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Conformational features of a furyl-substituted bis(tetrahydroindenyl)zirconium dichloride system[†]

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ABSTRACT: Treatment of 2-(5-methyl-2-furyl)tetrahydroindenyllithium with $ZrCl_4$ gave bis[2-(5-methyl-2-furyl)tetrahydroindenyl]zirconium dichloride (**8**). Dynamic ^1H NMR spectroscopy revealed a Cp-furyl rotational barrier of $\Delta G^{\neq}_{\text{Arrot}}$ (148 K) = 6.8 ± 0.4 kcal mol^{-1}. The x-ray crystal structure analysis of **8** showed the presence of a *rac*-like metallocene conformation in which the furyl rings are oriented coplanar with the Cp moiety of the tetrahydroindenyl ligand systems, but the two furyl rings are oriented differently: one has the oxygen atom oriented toward the open front side, whereas the other has the furyl oxygen pointing toward the narrow back side of the bent metallocene wedge. The **8**–MAO Ziegler–Natta catalyst system produces an atactic polypropylene oil. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: zirconocene; metallocene conformation; homogeneous Ziegler–Natta catalyst; polypropylene

INTRODUCTION

The conformational properties of specific Group 4 bent metallocene complexes can be of decisive importance for the stereochemical characteristics of carbon–carbon bond formation at the active catalysts derived from them. We had demonstrated this a few years ago with first examples of a series of bis(1-terpenylindenyl)zirconium complexes, whose metallocene conformational features—determined by the nature of the specific terpenyl substituent used—were shown to determine the stereospecificity of polypropylene formation at the respective Ziegler–Natta catalysts derived from them.[1] Later, these optically pure metallocenes were successfully employed as catalysts in organic asymmetric synthesis, again making use of their specific and very characteristic conformational features.[2]

Waymouth and co-workers found that bis(2-arylindenyl)$ZrCl_2$-derived homogeneous Ziegler–Natta catalysts can be used to make elastomeric polypropylenes. They proposed that the conformational ‘switching’ between chiral (C_2-symmetric), *rac*-like and achiral, *meso*-like metallocene conformations might represent the decisive mechanistic feature to determine the necessary change between the alternating production of isotactic and atactic polypropylene segments in this process.[3]

We have recently introduced a series of related bis(2-hetarylindenyl) Group 4 metallocene complexes into this chemistry, and found that some of these systems produce highly elastomeric polypropylene samples with excellent catalyst efficiencies. In several cases we were able to carry out the conformational analysis at the stage of the neutral catalyst precursors by dynamic NMR spectroscopy in solution, supported by an identification of several examples of the rotameric structural types in the solid state by x-ray crystal structure analyses.[4,5] We have now structurally identified the first example of a C_1-symmetric bis(2-furyltetrahydroindenyl)$ZrCl_2$ complex that exhibits both the two most often observed Cp-furyl conformational orientations in a single molecule. The preparation, structural characterization and some catalytic features of this special bis(2-furyltetrahydroindenyl)$ZrCl_2$ example is described in this paper.

RESULTS AND DISCUSSION

Synthesis and characterization of the furyl-substituted bis(tetrahydroindenyl)$ZrCl_2$ system 8

Tetrahydroindenyl complexes of the Group 4 metals can be synthesized by two principal routes, either by selective catalytic hydrogenation of the corresponding indenyl metal complexes[6] or by attachment of a preformed tetrahydroindenyl anion equivalent to the transition metal center. In this study, we chose the second alternative; we

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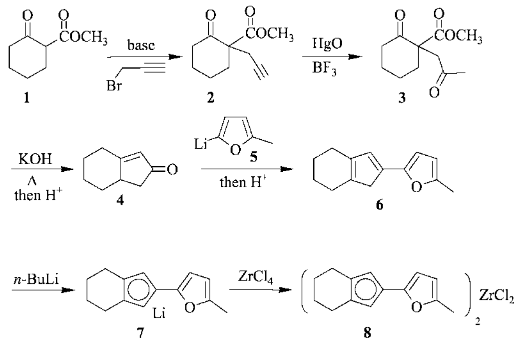


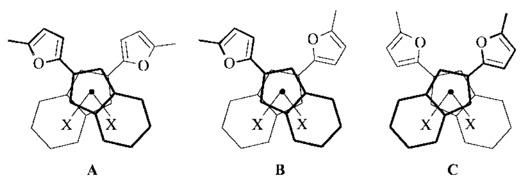
Scheme 1

adopted a procedure recently described by Polo *et al.*[7] and developed it into a synthesis of the required 2-(5-methyl-2-furylindenyl) ligand system (see Scheme 1).

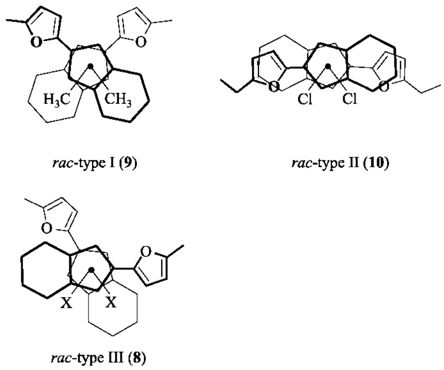
In this case, 2-methylfuran was treated with n-butyllithium to generate the 2-lithio-5-methylfuran reagent (**5**), which was then reacted at $-20\,^\circ$C with the bicyclic cyclopentenone derivative **4**. Hydrolytic workup and chromatographic purification eventually gave the sensitive furyl-substituted cyclopentadiene derivative **6** in ca 85% yield. This was subsequently deprotonated by treatment with n-butyllithium in diethyl ether–hexane to give **7** [^{1}H NMR (in benzene -d_6/THF -d_8, 10:1): δ 6.05 (s, 2H, 1-/3-H), 5.98, 5.90 (furyl-H)]. Zirconium tetrachloride was then added to a suspension of **7** at low temperature. Removal of the precipitated lithium chloride and workup involving crystallization from toluene at $-20\,^\circ$C eventually furnished the Group 4 metallocene complex **8** in ca 20% yield.

We had previously shown that bis(2-furylindenyl)zirconium complexes can attain three different *rac*-type conformational isomers (**A, B** and **C** in Scheme 2).[4,5] They originate from freezing out two different rotational processes, namely the rotation around the metal-η^5-indenyl ligand vector *and* that around the indenyl–furyl σ-bond connection. Examples of all three rotational isomeric types were observed by dynamic NMR spectroscopy in solution, but only the C_2-symmetric rotamers **A** and **C** had been observed by x-ray diffraction in the solid state so far. The x-ray crystal structure analysis of complex **8** has now for the first time revealed the structure of an example of the previously unobserved **B**-type isomer (of C_1- symmetry) in the crystal.

Single crystals of **8** that were suitable for an x-ray crystal structure analysis were obtained from toluene. The zirconium center in complex **8** is pseudotetrahedrally coordinated to two 2-(5-methyl-2-furyl)tetrahydroindenyl ligands and two chlorides. The complex is of C_1 symmetry and, therefore, the two zirconium–chloride distances are slightly different at 2.435(1) Å (Zr—Cl1) and 2.428(1) Å (Zr—Cl2). The Cl1—Zr—Cl2 angle [97.29(4)°] is in the typical bent metallocene range. Both tetrahydroindenyl ligands are η^5-coordinated to zirconium. There is a slight asymmetry detectable in the Zr—Cp coordination, with the C11—to C19—Zr bond lengths being in a range between 2.487(3) Å (C11, see Fig. 1) and 2.580(3) Å (C17) and the corresponding C31—to C39—Zr bonds ranging between 2.468(3) Å (C31) and 2.596(3) Å (C37). These differences seem to be independent of a specific substituent influence, but probably merely reflect positional differences as the smaller values correspond to the sterically tighter situation at the back side and the larger values are found at the more open front side of the bent metallocene wedge.



Scheme 2



Scheme 3. Schematic representation of chiral metallocene conformational types that were observed experimentally for the complexes **8**–**10** in the solid state

It is the specific conformational arrangement of the bis[2-(5-methyl-2-furyl)tetrahydroindenyl]Zr unit that makes complex **8** structurally so interesting. We had previously observed that there are two structurally clearly distinguishable types of C_2-symmetric chiral metallocene conformer types observed for bis(2-hetarylindenyl)zirconium complexes[4,5] (for related 2-substituted examples, see Ref. 8). One (type I, see Scheme 3) has both the annelated six-membered rings (C_2-symmetrically) placed in front of the bent metallocene wedge above and below the adjacent Zr–(σ-ligand) vectors. The other (type II in Scheme 3) has the annelated rings oriented toward the lateral sectors of the bent metallocene wedge. Which of the two types is preferred and thus experimentally observed by x-ray crystallography depends on the σ-ligands X. Bis[2-(5-methyl-2-furyl)indenyl)$\mathrm{Zr(CH_3)_2}$ (**9**) is an example of a *rac*-type I conformer whereas the related molecule bis[2-(5-ethyl-2-furyl)indenyl]$\mathrm{ZrCl_2}$ (**10**) exhibits a *rac*-type II metallocene conformation in the crystal.[4,5]

Complex **8** exhibits a *rac*-type metallocene conforma-

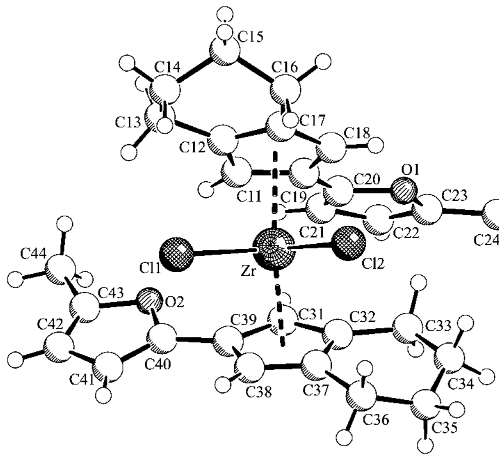


Figure 1. A front projection of the molecular structure of complex **8**. Selected bond lengths (Å) and angles (°): Zr—Cl1 2.435(1), Zr—Cl2 2.428(1), Zr—C11 2.487(3), Zr—C31 2.468(3), Zr—C12 2.574(3), Zr—C32 2.526(3), Zr—C17 2.580(3), Zr—C37 2.596(3), Zr—C18 2.541(3), Zr—C38 2.548(3), Zr—C19 2.543(3), Zr—C39 2.492(3), C19—C20 1.455(4), C39—C40 1.457(4), C20—O1 1.375(4), C40—O2 1.377(4), C20—C21 1.347(5), C40—C41 1.350(5), C21—C22 1.423(5), C41—C42 1.421(5), C22—C23 1.336(5), C42—C43 1.338(6), C23—O1 1.383(4), C43—O2 1.387(4); C11—Zr—Cl2 97.29(4), C11—C19—C20 126.2(3), C31—C39—C40 127.0(3), C18—C19—C20 126.1(3), C38—C39—C40 125.5(3), C19—C20—O1 115.4(3), C39—C40—O2 116.8(3), C19—C20—C21 134.6(3), C39—C40—C41 133.3(3), O1—C20—C21 109.9(3), O2—C40—C41 109.9(3), C20—O1—C23 106.5(3), C40—O2—C43 106.7(3), C20—C21—C22 106.4(3), C40—C41—C42 106.3(4), C21—C22—C23 107.7(3), C41—C42—C43 108.1(3), C22—C23—O1 109.4(3), C42—C43—O2 109.0(3)

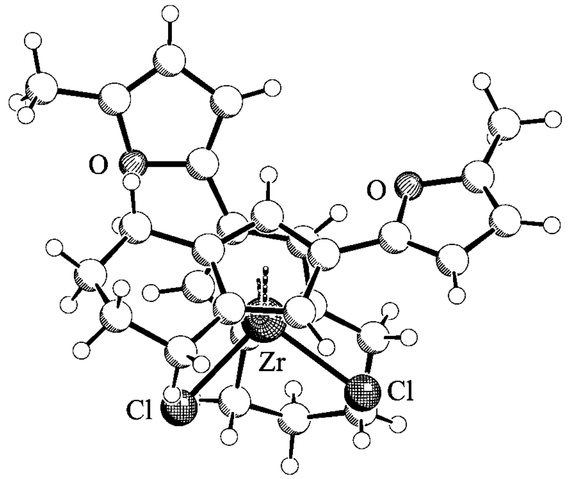


Figure 2. Top view of the molecular structure of **8**, showing the different conformational arrangements of the two η^5-2-(5-methyl-2-furyl)tetrahydroindenyl ligands inside the bent metallocene wedge

tion in the crystal that contains both rotational motifs from the complexes **9** and **10**, namely one tetrahydroindenyl ligand that exhibits its annelated saturated six-membered ring in the lateral sector whereas the other tetrahydroindenyl ring is oriented with its annelated cyclohexene moiety towards the front side of the metallocene wedge *syn*-positioned with one of the Zr—Cl vectors (see Scheme 3 and Figs 1 and 2).

The extraordinary structural feature of **8** is the arrangement of the furyl substituents on the metallocene framework. The furyl groups are oriented in-plane with the Cp section of the tetrahydroindenyl ligands, but the two furyl groups are arranged differently: one has its oxygen atom pointing in the direction of the metallocene front side whereas the other has its furyl oxygen atom oriented towards the narrow back side of the metallocene wedge. To our knowledge, this represents the first example of this specific combination of the conformational arrangement of the furyl substituents on a Group 4 metallocene framework. Aside from the unsymmetrical general arrangement of the two tetrahydroindenyl ligands relative to one another, this represents the first example of the **B**-type conformational arrangement depicted in Scheme 2, that had previously been found in solution by dynamic ^{1}H NMR spectroscopy, but that was unobserved so far in the crystal. The x-ray crystal structure analysis of **8** has thus revealed and characterized a first example of this important metallocene conformational type in the crystal, which may hence serve as a reference structure.

Complex **8** exhibits dynamic ^{1}H NMR spectra in $CDFCl_2$–CDF_2Cl solution in the temperature range 253–138 K, as expected. At the high temperature end it shows the spectra of a system that undergoes rapid conformational equilibration. At 193 K the ^{1}H NMR spectrum of complex **8** exhibits four separate multiplets of the annelated tetramethylene units at δ 1.42, 1.65, 2.24 and 2.38, three signals of the methylfuryl substituent (δ 2.40, CH_3; 6.03, 6.23, furyl 3-H/4-H) and a sharp singlet at δ 6.45 corresponding to the symmetry-equivalent tetrahydroindenyl protons 1-H and 3-H. The highly symmetrical appearance of the ^{1}H NMR spectrum, featuring the resonances of apparently two symmetry-equivalent ligands which show no distinction between a ligand 'front' and 'back' side, indicated that two conformational processes are proceeding rapidly on the 600 MHz ^{1}H NMR time-scale at this temperature in complex **8**, namely the rotation around the metal–Cp vector *and* the rotation around the Cp–furyl σ-bond.

Lowering the temperature of the NMR probe below 193 K leads to a broadening of all the tetrahydroindenyl resonances but not the 5-methylfuryl signals. At and below 143 K decoalescence of the tetrahydroindenyl 1-H/3-H singlet into two separate resonances is observed. Together with the massive splitting of the —$(CH_2)_4$— signals, this probably indicates freezing of the Cp–furyl rotation under these conditions.[5] From the dynamic 1-H/3-H resonances (δ 6.41 and 6.60 at 138 K) a Gibbs activation energy of $\Delta G^{\neq}_{\text{Arrot}}$ (148 K) = 6.8 ± 0.4 kcal mol^{-1}

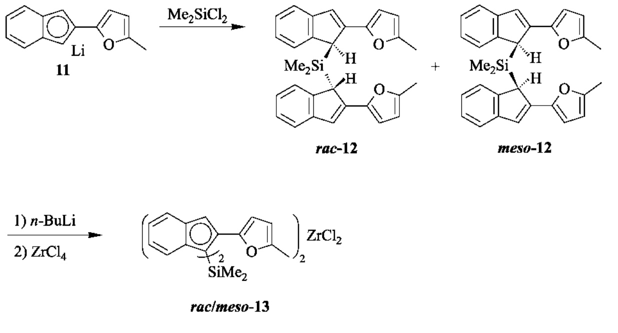
(1 kcal = 4.184 kJ) was obtained.[9] Under these conditions, the faster metal–Cp rotation is still rapid on the 600 MHz ^{1}H NMR time-scale. Only at the lowest monitoring temperature (138 K) did a beginning broadening of the low-field furyl ^{1}H NMR resonance signal the onset of the hindered rotation around the metal–Cp vector to become observable. However, the decoalescence point could not be reached under these experimental conditions.

We prepared a second 5-methylfuryl-substituted Group 4 metallocene complex, the hetaryl-substituted *ansa*-metallocene **13**, in the course of this study, which shows a structural arrangement of an indenyl–furyl moiety in the crystal that might serve as a static model of a possible transition state of the Cp–furyl–substituent rotation at a bent metallocene framework. The synthesis and structural characterization of the furyl-substituted *ansa*-metallocene complex **13** is described in the second part of this paper.

Synthesis and characterization of the 5-methylfuryl-substituted *ansa*-metallocene complex 13

Me_2Si-bridged bis(indenyl) *ansa*-Group 4 metallocenes have been of enormous importance for the practical development of homogeneous metallocene Ziegler–Natta catalysis.[10,11] Special substitution patterns especially with regard to aryl substituent attachment have been recognized that lead to very high reactivities of stereoselective polypropylene formation. Hetaryl groups have seldom been used, although some recent developments have shown the utility of annelated furan or thiophene rings in this chemistry.[12] Specifically substituted *ansa*-metallocenes have played a role in early metallocene-catalyzed elastomer formation.[13]

2-(5-Methyl-2-furyl)indenyllithium (**11**) was treated with Me_2SiCl_2 (2:1 ratio) in dilute ethereal solution to yield a 1:1 mixture of the diastereomers of the ligand precursor **12** (see Scheme 4) (the synthesis of **13** was carried out in analogy with published procedures[10] used for the preparation of aryl-substituted Me_2Si-bridged *ansa*-metallocenes). Double deprotonation was achieved by treatment with 2 equiv. of *n*-BuLi in hexane under reflux conditions. Subsequent transmetallation by the reaction with $ZrCl_4$ went smoothly to yield an 80:20 mixture of the *ansa*-metallocenes *rac*-**13** and *meso*-**13**. The *rac*-*ansa*-zirconocene isomer turned out to be of lower solubility in toluene than the *meso*-isomer, and was obtained isomerically pure after crystallization from this solvent (20% isolated). The C_2-symmetric *rac*-**13** *ansa*-metallocene diastereomer is characterized by the appearance of a single Me_2Si ^{1}H NMR resonance at δ 1.14 (in CD_2Cl_2 solution). It shows indenyl 4-H and 7-H ^{1}H NMR signals at δ 7.51 and δ 6.95. The corresponding 5-H/6-H signals appear at δ 7.30/6.71, and the indenyl 3-H signal is observed at δ 6.83 [with a characteristic ^5J(3-H,7-H) = 0.6 Hz coupling constant;[1,14] methylfuryl signals at δ 6.25, 6.10 and 2.43].



Scheme 4

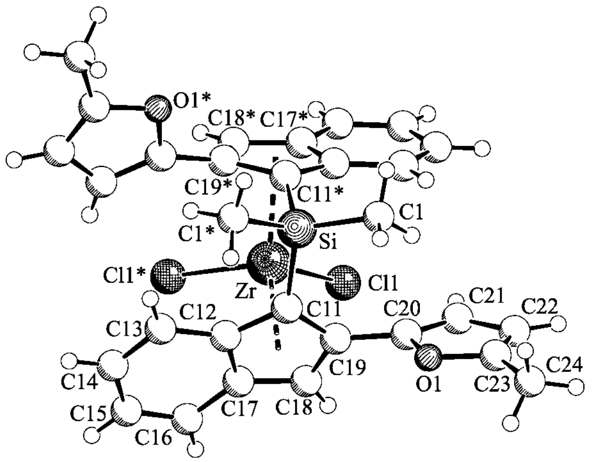


Figure 3. A view of the molecular structure of complex *rac*-**13**. Selected bond lengths (Å) and angles (°): Zr—Cl1 2.425(1), Zr—C11 2.473(3), Zr—C12 2.530(3), Zr—C17 2.629(3), Zr—C18 2.597(3), Zr—C19 2.526(3), C11—Si 1.882(3), C1—Si 1.856(3), C19—C20 1.467(4), C20—O1 1.384(3), C20—C21 1.340(4), C21—C22 1.420(5), C22—C23 1.340(5), C23—O1 1.378(4); Cl1—Zr—Cl1* 97.66(4), C11—Si—C11* 95.2(2), C11—C19—C20 126.2(3), C18—C19—C20 123.0(3), C19—C20—O1 114.1(2), C19—C20—C21 136.3(3), O1—C20—C21 109.3(3), C20—O1—C23 106.8(2), C20—C21—C22 107.2(3), C21—C22—C23 107.4(3), C22—C23—O1 109.3(3)

Complex *rac*-**13** was characterized by an x-ray crystal structure analysis. The view of the molecular structure (see Fig. 3) shows a distorted pseudotetrahedral coordination geometry around zirconium. The Zr—Cl1 bond length in the crystallographically C_2-symmetric molecule of *rac*-**13** is 2.425(1) Å. The corresponding Cl1—Zr—Cl1* angle was found to be 97.66(4)°. The *ansa*-metallocene framework in *rac*-**13** is rather strained. This shows up in the rather unsymmetrical η^5-Cp coordination of the indenyl five-membered ring. The 'distal' Zr—C17 and Zr—C18 bond lengths inside this subunit are rather long at 2.629(3) and 2.597(3) Å, respectively, while the 'proximal' Zr—C12 and Zr—C19 bonds are markedly shorter at 2.530(3) and 2.526(3) Å, respectively. The Zr—C11 bond is the shortest [2.473(3) Å], as expected.

Table 1. Propene polymerization reactions with the **8**–MAO and *rac*-**13**–MAO Ziegler–Natta catalyst systems at three temperatures

Compound	Catalyst (mg)	Al/Zr	*T* (°C)	Reaction time (h)	gPP[a]	Act[b]	mmmm (%)[c]
8	10	1930	+20	2.00	14.0	196	9
13	16	1400	+20	1.00	4.0	82	88
8	9	2150	0	2.00	13.5	210	11
13	17	1330	0	0.75	15.0	385	90
8	9	2150	−20	2.00	18.5	288	14
13	15	1500	−20	0.75	18.0	471	95

[a] g polypropylene.
[b] Activity in g polypropylene mmol^{-1} [Zr] h bar.
[c] From ^{13}C NMR pentad analysis.

The strain of the ligand framework is also reflected by the bonding geometry around the bridging silicon atom. While the C1—Si—C1* angle is close to ideally tetrahedral as expected [109.7(2)°], with the C1—Si—C11 angle at 111.4(1) Å not deviating much, the C11—Si—C11* angle is considerably reduced at 95.2(2)° (see Ref. 15 for a comparison).

A remarkable structural feature of the solid-state structure of complex *rac*-**13** is the observed conformational orientation of the furyl groups on the indenyl ligand framework. In complex *rac*-**13** the furyl groups are rotated markedly from the indenyl plane, which is different from all the structurally characterized examples of non-bridged 2-furylindenyl Group 4 metal complexes. In *rac*-**13** the respective dihedral angles, that characterize the furyl/indenyl rotation, are θ C11—C19—C20—O1 = +60.4(3)° and θ C18—C19—C20—O1 = −111.6(3)°. Potentially, this structural feature may serve as a model to approach structurally the transition-state geometry of the hetarene–Cp rotation during the conformational equilibration of the open non-bridged bis(furylindenyl)ZrX_2 complexes studied previously by dynamic NMR spectroscopic techniques in solution.

Polymerization reactions

Scouting propene polymerization reactions were carried out using the new complexes **8** and *rac*-**13**. In both cases the catalyst generation was carried out by treatment of the metallocene dichloride complexes with a >1000 molar excess of methylalumoxane.[16] Polymerization reactions were carried out at three different temperatures with each system.

The ansa-metallocene shows a typical catalyst activity for isotactic polypropylene formation (see Table 1). Solid, hard polypropylene was obtained at each temperature. At −20 °C a sample was obtained that exhibited a 95% mmmm pentad signal intensity in the ^{13}C NMR spectrum (for ^{13}C NMR methyl pentad analysis, see Ref. 17; for the statistical treatment of the NMR data obtained see Ref. 18). At the higher temperatures a slightly less isotactic polypropylene was obtained with the *rac*-**13**–MAO catalyst system. Overall, this catalyst showed features similar to many examples of the well studied aryl-substituted Me_2Si-bridged bis(indenyl)ZrX_2 Ziegler–Natta catalyst family.[10]

The non-bridged 2-furyltetrahydroindenyl-derived metallocene catalyst system **8**–MAO showed a similarly high propene polymerization activity under these conditions (see Table 1). In this case, near to atactic polypropylene oils were obtained in the temperature range between −20 and +20 °C.

EXPERIMENTAL

General remarks. Reactions were carried out under an argon atmosphere using Schlenk-type glassware or in a glove-box. Solvents (including deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. NMR spectra were recorded on a Varian Unity Plus NMR spectrometer (^{1}H, 600 MHz; ^{13}C, 150 MHz) at variable temperature. 1,4,5,6,7,7a-Hexahydroinden-2-one (**4**),[7] 2-lithio-5-methylfuran (**5**) and 2-(5-methyl-2-furyl)indenyllithium (**11**)[4] were prepared according to literature procedures. Most of the compounds were characterized by additional GCOSY, GHSQC and GHMBC NMR experiments.[19] IR spectra were aquired on a Nicolet 5 DXC Fourier transform IR spectrometer. Melting-points were obtained by differential scanning calorimetry (DuPont 910) and elemental analyses were performed on a Foss-Heraeus CHN-Rapid elemental analyzer.

*2-(5-Methyl-2-furyl)-4,5,6,7-tetrahydro-1H-indene (**6**).* 2-Methylfuran (0.60 g, 7.31 mmol) in diethyl ether (70 ml) was reacted with *n*-butyllithium (4.60 ml, 7.31 mmol, 1.6 M solution in *n*-hexane) to obtain 2-lithio-5-methylfuran (**5**). The dark brown solution was cooled to −20 °C and 1,4,5,6,7,7a-hexahydroinden-2-one[(**4**, 1.00 g (7.31 mmol)] was added. The reaction mixture was stirred for 2 h at −20 °C before warming to room temperature. The yellow solution was hydrolyzed with H_2O (40 ml) and extracted with diethyl ether (3 × 50 ml). The combined organic portions were dried with magnesium sulfate and the solvent was removed by rotary evaporation. The residue was filtered over silica gel with 1.5 l of isohexane. The solution was dried *in vacuo* and 1.50 g (6.32 mmol, yield 86%) of a yellow oil was obtained. Compound **6** has to be reacted immediately with *n*-butyllithium owing to the possible Diels–Alder dimerization. ^{1}H NMR (dichloromethane-d_2, 599.9 MHz): $\delta = 6.45$ (s,1H, 3-H), 6.12 (d, 1H, 3-H_{furyl}, $^3J = 3.0$ Hz), 5.96 (dq, 1H, 4-H_{furyl}, $^3J = 3.0$ Hz, $^4J = 1.2$ Hz), 3.48 [q, 4H, $(CH_3CH_2)_2O$, $^3J = 6.6$ Hz], 3.16 (s, 2H, 1-H), 2.33–2.27 (m, 4H, 4-H, 7-H), 2.31 (s, 3H, CH_3), 1.72 (m, 4H, 5-H, 6-H), 1.21 [t, 6H, $(CH_3CH_2)_2O$, $^3J = 6.6$ Hz]. ^{13}C NMR (dichloromethane-d_2, 150.1 MHz): $\delta = 151.9$ (C, C-5_{furyl}), 151.1 (C, C-3a), 139.2 (C, C-2_{furyl}), 138.1 (C, C-7a), 134.1 (C, C-2), 127.7 (CH, C-3), 107.9 (CH, C-4_{furyl}), 105.4 (CH, C-3_{furyl}), 66.4 [CH_2, $(CH_3CH_2)_2O$], 43.1 (CH_2, C-1), 26.0 (CH_2, C-4 or C-7), 25.0 (CH_2, C-4 or C-7), 23.8 (CH_2, C-5 or C-6), 23.6 (CH_2, C-5 or C-6), 15.9 [CH_3, $(CH_3CH_2)_2O$], 14.2 (CH_3, CH_3).

*2-(5-Methyl-2-furyl)-4,5,6,7-tetrahydroindenyllithium (**7**).* *n*-Butyllithium (3.87 ml, 6.19 mmol, 1.6 M solution in *n*-hexane) was added to 2-(5-methyl-2-furyl)-4,5,6,7-tetrahydroindene [**6**, 1.24 g (6.19 mmol)] in diethyl ether (50 ml) at room temperature. The yellow solution was stirred overnight and the solvent was removed in vacuum. Pentane (20 ml) was added to the reddish residue and the resulting slurry was stirred for 10 h, filtered and washed with 5 ml of pentane to yield 0.64 g (3.10 mmol, 50%) of an off-white powder. ^{1}H NMR [benzene-d_6–tetrahydrofuran-d_8 (10:1), 200.1 MHz]: $\delta = 6.05$ (s, 2H, 1-H, 3-H), 5.98 (d, 1H, 3-H_{furyl}, $^3J = 3.2$ Hz), 5.90 (dq, 1H, 4-H_{furyl}, $^3J = 3.2$ Hz, $^4J = 1.2$ Hz), 2.79 (m, 4H, 4-H, 7-H), 2.17 (s, 3H, CH_3), 1.82 (m, 4H, 5-H, 6-H).

*Bis[2-(5-methyl-2-furyl)tetrahydroindenyl]dichlorozirconium (**8**).* Under argon zirconium tetrachloride powder (0.23 g, 0.97 mmol) was added to a suspension of 0.40 g (1.94 mmol) of the lithium salt **7** in 30 ml of toluene at −78 °C. The reaction mixture was stirred overnight and filtered using a Schlenk frit. The solvent was reduced in vacuum and the product crystallized at −30 °C. Together with a second crystallization a yield of 120 mg (0.22 mmol, 22%) of a yellow solid was obtained, m.p. 117 °C. ^{1}H NMR (dichloromethane-d_2, 599.9 MHz): $\delta = 6.27$ (s, 4H, 1-H, 3-H), 6.26 (m, 2H, 3-H_{furyl}), 6.05 (dq, 2H, 4-H_{furyl}, $^3J = 3.6$ Hz, $^4J = 1.2$ Hz), 2.42 (m, 8H, 4-H, 7-H), 2.38 (s, 6H, CH_3), 1.76 (m, 4H, 5-H or 6-H), 1.49 (m, 4H, 5-H or 6-H). ^{13}C NMR (dichloromethane-d_2, 150.1 MHz): $\delta = 152.0$ (C, C-5_{furyl}), 147.4 (C, C-2_{furyl}), 130.2 (C, C-3a, C-7a), 117.2 (C, C-2), 110.9 (CH, C-1, C-3), 108.1 (CH, C-4_{furyl}), 107.5 (CH, C-3_{furyl}), 24.1 (CH_2, C-4, C-7), 22.4 (CH_2, C-5, C-6), 13.8 (CH_3, CH_3). IR (KBr): $\tilde{\nu} = 3103$ (m), 2936 (vs), 2865 (s), 1615 (m), 1579 (vs), 1496 (s), 1443 (vs), 1360 (w), 1324 (w), 1301 (w), 1200 (vs), 1105 (s), 1075 (s), 975 (vs), 892 (s), 856 (vs), 791 (vs), cm^{-1}. $C_{28}H_{30}O_2Cl_2Zr$ calcd C 59.98, H 5.39; found C 60.60, H 4.49%.

*X-ray crystal structure analysis of **8**.* Formula $C_{28}H_{30}O_2Cl_2Zr$, $M = 560.64$, yellow crystal 0.20 × 0.10 × 0.05 mm, $a = 10.497(1)$, $b = 11.279(1)$, $c = 12.055(1)$ Å, $\alpha = 110.33(1)$, $\beta = 108.84(1)$, $\gamma = 91.48(1)°$, $V = 1251.2(2)$ Å^3, $\rho_{calc} = 1.488$ g cm^{-3}, $\mu = 6.76$ cm^{-1}, empirical absorption correction via SORTAV ($0.877 \le T \le 0.967$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 8749 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.68$ Å^{-1}, 6207 independent ($R_{int} = 0.029$) and 4797 observed reflections [$I \ge 2\sigma(I)$], 300 refined parameters, $R = 0.049$, $wR^2 = 0.097$, maximum residual electron density 0.67 (−0.75) e Å^{-3}, hydrogens calculated and refined as riding atoms. Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used were data collection COLLECT (Nonius, 1998), data reduction Denzo-SMN,[20] absorption correction SORTAV,[21] structure solution SHELXS-97,[22] structure refinement SHELXL-97 (G. M. Sheldrick, Universität Göttingen, 1997) and graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

*rac- and meso-Dimethylbis[2-(5-methyl-2-furyl)indenyl]silane (**12**).* $SiMe_2Cl_2$ (1.12 g, 8.66 mmol) was added to a solution of 2-(5-methyl-2-furyl)indenyllithium (**11**, 3.50 g, 17.3 mmol) in diethyl ether (50 ml) at −78 °C. The reaction mixture was stirred overnight and allowed to warm to room temperature over night. The solution was hydrolyzed with H_2O (40 ml) and extracted three times with diethyl ether (100 ml). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent was removed by rotary evaporation. Column chromatography over silica gel with isohexane–dichloromethane (9:1) resulted in a colorless oil, 1.75 g (3.89 mmol, 79%). *rac*-^{1}H NMR (dichloromethane-d_2, 599.9 MHz): $\delta = 7.44$ (m, 4H, 4-H, 7-H), 7.26 (m, 2H, 5-H, or 6-H), 7.17 (m, 2H, 5-H, or 6-H), 7.05 (s, 2H, 3-H), 6.29 (d, 2H, 3-H_{furyl}, $^3J = 3.0$ Hz), 6.00 (dq, 2H, 4-H_{furyl}, $^3J = 3.0$ Hz, $^4J = 1.2$ Hz), 4.34 (s, 2H, 1-H), 2.29 (s, 6H, CH_3), −0.68 [s, 6H, $Si(CH_3)_2$]. *rac*-^{13}C NMR (dichloromethane-d_2, 150.1 MHz): $\delta = 152.2$ (C, C-5_{furyl}), 150.7 (C, C-2_{furyl}), 145.0 (C, C-3a), 144.8 (C, C-7a), 139.8 (C, C-2), 125.8 (CH, C-5), 123.9 (CH, C-6), 123.6 (CH, C-3), 123.4 (CH, C-7), 121.4 (CH, C-4), 109.0 (CH, C-3_{furyl}), 108.0 (CH, C-4_{furyl}), 43.6 (CH, C-1), 13.7 (CH_3, CH_3), −5.3 [CH_3, $Si(CH_3)_2$]. *meso*-^{1}H NMR (dichloromethane-d_2, 599.9 MHz): $\delta = 7.59$ (d, 2H, 4-H or 7-H, $^3J = 7.2$ Hz), 7.44 (m, 2H, 4-H or 7-H), 7.26 (m, 2H, 5-H or 6-H), 7.17 (m, 2H, 5-H, or 6-H), 7.07 (s, 2H, 3-H), 6.31(d, 2H, 3-H_{furyl}, $^3J = 3.0$ Hz), 6.05 (dq, 2H, 4-H_{furyl}, $^3J = 3.0$ Hz, $^4J = 1.2$ Hz), 4.10 (s, 2H, 1-H), 2.30 (s, 6H, CH_3), −0.71

and −0.75 [each s, each 3H, each Si(CH_3)$_2$]. *meso*-^{13}C NMR (dichloromethane-d_2, 150.1 MHz): $\delta = 152.4$ (C, C-5$_{\text{furyl}}$), 150.8 (C, C-2$_{\text{furyl}}$), 145.1 (C, C-3a), 144.8 (C, C-7a), 139.7 (C, C-2), 125.7 (CH, C-5), 124.0 (CH, C-6), 123.8 (CH, C-7), 123.6 (CH, C-3), 121.3 (CH, C-4), 108.7 (CH, C-3$_{\text{furyl}}$), 108.1 (CH, C-4$_{\text{furyl}}$), 43.7 (CH, C-1), 13.8 (CH_3, CH_3), −5.5 [CH_3, Si(CH_3)$_2$], −7.02 [CH_3, Si(CH_3)$_2$]. IR (KBr): $\tilde{\nu} = 3063$ (w), 3012 (w), 2961 (m), 2916 (m), 2870 (w), 1709 (m), 1648 (m), 1612 (m), 1590 (w), 1454 (m), 1408 (w), 1363 (w), 1261 (s), 1102 (s), 1023 (vs), 881 (w), 847 (s), 813 (vs), 757 (s) cm^{-1}. HRMS: found, *m/z* 448.1858; calcd for $C_{30}H_{28}O_2Si$, 448.1842.

*rac-{Dimethylsilanediylbis[2-(5-methyl-2-furyl)-indenyl]}dichlorozirconium (**13**).* Compound **12** (2.19 g, 4.87 mmol) was dissolved in toluene (100 ml) and tetrahydrofuran (5 ml). *n*-Butyllithium (6.09 ml, 9.74 mmol, 1.6 M solution in *n*-hexane) were added at room temperature. The reaction mixture was heated under reflux for 3 h and then cooled to −25 °C. Zirconium tetrachloride (1.14 g, 4.87 mmol) was added and the resulting suspension was allowed to warm to room temperature over a period of 2 h. A *rac*- to *meso*- ratio of the crude product of 80:20 was determined by ^{1}H NMR spectroscopy. The LiCl formed was filtered off and the solvent was reduced in vacuum. Crystallization at −30 °C resulted after filtration in 593 mg (0.97 mmol, 20%) of the pure orange *rac*-isomer, m.p. 251 °C. ^{1}H NMR (dichloromethane-d_2, 599.9 MHz): $\delta = 7.51$ (d, 2H, 4-H, $^3J = 8.4$ Hz), 7.30 (m, 2H, 5-H), 6.95 (dd, 2H, 7-H, $^3J = 9.0$ Hz, $^5J = 0.6$ Hz), 6.83 (d, 2H, 3-H, $^5J = 0.6$ Hz), 6.71 (m, 2H, 6-H), 6.25 (d, 2H, 3-H$_{\text{furyl}}$, $^3J = 3.6$ Hz), 6.10 (dq, 2H, 4-H$_{\text{furyl}}$, $^3J = 3.6$ Hz, $^4J = 1.2$ Hz), 2.43 (s, 6H, CH_3), 1.14 [s, 6H, Si(CH_3)$_2$]. ^{13}C NMR (dichloromethane-d_2, 150.1 MHz): $\delta = 152.8$ (C, C-5$_{\text{furyl}}$), 147.2 (C, C-2$_{\text{furyl}}$), 133.7 (C, C-3a), 128.8 (C, C-2), 127.7 (CH, C-5), 126.6 (C, C-7a), 126.1 (CH, C-7), 125.8 (CH, C-4), 125.5 (CH, C-6), 117.9 (CH, C-3), 113.4 (CH, C-3$_{\text{furyl}}$), 108.6 (CH, C-4$_{\text{furyl}}$), 84.7 (C, C-1), 13.9 (CH_3, CH_3), 4.2 [CH_3, Si(CH_3)$_2$]. IR (KBr): $\tilde{\nu} = 3107$ (w), 3084 (w), 3027 (w), 2969 (m), 2918 (m), 1960 (w), 1616 (s), 1564 (vs), 1535 (s), 1449 (vs), 1398 (vs), 1340 (vs), 1214 (vs), 1094 (m), 1031 (vs), 956 (vs), 841 (vs), 795 (vs), 749 (vs) cm^{-1}. $C_{30}H_{26}O_2Cl_2SiZr$: calcd C 59.19, H 4.31; found C 60.19, H 5.21%.

*X-ray crystal structure analysis of **13**.* Formula $C_{30}H_{26}O_2Cl_2SiZr{\cdot}CH_2Cl_2$, $M = 693.64$, yellow–orange crystal 0.20 × 0.15 × 0.05 mm, $a = 21.965(1)$, $b = 12.275(1)$, $c = 11.239(1)$ Å, $\beta = 105.21(1)°$, $V = 2924.1(4)$ Å^3, $\rho_{\text{calc}} = 1.576$ g cm^{-3}, $\mu = 8.11$ cm^{-1}, empirical absorption correction via SORTAV ($0.855 \le T \le 0.961$), $Z = 4$, monoclinic, space group *C*2/*c* (No. 15), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 7027 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.68$ Å^{-1}, 3746 independent ($R_{\text{int}} = 0.032$) and 3030 observed reflections [$I \ge 2\sigma(I)$], 184 refined parameters, $R = 0.045$, $wR^2 = 0.104$, maximum residual electron density 1.06 (−0.99) e Å^{-3} close to the solvate molecule, hydrogens calculated and refined as riding atoms (for details, see *X-ray crystal structure analysis of **8***).

Polymerization reactions. All polymerizations were carried out in a 1 l Büchi glass autoclave charged with toluene (150 ml) and methylalumoxane (20 ml, 10.5 wt% solution in toluene). At the respective temperature the stirred (600 rpm) mixture was saturated with propene at a pressure of 2 bar for 30 min. The catalyst precursors were injected and the polymerizations were carried out at a constant propene pressure for 2 h. The reaction mixture was hydrolyzed cautiously with a 1:1 mixture of methanol and 2 M HCl and treated additionally with HCl (6 M, 100 ml). The organic layer was separated, the toluene evaporated and the residue dried in vacuum overnight.

Crystallographic data. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCD 166598 and 166599. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax +44 1223 336033, E-mail deposit@ccdc.cam.ac.uk).

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