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Preparation and structural features of 1-(2-pyridyl)- and 1-(2-furyl)indenyl-zirconium complexes

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

Abstract

Addition of 2-lithiopyridine to 1-indanone followed by aqueous workup gave 1-(2-pyridyl)indanol (**3**); subsequent H^+-catalyzed H_2O-elimination gave 3-(2-pyridyl)indene **4**. Deprotonation with *n*-butyllithium yielded the corresponding anionic reagent **5**. Treatment of **4** with $Zr(NR_2)_4$ ($R = CH_3$ or C_2H_5) yielded the half-sandwich complexes η^5-[1-(2-pyridyl)indenyl]$Zr(NR_2)_3$ (**7a**, **7b**). Reaction of **5** with $CpZrCl_3$ led to the formation of η^5-[1-(2-pyridyl)indenyl]$CpZrCl_2$ (**8**). The compounds **3**, **4**, and **8** were characterized by X-ray diffraction. Analogous treatment of 1-indanone with 2-lithio-5-methylfuran, followed by H_2O-elimination and deprotonation gave the reagent [1-(5-methyl-2-furyl)indenyl]Li·(OEt_2) **13**. Its reaction with $ZrCl_4$ in a 2:1 ratio in toluene yielded a 60:40 mixture of *rac*- and *meso*-bis[η^5-1-(5-methyl-2-furyl)indenyl]$ZrCl_2$ (*rac*-**14** and *meso*-**14**). Crystallization gave pure *rac*-**14**, which was characterized by an X-ray crystal structure analysis. Treatment of *rac*-**14** with excess methylalumoxane (MAO) in toluene (Al:Zr ≈ 2000) gave an active homogeneous Ziegler catalyst for atactic propene polymerization, whereas the **8**–MAO system was inactive. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Homogeneous Ziegler–Natta catalysts; Indenyl lithium compounds; Polypropylene; Substituted zirconocenes

1. Introduction

Alkyl and aryl substituents may very specifically alter the catalytic behavior of Group 4 metallocene Ziegler–Natta catalysts [1]. Substituents that contain oxygen or nitrogen heteroatoms have served to introduce novel features into Group 4 metallocene chemistry [2,3], sometimes leading to the observation of unusual new reaction pathways. It was uncertain which role hetaryl substituents attached at the metallocene Cp- or indenyl-rings might play, because previously such examples were scarce [4,5]. They may just serve as specific examples of aryl substituents that introduce increased (e.g. furyl, thienyl) or decreased (e.g. pyridyl) electron density at the ligand–metal system. Alternatively, a direct participation of the heteroatom as an inter- or intramolecular donor-ligand functionality may be envisaged. In order to learn more about the structural role of 2-furyl or 2-pyridyl substituents in Group 4 bent metallocene chemistry we have prepared selected 2-hetaryl-substituted indenyl ligand systems and their Group 4 metal complexes, and investigated the structural properties of the respective hetaryl-substituted bent metallocene complexes.

2. Results and discussion

2.1. [1-(2-Pyridyl)indenyl] zirconium complexes

The construction of the indenyl ligand system, bearing a 2-pyridyl substituent at the 1-position, follows a literature pathway [6] starting from 1-indanone (**1**). Addition of 2-lithiopyridine (**2**), generated from 2-bromopyridine by treatment with *n*-butyllithium in ether, to 1-indanone, followed by aqueous workup gave 1-(2-pyridyl)indanol (**3**) (Scheme 1, Fig. 1), which was isolated in ca. 70% yield after recrystallization and

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[1] X-ray crystal structure analyses.

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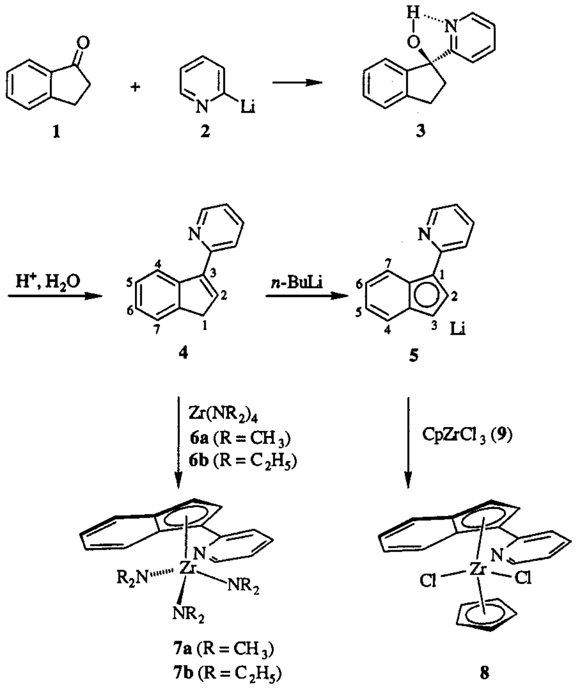
characterized by X-ray diffraction (for details see Sections 4 and 5). In the crystal the 2-pyridyl substituent is rotated markedly from the indane plane (dihedral angles C2–C1–C2′–N: 115.5(1)°; C7a–C1–C2′–C3′: 51.3(2)°). This is due to an internal hydrogen bridge between the indanol O–H group and the basic pyridyl nitrogen atom (O8···N separation: 2.584(1) Å, dihedral angle O8–C1–C2′–N: − 7.8(1)°; H8 observed, O8–H8 0.95(2) Å, angle O8–H8–N: 125(2)°, H8–N 1.92(2) Å), which results in a heterocyclic spiro-structure of compound **3**. The internal hydrogen bridge is probably retained in solution (^{1}H-NMR in $CDCl_3$: δ 5.94 (OH), IR (KBr): $\tilde{\nu} = 3361$ cm^{-1}).



Scheme 1. Preparation of the [η^5-1-(2-pyridyl)indenyl]zirconium complexes.

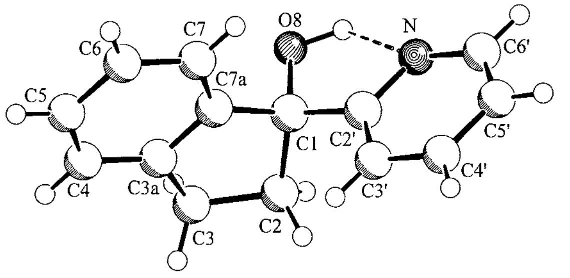


Fig. 1. A view of the structure of **3** in the crystal featuring the internal hydrogen bridge.

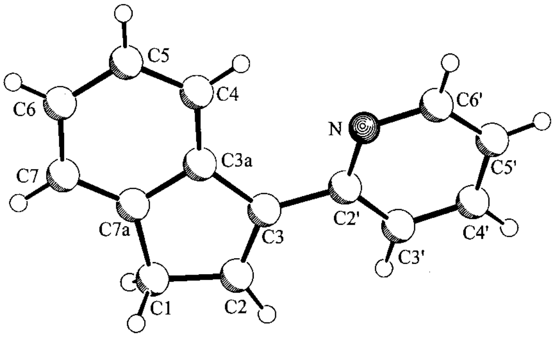


Fig. 2. Molecular structure of **4**.

Dehydration of **3** was achieved by treatment with sulfuric acid to yield 1-(2-pyridyl)indene (**4**, ca. 80% isolated). The NMR analysis showed a pronounced shift of the indene-4-H signal to a high δ value of 8.71 (5-H: δ 7.36; 6-H: δ 7.20; 7-H: δ 7.33). The X-ray crystal structure analysis (see Fig. 2) shows a conformational arrangement of **4** in the crystal that brings the hydrogen atom H-4 at the annelated arene ring rather close to the pyridyl nitrogen atom (C4···N separation 3.038(2) Å, H4···N: 2.48 Å, angle C4–H4–N 118°, the dihedral angle C3a–C3–C2′–N amounts to 14.4(2)°; for details see Sections 4 and 5).

Deprotonation of **4** was carried out by treatment with *n*-butyllithium in ether to yield **5** (ca. 70% isolated). The ^{1}H-NMR spectrum of **5** (in benzene-d_6/THF-d_8 10:1) shows an AX pair of signals of equal intensity at δ 7.26 and 6.72 ($^3J = 4.2$ Hz) of the indenyl 2-H and 3-H protons. The indene 7-H ^{1}H-NMR resonance of **5** is observed at δ 7.82 in the 'normal' region, in contrast to the corresponding 4-H value of δ 8.71 (see above) of its neutral precursor **4**. This probably indicates that the pyridyl nitrogen atom of **5** does not affect the C7–H7 bond any more. The strong electronic or even coordinative participation of the pyridyl nitrogen atom in the structural stabilization of the lithioindene system **5** is supported by its markedly deshielded ^{15}N-NMR resonance (**5**: δ − 122.5) relative to **4** (^{15}N: δ − 69.5) [3a,b,7].

Both the neutral pyridylindene **4** and the anionic pyridylindenyl system **5** were employed as precursors for the preparation of zirconium complexes. The neutral compound **4** was treated with one molar equivalent of $Zr(NMe_2)_4$ (**6a**) in toluene at ambient temperature [8]. During several hours deprotonation of the ligand, with formation of $HNMe_2$, the half-sandwich complex [η^5-1-(2-pyridyl)indenyl]$Zr(NMe_2)_3$ (**7a**) was obtained in almost quantitative yield (see Scheme 1). The ^{1}H-NMR spectrum of **7a** shows a singlet of relative intensity 18 for the three symmetry-equivalent dimethylamido ligands at δ 2.63 (in toluene-d_8). In contrast to the [1-(2-pyridyl)indenyl]Li system **5**, complex **7a** exhibits two ^{1}H-NMR resonances at high δ values, namely the pyridyl 6-H resonance at typical δ 8.46 *and* again the indene 7-H signal at δ 8.83. The latter value probably indicates a conformational arrangement of the pyridylindenyl moiety of **7a** similar to that observed for **4** (see above and Fig. 2), where the pyridyl nitrogen atom is located towards the respective

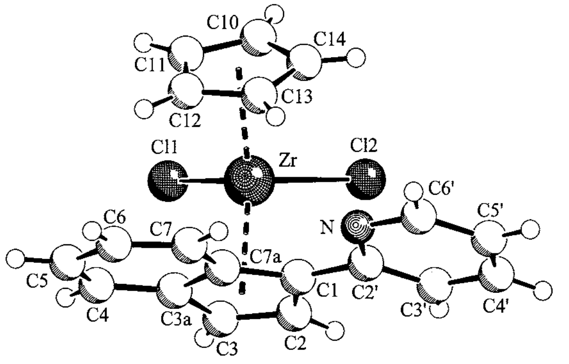
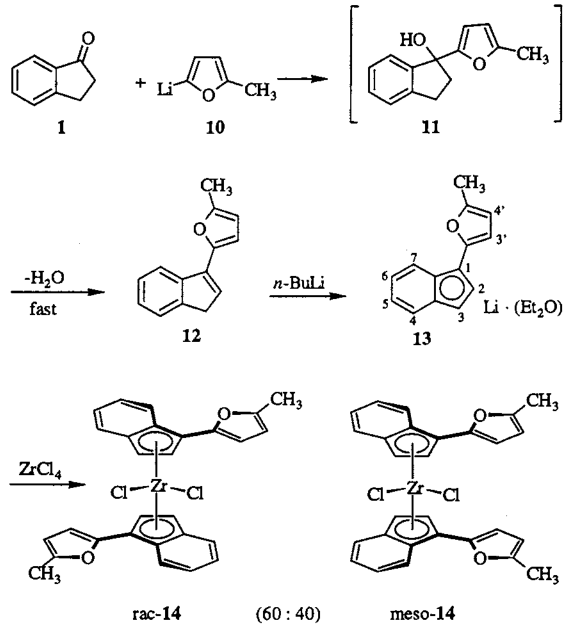


Fig. 3. Molecular structure of complex **8**. Selected bond lengths (Å) and angles (°): Zr–Cl1, 2.441(1); Zr–Cl2, 2.426(1); Zr–C1, 2.504(3); Zr–C2, 2.507(3); Zr–C3, 2.508(3); Zr–C3a, 2.558(3); Zr–C7a, 2.591(3); Zr–C10, 2.528(3); Zr–C11, 2.521(3); Zr–C12, 2.461(3); Zr–C13, 2.461(3); Zr–C14, 2.503(3); C1–C2, 1.434(4); C1–C7a, 1.435(5); C2–C3, 1.388(6); C3–C3a, 1.432(5); C3a–C7a, 1.437(5); C1–C2′, 1.466(5); C3a–C4, 1.411(5); C4–C5, 1.363(5); C5–C6, 1.417(5); C6–C7, 1.360(5); C7–C7a, 1.429(4); C2′–N, 1.350(4); C2′–C3′, 1.384(5); C3′–C4′, 1.365(6); C4′–C5′, 1.378(6); C5′–C6′, 1.383(5); C6′–N, 1.327(5); Cl1–Zr–Cl2, 96.8(1); C1–C2–C3, 110.5(3); C2–C3–C3a, 107.9(3); C3–C3a–C7a, 107.1(3); C3a–C7a–C1, 108.7(3); C2–C1–C2′, 126.0(3); C7a–C1–C2′, 128.2(3); C1–C2′–N, 116.7(3); C1–C2′–C3′, 121.8(3); N–C2′–C3′, 121.5(4); C2′–N–C6′, 117.0(3).



Scheme 2. Preparation of the bis[η^5-1-(5-methyl-2-furyl)indenyl]ZrCl$_2$ complexes.

C4–H vector (see Scheme 1). The ^{15}N-NMR spectrum of **7a** is characterized by two typical resonances at δ -76.2 (pyridyl-N) and δ -232.4 (NMe$_2$). Treatment of **4** with Zr(NEt$_2$)$_4$ (**6b**) proceeded analogously and yielded the analogous complex **7b** (for details see Section 4).

The [1-(2-pyridyl)indenyl]Li reagent (**5**) was also used for the preparation of a pyridyl-substituted Group 4 bent metallocene complex. Although the reaction of **5** with the strongly Lewis acidic zirconium tetrachloride has not yielded sufficiently clean products so far, treatment of **5** with the weaker Lewis acid CpZrCl$_3$ [9] in a 1:1 ratio in benzene at room temperature gave the substituted η^5-indenyl/η^5-Cp bent metallocene dihalide **8** in a moderate yield of ca. 40%. The ^{1}H-NMR spectrum of **8** again shows the typical feature of the indene 7-H resonance occurring at a high δ value of δ 8.97, indicating a syn-conformational arrangement with the pyridyl nitrogen atom.

This was confirmed by the X-ray crystal structure analysis of **8** (single crystals were obtained from benzene; Fig. 3). The Zr–C(Cp) distances vary between 2.461(3) and 2.528(3) Å (average value: 2.495(3) Å). The average C(η^5-indenyl)–Zr bond lengths amount to 2.534(3) Å [with short Zr–C(1) to C(3) distances of ca. 2.507 Å and long Zr–C3a (2.558(3) Å) and Zr–C7a (2.591(3) Å) bonds]. The 2-pyridyl substituent is oriented almost coplanar with the indenyl ligand (dihedral angle C7a–C1–C2′–N: $-9.8(4)$°), and the pyridyl nitrogen atom is syn-oriented with the annelated indenyl six-membered ring, and is pointing toward the C(7)–H(7) bond.

We tried to use the pyridyl-substituted metallocene dichloride **8** as a precursor for the generation of an active homogeneous Ziegler-type catalyst. For this purpose, complex **8** was treated with a ca. 1000-fold excess of methylalumoxane (MAO) in toluene solution. Propene polymerization was tried at 0°C and at 20°C, but in neither case did we observe the formation of polypropylene.

2.2. [1-(2-Furyl)indenyl]zirconium complexes

Next we investigated whether 2-furyl substituents could analogously be introduced at the 1-position of indenyl ligands of zirconium complexes and studied if active homogeneous Ziegler catalyst systems could be obtained from these metallocene complexes. For this specific study we used the 5-methyl-2-furyl substituent.

Treatment of 2-methylfuran with *n*-butyllithium in ether generated the 2-lithio-5-methylfuran reagent (**10**), which was subsequently added to 1-indanone (**1**). Workup with aqueous HCl resulted in the formation of 1-(5-methyl-2-furyl)indene (**12**); this was formed directly by dehydration from the intermediate **11**, which was not stable under the applied reaction conditions. Deprotonation of **12** was achieved by treatment with *n*-butyllithium in ether. The [1-(5-methyl-2-furyl)indenyl]Li reagent **13** was obtained in >90% yield (Scheme 2). The solid material contained one equivalent of ether attached, as judged from solution ^{1}H-NMR spectra of representative samples.

Treatment of reagent **13** with ZrCl$_4$ in toluene resulted in the formation of bis[η^5-1-(5-methyl-2-

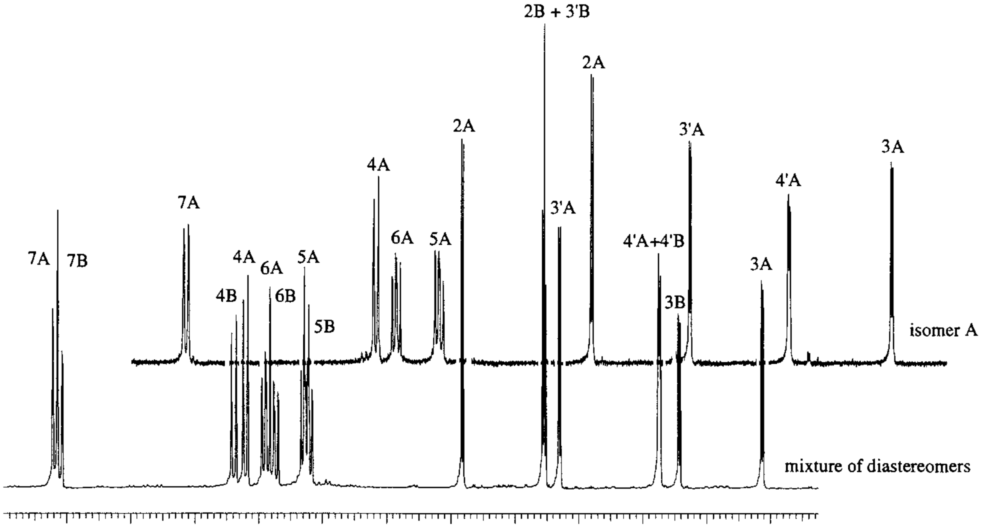


Fig. 4. ^{1}H-NMR spectra (600 MHz, 300 K, in CD_2Cl_2) of the *rac*-**14** (**A**)/*meso*-**14** (**B**) (60:40) mixture (bottom) obtained from the reaction of **13** with $ZrCl_4$ and of the pure *rac*-**14** diastereoisomer (**A**) (top), separated from the mixture by fractional crystallization.

furyl)indenyl]zirconium dichloride (**14**). A 60:40 mixture of the two diastereoisomers *rac*-**14** and *meso*-**14** was obtained (see Fig. 4). The product was recrystallized twice from toluene to give a small amount of the major diastereomer in a pure form. The mother liquor was enriched (ca. 90%) in the minor diastereomer. This mixture was treated with methyllithium to yield the corresponding furyl-substituted bis(indenyl)Zr$(CH_3)_3$ complexes. The ^{1}H-NMR spectrum showed the presence of two Zr–$C\underline{H}_3$ signals of equal intensity, indicating that the diastereomer remaining in the mother liquor was *meso*-**14** (for details see Section 4) [10]. The pure material obtained from the recrystallization process (see above) was thus identified as the *rac*-**14** isomer.

Single crystals of the complex *rac*-**14** were obtained from the *rac*-**14**/*meso*-**14** mixture (60:40) in dichloromethane–pentane at ambient temperature. The molecular structure of *rac*-**14** is C_2-symmetric in the crystal. The metallocene conformation observed features the annelated six-membered arene rings of the symmetry-equivalent η^5-indenyl units oriented toward the front sector of the bent metallocene wedge. They occupy the space above and below the respective Zr–Cl vectors in the chiral C_2-symmetric arrangement (see Fig. 5) [11]. The 2-furyl ring systems are oriented coplanar with their indenyl frameworks (dihedral angle C2–C1–C12–O11: 176.9(2)°). They are arranged toward the respective lateral sectors of the bent metallocene framework.

The oxygen atoms of the furyl rings are oriented toward the bent metallocene front side as in the pyridyl–indenyl ligand in **8** (see above and Fig. 3); the heteroatom of the hetaryl substituent in *rac*-**14** is in a syn-position with the arene C7–H vector with a C7–H···O separation of 3.055(4) Å (H7···O: 2.53 Å; C7–H7–O11: 115°).

The substituted indenyl rings in *rac*-**14** are η^5-coordinated to zirconium. The Zr–C3a (2.595(3) Å) and Zr–C7a (2.596(2) Å) linkages are longer than the remaining Zr–C(indenyl) bonds [Zr–C2 (2.484(3) Å), Zr–C3 (2.464(3) Å), Zr–C1 (2.535(2) Å)]. The averaged Zr–C(1)–(3)/(3a)/(7a) bond length in *rac*-**14** is 2.535(3) Å, which is identical to that in **8** (2.534(3) Å). The C–C bonds inside the five-membered indene carbocycle in *rac*-**14** are within a narrow range between 1.412(4) and 1.443(4) Å. There is a noticeable bond

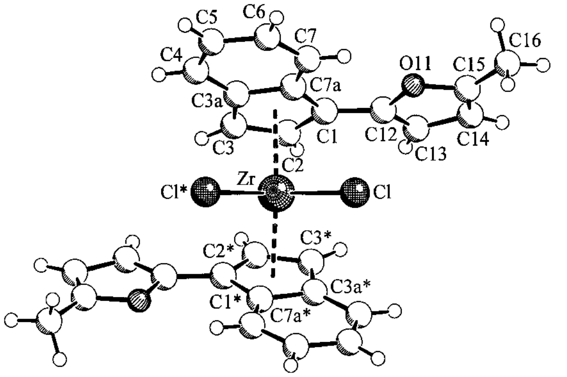


Fig. 5. Molecular structure of *rac*-**14**. Selected bond lengths (Å) and angles (°): Zr–Cl, 2.425(1); Zr–C1, 2.535(2); Zr–C2, 2.484(3); Zr–C3, 2.464(3); Zr–C3a, 2.595(3); Zr–C7a, 2.596(2); C1–C2, 1.412(4); C1–C7a, 1.443(4); C2–C3, 1.414(4); C3–C3a, 1.415(4); C3a–C7a, 1.438(3); C1–C12, 1.455(3); C3a–C4, 1.421(4); C4–C5, 1.354(5); C5–C6, 1.417(4); C6–C7, 1.355(4); C7–C7a, 1.416(4); C12–O11, 1.362(3); C12–C13, 1.348(4); C13–C14, 1.418(4); C14–C15, 1.338(6); C15–O11, 1.376(3); C15–C16, 1.479(5); Cl–Zr–Cl*, 98.49(4); C1–C2–C3, 109.2(2); C2–C3–C3a, 107.9(2); C3–C3a–C7a, 108.2(2); C3a–C7a–C1, 106.9(3); C2–C1–C12, 124.3(3); C7a–C1–C12, 128.0(3); C1–C12–O11, 117.3(2); C1–C12–C13, 132.9(3); O11–C12–C13, 109.8(2); C12–O11–C15, 106.8(2).

Table 1
Propene polymerization reactions carried out with the homogeneous *rac*-**14**–MAO Ziegler–Natta catalyst system[a]

Polymer	PP1	PP2	PP3	PP4	PP5	PP6
T_{react} (°C)	20	20	0	0	−20	−20
14 (μmol)	7.2	18.1	18.1	18.1	14.5	18.1
MAO (mmol)	34.5	34.5	34.5	34.5	34.5	34.5
Al/Zr	4700	1900	1900	1900	2400	1900
PP (g)	0.65	1.93	3.94	4.37	3.25	3.40
Activity[b] ($g\,h^{-1}\,bar^{-1}$)	22	26	54	60	45	47
mmmm[c] (%)	14	12	12	10	13	12

[a] 2 h reaction time, 2 bar propene pressure.

[b] PP/mmol(Zr).

[c] From ^{13}C-NMR pentade analysis.

alternation present at the far end of the indenyl six-membered ring system (C3a–C4: 1.421(4) Å, C4–C5: 1.354(5) Å, C5–C6: 1.417(4) Å, C6–C7: 1.355(4) Å, C7–C7a: 1.416(4) Å), which is a typical feature in η^5-indenyl metal complexes. The Zr–Cl bond length in *rac*-**14** is 2.425(1) Å, the Cl*–Zr–Cl angle amounts to 98.49(4)°, and the Cp(centroid)–Zr–Cp(centroid) angle is found to be 129.5°.

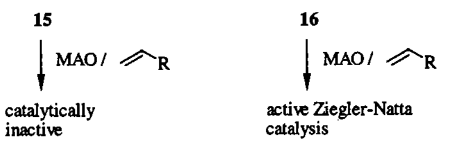
The pure *rac*-**14** diastereomer was used for the generation of an active homogeneous Ziegler–Natta catalyst, that was employed in a small series of scouting propene polymerization reactions. For this purpose samples of *rac*-**14** were activated by treatment with a ca. 2000 fold molar excess of MAO in toluene solution [12]. The *rac*-**14**–MAO system is an active propene polymerization catalyst. Polymerization reactions were carried out at −20, 0, and +20°C. Propene polymerization activities in the range of ca. 24 to 57 $g\,h^{-1}\,bar^{-1}$ of polypropylene per millimole of zirconium catalyst were obtained (for details see Table 1). The polymer samples obtained were all close to atactic as judged from the ^{13}C-NMR pentade analyses [13].

3. Conclusions

The structural features of the η^5-[1-(2-pyridyl)-indenyl]Zr and the η^5-[1-(5-methyl-2-furyl)indenyl]Zr moieties in the complexes **8** and *rac*-**14** are very similar. In the X-ray crystal structure analyses of these two complexes the averaged Zr–C(indenyl) bond lengths are identical. The conformational arrangements of the hetaryl–indenyl moieties are also comparable, both with regard to the relative positioning of their characteristic groups inside the bent metallocene sectors and the conformational orientation of the hetaryl substituent at the indenyl moiety. Nevertheless, the catalytic potential of the two systems **8** and *rac*-**14** is dramatically different: complex *rac*-**14** produces an active homogeneous Ziegler–Natta catalyst for polypropylene formation upon conventional activation with MAO, whereas the corresponding **8**–MAO system is catalytically inactive under the conditions tested.

It is likely that the basicity of the pyridyl nitrogen atom is responsible for the fundamental difference observed. We assume that the pyridyl nitrogen lone pair, whose influence has already been noticed in the ^{1}H-NMR spectra of 1-(2-pyridyl)indene and the ligands derived from it (see Section 2.1), is probably actively employed in coordinating the strongly Lewis acidic MAO activator and thereby may lead to a steric shielding of the Group 4 metal center in the activated complex. A related deactivation was indirectly indicated recently for the remotely related system **15** (see Scheme 3), which contains a rather nucleophilic iminoate nitrogen center. Complex **15** was also not active in α-olefin polymerization upon treatment with MAO, but gave an active Ziegler–Natta catalyst after the nitrogen lone pair was occupied by a suitable organometallic protecting group [14] (here introduced by hydroboration with $HB(C_6F_5)_2$ [15] to give **16**).

Our present study thus provides additional evidence that strongly nucleophilic centers at substituents may prohibit the formation of active Group 4 metallocene Ziegler–Natta catalysts. In contrast to the pyridyl system the furyl substituent does not show these adverse effects and may thus be used as a variant of an aryl substituent to alter and potentially control the features of active Group 4 metallocene catalyst systems by its steric and electronic influences [4].



Scheme 3. Activation of a metallocene catalyst by attachment of a protecting group.

4. 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, a Bruker AMX 400 NMR spectrometer at 300 K, or a Varian Unity Plus NMR spectrometer (^{1}H: 600 MHz; ^{13}C: 150 MHz) at 298 K. Assignments were usually secured by GCOSY, GHSQC, and GHMBC 2D NMR experiments [16]. Primed atom numbers are used for the pyridyl or furyl substituents. The complexes $Zr(NMe_2)_4$ **6a**, $Zr(NEt_2)_4$ **6b** [8d] and $CpZrCl_3$ **9** [9] were prepared according to literature procedures.

*4.1. Preparation of 1-(2-pyridyl)indanol (**3**)*

A solution of 12.8 g (81.0 mmol) of 2-bromopyridine in 50 ml of diethyl ether was added dropwise at − 60°C to 48.0 ml (81.0 mmol) of *n*-butyllithium (1.6 M in *n*-hexane). The resulting reaction mixture was stirred for 20 min at this temperature. Thereafter, 10.0 g (81.0 mmol) of 1-indanone dissolved in 70 ml of diethyl ether was added to the stirred solution within 20 min. After a reaction time of 2 h at − 40 to −60°C the dry-ice–isopropanol bath was removed and the reaction hydrolyzed with 50 ml of saturated ammonium chloride solution. Organic workup and recrystallization yielded 12.4 g (72%) of **3** as a light yellow crystalline solid, m.p. 80°C. ^{1}H-NMR (chloroform-d_1, 599.9 MHz): $\delta = 8.54$ (ddd, 1H, 6′-H, $^{3}J = 4.8$ Hz, $^{4}J = 1.2$ Hz, $^{5}J = 0.6$ Hz), 7.57 (ddd, 1H, 4′-H, $^{3}J = 7.8$ Hz, $^{3}J = 7.8$ Hz, $^{4}J = 1.2$ Hz), 7.31 (d, 1H, 7-H, $^{3}J = 7.2$ Hz), 7.26 (ddd, 1H, 6-H, $^{3}J = 7.8$ Hz, $^{3}J = 7.2$ Hz, $^{4}J = 1.2$ Hz), 7.16 (m, 2H, 5-H, 5′-H), 7.02 (dd, 1H, 4-H, $^{3}J = 8.4$ Hz, $^{4}J = 1.2$ Hz), 7.01 (dd, 1H, 3′-H, $^{3}J = 7.8$ Hz, $^{4}J = 1.2$ Hz), 5.94 (broad s, 1H, OH), 3.24, 3.03 (m, each 1H, 3-Ha, 3-Hb), 2.52 (m, 2H, 2-H) ppm. ^{13}C-NMR (chloroform-d_1, 150.8 MHz): $\delta = 164.2$ (C, C-2′), 147.6 (C, C-3a), 147.3 (CH, C-6′), 143.9 (C, C-7a), 137.1 (CH, C-4′), 128.5 (CH, C-6), 127.2 (CH, C-5), 125.0 (CH, C-7), 124.2 (CH, C-4), 122.3 (CH, C-5′), 120.4 (CH, C-3′), 84.4 (C, C-1), 43.0 (CH_2, C-2), 30.4 (CH_2, C-3) ppm. Anal. Found: C, 79.42; H, 6.27; N, 6.68. Calc. for $C_{14}H_{13}NO$ (211.3): C, 79.59; H, 6.20; N, 6.63%.

*4.1.1. X-ray crystal structure analysis of **3***

Formula $C_{14}H_{13}NO$, $M = 211.25$, light yellow crystal $0.50 \times 0.50 \times 0.20$ mm^3, $a = 9.307(1)$, $b = 9.419(1)$, $c = 12.974(1)$ Å, $\beta = 108.38(1)$°, $V = 1079.3(2)$ Å^3, $\rho_{calc} = 1.300$ g cm^{-3}, $\mu = 6.46$ cm^{-1}, empirical absorption correction via ψ scan data ($0.738 \le T \le 0.882$), $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 1.541\ 78$ Å, $T = 223$ K, ω–2θ scans, 2339 reflections collected ($+h$, $+k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 2203 independent ($R_{int} = 0.016$) and 2092 observed reflections [$I \ge 2\sigma(I)$], 150 refined parameters, $R = 0.040$, $wR^2 = 0.110$, max. residual electron density 0.27 (− 0.15) e$^-$ Å^{-3}, hydrogen at O8 from difference Fourier calculations, refined independently, all others calculated and refined as riding atoms.

*4.2. Preparation of 3-(2-pyridyl)indene (**4**)*

Following a modified literature procedure [6] a sample of 10.0 g (47.0 mmol) of **3** was treated at 0°C dropwise with 100 ml of sulfuric acid (85%). The dark red solution was stirred for 2 h at this temperature and then poured into 150 g of ice. The resulting reaction mixture was neutralized with solid sodium hydroxide and then washed with diethyl ether. After organic workup and recrystallization, 7.08 g (78%) of white solid **4** was obtained, m.p. 80°C. ^{1}H-NMR (benzene-d_6): $\delta = 8.71$ (d, 1H, 4-H, $^{3}J = 7.8$ Hz), 8.60 (ddd, 1H, 6′-H, $^{3}J = 4.8$ Hz, $^{4}J = 1.2$ Hz, $^{5}J = 0.6$ Hz), 7.36 (ddd, 1H, 5-H, $^{3}J = 7.8$ Hz, $^{3}J = 7.8$ Hz, $^{4}J = 1.2$ Hz,), 7.34 (ddd, 1-H, 3′-H, $^{3}J = 8.4$ Hz, $^{4}J = 1.2$ Hz, $^{5}J = 0.6$ Hz), 7.32 (ddd, 1H, 7-H, $^{3}J = 7.2$ Hz, $^{4}J = 1.2$ Hz, $^{5}J = 0.6$ Hz), 7.20 (ddd, 1H, 6-H, $^{3}J = 7.8$ Hz, $^{3}J = 7.2$ Hz, $^{4}J = 1.2$ Hz), 7.11 (ddd, 1H, 4′-H, $^{3}J = 8.4$ Hz, $^{3}J = 7.2$ Hz, $^{4}J = 1.2$ Hz), 6.67 (ddd, 1H, 5′-H, $^{3}J = 7.2$ Hz, $^{3}J = 4.8$ Hz, $^{4}J = 1.2$ Hz), 6.65 (t, 1H, 2-H, $^{3}J = 1.8$ Hz), 3.11 (d, 2H, 1-H, $^{3}J = 1.8$ Hz) ppm. ^{13}C-NMR (benzene-d_6): $\delta = 155.6$ (C, C-2′), 149.5 (CH, C-6′), 145.0 (C, C-7a), 144.5 (C, C-3), 143.6 (C, C-3a), 135.9 (CH, C-4′), 133.5 (CH, C-2), 126.6 (CH, C-5), 125.4 (CH, C-6), 124.0 (CH, C-7), 123.7 (CH, C-4), 121.9 (CH, C-5′), 121.7 (CH, C-3′), 38.2 (CH_2, C-1) ppm. ^{15}N/^{1}H-GHMBC-NMR (benzene-d_6): δ (ppm) = − 69.5/8.60 (pyridyl-N/6′-H). Anal. Found: C, 86.03; H, 5.62; N, 7.20. Calc. for $C_{14}H_{11}N$ (193.2): C, 87.01; H, 5.74; N, 7.25%.

*4.2.1. X-ray crystal structure analysis of **4***

Formula $C_{14}H_{11}N$, $M = 193.24$, yellow crystal $0.30 \times 0.30 \times 0.10$ mm^3, $a = 5.706(1)$, $b = 10.210(1)$, $c = 17.262(1)$ Å, $\beta = 94.24(1)$°, $V = 1002.9(2)$ Å^3, $\rho_{calc} = 1.280$ g cm^{-3}, $\mu = 5.74$ cm^{-1}, empirical absorption correction via ψ scan data ($0.847 \le T \le 0.945$), $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda = 1.541\ 78$ Å, $T = 223$ K, ω–2θ scans, 2247 reflections collected ($+h$, $+k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 2040 independent ($R_{int} = 0.020$) and 1747 observed reflections [$I \ge 2\sigma(I)$], 137 refined parameters, $R = 0.041$, $wR^2 = 0.114$, max. residual electron density 0.23 (− 0.16) e$^-$ Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

4.3. General procedure for the preparation of the substituted indenyllithium compounds

A solution of 18.8 ml (30.0 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) at 0°C was added dropwise to a solution of 30.0 mmol of the corresponding indene in 150 ml of diethyl ether. After stirring for 1 h at 0°C and another 1 h at room temperature (r.t.) the solvent was removed in vacuo and the resulting reaction mixture was suspended in 100 ml of pentane and stirred overnight. The suspension was filtered, washed with 10 ml of pentane and dried in vacuum.

*4.3.1. Preparation of [1-(2-pyridyl)indenyl]lithium (**5**)*

Deprotonation of 2.00 g (10.3 mmol) of 3-(2-pyridyl)indene (**4**) with 6.45 ml (10.3 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) yielded 1.50 g (73%) of the product **5** as a dark red solid. ^{1}H-NMR (benzene-d_6/tetrahydrofuran-d_8 (10:1)): $\delta = 8.11$ (d, 1H, 7-H, $^{3}J = 7.2$ Hz), 7.86 (d, 1H, 6′-H, $^{3}J = 4.2$ Hz), 7.82 (dd, 1H, 4-H, $^{3}J = 6.6$ Hz, $^{4}J = 1.2$ Hz), 7.55 (d, 1H, 3′-H, $^{3}J = 8.4$ Hz), 7.26 (d, 1H, 2-H, $^{3}J = 4.2$ Hz), 7.16 (ddd, 1H, 4′-H, $^{3}J = 8.4$ Hz, $^{3}J = 7.2$ Hz, $^{4}J = 1.2$ Hz), 7.02 (m, 2H, 5-H, 6-H), 6.72 (d, 1H, 3-H, $^{3}J = 4.2$ Hz), 6.33 (dd, 1H, 5′-H, $^{3}J = 7.2$ Hz, $^{3}J = 4.2$ Hz) ppm. ^{13}C-NMR (benzene-d_6/tetrahydrofuran-d_8 (10:1)): $\delta = 161.2$ (C, C-2′), 148.0 (CH, C-6′), 136.4 (CH, C-4′), 129.0 (C, C-3a or C-7a), 127.1 (C, C-3a or C-7a), 121.2 (CH, C-4), 120.3 (CH, C-3′), 120.2 (CH, C-2), 118.2 (CH, C-5 or C-6), 116.1 (CH, C-5 or C-6), 114.3 (CH, C-7), 113.3 (CH, C-5′), 108.0 (C, C-1), 103.8 (CH, C-3) ppm. ^{15}N-NMR (benzene-d_6/tetrahydrofuran-d_8 (10:1)): $\delta = -122.5$ (pyridyl-N) ppm.

4.4. General procedure for the preparation of the trisamido[1-(2-pyridyl)indenyl]zirconium complexes

To a solution of 0.50 g (2.59 mmol) of 3-(2-pyridyl)indene in 15 ml toluene was added 2.59 mmol of the corresponding tetrakis(dialkylamido)zirconium reagent dissolved in 20 ml of toluene. The yellow solution changed color to dark brown. The liberated amine was removed with the solvent in vacuo and the product was dried overnight.

*4.4.1. Preparation of [1-(2-pyridyl)indenyl]tris(dimethylamido)zirconium (**7a**)*

By reacting 0.75 g (3.88 mmol) of 3-(2-pyridyl)indene (**4**) with 1.04 g (3.88 mmol) of tetrakis(dimethylamido)zirconium and removal of the solvent 1.60 g (99%) of the product **7a** was obtained, m.p. 61°C. IR (KBr): $\tilde{\nu} = 3054$ (m), 2826 (vs), 2768 (vs), 1587 (vs), 1562 (m), 1492 (vs), 1243 (s), 1155 (s), 942 (vs), 788 (s), 751 (m). ^{1}H-NMR (toluene-d_8): $\delta = 8.83$ (ddd, 1H, 7-H, $^{3}J = 8.4$ Hz, $^{4}J = 1.2$ Hz, $^{5}J = 0.6$ Hz), 8.46 (ddd, 1H, 6′-H, $^{3}J = 4.8$ Hz, $^{4}J = 1.2$ Hz, $^{5}J = 0.6$ Hz), 7.45 (ddd, 1H, 4-H, $^{3}J = 8.4$ Hz, $^{4}J = 1.2$ Hz, $^{5}J = 0.6$ Hz), 7.25 (ddd, 1H, 3′-H, $^{3}J = 7.8$ Hz, $^{4}J = 1.2$ Hz, $^{5}J = 0.6$ Hz), 7.11 (ddd, 1H, 4′-H, $^{3}J = 7.8$ Hz, $^{3}J = 7.2$ Hz, $^{4}J = 1.2$ Hz), 7.00 (ddd, 1H, 6-H, $^{3}J = 8.4$ Hz, $^{3}J = 6.6$ Hz, $^{4}J = 1.2$ Hz), 6.92 (ddd, 1H, 5-H, $^{3}J = 8.4$ Hz, $^{3}J = 6.6$ Hz, $^{4}J = 1.2$ Hz), 6.89 (d, 1H, 2-H, $^{3}J = 3.6$ Hz), 6.56 (ddd, 1H, 5′-H, $^{3}J = 7.2$ Hz, $^{3}J = 4.8$ Hz, $^{4}J = 1.2$ Hz), 6.30 (dd, 1H, 3-H, $^{3}J = 3.6$ Hz, $^{5}J = 0.6$ Hz), 2.63 (s, 18H, $N(C\underline{H}_3)_2$) ppm. ^{13}C-NMR (toluene-d_8): $\delta = 156.7$ (C, C-2′), 149.3 (CH, C-6′), 135.6 (CH, C-4′), 127.6 (C, C-3a), 125.4 (CH, C-7), 124.5 (C, C-7a), 123.6 (CH, C-6), 123.3 (CH, C-5), 122.8 (CH, C-4), 119.9 (CH, C-3′), 119.5 (CH, C-5′), 115.7 (CH, C-2), 111.4 (C, C-1), 99.6 (CH, C-3), 43.8 (CH_3, $N(\underline{C}H_3)_2$) ppm. ^{15}N/^{1}H-GHMBC-NMR (toluene-d_8): $\delta = -76.2/8.46$ (pyridyl-N/6′-H) ppm. Anal. Found: C, 57.21; H, 7.16; N, 13.36. Calc. for $C_{20}H_{28}N_4Zr$ (415.7): C, 57.79; H, 6.79; N, 13.48%.

*4.4.2. Preparation of [1-(2-pyridyl)indenyl]tris(diethylamido)zirconium (**7b**)*

Reaction of 0.50 g (2.59 mmol) 3-(2-pyridyl)indene (**4**) dissolved in 20 ml of toluene with 0.98 g (2.59 mmol) of tetrakis(diethylamido)zirconium yielded 1.28 g (99%) of **7b** as a dark brown oil. IR (KBr): $\tilde{\nu} = 3043$ (m), 2974 (vs), 2933 (s), 2843 (s), 1597 (vs), 1563 (m), 1494 (vs), 1370 (s), 1146 (s), 1005 (vs), 785 (vs). ^{1}H-NMR (benzene-d_6) $\delta = 8.95$ (ddd, 1H, 7-H, $^{3}J = 8.4$ Hz, $^{4}J = 1.2$ Hz, $^{5}J = 0.6$ Hz), 8.57 (ddd, 1H, 6′-H, $^{3}J = 4.8$ Hz, $^{4}J = 1.2$ Hz, $^{5}J = 0.6$ Hz), 7.60 (ddd, 1H, 4-H, $^{3}J = 8.4$ Hz, $^{4}J = 1.2$ Hz, $^{5}J = 0.6$ Hz), 7.43 (ddd, 1H, 3′-H, $^{3}J = 7.8$ Hz, $^{4}J = 1.2$ Hz, $^{5}J = 0.6$ Hz), 7.18 (ddd, 1H, 4′-H, $^{3}J = 7.8$ Hz, $^{3}J = 7.2$ Hz, $^{4}J = 1.2$ Hz), 7.10 (ddd, 1H, 6-H, $^{3}J = 8.4$ Hz, $^{3}J = 6.6$ Hz, $^{4}J = 1.2$ Hz), 7.07–6.99 (m, 2H, 2-H, 5-H), 6.56 (ddd, 1H, 5′-H, $^{3}J = 7.2$ Hz, $^{3}J = 4.8$ Hz, $^{4}J = 1.2$ Hz), 6.30 (dd, 1H, 3-H, $^{3}J = 3.6$ Hz, $^{5}J = 0.6$ Hz), 3.19 (q, 12H, $N(C\underline{H}_2CH_3)_2$, $^{3}J = 6.8$ Hz), 0.88 (t, 18H, $N(CH_2C\underline{H}_3)_2$, $^{3}J = 6.8$ Hz) ppm. ^{13}C-NMR (benzene-d_6) $\delta = 156.9$ (C, C-2′), 149.4 (CH, C-6′), 135.6 (CH, C-4′), 128.2 (C, C-3a), 125.8 (CH, C-7), 125.3 (C, C-7a), 123.5 (CH, C-6), 123.1 (CH, C-5), 122.9 (CH, C-4), 120.4 (CH, C-3′), 119.4 (CH, C-5′), 116.3 (CH, C-2), 111.3 (C, C-1), 99.3 (CH, C-3), 43.8 (CH_2, $N(\underline{C}H_2CH_3)_2$), 15.0 ($CH_3$, $N(\underline{C}H_2\underline{C}H_3)_2$) ppm. Anal. Found: C, 61.79; H, 8.89; N, 10.90. Calc. for $C_{26}H_{40}N_4Zr$ (499.8): C, 62.48; H, 8.07; N, 11.21%.

*4.5. Dichloro(η^5-cyclopentadienyl)[1-(2-pyridyl)indenyl]zirconium (**8**)*

To a suspension of 0.66 g (2.51 mmol) of (η^5-cyclopentadienyl)zirconiumtrichloride (**9**) in 20 ml of benzene a suspension of 0.50 g (2.51 mmol) [1-(2-pyridyl)-indenyl]lithium (**5**) in benzene was added. After stirring overnight the precipitated lithium chloride was filtered off and the solvent was removed in vacuo. The resulting solid was suspended in 20 ml of pentane, the insoluble solid product **8** was collected by filtration and dried overnight in vacuo to yield 0.45 g (43%) of **8**, m.p. 76°C. IR (KBr): $\tilde{\nu} = 3104$ (m), 3057 (w), 2967 (w), 2933 (w), 1608 (m), 1587 (s), 1563 (s), 1391 (m), 1164 (w), 1019 (s), 819 (vs), 771 (s). ^{1}H-NMR (benzene-d_6) $\delta =$ 8.97 (dd, 1H, 7-H, $^3J = 8.4$ Hz, $^5J = 0.6$ Hz), 8.48 (ddd, 1H, 6′-H, $^3J = 4.8$ Hz, $^4J = 1.2$ Hz, $^5J = 0.6$ Hz), 7.46 (ddd, 1H, 4-H, $^3J = 8.4$ Hz, $^4J = 1.2$ Hz, $^5J = 0.6$ Hz), 7.35 (ddd, 1H, 3′-H, $^3J = 7.8$ Hz, $^4J = 1.2$ Hz, $^5J =$ 0.6 Hz), 7.27 (d, 1H, 2-H, $^3J = 3.6$ Hz), 7.09 (ddd, 1H, 4′-H, $^3J = 7.8$ Hz, $^3J = 7.2$ Hz, $^4J = 1.2$ Hz), 7.03 (ddd, 1H, 6-H, $^3J = 8.4$ Hz, $^3J = 6.6$ Hz, $^4J = 1.2$ Hz), 6.84 (ddd, 1H, 5-H, $^3J = 8.4$ Hz, $^3J = 6.6$ Hz, $^4J = 1.2$ Hz), 6.58 (ddd, 1H, 5′-H, $^3J = 7.2$ Hz, $^3J = 4.8$ Hz, $^4J =$ 1.2 Hz), 6.57 (dd, 1H, 3-H, $^3J = 3.6$ Hz, $^5J = 0.6$ Hz), 5.72 (s, 5H, CpH) ppm. ^{13}C-NMR (benzene-d_6) $\delta =$ 154.7 (C, C-2′), 149.3 (CH, C-6′), 136.3 (CH, C-4′), 128.3 (C, C-1), 127.7 (CH, C-7), 127.0 (CH, C-6), 126.5 (CH, C-4), 126.2 (CH, C-2), 125.7 (CH, C-5), 125.3 (C, C-3a), 124.2 (C, C-7a), 121.1 (CH, C-3′), 121.0 (CH, C-5′), 118.2 (CH, C-Cp), 108.6 (CH, C-3) ppm.

4.5.1. X-ray crystal structure analysis of *8*

Formula $C_{19}H_{15}NCl_2Zr$, $M = 419.44$, yellow crystal $0.40 \times 0.25 \times 0.25$ mm^3, $a = 7.929(2)$, $b = 12.317(2)$, $c = 17.676(3)$ Å, $\beta = 99.97(2)°$, $V = 1700.2(6)$ Å^3, $\rho_{calc} = 1.639$ g cm^{-3}, $\mu = 9.58$ cm^{-1}, empirical absorption correction via ψ scan data ($0.700 \leq T \leq 0.796$), $Z = 4$, monoclinic, space group $P2_1/c$ (no. 14), $\lambda =$ 0.710 73 Å, $T = 223$ K, ω–2θ scans, 3687 reflections collected ($-h$, $-k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 3435 independent ($R_{int} = 0.034$) and 2363 observed reflections [$I \geq 2\sigma(I)$], 208 refined parameters, $R = 0.032$, $wR^2 = 0.071$, max. residual electron density 0.38 (-0.57) e$^-$ Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

4.6. Preparation of 3-(5-methyl-2-furyl)indene (*12*)

A solution of 60.9 ml of *n*-butyllithium (97.4 mmol, 1.6 M in hexane) was added to a stirred solution of 2-methylfuran (8.00 g, 97.4 mmol) in 70 ml of diethyl ether. After stirring at r.t. for 12 h the solvent was removed under reduced pressure and the resulting crude product was used for the reaction with 1-indanone. To a solution of the thus-obtained 5-lithio-2-methylfuran (**10**) [8.60 g (97.6 mmol), see above] dissolved in 100 ml of diethyl ether was added dropwise a solution of 12.9 g (97.6 mmol) of 1-indanone in 100 ml of diethyl ether at −60°C. The resulting dark brown reaction mixture was stirred for an additional 2 h between −60 and −40°C before hydrolysis with 75 ml of HCl (2 N) was carried out. Chromatography at silica gel using isohexane/diethyl ether 1:1 and additional triethylamine (5%) as eluent gave 15.0 g (79%) of **12** as a yellow oil, which was stored under argon at −20°C to prevent decomposition. IR (KBr): $\tilde{\nu} = 3067$ (m), 3031 (m), 2925 (s), 2890 (m), 2878 (m), 1725 (vs), 1664 (s), 1603 (m), 1460 (s), 1392 (s), 1380 (w), 1223 (s), 1221 (vs), 1090 (vs), 975 (s), 920 (m), 913 (m). ^{1}H-NMR (chloroform-d_1) $\delta = 7.78$ (d, 1H, 4-H, $^3J = 7.8$ Hz), 7.49 (dd, 1H, 7-H, $^3J = 7.2$ Hz, $^4J = 0.7$ Hz), 7.35 (ddd, 1H, 5-H, $^3J = 7.8$ Hz, $^3J =$ 7.4 Hz, $^4J = 0.7$ Hz), 7.24 (ddd, 1H, 6-H, $^3J = 7.4$ Hz, $^3J = 7.2$ Hz, $^4J = 1.7$ Hz), 6.75 (t, 1H, 2-H, $^3J = 2.4$ Hz), 6.62 (d, 1H, 3′-H, $^3J = 3.2$ Hz), 6.08 (dq, 1H, 4′-H, $^3J = 3.2$ Hz, $^4J = 1.0$ Hz), 3.51 (d, 2H, 1-H, $^3J =$ 2.4 Hz), 2.39 (dd, 3H, 6′-H, $^4J = 1.0$ Hz, $^5J = 0.4$ Hz) ppm. ^{13}C-NMR (chloroform-d_1) $\delta = 151.6$ (C, C-2′), 148.9 (C, C-5′), 144.5 (C, C-3a), 141.8 (C, C-7a), 134.3 (C, C-3), 127.5, 126.2 (each CH, C-4, C-7), 124.9, 123.9 (each CH, C-5, C-6), 120.8 (CH, C-2), 107.6 (CH, C-3′), 107.2 (CH, C-4′), 38.1 (CH_2, C-1), 13.7 (CH_3, C-6′). GC–MS (30 eV) $m/z = 196$ (100) [M$^+$], 181 (12) [M$^+$ $-$ CH$_3$], 165 (12) [M$^+$ $-$ CH$_3$O], 153 (73) [M$^+$ $-$ C$_2$H$_3$O], 115 (10) [M$^+$ $-$ C$_5$H$_5$O], 89 (7) [M$^+$ $-$ C$_7$H$_7$O].

4.7. Preparation of [1-(5-methyl-2-furyl)indenyl]lithium (*13*)

Following the general procedure (see Section 4.3), 7.22 g (36.0 mmol) of 3-(5-methyl-2-furyl)indene (**12**) was treated with 23.0 ml of *n*-butyllithium (36.8 mmol, 1.6 M in *n*-hexane) to yield 9.31 g of a beige-colored solid. The ^{1}H-NMR spectra of the compound showed that one equivalent of diethyl ether was coordinated (yield 94%). ^{1}H-NMR (benzene-d_6/tetrahydrofuran-d_8 (10:1)) $\delta = 8.16$ (ddd, 1H, 7-H, $^3J = 7.8$ Hz, $^4J = 1.2$ Hz, $^5J = 0.6$ Hz), 7.69 (ddd, 1H, 4-H, $^3J = 7.8$ Hz, $^4J =$ 1.2 Hz, $^5J = 0.6$ Hz), 7.24 (d, 1H, 2-H, $^3J = 3.6$ Hz), 7.06 (ddd, 1H, 6-H, $^3J = 7.8$ Hz, $^3J = 6.6$ Hz, $^4J =$ 1.2 Hz), 6.97 (ddd, 1H, 5-H, $^3J = 7.8$ Hz, $^3J = 6.6$ Hz, $^4J = 1.2$ Hz), 6.27 (dd, 1H, 3-H, $^3J = 3.6$ Hz, $^5J =$ 0.6 Hz), 6.22 (d, 1H, 3′-H, $^3J = 3.0$ Hz), 6.05 (dq, 1H, 4′-H, $^3J = 3.0$ Hz, $^4J = 1.2$ Hz), 3.25 (q, 4H, $(CH_3C\underline{H}_2)_2O$, $^3J = 6.6$ Hz), 2.27 (d, 3H, 6′-H, $^4J =$ 1.2 Hz), 1.07 (t, 6H, $(C\underline{H}_3CH_2)_2O$, $^3J = 6.6$ Hz) ppm. ^{13}C-NMR (benzene-d_6/tetrahydrofuran-d_8 (10:1)) $\delta =$ 157.2 (C, C-2′), 144.6 (C, C-5′), 130.9 (C, C-3a), 126.1 (C, C-7a), 120.1 (CH, C-4), 119.6 (CH, C-7), 116.2 (CH, C-6), 115.4 (CH, C-5), 114.3 (CH, C-2), 107.4 (CH, C-4′), 100.4 (C, C-1), 96.6 (CH, C-3′), 93.1 (CH, C-3), 65.9 (CH_2, $(CH_3\underline{C}H_2)_2O$), 15.5 ($CH_3$, $(\underline{C}H_3CH_2)_2O$), 13.9 ($CH_3$, C-6′) ppm.

4.8. Dichlorobis[1-(5-methyl-2-furyl)indenyl]zirconium (*14*)

To a suspension of 3.00 g (10.8 mmol) of [1-(5-methyl-2-furyl)indenyl]lithium (**13**) in 100 ml of toluene was added at $-78°C$ 1.26 g (5.40 mmol) of $ZrCl_4$. The reaction mixture was allowed to warm to r.t. overnight and the lithium chloride formed was filtered off. The resulting solution was concentrated in vacuo to about 40 ml and the product crystallized at $-20°C$. The solid was collected by filtration and the diastereomeric ratio determined by ^1H-NMR spectroscopy. The overall yield of the 60:40 mixture of *rac*-**14** and *meso*-**14** was 2.00 g (67%). After fractional crystallization, 0.23 g of pure isomer **A** (i.e. *rac*-**14**) was obtained, m.p. 246°C. Anal. Found: C, 59.20; H, 4.01. Calc. for $C_{28}H_{22}Cl_2O_2Zr$ (552.6): C, 60.86; H, 4.01%.

rac-**14**. ^1H-NMR (dichloromethane-d_2, 599.9 MHz): $\delta = 8.03$ (dd, 1H, 7-H, $^3J = 8.4$ Hz, $^5J = 0.6$ Hz), 7.43 (ddd, 1H, 4-H, $^3J = 8.4$ Hz, $^4J = 1.2$ Hz, $^5J = 0.6$ Hz), 7.37 (ddd, 1H, 6-H, $^3J = 8.4$ Hz, $^3J = 6.6$ Hz, $^4J = 1.2$ Hz), 7.23 (ddd, 1H, 5-H, $^3J = 8.4$ Hz, $^3J = 6.6$ Hz, $^4J = 1.2$ Hz), 6.76 (d, 1H, 2-H, $^3J = 3.0$ Hz), 6.45 (d, 1H, 3′-H, $^3J = 3.6$ Hz), 6.14 (dq, 1H, 4′-H, $^3J = 3.6$ Hz, $^4J = 1.2$ Hz), 5.82 (dd, 1H, 3-H, $^3J = 3.0$ Hz, $^5J = 0.6$ Hz), 2.45 (d, 3H, 6′-H, $^4J = 1.2$ Hz) ppm. ^{13}C-NMR (dichloromethane-d_2, 150.8 MHz): $\delta = 152.4$ (C, C-5′), 147.7 (C, C-2′), 127.5 (C, C-3a), 127.4 (CH, C-6), 126.6 (CH, C-5), 126.4 (CH, C-4), 125.1 (CH, C-7), 124.1 (C, C-7a), 116.2 (CH, C-2), 111.0 (C, C-1), 108.5 (CH, C-3′), 108.0 (CH, C-4′), 103.5 (CH, C-3), 13.9 (CH_3, C-6′) ppm.

meso-**14**. ^1H-NMR (dichloromethane-d_2, 599.9 MHz, values obtained from the 60:40 mixture of the diastereoisomers): $\delta = 8.01$ (dd, 1H, 7-H, $^3J = 8.4$ Hz, $^5J = 0.6$ Hz), 7.48 (ddd, 1H, 4-H, $^3J = 8.4$ Hz, $^4J = 1.2$ Hz, $^5J = 0.6$ Hz), 7.35 (ddd, 1H, 6-H, $^3J = 8.4$ Hz, $^3J = 6.6$ Hz, $^4J = 1.2$ Hz), 7.25 (ddd, 1H, 5-H, $^3J = 8.4$ Hz, $^3J = 6.6$ Hz, $^4J = 1.2$ Hz), 6.51 (d, 1H, 2-H, $^3J = 3.0$ Hz), 6.50 (d, 1H, 3′-H, $^3J = 3.0$ Hz), 6.14 (dq, 1H, 4′-H, $^3J = 3.0$ Hz, $^4J = 1.2$ Hz), 6.08 (dd, 1H, 3-H, $^3J = 3.0$ Hz, $^5J = 0.6$ Hz), 2.46 (d, 3H, 6′-H, $^4J = 1.2$ Hz) ppm. ^{13}C-NMR (dichloromethane-d_2, 150.8 MHz): $\delta = 152.5$ (C, C-5′), 147.8 (C, C-2′), 127.1 (CH, C-6), 126.8 (C, C-3a), 126.5 (CH, C-5), 126.1 (CH, C-4), 125.1 (CH, C-7), 124.0 (C, C-7a), 116.6 (CH, C-2), 111.8 (C, C-1), 108.6 (CH, C-3′), 107.9 (CH, C-4′), 102.2 (CH, C-3), 13.8 (CH_3, C-6′).

4.8.1. *X-ray crystal structure analysis of rac-**14***

Formula $C_{28}H_{22}O_2Cl_2Zr$, $M = 552.58$, yellow crystal $0.25 \times 0.20 \times 0.10$ mm^3, $a = 21.039(3)$, $b = 34.581(7)$, $c = 6.485(1)$ Å, $V = 4718.2(14)$ Å^3, $\rho_{calc} = 1.556$ g cm^{-3}, $\mu = 7.17$ cm^{-1}, empirical absorption correction via ψ scan data ($0.841 \leq T \leq 0.932$), $Z = 8$, orthorhombic, space group *Fdd*2 (no. 43), $\lambda = 0.710$ 73 Å, $T = 223$ K, ω–2θ scans, 1300 reflections collected $(-h, k, l)$, $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 1300 independent and 1239 observed reflections $[I \geq 2\sigma(I)]$, 151 refined parameters, $R = 0.019$, $wR^2 = 0.046$, max. residual electron density 0.28 (-0.22) e$^-$ Å^{-3}, Flack parameter 0.02(5), hydrogen atoms calculated and refined as riding atoms. Data sets were collected with Enraf–Nonius CAD4 diffractometers, in the case of Mo radiation equipped with a Nonius rotating anode generator FR591. Programs used: data collection EXPRESS (Nonius B.V., 1994), data reduction MOLEN (K. Fair, Enraf–Nonius B.V., 1990), structure solution SHELXS-97 [17], structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).

4.9. *Chemical identification of meso-**14***

After the crystallization of the pure isomer **A** (i.e. *rac*-**14**) was performed, another crystallization of the remaining solution yielded 0.50 g of a 10%:90% **A**:**B** mixture. This rac/meso mixture was treated on an NMR scale with two equivalents of methyllithium. Therefore, 35.0 mg (63.3 μmol) of this mixture was dissolved in benzene-d_6/tetrahydrofuran-d_8 (10:1), and 3 mg (136 μmol) of methyllithium was added. The color turned immediately from yellow to dark red, and as the main product the corresponding dimethylzirconocene compound of the meso isomer was identified by NMR. ^1H-NMR (benzene-d_6/tetrahydrofuran-d_8, 599.9 MHz): $\delta = 7.87$ (d, 2H, 7-H, $^3J = 9.0$ Hz), 7.13 (m, 2H, 4-H), 7.02 (m, 2H, 5-H or 6-H), 6.91 (m, 2H, 5-H or 6-H), 6.27 (d, 2H, 3′-H, $^3J = 3.6$ Hz), 5.97 (d, 2H, 2-H, $^3J = 3.6$ Hz), 5.90 (m, 2H, 4′-H), 5.77 (d, 2H, 3-H, $^3J = 3.6$ Hz), 2.13 (s, 6H, 6′-H), -0.86 (s, 3H, $ZrCH_3$), -1.42 (s, 3H, $ZrCH_3$) ppm.

4.10. *Polymerization reactions*

All polymerizations were carried out in an 1 l glass autoclave charged with 150 ml of toluene and 20 ml of MAO (10.5 wt% solution in toluene). At the given 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 carried out at a permanent pressure of propene (2 bar) for 2 h. Thereafter the reaction mixture was cautiously hydrolyzed by treatment 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 solvent evaporated and the residue dried in vacuo overnight. The polymerizations were carried out with complexes **8** and *rac*-**14**. For details see Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication Nos CCDC-145076–

145079. 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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References

[1] (a) M. Aulbach, F. Küber, Chem. Unserer Zeit 28 (1994) 197 and references cited therein. (b) H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. 107 (1995) 1255; Angew. Chem. Int. Ed. Engl. 34 (1995) 1143 and references cited therein. (c) M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 255 and references cited therein. (d) W. Kaminsky, J. Chem. Soc. Dalton Trans. (1998) 1413 and references cited therein. (e) A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587 and references cited therein.

[2] (a) E.E.C.G. Gielms, J.Y. Tiesnitsch, B. Hessen, J.H. Teuben, Organometallics 17 (1998) 1652. (b) P. Foster, M.D. Rausch, J.C.W. Chien, J. Organomet. Chem. 527 (1997) 71. (c) A.A.H. van der Zeijden, C. Mattheis, R. Fröhlich, F. Zippel, Inorg. Chem. 36 (1997) 4444. (d) A.A.H. van der Zeijden, C. Mattheis, R. Fröhlich, Organometallics 16 (1997) 2651. (e) A.A.H. van der Zeijden, C. Mattheis, R. Fröhlich, Chem. Ber./Recueil 130 (1997) 1231. (f) Y. Qian, G. Li, W. Chen, B. Li, X. Jin, J. Organomet. Chem. 373 (1989) 185.

[3] (a) J. Pflug, G. Erker, G. Kehr, R. Fröhlich, Eur. J. Inorg. Chem. (2000) 1795. (b) J. Pflug, A. Bertuleit, G. Kehr, R. Fröhlich, G. Erker, Organometallics 18 (1999) 3818. (c) P. Jutzi, T. Redeker, B. Neumann, H.-G. Stammler, Organometallics 15 (1996) 4153. (d) R. Beckhaus, J. Oster, B. Ganter, U. Englert, Organometallics 16 (1997) 3902. (e) M.S. Blais, J.C.W. Chien, M.D. Rausch, Organometallics 17 (1998) 3775. (f) M. Galakhov, P. Gómez-Sal, A. Martin, M. Mena, C. Yélamos, Eur. J. Inorg. Chem. (1998) 1319. Reviews: (g) G.W. Klumpp, Recl. Trav. Chim. Pays-Bas 105 (1986) 1. (h) P. Jutzi, J. Dahlhaus, Coord. Chem. Res. 137 (1994) 179. (i) P. Jutzi, T. Redeker, Eur. J. Inorg. Chem. (1998) 663. (k) J. Okuda, Comments Inorg. Chem. 16 (1994) 185.

[4] (a) T. Dreier, G. Erker, R. Fröhlich, B. Wibbeling, Organometallics 19 (2000) 4095. (b) J.A. Ewen, R.L. Jones, M.J. Elder, A.L. Rheingold, L.M. Liable-Sands, J. Am. Chem. Soc. 120 (1998) 10 786. (c) C. Qian, D. Zhu, J. Chem. Soc. Dalton Trans. (1994) 1599. (d) P. Burger, J. Diebold, S. Gutmann, H.-U. Hund, H.-H. Brintzinger, Organometallics 11 (1992) 1319. (e) J. Amarasekera, T.B. Rauchfuss, Inorg. Chem. 28 (1989) 3875.

[5] (a) K.H. Thiele, C. Schließburg, B. Neumüller, Z. Anorg. Allg. Chem. 621 (1995) 1106. (b) G. Paolucci, G. Pojana, J. Zanon, V. Lucchini, E. Avtomonov, Organometallics 16 (1997) 5312. (c) M. Enders, R. Rudolph, H. Pritzkow, Chem. Ber. 129 (1996) 459. J. Organomet. Chem. 549 (1997) 251. (d) U. Siemeling, U. Vorfeld, B. Neumann, H.-G. Stammler, Chem. Ber. 128 (1995) 481. (e) M.L. Hays, T.P. Hanusa, T.A. Nile, J. Organomet. Chem. 514 (1996) 73.

[6] P.A. Barrett, J. Chem. Soc. (1958) 325.

[7] See for a comparison: H.G. Alt, K. Föttinger, W. Milius, J. Organomet. Chem. 572 (1999) 21.

[8] (a) G. Chandra, M.F. Lappert, J. Chem. Soc. A (1968) 1940. (b) W.A. Herrmann, M.J.A. Morawietz, T. Priermeier, Angew. Chem. 106 (1994) 2025; Angew. Chem. Int. Ed. Engl. 33 (1994) 1996. (c) G.M. Diamond, S. Rodewald, R.F. Jordan, Organometallics 14 (1995) 5. (d) D.C. Bradley, I.M. Thomas, J. Chem. Soc. (1960) 3857.

[9] G. Erker, K. Berg, L. Treschanke, K. Engel, Inorg. Chem. 21 (1982) 1277.

[10] For specific solutions of the rac-/meso selectivity problem see e.g. (a) M. Könemann, G. Erker, R. Fröhlich, S. Kotila, Organometallics 16 (1997) 2900. (b) G.M. Diamond, R.F. Jordan, J.L. Petersen, J. Am. Chem. Soc. 118 (1996) 8024.

[11] (a) G. Erker, M. Aulbach, M. Knickmeier, D. Wingbermühle, C. Krüger, M. Nolte, S. Werner, J. Am. Chem. Soc. 115 (1993) 4590. (b) M. Knickmeier, G. Erker, T. Fox, J. Am. Chem. Soc. 118 (1996) 9623.

[12] H. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18 (1980) 99.

[13] ^{13}C-NMR methyl pentade analysis: (a) F.A. Bovey, G.V.D. Tiers, J. Polym. Sci. 44 (1960) 173. (b) R.A. Sheldon, T. Fueno, R. Tsuntsuga, J. Kurukawa, J. Polym. Sci. Part B 3 (1965) 23. (c) A. Zambelli, P. Locatelli, G. Bajo, F.A. Bovey, Macromolecules 8 (1975) 687. (d) M. Farina, Top. Stereochem. 17 (1987) 1. For the statistical treatment see: (e) J. Inoue, Y. Itabashi, R. Chujo, Y. Doi, Polymer 25 (1984) 1640. (f) G. Erker, R. Nolte, Y.-H. Tsay, C. Krüger, Angew. Chem. 101 (1989) 642; Angew. Chem. Int. Ed. Engl. 28 (1989) 628.

[14] D. Kunz, G. Erker, R. Fröhlich, G. Kehr, Eur. J. Inorg. Chem. (2000) 409.

[15] (a) D.J. Parks, R.E.v.H. Spence, W.E. Piers, Angew. Chem. 107 (1995) 895; Angew. Chem. Int. Ed. Engl. 34 (1995) 809. (b) D.J. Parks, W.E. Piers, G.P.A. Yap, Organometallics 17 (1998) 5492.

[16] S. Braun, H.-O. Kalinowski, S. Berger, 150 and More Basic NMR Experiments, VCH, Weinheim, 1998 and references cited therein.

[17] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.