

Synthesis, Characterization, and Catalytic Properties of *ansa*-Zirconocenes [Zr{1-Me₂Si(3- η^5 -C₉H₅R)₂}Cl₂] (R = Me, *n*Pr, *n*Bu, and Bz)

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Dedicated to Professor Victor Riera on the occasion of his 70th birthday^[‡]

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The *ansa*-indene ligands [1-Me₂Si(3-C₉H₆R)₂] [R = Me (**1**), *n*Pr (**2**), *n*Bu (**3**), and Bz (**4**)] were prepared by alkylation of the unsubstituted *ansa*-indene. These ligands were converted, by reaction with *n*BuLi, to the di-lithium compounds [Li₂{1-Me₂Si(3-C₉H₅R)₂}] [R = Me (**5**), *n*Pr (**6**), *n*Bu (**7**), and Bz (**8**)]. *ansa*-Zirconocenes, [Zr{1-Me₂Si(3- η^5 -C₉H₅R)₂}Cl₂] [R = Me (**9**), *n*Pr (**10**), *n*Bu (**11**), and Bz (**12**)], have been prepared by the reaction of ZrCl₄ with **5–8** in diethyl ether/toluene at –78 °C. The molecular structure of *meso*-[Zr{1-Me₂Si[3- η^5 -C₉H₅(CH₃)₂]₂}Cl₂] (**9**) and *rac*-[Zr{1-Me₂Si[3- η^5 -C₉H₅(CH₂CH₂CH₃)₂]₂}Cl₂] (**10**) have been determined by single-

crystal X-ray diffraction studies. Ethylene polymerization catalysis has been studied for complexes **9–12** as a mixture of *meso* and *rac* isomers in the presence of methylaluminoxane (MAO) as cocatalyst. Complexes **9–12** exhibit high activities and give rise to polyethylene with low molecular weights without the introduction of molecular hydrogen. In addition, active species from these complexes were found to be very stable in comparison with unsubstituted analogues.

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Introduction

A large number of new catalysts for olefin polymerization, classified as metallocene catalysts, have been prepared during the last decade.^[1] The majority of these catalysts consist of a zirconium complex with the general formula LL'ZrCl₂ and these systems are activated by methylaluminoxane (MAO). The ligands L and L' are typically equal or different dienyl ligands that may be linked together by a bridge. A major evolution has been achieved in the field of polypropylene, which can now be produced with different types and degrees of stereoregularity.^[2] In fact, a new class of catalysts based on C₂-symmetric metallocenes, with *ansa*-bis(indenyl) ligands, produce almost isotactic polypropylenes. The best-known example is Brintzinger's *rac*-[Zr{1-(C₂H₄)(η^5 -C₉H₆)₂}Cl₂].^[3] Although the introduction of an alkyl substituent in the cyclopentadienyl fragment of the

indenyl group has been studied,^[4] few examples of *ansa*-bis-indenyl complexes, bearing SiMe₂ bridges, have been described^[5–9] and, to the best of our knowledge, there is not a complete structural characterization of these complexes. The target for these catalysts was to study the influence of the metallocene structure in the performance of propylene polymerization. Less attention has been paid to the study of the influence on the properties of the polyethylene obtained with these catalysts, i.e., on the molecular weight of the obtained polymer. Usually, this parameter can be controlled during the polymerization by either adjusting the temperature of the polymerization or by adding molecular hydrogen, which acts as a chain transfer agent.^[10]

With this in mind, and as part of our continued interest in this field,^[11] we have developed new examples of *ansa*-zirconocene catalysts of the general formula [Zr{1-Me₂Si(3- η^5 -C₉H₅R)₂}Cl₂]. These catalysts have proved to be very active and are able to produce polyethylene with low molecular weight without introducing molecular hydrogen to control the process. It was of particular interest to compare the results with the analogous unsubstituted complex [Zr{1-Me₂Si(η^5 -C₉H₆)₂}Cl₂].^[12]

Here we provide the details of the preparation and polymerization behavior of four members of this class of catalysts [Zr{1-Me₂Si(3- η^5 -C₉H₅R)₂}Cl₂] [R = Me (**9**), *n*Pr (**10**), *n*Bu (**11**), and Bz (**12**)]. The activities of these systems in the polymerization of ethylene and the molecular weights

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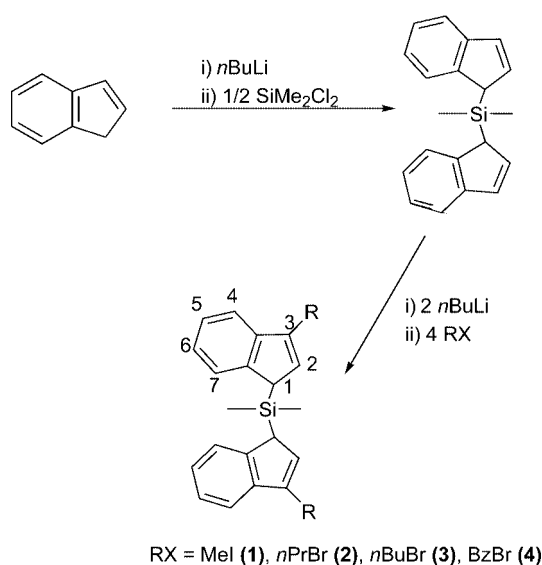
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[‡] In recognition of his important contribution to organometallic chemistry and as a mark of friendship.

of the resulting polymers are discussed. In addition, the molecular structures of *rac*-**10** and *meso*-**9** have been determined by X-ray diffraction methods.

Results and Discussion

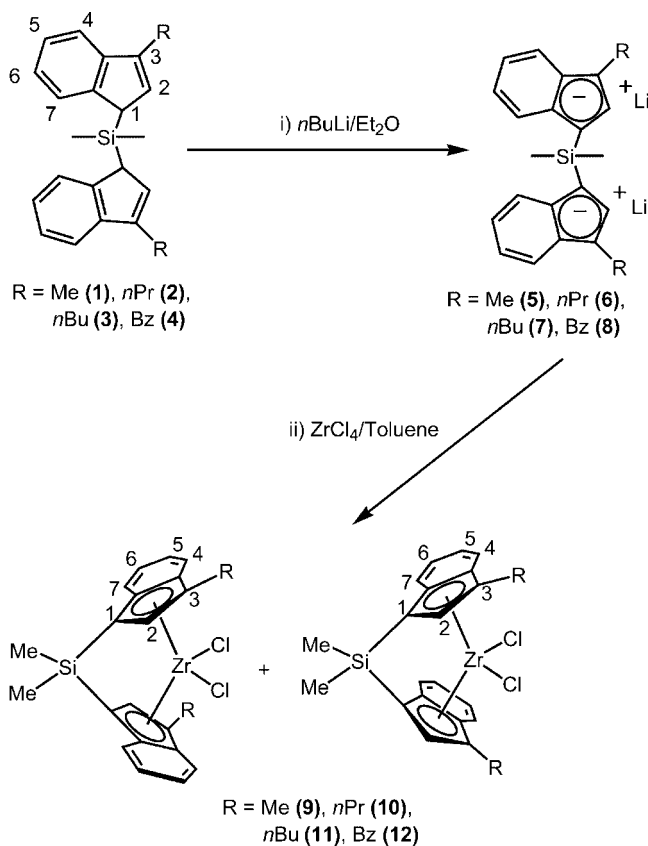
The preparation of the substituted *ansa*-indene precursors $\{1\text{-Me}_2\text{Si}(3\text{-C}_9\text{H}_6\text{R})_2\}$ [**R** = Me (**1**), *n*Pr (**2**), *n*Bu (**3**) and Bz (**4**)] was achieved by alkylation of the dilithium salt of $\{1\text{-Me}_2\text{Si}(3\text{-C}_9\text{H}_7)_2\}$, generated with *n*BuLi in Et₂O, with a large excess of RX (X = I and R = Me for **1**, X = Br and R = *n*Pr for **2**, X = Br and R = *n*Bu for **3**, and X = Br and R = Bz for **4**) (Scheme 1). Column chromatography was used to purify the ligands **1–4**.



Scheme 1.

This is the preferred route because of the very simple synthesis and purification of the intermediate $\{1\text{-Me}_2\text{Si}(\text{C}_9\text{H}_7)_2\}$ and because of its intrinsic versatility. In fact, $\{1\text{-Me}_2\text{Si}(\text{C}_9\text{H}_7)_2\}$ is a convenient starting material for the synthesis of a series of different 3-alkyl- and 3-silyl-*ansa*-bisindenyl ligands.^[13] The ¹H NMR spectra show the *meso*-isomer as the major isomer for derivatives **1–4**, with two singlets for the *ansa*-bridge methyl groups, a doublet for H1, a doublet for H2, and four multiplets corresponding to the protons of the C₆ ring of the indenyl moiety. In addition, the corresponding signals were observed for the pendant alkyl chain (see Exp. Sect.).

As shown in Scheme 2, the deprotonation of **1–4** with *n*BuLi gave the lithium salts $[\text{Li}_2\{1\text{-Me}_2\text{Si}(3\text{-C}_9\text{H}_5\text{R})_2\}]$ [**R** = Me (**5**), *n*Pr (**6**), *n*Bu (**7**), and Bz (**8**)]. The subsequent reaction of the lithium salts with ZrCl₄ in diethyl ether/toluene, gave the corresponding zirconocene complexes $[\text{Zr}\{1\text{-Me}_2\text{Si}(3\text{-}\eta^5\text{-C}_9\text{H}_5\text{R})_2\}\text{Cl}_2]$ [**R** = Me (**9**), *n*Pr (**10**), *n*Bu (**11**), and Bz (**12**)]. The orange solids obtained are sensitive towards air and moisture and are soluble in polar solvents.



Scheme 2.

While the total yield of this last step is satisfactory, a random *rac*/*meso* ratio is obtained. In general, the *rac*/*meso* ratio ranges from 0.6:1 (**10**) to 1.86:1 (**12**). For complex **9**, samples of the pure *meso* diastereomer and a product enriched in the *rac* isomer (11.5:1) were obtained by careful recrystallization from CH₂Cl₂/Et₂O.

The ¹H NMR spectra for the *meso* isomers of the complexes **9–12** show the following signals: two singlets for the *ansa*-bridge methyl groups, a singlet for the proton of the indenyl C₅ ring, and four multiplets corresponding to the protons of the C₆ ring of the indenyl moiety. In addition, the appropriate signals were observed for the pendant alkyl chain (see Exp. Sect.). Furthermore, the following signals were observed for the *rac* isomers of the complexes **9–12**: a singlet for the *ansa*-bridge methyl groups, a singlet for the proton of the indenyl C₅ ring, and four multiplets corresponding to the protons of the C₆ ring of the indenyl moiety. In addition, several signals were observed for the pendant alkyl chain (see Exp. Sect.).

¹H NMR nuclear Overhauser effect (NOE) difference spectroscopy allowed unambiguous identification of each isomer. Irradiation of the signal due to H2 in the *meso* isomer (which appears as a singlet in the NMR spectrum) led to measurable enhancement of the protons of the C3-alkyl substituent and the protons in one of the methyl groups of the SiMe₂ bridge. However, a similar irradiation in the *rac* isomer led to enhancement of the corresponding signals due to the C3-alkyl and the silicon methyl groups as well as the

aromatic proton H7 on the opposite indenyl ring (Figure 1). In the *meso* isomer, these SiMe₂ methyl groups are located in very different chemical environments (one is sandwiched between the two C₆ aromatic rings, and the other is only flanked by the Cp rings), while in the *rac* isomer the two methyl groups are equivalent.

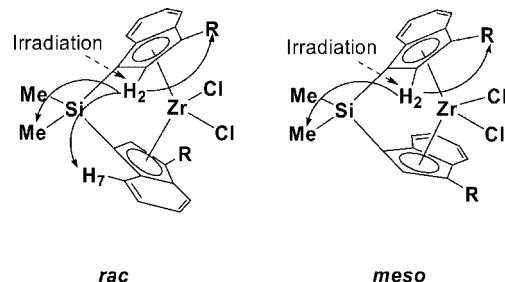


Figure 1. ¹H NOE difference experiments provide information on the spatial proximity between protons.

The carbon signal assignments were made following a procedure on the basis of ¹H and ¹³C NMR correlated spectroscopy (HETCOR) (see Exp. Sect.). For the *meso* isomer of these compounds **9–12**, the ¹³C analysis showed two signals for the *ansa*-bridge methyl groups, a signal for the carbon C2 of the indenyl C₅ ring, and four signals corresponding to the carbons (C4–C7) of the C₆ ring of the indenyl moiety. For the *rac* isomers, only one signal was found for the *ansa*-bridge methyl groups. In addition, a signal of the carbon C2 of the indenyl C₅ ring was observed, and four signals corresponding to the carbons (C4–C7) of the C₆ ring of the indenyl moiety. The corresponding signals were observed for the pendant alkyl chain for both isomers (see Exp. Sect.).

X-ray Molecular Structures of Complexes *meso-9* and *rac-10*

Single crystals of *meso-9* and *rac-10* that were suitable for X-ray diffraction were obtained from CH₂Cl₂/ether and toluene. Their molecular structures, as determined by the crystallographic analysis, are depicted in Figure 2.

The *meso-9* complex crystallizes in the triclinic space group *P* $\bar{1}$. The crystal structure reveals the existence of one unique isomer. The *rac-10* complex crystallizes in the monoclinic space group *P*₂/*c* with a solvate toluene molecule. The crystal structure reveals the existence of two racemic enantiomers. The bonding parameters for *meso-9* and *rac-10* are summarized in Table 1. The mutual arrangement of the indenyl fragments corresponds to C₂ symmetry for *rac* and C_s for *meso*.

In both cases the zirconium atom is in a pseudotetrahedral environment formed by the two chloride ligands and two η^5 -coordinated indenyl ligands. The Zr–C bond lengths of five-membered rings range between 2.448(6) and 2.662(6) Å. These values are close to that found in other *ansa*-bis(indenyl) zirconocene complexes (2.5 Å).^[14] The Zr–Cl distances for these complexes are within the range

Table 1. Selected bond lengths [Å] and angles [°] for *meso-9* and *rac-10*.

	<i>meso-9</i>	<i>rac-10</i>
Bond lengths		
Zr(1)–Cent(1) ^[a]	2.246(1)	2.243
Zr(1)–Cent(2) ^[b]	2.252(1)	
av ^[c] Zr(1)–C[Cent(1)] ^[a]	2.550(6)	2.548(3)
av ^[c] Zr(1)–C[Cent(2)] ^[b]	2.556(6)	
Zr(1)–Cl(1)	2.409(2)	2.4130(11)
Zr(1)–Cl(2)	2.4375(19)	
Zr(1)–C(1)	2.448(6)	2.451(3)
Zr(1)–C(2)	2.467(6)	2.483(3)
Zr(1)–C(3)	2.631(6)	2.619(3)
Zr(1)–C(4)	2.662(6)	2.656(3)
Zr(1)–C(5)	2.540(6)	2.529(3)
Bond angles		
Cent(1) ^[a] –Zr–Cent(2) ^[b]	128.84	128.81
Si(1)–C(1)–Cent(1) ^[a]	163.6(4)	163.5
Si(1)–C(11)–Cent(2) ^[b]	163.5	
Cl(1)–Zr–Cent(1) ^[a]	106.71	106.76(3)
Cl(1)–Zr–Cent(2) ^[b]	106.65(5)	106.82(2)
Cl(2)–Zr–Cent(1) ^[a]	106.40	
Cl(2)–Zr–Cent(2) ^[b]	106.97	

[a] Cent(1) is the centroid of C(1)–C(5) for both complexes. [b] Cent(2) is the centroid of C(11)–C(15) for the complex *meso-9*. [c] Refers to the average bond length between Zr(1) and the carbon atoms of the C₅ ring of the cyclopentadienyl moiety.

observed previously for other bis(indenyl)-zirconium dichlorides [2.407(1)–2.465(2) Å].^[15–20]

The angles between some relevant planes are collected in Table 2 along with the geometrical parameters described in Figure 3 for compounds *meso-9*, *rac-10*, and the unsubstituted parent *rac*-[Zr{1-Me₂Si(η^5 -C₉H₆)₂}Cl₂].^[12] As usual for bent metallocenes, the overall coordination environment is best described by the set of parameters depicted in Figure 3, which describes the metal accessibility. In particular, the smaller the “bite angle” β and the larger the Cp–M–Cp' α angle, the more the metal is tucked into the ligand envelope.

The main geometrical difference of *meso-9* and *rac-10* from *rac*-[Zr{1-Me₂Si(η^5 -C₉H₆)₂}Cl₂] is associated with the angle β and the range of Zr–C_{Cp} bond lengths. β , in *meso-9* (63.9°) and *rac-10* (62.9°), is increased compared to that of *rac*-[Zr{1-Me₂Si(η^5 -C₉H₆)₂}Cl₂] (60.2°). The range of Zr–C_{Cp} for both complexes (0.21 Å for *meso-9* and 0.20 Å for *rac-10*) is similar to that in *rac*-[Zr{1-Me₂Si(η^5 -C₉H₆)₂}Cl₂] (0.20 Å).

These differences are, likely, caused by the bulky R substituents at C(3) of both indenyl fragments. This conclusion is supported by significant displacements of the C(3)–R bonds from the planes of the parent cyclopentadienyl rings opposite to Zr (4.1° and 4.5° for *meso-9*, and 4.2° for *rac-10*).

It can be seen from Figure 2 that, for the structures of the complexes *meso-9* and *rac-10*, both C₅ rings are eclipsed, including, in the case of *meso-9*, the methyl-substituent in position 3. In *meso-9*, it can be observed that one of the chloride ligands is very close to the C₆ aromatic rings, whereas the other one is in an intermediate location between the methyl-substituents. In the case of *rac-10*, each

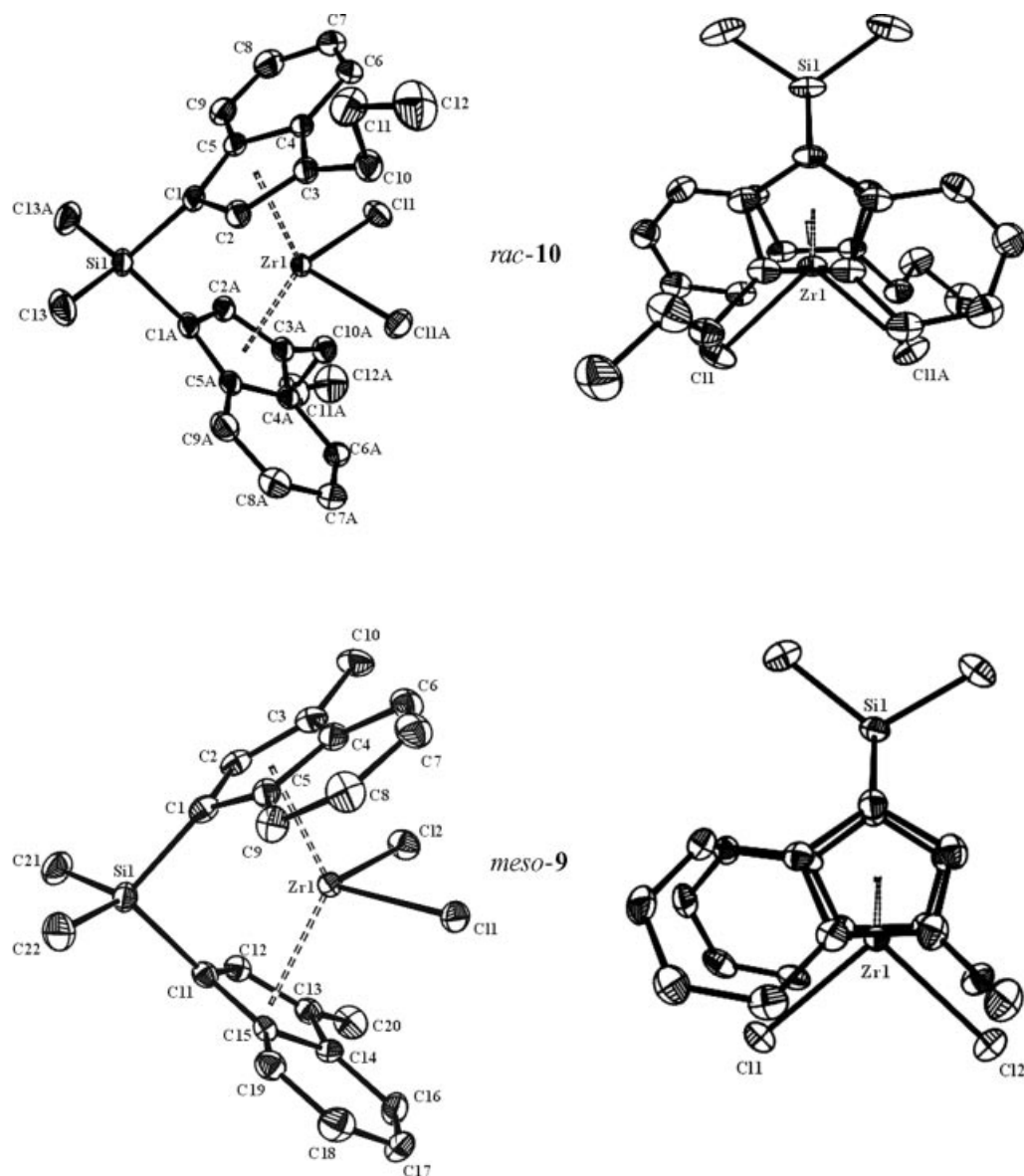


Figure 2. Solid state structure of *rac*-10 and *meso*-9 (hydrogen atoms are omitted for clarity).

Table 2. Relevant geometrical parameters.^[a]

	<i>meso</i> -9	<i>rac</i> -10	<i>rac</i> -[Me ₂ Si(Ind) ₂]ZrCl ₂
<i>a</i>	128.7	128.8	127.8
<i>β</i>	63.9	62.9	60.2
<i>δ</i>	83.6, 83.4	83.9	85.7
<i>φ</i>	95.3	95.3	94.4
<i>γ</i>	15.6, 15.8	16.1	17.8; 16.4
<i>r</i> (Zr–CCp), Å	2.45–2.66	2.45–2.65	2.46–2.66, 0.20
<i>Δr</i>	0.21	0.20	

[a] All quantities in degrees, apart from *Δ* (Å). The angles *α*, *β*, *γ*, *δ*, and *φ* are defined in Figure 3. *Δ* is the distance between the perpendicular projection of the heavy atom on the ring least-squares plane and the ring centroid.

chloride ligand is between a ring and an alkyl substituent. This situation could give rise to a great influence of the rings and their alkyl substituents on the positions occupied by the active sites of the catalysts. These features could be

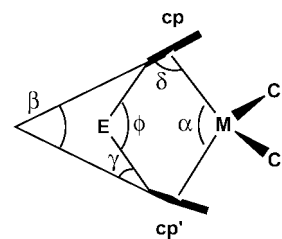


Figure 3. Schematic representation of an *ansa*-metallocene detailing the angles listed in Table 2.

established to control the molecular weight of the polymers obtained.

Polyethylene Polymerization using Complexes 9–12

Complexes 9–12, used as *rac/meso* mixtures, after being activated with methylaluminoxane (MAO), are very active

Table 3. Homogeneous ethylene polymerization results for **9–12** and $[\text{Zr}\{\text{1-Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_6)_2\}\text{Cl}_2]$ as reference. Conditions: 343 K, 1.5 bar monomer pressure, 6 μmol Zr, MAO/Zr = 2000, 100 mL toluene, t_{pol} = 30 min.

Complex	Activity ^[a] [kg _{PE} /mol _{Zr} × h]	Activity (after 12 h) ^{[a][b]} [kg _{PE} /mol _{Zr} × h]	M_w [g mol ⁻¹]	M_n	M_w/M_n	M.p. [°C]
$[\text{Zr}\{\text{1-Me}_2\text{Si}[3-(\eta^5\text{-C}_9\text{H}_5)\text{Me}]_2\}\text{Cl}_2]$ (9)	6333	1757	82000	21000	3.82	132
$[\text{Zr}\{\text{1-Me}_2\text{Si}[3-(\eta^5\text{-C}_9\text{H}_5)n\text{Pr}]_2\}\text{Cl}_2]$ (10)	3473	2333	87000	26000	3.40	134
$[\text{Zr}\{\text{1-Me}_2\text{Si}[3-(\eta^5\text{-C}_9\text{H}_5)n\text{Bu}]_2\}\text{Cl}_2]$ (11)	2946	1856	74000	17000	4.35	132
$[\text{Zr}\{\text{1-Me}_2\text{Si}[3-(\eta^5\text{-C}_9\text{H}_5)\text{Bz}]_2\}\text{Cl}_2]$ (12)	1849	1843	70000	17000	4.06	134
$[\text{Zr}\{\text{1-Me}_2\text{Si}(\text{Ind})_2\}\text{Cl}_2]$	3573	No reaction	166000	53000	3.16	136

[a] Average value for three different runs. [b] Precatalyst/MAO solutions were aged for 12 h, at room temperature, before monomer introduction.

catalysts for the polymerization of ethylene. In the present study, we used a 10% solution of MAO in toluene, which contains about 20–30% of AlMe_3 . In all polymerization experiments, $\text{Al}(\text{iBu})_3$ was used to scavenge possible impurities in the monomer. The polymerization results are compared with those of one of the best zirconocene catalysts, i.e., $[\text{Zr}\{\text{1-Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_6)_2\}\text{Cl}_2]$.^[12] The polymerization results and the available polymer characterization data are shown in Table 3.

Complexes **9–12** show similar or higher activities than the reference complex and, moreover, these new catalysts produced lower molecular weight polyethylene than the reference catalyst. Although it is not possible to establish any relation between the size of the substituent and the polymer molecular weight, we suggest that this low molecular weight arises due to the steric influence of the substituents. The activities of complexes **9–12** decrease as the bulk of the substituent in position 3 increases.

In addition, the melting points of all the polymers were determined (see Table 3). The catalysts **9–12** produced crystalline materials with relatively high melting points (near 130 °C).

The stability of metallocene complexes is one of the most important variables for its future industrial use. The activities of activated forms of complexes **9–12** were tested after 12 h of contact between the complexes and MAO solution. It is worth noting that these complexes maintained a reasonable level of activity after this contact time. In contrast, the reference complex ($[\text{Zr}\{\text{1-Me}_2\text{Si}(\eta^5\text{-C}_9\text{H}_6)_2\}\text{Cl}_2]$) did not give any reaction with ethylene after the same time of contact with MAO. It therefore appears that an increase in the volume of the substituent in the 3-position leads to an increase in the stability of the catalyst.

Conclusions

We have carried out the synthesis of new examples of *ansa*-bis-indenylzirconocene complexes, bearing a SiMe_2 bridge, with alkyl substituents in the 3 position. The presence of these groups allows stable and very active catalysts to be obtained in ethylene polymerization, producing polyethylenes of low molecular weight, in comparison with the unsubstituted analogue. In addition, complexes *meso*- $[\text{Zr}\{\text{1-Me}_2\text{Si}[3-\eta^5\text{-C}_9\text{H}_5(\text{CH}_3)_2]\}\text{Cl}_2]$ and *rac*- $[\text{Zr}\{\text{1-Me}_2\text{Si}[3-\eta^5\text{-C}_9\text{H}_5(\text{CH}_2\text{CH}_2\text{CH}_3)]_2\}\text{Cl}_2]$ have been characterized by X-ray diffraction methods.

Experimental Section

General Remarks: All reactions were carried out using standard Schlenk-tube and glove-box techniques in dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. ZrCl_4 , indene, SiMe_2Cl_2 , ICH_3 , $\text{BrCH}_2\text{CH}_2\text{CH}_3$, $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, and BrCH_2Ph were purchased from Aldrich and used directly. ^1H and ^{13}C spectra were recorded with Varian GEMINI FT-400 and Varian INNOVA FT-500 spectrometers and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin–Elmer 2400 microanalyzer. Mass spectrometry was performed with a Hewlett–Packard 5988A (m/z = 50–1000) (electron impact) spectrometer.

Preparation of $\{\text{1-Me}_2\text{Si}[3-\text{C}_9\text{H}_6(\text{CH}_3)_2]\}_2$ (1**):** $n\text{BuLi}$ (1.60 M in hexane) (38.00 mL, 60.74 mmol) was added over 15 min to a cooled (–78 °C) solution of $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_7)]$ (7.30 g, 25.31 mmol) in Et_2O (100 mL) in a 250-mL Schlenk tube. At the end of the addition the solution was allowed to reach room temperature and stirred for 4 h, cooled again to –78 °C, and MeI (14.37 g, 101.24 mmol) was added. The reaction mixture was allowed to reach room temperature and stirred for 16 h. The solvent was removed in vacuo and hexane (100 mL) was added. Water (200 mL) was added, the organic product was extracted with hexane, the aqueous layer was washed with hexane (3 × 50 mL), the organic layers combined, dried with MgSO_4 , filtered and the solvent removed from the filtrate under reduced pressure to yield the title compound as a yellow oil. Compound **1** was purified by column chromatography (Et_2O /hexane, 1:9) (yield 7.05 g, 88%). ^1H NMR (400 MHz, CDCl_3) (for the predominant isomer): δ = 0.10 and 0.14 (2s, each 3 H, SiMe_2), 0.82 (m, 6 H, CH_3), 3.56 (d, J = 1.8 Hz, 2 H, 1-H), 6.82 (d, J = 1.8 Hz, 2 H, 2-H), 7.11–7.37 (m, 8 H, 4-H–7-H) ppm. MS electron impact: m/z (%) = 316 (3) $[\text{M}, \{\text{1-Me}_2\text{Si}[3-\text{C}_9\text{H}_6(\text{CH}_3)_2]\}_2]^+$, 187 (100) $[\text{M} - (3\text{-Me} - \text{C}_9\text{H}_6)]^+$, 129 (56) $[\text{M} - \text{Me}_2\text{Si}]^+$.

Preparation of $\{\text{1-Me}_2\text{Si}(3-\text{C}_9\text{H}_6(\text{CH}_2\text{CH}_2\text{CH}_3))_2\}_2$ (2**):** The synthesis of **2** was carried out in an identical manner to **1**. $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_7)]$ (7.30 g, 25.31 mmol), $n\text{BuLi}$ (1.60 M in hexane) (38.00 mL, 60.74 mmol), and $\text{BrCH}_2\text{CH}_2\text{CH}_3$ (12.45 g, 101.24 mmol). Yield 8.48 g (89%). ^1H NMR (400 MHz, CDCl_3) (for the predominant isomer): δ = 0.19 and 0.32 (2s, each 3 H, SiMe_2), 0.95 (m, 6 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.39–2.73 (m, 8 H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.50 (d, J = 1.8 Hz, 2 H, 1-H), 6.98 (d, J = 1.8 Hz, 2 H, 2-H), 7.10–7.50 (m, 8 H, 4-H–7-H) ppm. MS electron impact: m/z (%) = 372 (3) $[\text{M}, \{\text{1-Me}_2\text{Si}(3-\text{C}_9\text{H}_6(\text{CH}_2\text{CH}_2\text{CH}_3))_2\}_2]^+$, 216 (100) $[\text{M} - (3\text{-Pr} - \text{C}_9\text{H}_6)]^+$, 156 (23) $[\text{M} - \text{Me}_2\text{Si}]^+$.

Preparation of $\{\text{1-Me}_2\text{Si}(3-\text{C}_9\text{H}_6(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3))_2\}_2$ (3**):** The synthesis of **3** was carried out in an identical manner to **1**. $[\text{Me}_2\text{Si}(\text{C}_9\text{H}_7)]$ (7.30 g, 25.31 mmol), $n\text{BuLi}$ (1.60 M in hexane) (38.00 mL, 60.74 mmol), and $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (13.87 g, 101.24 mmol). Yield 9.13 g (90%). ^1H NMR (400 MHz, CDCl_3) (for the predominant isomer): δ = 0.22 and 0.08 (2s, each 3 H,

SiMe₂), 0.95–2.73 (m, 18 H, -CH₂CH₂CH₂CH₃), 3.80 (d, $J = 1.8$ Hz, 2 H, 1-H), 6.89 (d, $J = 1.8$ Hz, 2 H, 2-H), 7.10–7.50 (m, 8 H, 4-H–7-H) ppm. MS electron impact: m/z (%) = 400 (3) [M, {1-Me₂Si(3-C₉H₆(CH₂CH₂CH₃))₂}]⁺, 228 (100) [M – (3-Bu-C₉H₆)]⁺, 59 (55) [M – Me₂Si(C₉H₆)]⁺.

Preparation of {1-Me₂Si(3-C₉H₆(CH₂C₆H₅))₂} (4): The synthesis of **4** was carried out in an identical manner to **1**. [Me₂Si(C₉H₇)] (7.30 g, 25.31 mmol), *n*BuLi (1.60 M in hexane) (38.00 mL, 60.74 mmol), and BrCH₂C₆H₅ (8.66 g, 50.62 mmol). Yield 5.34 g (45%). ¹H NMR (400 MHz, CDCl₃) (for the predominant isomer): $\delta = 0.16$ and 0.13 (2s, each 3 H, SiMe₂), 2.72–3.00 (m, 4 H, -CH₂C₆H₅), 3.54 (d, $J = 1.8$ Hz, 2 H, 1-H), 6.78 (d, $J = 1.8$ Hz, 2 H, 2-H), 7.14–7.39 (m, 18 H, 4-H–7-H, CH₂C₆H₅) ppm. MS electron impact: m/z (%) = 468 (2) [M, {1-Me₂Si(3-C₉H₆(CH₂C₆H₅))₂}]⁺, 264 (83) [M – (3-Bz-C₉H₆)]⁺, 91 (100) [M – Me₂Si(C₉H₆)]⁺.

Preparation of Li₂{1-Me₂Si(3-C₉H₅(CH₃))₂} (5): *n*BuLi (1.60 M in hexane) (23.79 mL, 37.92 mmol) was added dropwise over 15 min to a cooled (–80 °C), stirred solution of {1-Me₂Si(3-C₉H₆(CH₃))₂} (**1**) (5.00 g, 15.80 mmol) in Et₂O (80 mL) in a 250-mL Schlenk tube. The solution was warmed up to room temperature and stirred for 4 h. An increasing turbidity developed and this finally led to the formation of a yellow-orange suspension. The solvent was removed in vacuo to give a yellow solid, which was washed with hexane (2 × 50 mL) and dried under vacuum to yield **5** as a free flowing yellow solid (yield 3.94 g, 76%). C₂₂H₂₂Li₂Si (328.28): calcd. C 80.47, H 6.75; found C 80.53, H 6.80.

Preparation of Li₂{1-Me₂Si(3-C₉H₅(CH₂CH₂CH₃))₂} (6): The synthesis of **6** was carried out in an identical manner to **5**. {1-Me₂Si(3-C₉H₆(CH₂CH₂CH₃))₂} (**2**) (5.00 g, 13.28 mmol), *n*BuLi (1.60 M in hexane), and (19.91 mL, 31.85 mmol). Yield 4.48 g (87%). C₂₆H₃₀Li₂Si (384.48): calcd. C 81.22, H 7.86; found C 81.43, H 7.93.

Preparation of Li₂{1-Me₂Si(3-C₉H₅(CH₂CH₂CH₂CH₃))₂} (7): The synthesis of **7** was carried out in an identical manner to **5**. {1-Me₂Si(3-C₉H₆(CH₂CH₂CH₂CH₃))₂} (**3**) (5.00 g, 12.48 mmol) and *n*BuLi (1.60 M in hexane) (18.72 mL, 29.95 mmol). Yield (4.37 g, 85%). C₂₈H₃₄Li₂Si (412.54): calcd. C 81.52, H 8.31; found C 81.43, H 8.40.

Preparation of Li₂{1-Me₂Si(3-C₉H₅(CH₂C₆H₅))₂} (8): The synthesis of **8** was carried out in an identical manner to **5**. {1-Me₂Si(3-C₉H₆(CH₂C₆H₅))₂} (**4**) (5.00 g, 10.67 mmol) and *n*BuLi (1.60 M in hexane) (16.00 mL, 26.21 mmol). Yield 4.10 g (80%). C₃₄H₃₀Li₂Si (480.57): calcd. C 84.97, H 6.29; found C 84.83, H 6.34.

Preparation of [Zr{1-Me₂Si(3-η⁵-C₉H₅(CH₃))₂}Cl₂] (9): A cooled (–78 °C) slurry of ZrCl₄ (2.79 g, 12.00 mmol) in toluene (80 mL) was rapidly added to a cooled (–78 °C) solution of Li₂{1-Me₂Si(3-C₉H₅(CH₃))₂} (**5**) (3.94 g, 12.00 mmol) in Et₂O (80 mL) in a 250-mL Schlenk tube. The reaction mixture was stirred for 30 min at –20 °C and then overnight at room temperature (16 h). The orange suspension was filtered through a G4 frit with Celite. The filtrate was evaporated to dryness under reduced pressure to yield a sticky dark-orange product. The product was washed with Et₂O (30 mL) and the residue was dried to give an orange solid (0.86 g, 15%). *rac*/*meso* = 55:45. For this complex, samples of the pure *meso* diastereomer and a product enriched in the *rac* isomer (11.5:1) were obtained by careful recrystallization from CH₂Cl₂/Et₂O.

meso Isomer: ¹H NMR (500 MHz, CD₂Cl₂): $\delta = 0.80$ [s, 3 H, Si(CH₃)₂ *exo*], 1.27 [s, 3 H, Si(CH₃) *endo*], 2.35 (s, 6 H, CH₃), 5.50 (s, 2 H, 2-H), 6.83 and 7.09 (2t, $J = 8.8$ Hz, each 2 H, 5-H, 6-H), 7.32 and 7.44 (2d, $J = 8.8$ Hz, each 2 H, 4-H, 7-H) ppm. ¹³C{¹H} NMR (125 MHz, CD₂Cl₂): $\delta = 13.03$ [Si(CH₃) *exo*], 13.62 [Si(CH₃)

endo], 43.62 (CH₃), 76.78, 86.00 (C1, C3), 118.40 (C2), 123.21 and 125.11 (C5, C6), 126.15, 126.48 (C4, C7) ppm.

rac Isomer: ¹H NMR (500 MHz, CD₂Cl₂): $\delta = 1.09$ [s, 6 H, Si(CH₃)₂], 2.22 (s, 6 H, CH₃), 5.68 (s, 2 H, 2-H), 6.97 and 7.23 (2t, $J = 8.8$ Hz, each 2 H, 5-H, 6-H), 7.35 and 7.38 (2d, $J = 8.8$ Hz, each 2 H, 4-H, 7-H) ppm. ¹³C NMR (125 MHz, CD₂Cl₂): $\delta = -1.44$ ppm [Si(CH₃)₂], 13.34 (CH₃), 78.04, 86.40 (C1, C3), 119.32 (C2), 124.25 and 125.06 (C5, C6), 126.55 and 126.85 (C4, C7) ppm.

Both Isomers: C₂₂H₂₂Cl₂Zr (476.6): calcd. C 55.44, H 4.65; found C 55.63, H 4.68.

Preparation of [Zr{1-Me₂Si[3-η⁵-C₉H₅(CH₂CH₂CH₃)]₂]Cl₂] (10): The synthesis of **10** was carried out in an identical manner to **9**. Li₂{1-Me₂Si[3-C₉H₅(CH₂CH₂CH₃)]₂} (**6**) (4.48 g, 11.65 mmol) and ZrCl₄ (2.72 g, 11.65 mmol). Yield 1.61 g (26%). *rac*/*meso* = 38:62.

meso Isomer: ¹H NMR (500 MHz, CDCl₃): $\delta = 1.04$ [s, 3 H, Si(CH₃) *exo*], 1.51 [s, 3 H, Si(CH₃) *endo*], 1.07 (t, 6 H, $J = 7.9$ Hz, CH₂CH₂CH₃), 1.74 (m, 4 H, CH₂CH₂CH₃), 2.98 (m, 4 H, CH₂CH₂CH₃), 5.73 (s, 2 H, 2-H), 7.07 and 7.32 (2t, $J = 8.8$ Hz, each 2 H, 5-H, 6-H), 7.57 and 7.65 (2d, $J = 8.8$ Hz, each 2 H, 4-H, 7-H) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): $\delta = -2.45$ [Si(CH₃) *exo*], -0.71 [Si(CH₃) *endo*], 14.46 (CH₂CH₂CH₃), 23.62 (CH₂CH₂CH₃), 30.78 (CH₂CH₂CH₃), 77.30, 80.10 (C1, C3), 117.27 (C2), 124.36 and 126.04 (C5, C6), 126.30 and 126.47 (C4, C7) ppm.

rac Isomer: ¹H NMR (500 MHz, CDCl₃): $\delta = 1.25$ [s, 6 H, Si(CH₃)₂], 1.03 (t, 6 H, $J = 7.9$ Hz, CH₂CH₂CH₃), 1.65 (m, 4 H, CH₂CH₂CH₃), 2.84 (m, 4 H, CH₂CH₂CH₃), 5.91 (s, 2 H, 2-H), 7.19 and 7.47 (2t, $J = 8.8$ Hz, each 2 H, 5-H, 6-H), 7.57 and 7.65 (2d, $J = 8.8$ Hz, each 2 H, 4-H, 7-H) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): $\delta = -1.12$ ppm [Si(CH₃)₂], 14.34 (CH₂CH₂CH₃), 23.54 (CH₂CH₂CH₃), 30.49 (CH₂CH₂CH₃), 77.40, 85.31 (C1, C3), 117.27 (C2), 124.55 and 124.92 (C5, C6), 126.62 and 126.72 (C4, C7) ppm.

Both Isomers: C₂₆H₃₀Cl₂Zr (532.73): calcd. C 58.62, H 5.68; found C 58.71, H 5.69.

Preparation of [Zr{1-Me₂Si[3-η⁵-C₉H₅(CH₂CH₂CH₂CH₃)]₂]Cl₂] (11): The synthesis of **11** was carried out in an identical manner to **9**. Li₂{1-Me₂Si[3-C₉H₅(CH₂CH₂CH₂CH₃)]₂} (**7**) (4.37 g, 10.59 mmol) and ZrCl₄ (2.47 g, 10.59 mmol). Yield 2.08 g (35%). *rac*/*meso* = 59:41.

meso Isomer: ¹H NMR (500 MHz, CDCl₃): $\delta = 0.87$ [s, 3 H, Si(CH₃) *exo*], 1.36 [s, 3 H, Si(CH₃) *endo*], 0.89 (t, $J = 7.9$ Hz, 6 H, CH₂CH₂CH₂CH₃), 1.34 (m, 4 H, CH₂CH₂CH₂CH₃), 1.51 (m, 4 H, CH₂CH₂CH₂CH₃), 2.72 (m, 4 H, CH₂CH₂CH₂CH₃), 5.58 (s, 2 H, 2-H), 6.91 and 7.16 (2t, $J = 8.8$ Hz, each 2 H, 5-H, 6-H), 7.41 and 7.49 (2d, $J = 8.8$ Hz, each 2 H, 4-H, 7-H) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): $\delta = -2.69$ [Si(CH₃) *exo*], -0.96 [Si(CH₃) *endo*], 13.95 (CH₂CH₂CH₂CH₃), 22.77 (CH₂CH₂CH₂CH₃), 28.24 (CH₂CH₂CH₂CH₃), 32.29 (CH₂CH₂CH₂CH₃), 77.10, 84.81 (C1, C3), 116.88 (C2), 123.98 and 125.77 (C5, C6), 126.03, 126.19 (C4, C7) ppm.

rac Isomer: ¹H NMR (500 MHz, CDCl₃): $\delta = 1.11$ [s, 6 H, Si(CH₃)₂], 0.90 (t, 6 H, $J = 7.9$ Hz CH₂CH₂CH₂CH₃), 1.34 (m, 4 H, CH₂CH₂CH₂CH₃), 1.51 (m, 4 H, CH₂CH₂CH₂CH₃), 2.82 (m, 4 H, CH₂CH₂CH₂CH₃), 5.77 (s, 2 H, 2-H), 7.06 and 7.32 (2t, $J = 8.8$ Hz, each 2 H, 5-H, 6-H), 7.41 and 7.49 (2d, $J = 8.8$ Hz, each 2 H, 4-H, 7-H) ppm. ¹³C{¹H} NMR (125 MHz, CDCl₃): $\delta = -1.37$ [Si(CH₃)₂], 13.95 (CH₂CH₂CH₂CH₃), 22.77 (CH₂CH₂CH₂CH₃), 28.12 (CH₂CH₂CH₂CH₃), 32.29 (CH₂CH₂CH₂CH₃), 77.69, 85.06 (C1, C3), 117.00 (C2), 124.08 and 124.67 (C5, C6), 126.34 and 126.43 (C4, C7) ppm.

Both Isomers: $C_{28}H_{34}Cl_2SiZr$ (560.79): calcd. C 59.97, H 6.11; found C 60.21, H 6.19.

Preparation of $[Zr\{1-Me_2Si[3-\eta^5-C_9H_5(CH_2C_6H_5)]_2\}Cl_2]$ (12): The synthesis of **12** was carried out in an identical manner to **9**. $Li_2\{1-Me_2Si[3-C_9H_5(CH_2C_6H_5)]_2\}$ (**8**) (4.10 g, 8.53 mmol) and $ZrCl_4$ (2.00 g, 8.53 mmol). Yield 2.15 g (40%). *rac/meso* = 65:35.

meso Isomer: 1H NMR (500 MHz, $CDCl_3$): δ = 1.01 [s, 3 H, $Si(CH_3)$ *exo*], 1.29 [s, 3 H, $Si(CH_3)$ *endo*], δ_A = 4.28, δ_B = 4.22 (AB, J_{AB} = 21.6 Hz, 4 H, $CH_2C_6H_5$), 5.77 (s, 2 H, 2-*H*), 7.02–7.48 (m, 8 H, 4-*H*–7-*H*), 7.02–7.48 (m, 10 H, $CH_2C_6H_5$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = –1.40 [$Si(CH_3)$ *exo*], –0.99 [$Si(CH_3)$ *endo*], 34.22 ($CH_2C_6H_5$), 65.84, 85.90 (C1, C3), 118.12 (C2), 124.06 and 125.85 (C5, C6), 126.12 and 126.14 (C4, C7), 118.04–140.17 ($CH_2C_6H_5$) ppm.

rac Isomer: 1H NMR (500 MHz, $CDCl_3$): δ = 0.79 [s, 6 H, $Si(CH_3)$], δ_A = 4.17, δ_B = 4.04 (AB, J_{AB} = 19.6 Hz, 4 H, $CH_2C_6H_5$), 5.59 (s, 2 H, 2-*H*), 7.02–7.48 (m, 8 H, 4-*H*–7-*H*), 7.02–7.48 (m, 10 H, $CH_2C_6H_5$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = –2.85 [$Si(CH_3)_2$], 34.58 ($CH_2C_6H_5$), 65.94, 86.32 (C1, C3), 118.04 (C2), 124.25 and 124.74 (C5, C6), 126.57 and 126.78 (C4, C7), 118.04–140.17 ($CH_2C_6H_5$) ppm.

Both Isomers: $C_{34}H_{30}Cl_2SiZr$ (628.82): calcd. C 64.94, H 4.81; found C 65.02, H 4.86.

Polymerization Experiments: Polymerizations (three runs for catalyst) were carried out in a 250 mL glass reactor using toluene as a solvent (100 mL). Catalysts (6 μ mol) were treated with the appropriate quantity (Al/Zr = 2000) of a commercial (CROPTOM) solution of MAO in toluene (10% Al) for 15 min. Toluene (80 mL), $Al(iBu)_3$ scavenger (2 mL), and activated catalyst were introduced, in this order, into the reactor and the temperature was maintained at 343 K. The nitrogen atmosphere was removed and a continuous flow of ethylene (1.5 bar) was introduced over 30 min. The reaction mixture was then quenched by the addition of acidified methanol. The polymer was collected by filtration, washed with methanol, and dried under vacuum at room temperature for 24 h.

Polymer Analysis Procedures: M_w , M_n , and M_w/M_n were measured with an Alliance GPC-2000 high temperature GPC device from Waters Corp., Milford, MA, USA. The mobile phase was 2,4,5-trichlorobenzene (HPLC grade, J. T. Baker Ltd.) at 150 °C. Prior to use as a mobile phase, TCB was filtered through a 0.2- μ fiberglass filter (PALL Corp.). The GPC device was completed with 3 Styragel® columns (Waters Corp.) and an additional GARD column. All columns were placed in an oven and heated to 150 °C. The RI detector at 150 °C was used for MW determination by the relative method. Data processing was performed using Millennium® ver. 4.2 Software (Waters Corp.). The sample (0.020 g) was dissolved in 2,4,5-trichlorobenzene (10.0 mL) (HPLC grade, J. T. Baker Ltd.) at 150 °C over 7 h. The solution was stirred four times during this period. The hot solution (7 mL) of each sample was placed into the metal vial equipped with a mechanism for automatic filtration through 0.2- μ metal filters prior to injection. The vials were immediately placed in an autosampler heated continually at 150 °C. The sample was stirred for 15 min in the autosampler prior to injection. 12 PS narrow standards in the range of M_w from 2430 Dalton to 1.800.000 Dalton (Aldrich) were used for the calibration of the GPC device. The standards were prepared analogous to the sample preparation. The concentrations of standard solutions were calculated according the recommendations of Aldrich. The calibration curve is linear in all range of M_w and indicates the good working order of the device and especially the columns.

X-ray Crystal Structure Determination of *meso*-9 and *rac*-10: Intensity data were collected with a Nonius-MACH3 diffractometer equipped with a graphite monochromator and a Mo- K_α radiation source (λ = 0.71073 Å) using a $\omega/2\theta$ -scan technique. The final unit cell parameters were determined from 25 well-centered reflections and refined by least-squares methods. Data were corrected for Lorentz and polarization effects and a semi-empirical absorption correction (Psi-scans) was made.^[21]

The structures were solved using direct methods,^[22] completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures on F^2 .^[23] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed using a “riding model” and included in the refinement at calculated positions. Weights were optimized in the final cycles. Crystallographic data are given in Table 4.

Table 4. Crystal data and structure refinement for *meso*-9 and *rac*-10.

	<i>meso</i> -9	<i>rac</i> -10
Empirical formula	$C_{22}H_{22}Cl_2SiZr \cdot CH_2Cl_2$	$C_{26}H_{30}Cl_2SiZr \cdot 0.5C_7H_8$
Formula weight	561.53	578.78
Temperature [K]	290(2)	250(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
<i>a</i> [Å]	9.994(5)	11.062(4)
<i>b</i> [Å]	10.430(8)	12.206(4)
<i>c</i> [Å]	12.264(5)	11.311(3)
α [°]	86.23(4)	
β [°]	70.28(4)	91.59(3)
γ [°]	78.74(6)	
Volume [Å ³]	1180(1)	1526.7(8)
<i>Z</i>	2	2
Density (calculated) [g/cm ³]	1.580	1.259
Absorption coefficient [cm ^{–1}]	9.78	5.89
<i>F</i> (000)	568	598
Crystal size [mm]	0.3 × 0.2 × 0.1	0.4 × 0.3 × 0.2
Index ranges	–12 ≤ <i>h</i> ≤ 13 –13 ≤ <i>k</i> ≤ 13 0 ≤ <i>l</i> ≤ 16	–14 ≤ <i>h</i> ≤ 14 0 ≤ <i>k</i> ≤ 16 0 ≤ <i>l</i> ≤ 14
Reflections collected	5894	3858
Independent reflections	5638 [<i>R</i> (int) = 0.0497]	3674 [<i>R</i> (int) = 0.0168]
Data/restraints/parameters	5638/0/266	3674/0/147
Goodness-of-fit on <i>F</i> ₂	1.056	1.111
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0630 <i>wR</i> ₂ = 0.1479	<i>R</i> ₁ = 0.0466 <i>wR</i> ₂ = 0.1460
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1260 <i>wR</i> ₂ = 0.1745	<i>R</i> ₁ = 0.0656 <i>wR</i> ₂ = 0.1567
Largest diff. peak/hole [e·Å ^{–3}]	1.076/–1.384	1.218/–0.461
$R_1 = \Sigma F_o - F_c /\Sigma F_o $; $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^{0.5}]$		

CCDC-283808 and -283809 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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