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Group 4 metallocenes containing hetaryl substituents at their π-ligands: synthesis and characterization of the parent bis[2-(2-furyl)indenyl]zirconocene system

Thorsten Dreier, Gesa Unger, Gerhard Erker *, Birgit Wibbeling [1], Roland Fröhlich[1]

Organisch-Chemisches Institut der Universität Münster, Corrensstrasse 40, D-48149 Munster, Germany

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Abstract

2-Lithiofuran was added to 2-indanone to yield 2-(2-furyl)indene (**4**) after hydrolytic workup. Treatment of **4** with *n*-butyllithium gave 2-(2-furyl)indenyllithium (**5**). Subsequent reaction of **5** with 0.5 molar equivalents of zirconium tetrachloride in toluene yielded bis[2-(2-furyl)indenyl]zirconium dichloride (**6**) that was characterized by X-ray diffraction. The homogeneous **6**–methylalumoxane Ziegler-Natta catalyst produced elastomeric polypropylene. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zirconocene complexes; Homogeneous Ziegler-Natta catalysis; Elastomeric polypropylene; Metallocene conformation

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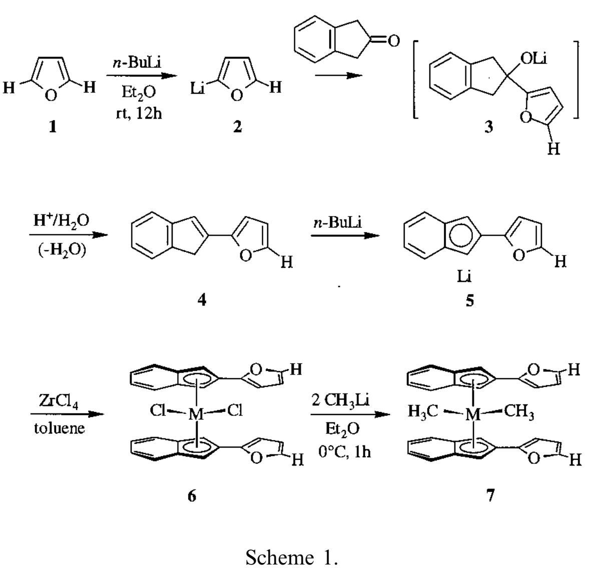
1. Introduction

Bis(2-arylindenyl)zirconium complexes have served as transition metal components for the generation of active homogeneous metallocene Ziegler-Natta catalysts that produce elastomeric polypropylenes [1,2]. We have recently shown that related bis(2-hetarylindenyl)-zirconium-derived catalysts behave similarly. They lead to the production of polypropylenes with interesting elastomeric properties [3], in the case of attachment of 2-furyl or 2-thienyl substituents [4,5]. The corresponding 2-*N*-methyl-pyrrolyl-substituted systems had poor catalyst performance. The cases reported in our recent publication [3] contained the 5-methyl-2-furyl (or -2-thienyl) substituent that was readily introduced into the ligand system via the 2-lithio-5-methylfuran reagent which, in turn, is readily available from 2-methylfuran by means of a selective deprotonation reaction by treatment with *n*-butyllithium [6]. We were curious to learn whether the same, very simple and straightforward synthetic procedure could be applied for the preparation of the parent system, the metallocene bis[2-(2-furyl)indenyl]$ZrCl_2$ (**6**). Our results, which are described below in this paper, have revealed that the remaining furyl-5-hydrogen atom does not adversely interfere with the necessary strongly basic reaction conditions during the synthesis and subsequent transformations of the system **6**, and that **6** can easily be activated by treatment with methylalumoxane [7] to give an active metallocene Ziegler-Natta catalyst [8].



Scheme 1.

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* Corresponding author. Tel.: +49-251-8333221; fax: +49-251-8336503.

E-mail address: erker@uni-muenster.de (G. Erker).

[1] X-ray crystal structure analysis.

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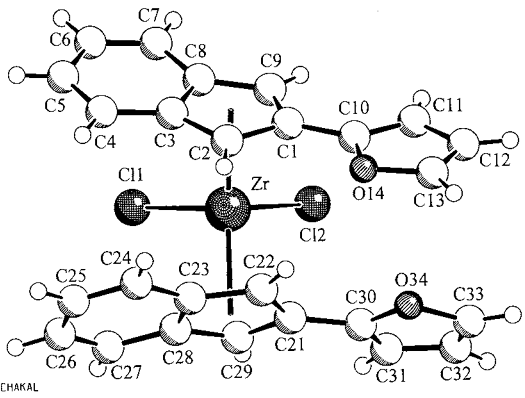

Fig. 1. Molecular structure of complex **6** in the crystal. Selected bond lengths (Å) and angles (°): Zr–Cl1 2.408(1), Zr–Cl2 2.430(1), C1–C2 1.416(6), C21–C22 1.416(5), C1–C9 1.411(6), C21–C29 1.397(5), C1–C10 1.428(6), C21–C30 1.449(5), C2–C3 1.425(6), C22–C23 1.431(5), C3–C4 1.427(6), C23–C24 1.426(5), C3–C8 1.438(6), C23–C28 1.423(5), C4–C5 1.346(6), C24–C25 1.355(6), C5–C6 1.420(7), C25–C26 1.409(6), C6–C7 1.344(6), C26–C27 1.349(6), C7–C8 1.410(6), C27–C28 1.431(5), C8–C9 1.418(6), C28–C29 1.424(5), C10–C11 1.344(6), C30–C31 1.323(5), C10–O14 1.370(5), C30–O34 1.360(5), C11–C12 1.411(7), C31–C32 1.374(7), C12–C13 1.322(7), C32–C33 1.333(8), C13–O14 1.378(6), C33–O34 1.409(6); Cl1–Zr–Cl2 95.91(4), C2–C1–C9 107.9(4), C22–C21–C29 108.1(3), C2–C1–C10 127.3(4), C22–C21–C30 125.5(4), C9–C1–C10 124.8(4), C29–C21–C30 126.4(4), C1–C2–C3 108.5(4), C21–C22–C23 107.8(3), C2–C3–C4 134.0(4), C22–C23–C24 133.4(4), C2–C3–C8 107.1(4), C22–C23–C28 107.5(3), C4–C3–C8 118.8(4), C24–C23–C28 119.0(4), C3–C4–C5 119.2(4), C23–C24–C25 119.3(4), C4–C5–C6 121.2(4), C24–C25–C26 121.6(4), C5–C6–C7 121.8(4), C25–C26–C27 121.4(4), C6–C7–C8 119.1(4), C26–C27–C28 119.1(4), C7–C8–C3 119.7(4), C27–C28–C23 119.5(3), C7–C8–C9 132.7(4), C27–C28–C29 133.2(3), C3–C8–C9 107.5(3), C23–C28–C29 107.3(3), C8–C9–C1 108.7(4), C28–C29–C21 108.8(3), C1–C10–C11 131.8(4), C21–C30–C31 125.0(9), C1–C10–O14 118.1(4), C21–C30–O34 122.6(4), C11–C10–O14 110.1(4), C31–C30–O34 112.4(4), C10–C11–C12 106.4(4), C30–C31–C32 106.2(4), C11–C12–C13 107.6(4), C31–C32–C33 109.1(4), C12–C13–O14 110.1(4), C32–C33–O34 108.5(5), C13–O14–C10 105.7(4), C33–O34–C30 103.8(4). For additional structural parameters see the text.

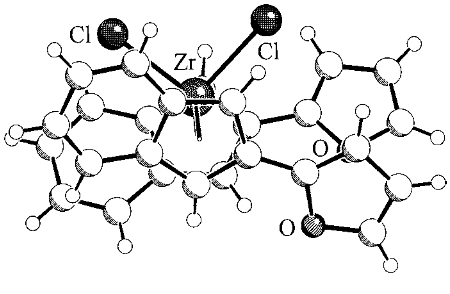

Fig. 2. Overhead view of the *meso*-like metallocene conformation of complex **6**.

2. Results and discussion

Furan was mono-deprotonated by treatment with *n*-butyllithium in ether at room temperature during 12 h to generate the reagent 2-lithiofuran (**2**). Addition of this furyl-anion equivalent to 2-indanone followed by hydrolytic workup proceeded directly with dehydration to give 2-(2-furyl)indene (**4**) that was isolated in 56% yield (see Scheme 1). Compound **4** was then treated with one molar equivalent of *n*-butyllithium in diethyl ether at 0°C. The $\mathrm{p}K_a$ difference between the indenyl C1–H and the remaining furyl C5–H is sufficiently large to allow for the selective formation of the 2-(2-furyl)indenyllithium system (**5**). It was obtained as an off-white solid and characterized by ^{1}H NMR spectroscopy in benzene-d_6–THF-d_8 (10:1) solution (furyl 5-H: $\delta = 7.22$, indenyl 1-H/3-H: $\delta = 6.73$). The 2-(2-furyl)indenyllithium reagent **6** was then reacted with zirconium tetrachloride in a 2:1 molar ratio in toluene. Crystallization from toluene (− 20°C) gave bis[2-(2-furyl)indenyl]zirconium dichloride (**6**) in 50% yield as pale yellow solid. Complex **6** was characterized by an X-ray crystal structure analysis (see below). The $[\mathrm{Zr}]\mathrm{Cl}_2$ unit in complex **6** can be converted to the $[\mathrm{Zr}](\mathrm{CH}_3)_2$ moiety by treatment with methyllithium. Again, the presence of an unprotected C–H bond at the furyl 5-position did not adversely influence the course of the reaction with the strongly basical alkyllithium reagent. Bis[2-(2-furyl)indenyl]zirconium dimethyl (**7**) was obtained by treatment of **6** with $\mathrm{CH_3Li}$ in ether at 0°C and isolated in a yield of 56%.

The X-ray crystal structure analysis of **6** (Fig. 1) shows a typical pseudotetrahedral coordination environment around zirconium with substituted η^5-indenyl ligands and two σ-Cl groups. The Zr–Cl bond lengths amount to 2.408(1) (Zr–Cl1) and 2.430(1) Å (Zr–Cl2). The Cl1–Zr–Cl2 angle is 95.91(4)°, and the Cp(centroid)–Zr–Cp(centroid) angle is found at 130.3°. The bond lengths between zirconium and the carbon atoms of the indenyl five-membered rings are in a range between 2.474(3) and 2.633(3) Å (C2, C1, C9, C3, C8) and 2.468(4) and 2.635(3) Å (C22, C21, C23, C29, C28), respectively. The corresponding C–C bond lengths inside the five-membered rings are found within a narrow range (1.397(5)–1.438(6) Å). The anellated indenyl six-membered rings exhibit a pronounced bond alternation with short C4–C5 (1.346(6) Å) and C6–C7 (1.344(6) Å) [C24–C25: 1.355(6), C26–C27: 1.349(6) Å] bonds connected by a long C5–C6 (1.420(7) Å) linkage [C25–C26: 1.409(6) Å].

Complex **6** in the crystal is found in a bent metallocene conformation (Fig. 2) where both indenyl six-membered rings are oriented laterally, and they are pointed toward the same side of the bent metallocene wedge [9]. The molecule has no plane of symmetry, but the rotation of the two η^5-indenyl ligands is not far from a *meso*-metallocene arrangement. The conformation found in the crystal is *meso*-like, similarly as it was found for the two bis[2-(5-methyl-2-furyl)indenyl]ZrCl_2

(**8**) and –HfCl$_2$ (**9**) examples that we had described earlier (see Chart I) [3]. The 2-furyl substituents in complex **6** are arranged coplanar with their attached indenyl ligands (connecting bonds C1–C10: 1.428(6) Å, C21–C30: 1.449(5) Å, dihedral angles C2–C1–C10–C11: − 178.1(4)°, C22–C21–C30–C31: − 178.4(4)°, see Fig. 1). We have not located the position of the oxygen atoms inside the unsubstituted 2-furyl substituents beyond doubt, but it appears reasonable to assume that they are oriented toward the narrow back side of the bent metallocene, just as it was found in the related 5-methyl-2-furyl-substituted complexes **8** and **9** [3]. The obtained bond lengths inside the furyl rings of **6** support this interpretation [C10–C11: 1.344(6) Å/C30–C31: 1.323(5) Å, C10–O14: 1.370(5) Å/C30–O34: 1.360(5) Å, C11–C12: 1.411(7) Å/C31–C32: 1.374(7) Å, C12–C13: 1.322(7) Å/C32–C33: 1.333(8) Å, C13–O14: 1.378(6) Å/C33–O34: 1.409(6) Å].

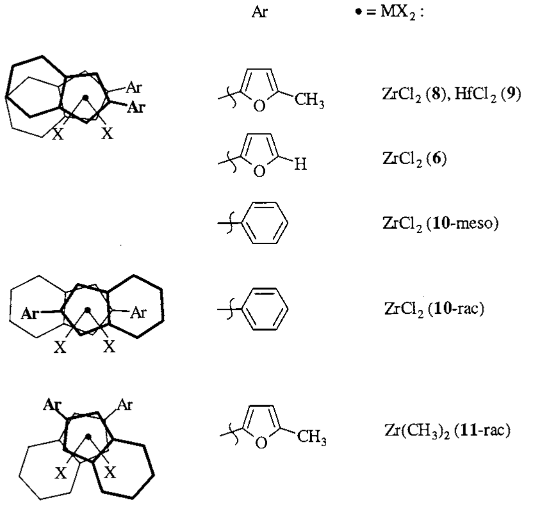

Chart I. Projections of the structurally observed metallocene conformations of bis[2-aryl-/2-hetaryl-indenyl]MX$_2$ (X = Cl, CH$_3$) complexes.

The new complex **6** was used in scouting propene polymerization reactions. Activation was carried out by treatment with a large excess of methylalumoxane (Al:Zr ratio $\geq$ 1500) in toluene. Polymerization reactions were carried out at three different temperatures, namely 20, 0, and − 20°C. Each experiment was performed twice under comparable reaction conditions in order to ensure reproducibility of the observations made. For the purpose of comparison a similar set of propene polymerization reactions was carried out employing Waymouth's bis(2-phenylindenyl)ZrCl$_2$–MAO catalyst (**10**–MAO) [1,2] under comparable conditions (to yield the polymer samples PP7 to PP12).

A comparison of the results (see Tables 1 and 2) has revealed that both the **6**–MAO and **10**–MAO catalysts show similar propene polymerization activities in the chosen temperature range. The furyl-substituted catalyst seems to be slightly more active at 0°C, but these differences are marginal. The ^{13}C-NMR methyl pentade analysis [10] has shown that the furyl system **6**–MAO causes slightly larger isotatic mmmm pentades (ca. 15% intensity) as compared to the **10**–MAO system, but again, these differences are not pronounced. The polypropylene samples obtained under these conditions at the **6**–MAO catalyst show elastomeric properties. These were characterized by the respective stress–strain curves (see Table 3 and Fig. 3). A comparison of the characteristic values between the polypropylenes obtained at the **6**–MAO and **10**–MAO catalysts shows that the recovery of the polypropylenes derived from the furyl-substituted catalyst system appears to be slightly better in the lower elongation experiments. However, the **6**–MAO-derived elastomers seem to yield more readily to the applied strain than the **10**–MAO-derived samples. Previous comparisons have shown slightly closer similarities between elastomers obtained from the **8**–MAO and **10**–MAO catalysts [3]. This

Table 1
Propene polymerization reactions with the **6**–MAO catalyst [a]

T_{react}	20°C		0°C		−20°C	
Polymer	PP1	PP2	PP3	PP4	PP5	PP6
Time (h)	2	2	2	2	2	2
μmol [Zr]	23	21	21	21	23	21
mmol MAO	34.5	34.5	34.5	34.5	34.5	34.5
Al/Zr	1500	1640	1640	1640	1500	1640
g PP obtained	16	14	22	19	38	2
Act [b]	178	165	255	219	426	27 [c]
%mmmm	13		15		15	

[a] Carried out in toluene at a constant propene pressure of 2 bar.

[b] In g polymer/mmol [Zr] h bar.

[c] Propene pressure decreased during the polymerization reaction.

Table 2
Propene polymerization reactions with the **10**–MAO catalyst for comparison [a]

T_{react}	20°C		0°C		−20°C	
Polymer	PP7	PP8	PP9	PP10	PP11	PP12
Time (h)	2.25	2.00	3.00	2.00	2.00	2.00
μmol [Zr]	22	9	22	7	16	6
mmol MAO	34.5	34.5	34.5	34.5	34.5	34.5
Al/Zr	1570	3830	1570	4920	2150	5750
g PP	16	5.5	24	4.8	28	5
Act	161	150	181	163	423	227
%mmmm	9		12		13	

[a] Under conditions comparable to those indicated in Table 1.

Table 3
Selected values from the stress–strain curves of the elastomeric polypropylenes PP5 and PP11 obtained at the **6**–MAO and **10**–MAO catalysts at −20°C

Elongation in %	**6**–MAO (PP5)	Stress (MPa)	**10**–MAO (PP11)	Stress (MPa)
100 [a]	9 [b]	0.78	21	0.72
200	21	0.89	49	0.74
300	39	0.86	91	0.66
400	65	0.78	147	0.59
500	110	0.69	220	0.56
600	165	0.59	299	0.54
700	246	0.48	400	0.54
800	353	0.37	493	0.55

[a] 100% denotes an elongation to double the original length.

[b] The recovery value of 9% denotes a total length of 109% of the initial value after recovery from the first elongation in the cycle.

could indicate that the alkyl substituents at the furyl- (or thienyl-) 5-positions might play an important role in controlling the specific properties of such catalyst types in detail [11]. Experiments to elucidate the influence of alkyl side chains attached at the hetaryl-substituents on the catalyst performance are currently carried out in our laboratory.

3. Experimental

Reactions were carried out under an argon atmosphere using Schlenk-type glassware or in a glovebox. Solvents (including the deuterated solvents used for NMR spectroscopy) were dried and distilled under argon prior to use. NMR spectra were recorded on a Bruker AC 200 P NMR spectrometer (^{1}H: 200 MHz, ^{13}C: 50 MHz) at 300 K or a Varian Unity Plus NMR spectrometer (^{1}H: 600 MHz, ^{13}C: 150 MHz) at 298 K. Most NMR assignments were secured by 2D NMR experiments (GCOSY, GHSQC, GHMBC) or NOE-difference spectra [12].

3.1. Preparation of 2-(2-furyl)indene (**4**)

A stirred solution of furan (0.94 ml, 45.5 mmol) in Et_2O (150 ml) was reacted with *n*-butyllithium (28.4 ml,

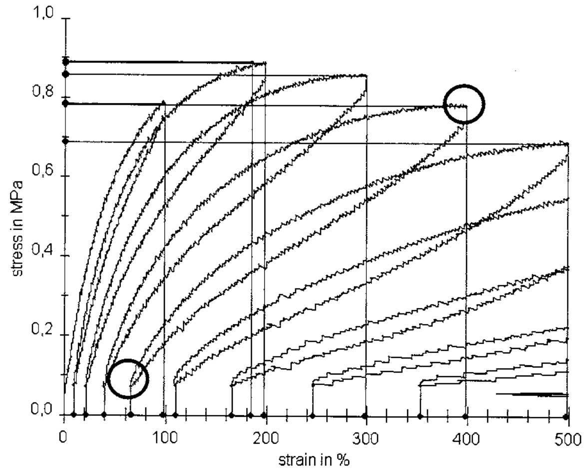

Fig. 3. Stress–strain curves obtained by elongation experiments with an elastomeric polypropylene sample obtained at the **6**–MAO catalyst at −20°C.

45.5 mmol, 1.6 M in hexane). After stirring at room temperature (r.t.) for 12 h, the dark solution was cooled to −60°C and solid 2-indanone (6.00 g, 45.5 mmol) was added in several portions over a period of 4 h. The resulting reaction mixture was stirred for another 2 h between −60 and −40°C before warming up to −25°C. Hydrolysis with 75 ml of 2 N HCl, separation of the layers, drying over $MgSO_4$ and removal of the solvent in vacuo yielded a dark red oil. The crude product was purified by column chromatography (silica gel) with isohexane–Et_2O 4:1 as eluent. Compound **4**, 4.63 g (56%), was obtained as a white solid. R_f (isohexane–Et_2O, 1:1) = 0.6, m.p. 99°C. ^1H-NMR (CH_2Cl_2-d_2): $\delta = 7.46$ (dd, $^3J = 1.8$, $^4J = 0.6$ Hz, 1H, furyl-5-H), 7.44 (dd, $^3J = 7.2$, $^4J = 1.2$ Hz, 1H, 7-H), 7.38 (d, $^3J = 7.2$ Hz, 1H, 4-H), 7.25 (dt, $^3J = 7.2$, $^4J = 0.6$ Hz, 1H, 5-H), 7.16 (dt, $^3J = 7.2$, $^4J = 1.2$ Hz, 1H, 6-H), 7.06 (s, 1H, 3-H), 6.51 (d, $^3J = 3.6$ Hz, 1H, furyl-3-H), 6.47 (dd, $^3J = 3.6$, $^3J = 1.8$ Hz, 1H, furyl-4-H), 3.73 (s, 2H, 1-H). ^{13}C-NMR (CH_2Cl_2-d_2): $\delta = 152.5$ (C, furyl-C-2), 145.4 (C, C-7a), 142.8 (C, C-3a), 142.6 (CH, furyl-C-5), 136.7 (C, C-2), 127.0 (CH, C-5), 125.4 (CH, C-3), 125.1 (CH, C-6), 124.0 (CH, C-7), 121.3 (CH, C-4), 112.0 (CH, furyl-C-4), 107.3 (CH, furyl-C-3), 38.6 (CH_2, C-1). IR (KBr): $\tilde{\nu} = 3134$ (w), 3057 (m), 3039 (w), 1600 (m), 1538 (m), 1451 (vs), 1386 (s), 1220 (s), 993 (vs), 915 (m), 868 (m), 854 (s), 807 (vs), 738 (vs) cm^{-1}. Anal. Calc. for $C_{13}H_{10}O$ (182.2): C, 85.69; H, 5.53. Found: C, 85.34; H, 5.89%.

*3.2. Preparation of 2-(2-furyl)indenyllithium (**5**)*

A solution of **4** (1.50 g, 8.28 mmol) in Et_2O (80 ml) was treated with *n*-butyllithium (5.18 ml, 8.29 mmol, 1.60 M in *n*-hexane) at 0°C. After 3 h the solvent was removed in vacuo and pentane (50 ml) was added. After stirring over night the suspension was filtered and 1.46 g (94%) of the product **5** was obtained. ^1H-NMR (benzene-d_6–THF-d_8): $\delta = 7.75$ (m, 2H, 4-H, 7-H), 7.22 (dd, $^3J = 1.8$, $^4J = 0.8$ Hz, 1H, furyl-5-H), 6.99 (m, 2H, 5-H, 6-H), 6.73 (s, 2H, 1-H, 3-H), 6.43 (dd, $^3J = 3.2$, $^4J = 0.8$ Hz, 1H, furyl-3-H), 6.31 (dd, $^3J = 3.2$, $^3J = 1.8$ Hz, 1H, furyl-4-H).

*3.3. Preparation of dichloro-bis[2-(2-furyl)indenyl]zirconium (**6**)*

A suspension of **5** (0.60 g, 3.20 mmol) in toluene was cooled to −78°C and solid zirconium tetrachloride (0.37 g, 1.60 mmol) was added. The reaction mixture was allowed to warm up to r.t. over night and then filtered. Crystallization from toluene at −20°C yielded 0.42 g (50%) of **6** as a yellow solid, m.p. 236°C. ^1H-NMR (CH_2Cl_2-d_2): $\delta = 7.60$ (dd, $^3J = 1.8$, $^4J = 0.6$ Hz, 2H, furyl-5-H), 7.32 (m, 4H, 4-H, 7-H), 7.14 (m, 4H, 5-H, 6-H), 6.62 (s, 4H, 1-H, 3-H), 6.58 (dd, $^3J = 3.0$, $^4J = 0.6$ Hz, 2H, furyl-3-H), 6.57 (dd, $^3J = 3.0$, $^3J = 1.8$ Hz, 2H, furyl-4-H). ^{13}C-NMR (CH_2Cl_2-d_2): $\delta = 148.9$ (C, furyl-C-2), 143.4 (CH, furyl-C-5), 126.9 (CH, C-5, C-6), 126.8 (C, C-3a, C-7a), 125.0 (CH, C-4, C-7), 124.8 (C, C-2), 112.4 (CH, furyl-C-4), 109.5 (CH, furyl-C-3), 101.3 (CH, C-1, C-3). IR (KBr): $\tilde{\nu} = 3117$ (w), 3095 (m), 1609 (w), 1598 (m), 1503 (s), 1432 (w), 1360 (s), 1218 (m), 1207 (s), 1011 (vs), 941 (s), 848 (vs), 836 (vs), 741 (vs) cm^{-1}. Anal. Calc. for $C_{26}H_{18}Cl_2O_2Zr$ (524.6): C, 59.53; H, 3.46. Found: C, 60.97; H, 4.14%.

*3.3.1. X-ray crystal structure analysis of **6***

Formula $C_{26}H_{18}O_2Cl_2Zr$, $M = 524.52$, yellow crystal $0.25 \times 0.15 \times 0.05$ mm, $a = 8.591(1)$, $b = 15.433(1)$, $c = 16.112(1)$ Å, $V = 2136.2(3)$ Å^3, $\rho_{calc} = 1.631$ g cm^{-3}, $\mu = 7.87$ cm^{-1}, empirical absorption correction via SORTAV ($0.828 \leq T \leq 0.962$), $Z = 4$, orthorhombic, space group $P2_12_12_1$ (no. 19), $\lambda = 0.71073$ Å, $T = 198$ K, ω and φ scans, 15 278 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.65$ Å^{-1}, 4850 independent ($R_{int} = 0.058$) and 4173 observed reflections [$I \geq 2\sigma(I)$], 280 refined parameters, $R = 0.042$, $wR^2 = 0.077$, max. residual electron density 0.77 (−0.39) e Å^{-3}, Flack parameter −0.05(5), the positions of the oxygen atoms in the furan rings could not be assigned unambiguously, hydrogen atoms calculated and refined riding.

Data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT [13], data reduction DENZO-SMN [14], absorption correction SORTAV [15], structure solution SHELXS-97 [16], structure refinement SHELXL-97 [17], graphics SCHAKAL [18].

*3.4. Preparation of dimethyl-bis[2-(2-furyl)indenyl]zirconium (**7**)*

Methyllithium (1.40 ml, 2.24 mmol, 1.60 M in Et_2O) was added to a suspension of **6** (0.59 g, 1.12 mmol) in 20 ml of Et_2O at 0°C. The reaction mixture was kept for 1 h at this temperature and then warmed up to r.t. After stirring for an additional 2 h, the solvent was removed in vacuo and 20 ml of pentane was added. Filtration and crystallization at −20°C yielded 0.30 g (56%) of **7** as an off-white powder, m.p. 157°C. ^1H-NMR (CH_2Cl_2-d_2): $\delta = 7.57$ (dd, $^3J = 1.8$, $^4J = 0.6$ Hz, 2H, furyl-5-H), 7.10 (m, 4H, 4-H, 7-H), 7.03 (m, 4H, 5-H, 6-H), 6.56 (dd, $^3J = 3.6$, $^3J = 1.8$ Hz, 2H, furyl-4-H), 6.48 (dd, $^3J = 3.6$, $^4J = 0.6$ Hz, 2H, furyl-3-H), 6.25 (s, 4H, 1-H, 3-H), −1.32 (s, 6H, Zr–CH_3). ^{13}C-NMR (CH_2Cl_2-d_2): $\delta = 150.0$ (C, furyl-C-2), 142.5 (CH, furyl-C-5), 124.9 (CH, C-5, C-6), 124.7 (CH, C-4, C-7), 124.4 (C, C-3a, C-7a), 120.3 (C, C-2), 112.2 (CH, furyl-C-4), 107.1 (CH, furyl-C-3), 96.4 (CH, C-1, C-3), 36.1 (CH_3, Zr–CH_3). IR (KBr): $\tilde{\nu} = 3115$ (w), 2940 (w), 2922 (w), 2863 (w), 1610 (w), 1505 (m), 1430 (s), 1357 (vs), 1298 (s), 1218 (s), 1110 (s), 1009 (vs), 883 (s), 837 (vs), 806 (vs), 741 (vs), 733 (vs) cm^{-1}. HRMS: $C_{27}H_{21}O_2Zr$ ($M^+ - CH_3$), HRMS Calc.: m/z 467.0589. Found: 467.0602.

3.5. Polymerization reactions

All polymerizations were carried out in a 1 l glass autoclave charged with 150 ml toluene and 20 ml methylalumoxane (10.5 weight% solution in toluene). At the respective temperature, the stirred (600 rpm) mixture was saturated for 30 min with propene at a pressure of 2 bar. The catalyst precursors were injected and the polymerizations were carried out for 2 h at a permanent propene pressure of 2 bar. The reaction mixture was hydrolyzed cautiously with a 1:1 mixture of methanol and 2 N HCl and treated additionally with HCl (6 N, 100 ml). The organic layer was separated, the toluene evaporated and the residue dried in vacuo over night. The elastomeric measurements were carried out as described previously [3].

The test samples were prepared according to DIN 53502 and DIN 53504. The elongation measurement were limited up to 15 iterations (for details see Table 3).

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 149191. 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 or www: http://www.ccdc.cam.ac.uk).

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