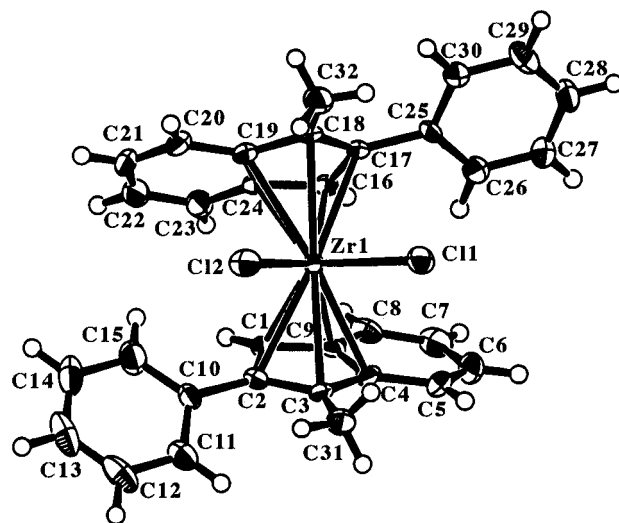
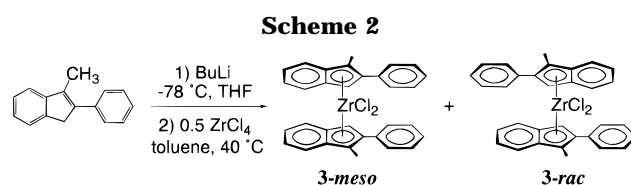


Figure 1. Molecular structure of complex **3-rac**, showing atom-labeling scheme.



of bis(1-methyl-2-phenylindene)zirconium dichloride in 60:40 ratio and 65% crude yield (Scheme 2). The two complexes were isolated by fractional crystallization. Orange rhombic crystals of **3-meso** were isolated from a methylene chloride solution stored at -18 °C overnight in 11% yield. Yellow rod-like crystals of complex **3-rac** crystallized out of a THF/pentane solution at room temperature in 10% yield. Only one narrow signal corresponding to the methyl protons (2.57 ppm for **3-meso**, 2.52 ppm for **3-rac**) and one narrow signal corresponding to the proton of the CH group of the five-membered ring (6.07 ppm for **3-meso**, 6.06 ppm for **3-rac**) were observed in the ^1H NMR spectra of the two complexes, consistent with the rapid ligand rotation at room temperature.²⁸

The two diastereomers were identified by X-ray crystallography. The ORTEP drawings and atom-labeling schemes of **3-rac** and **3-meso** are shown in Figures 1 and 2. In contrast to $(2\text{-PhInd})_2\text{ZrCl}_2$, **1**,¹³ only one rotamer in which the two methyl groups are on the more open side of the complex was found in the crystal cell for both substituted complexes: the *anti*-rotamer for **3-rac** and the *syn*-rotamer for **3-meso**. Typical Zr–Cl and Zr–centroid bond lengths and angles were observed for both complexes.^{13,14} However, a marked increase was found in the magnitude of the dihedral angle between the planes of the indenyl and the phenyl rings: 26–33° in **3-rac** and **3-meso** compared to 10–13° for complex **1** (Table 1), suggesting a strong steric interaction between the 1-methyl and 2-phenyl substituents. The increase of the dihedral angle was accompanied by a slight lengthening of the

(28) Note that in the conformations of **2-rac** and **2-meso** which are depicted in Scheme 2, the two CH_3 groups and the two Cp protons can be interconverted through symmetry operations, and thus, if the complexes are completely frozen in these conformations, the groups under consideration will be equivalent by NMR. However, closely related 2-arylindene metallocene dihalides are known to undergo rapid ligand rotation at room temperature.

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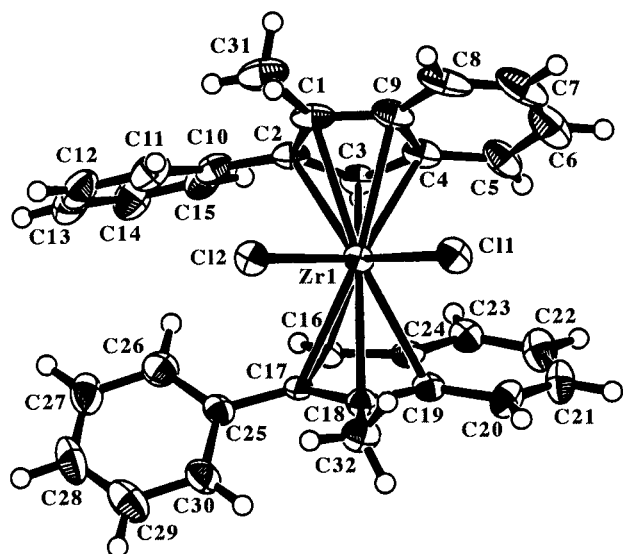


Figure 2. Molecular structure of complex **3-meso**, showing atom-labeling scheme.

Table 1. Selected Dihedral Angles and Bond Lengths for Complexes **3-rac** and **3-meso**

complex	dihedral angle (deg)		bond distance (Å)	
	plane 1/ plane 2 ^a	plane 3/ plane 4 ^b	C(2)–C(10)	C(17)–C(25)
3-rac	31.4(8)	27.9(9)	1.496(7)	1.480(7)
3-meso	26.4(8)	33.3(7)	1.482(8)	1.482(7)
1-anti ¹³	11.54	13.53	1.476(5)	1.472(6)
1-syn ¹³	10.44	12.72	1.468(7)	1.485(5)

^a Plane 1 = C(1)–C(9), plane 2 = C(10)–C(15). ^b Plane 3 = C(16)–C(24), plane 4 = C(25)–C(30).

Table 2. Ethylene Polymerization Using Complexes **1,3-rac** and **3-meso**^a

catalyst	productivity ^b	$M_w \times 10^{-3}$ ^c	MWD ^c
3-meso /MAO	3050	1966	4.0
1 /MAO	3570	2040	3.2
3-rac /MAO	7280	1034	3.4

^a Reaction conditions: $P_E = 25$ psig, $[Zr] = 5 \times 10^{-6}$ M, $t_{rxn} = 1$ h, $T = 20 \pm 1$ °C, $[Zr]:[MAO] = 1:2750$. ^b kg-PE/mol-Zr·h. ^c Determined by high-temperature GPC.

carbon–carbon bond connecting the 2-phenyl and the indenyl ring. The complete summary of structural parameters can be found in the Supporting Information.

Ethylene polymerization results are summarized in Table 2. Both substituted catalysts were characterized by fairly high ethylene polymerization productivities. Productivity and polyethylene molecular weight for **3-meso**/MAO were similar to those achieved with catalyst **1**/MAO. Catalyst **3-rac**/MAO had a higher productivity but made polyethylene of a lower molecular weight than the other two catalysts.

For the polymerization of propylene (Table 3), both **3-rac**/MAO and **3-meso**/MAO had a much lower productivity and produced polypropylene of a much lower molecular weight than unsubstituted catalyst **1**/MAO. As observed for ethylene polymerization, **3-rac**/MAO was more productive but generated polypropylene with a lower molecular weight than **3-meso**/MAO. For propylene polymerization catalyzed by **3-rac**/MAO, the productivity and polymer molecular weights increased with propylene concentration. Polymerization catalyzed by **3-meso**/MAO showed no dependence on monomer concentration. Both **3-rac**/MAO and **3-meso**/MAO pro-

duced polypropylene with a much broader molecular weight distribution (MWD) than **1**/MAO, which was especially noticeable in the case of polymerization in bulk propylene.

The isotactic pentad content determined by ¹³C NMR spectroscopy^{29–34} was much lower for polypropylene prepared with **3-rac**/MAO and **3-meso**/MAO than that for samples generated with **1**/MAO. No difference in %*mmmm* was observed for the samples prepared using catalyst **3-meso**/MAO in toluene solution at 75 psig of propylene (%*mmmm* = 12) or in bulk propylene (%*mmmm* = 11). Catalyst **3-rac**/MAO gave polypropylene with %*mmmm* = 20 in toluene solution at 75 psig of propylene, but in liquid propylene, %*mmmm* decreased to 14.³⁵ In contrast to polymerization catalyzed by **1**/MAO, polypropylene samples prepared with **3-rac**/MAO and **3-meso**/MAO were not elastomeric, which could be a consequence of their lower molecular weight and/or lower isotacticity.

Discussion

The crystal structures of **3-rac** and **3-meso** reveal that the 1-methyl substituents influence the dihedral angle of the 2-phenyl substituent relative to the plane of the cyclopentadienyl ligand. The dihedral angle between the planes of the indenyl and the phenyl ring has increased by as much as 15–23°, as compared to unsubstituted (2-PhInd)₂ZrCl₂, **1** (Table 1).

Electronically, both **3-rac**/MAO and **3-meso**/MAO appear to be suitable for α -olefin polymerization: both of them are quite active in polymerization of ethylene (Table 2). However, in polymerization of propylene, 1-methyl substitution results in a significant decrease of productivity as compared to unsubstituted catalyst **1**/MAO (Table 3). Most likely, the decrease in propylene polymerization productivity is due to the increased steric hindrance of the catalyst active sites introduced by the methyl substituents. A similar decrease in propylene polymerization productivity was reported for 3-methyl-substituted ethylene-bridged *rac*-Et(3-MeInd)₂ZrCl₂ and silicon-bridged *rac*-Me₂Si(3-MeInd)₂ZrCl₂ when compared to their unsubstituted analogs.^{36–38} It appears that in the case of a more open ethylene-bridged structure of *rac*-Et(3-MeInd)₂ZrCl₂ (metal–centroid angle, $\theta = 126.4^\circ$),³⁷ the steric effect of the methyl substituents is less dramatic (productivity is lowered by a factor of

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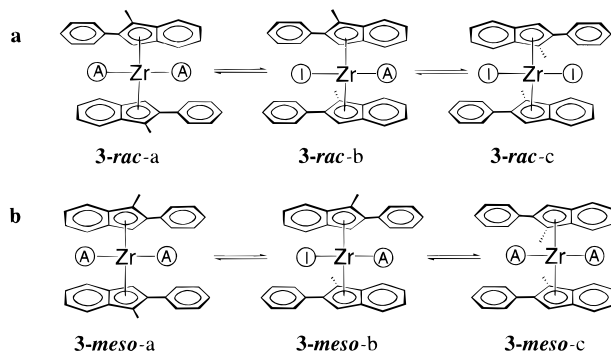
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Table 3. Propylene Polymerization Using Complexes **3-rac and **3-meso**^a**

catalyst	propylene	productivity ^b	%m ^c	%mmmm ^c	$M_w \times 10^{-3}$ ^d	MWD ^d
3-meso /MAO	75 psig	140	55	12	68.1	5.8
3-meso /MAO	bulk	140	54	11	69.1	8.6
3-rac /MAO	75 psig	220	60	20	41.3	4.2
3-rac /MAO	bulk	360	55	14	55.9	15.3
1 /MAO ¹⁴	75 psig	1700	70	33	369	3.9

^a Reaction conditions: $T = 20 \pm 1$ °C, $[\text{Zr}]:[\text{MAO}] = 1000$, $t_{\text{rxn}} = 1$ h, $[\text{Zr}] = 5 \times 10^{-5}$ M. ^b kg·PP/mol·Zr·h. ^c Determined from ¹³C NMR spectroscopy. ^d Determined by high-temperature GPC.

**Figure 3.** The possible rotamers of complexes (a) **3-rac** and (b) **3-meso**.

2) than in the case of unbridged complex **3-rac** ($\theta = 132.1^\circ$, productivity is lowered by a factor of 8).

The stereospecificity of bis(1-methyl-2-phenylindenyl)zirconocene catalysts **3-rac**/MAO and **3-meso**/MAO is lower than that of the unsubstituted bis(2-phenylindenyl)zirconocene **1**/MAO. At a propylene pressure of 75 psig, **3-rac**/MAO produces polypropylene with an isotactic index ($[mmmm] = 20\%$) which is higher than that of the polypropylene produced with **3-meso**/MAO under similar conditions ($[mmmm] = 12\%$). These results might be rationalized by the greater number of isospecific coordination sites available among the various rotameric forms of the chiral **3-rac** relative to the achiral **3-meso** (Figure 3; here olefin coordination sites are represented as isospecific (I) or aspecific (A)). However, in liquid propylene, there does not seem to be a significant difference in the stereospecificity of the two catalysts ($[mmmm] = 14\%$ for **3-rac**/MAO and 11% for **3-meso**/MAO). The decrease in stereospecificity for **3-rac**/MAO from $[mmmm] = 20\%$ at 75 psig of propylene to $[mmmm] = 14\%$ in liquid propylene is unusual and merits further investigation.³⁵ Typically, the isospecificity of 2-arylindene catalysts increases with increasing monomer concentration.^{13,14}

Broad ($M_w/M_n = 4\text{--}15$) and, in some cases, even bimodal molecular weight distributions were observed for polypropylenes generated with catalysts **3-rac**/MAO and **3-meso**/MAO. This may indicate that the rate of interconversion of their rotamers is lower than that in the case of catalyst **1**/MAO,³⁹ leading to the situation in which the growth of an individual polypropylene chain may be completed before the rotamers interconvert to form heterogeneous blend-like materials with molecular weight distributions being a superposition of molecular weights corresponding to individual rotamers. The slower rate of ligand rotation could be rationalized by the increased steric interaction of the phenyl groups,

(39) We assume that ligand rotation in the actual active species **3-rac**/MAO and **3-meso**/MAO is slower than that of the corresponding dichlorides (see ref 28) due to the interactions with the growing polymer chain and MAO anion.

which are twisted out of the plane of the indenyl ring by 1-methyl substituents, with each other as well as with the growing polymer chain. Due to their very low yield, no detailed fractionation study was conducted on polypropylene samples made with **3-rac**/MAO and **3-meso**/MAO.

The fact that in propylene polymerization **3-rac**/MAO is more productive but produces a polymer of lower molecular weight than **3-meso**/MAO deserves attention. It had been previously observed that in the case of some bridged bis(indenyl) complexes, the *rac*-isomer was more active and made polypropylene of higher molecular weight than the *meso*-isomer.⁴⁰ It is interesting that the behavior of our unbridged complexes partially correlates with this finding (**3-rac**/MAO is more productive than **3-meso**/MAO), but the order of the polymer molecular weights is not the same.

Conclusions

Propylene polymerization with unbridged bis(1-methyl-2-phenylindenyl)zirconocene catalysts yields amorphous polypropylenes under conditions where the bis(2-phenylindenyl)zirconocene catalysts yield elastomeric polypropylenes. 1-Methyl substitution of the 2-phenylindene ligand lowered propylene polymerization productivity, polymer molecular weights, and catalyst stereospecificity. In addition, broad molecular weight distributions of the polymers prepared with the substituted catalysts suggested the possibility of slower ligand rotation than in the case of unsubstituted catalyst **1**/MAO. These results underscore the subtle balance that is necessary for these dynamic unbridged metallocenes to produce stereoblock, elastomeric polypropylenes.

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Supporting Information Available: Text giving a complete description of the X-ray structure determination of complexes **3-rac** and **3-meso** and tables of crystallographic parameters, atomic coordinates, anisotropic thermal coefficients, bond lengths and angles, and torsion angles (20 pages). Ordering information is given on any current masthead page.

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