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Dissymmetric ansa zirconocene complexes with di- and trisubstituted indenyl ligands as catalysts for homogeneous ethylene homo- and ethylene/1-hexene copolymerization reactions

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ABSTRACT

Different routes for the synthesis of 1,2- and 1,2,3-substituted indene derivatives are described. Representative substituents are: Me, Ph, PhCH₂, PhCH₂CH₂, PhCH₂CH₂, CH₂CH = CH₂. Subsequent deprotonation of these substituted indenes and reaction with indenyl zirconium trichloride gave the corresponding dissymmetric bis(indenyl) zirconium complexes. After activation with methylaluminoxane (MAO) these complexes show high activities both in ethylene homopolymerisation and ethylene/1-hexene copolymerisation. The rate of comonomer incorporation can reach 33.3% (**15**/MAO). The copolymers exhibit lower melting points than the homopolymers and their crystallinities α are lower compared with the homopolymers.

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1. Introduction

Multinuclear or dissymmetric mononuclear complexes can be used as catalysts to produce polyolefins with bimodal or multimodal molecular weight distributions [1–9]. Such polyolefins show an advantageous processability because of their broad melting range. Another option comprises the copolymerisation of at least two monomers [10]. Suitable systems are ethylene and short chain α -olefins like 1-hexene [11,12]. The copolymerisation of ethylene and 1-hexene is a typical way to introduce short chain branches into the linear polyolefin backbone to produce low density polyethylene (LLDPE). An essential element of this process is the selectivity of the catalyst towards ethylene and the respective α -olefin. Since each catalyst incorporates different amounts of the α -olefin into the polymer backbone resulting in polymers with different branching patterns, it is possible to obtain a variety of new polymers with different contents of comonomer and molecular weight distributions. Compared to their corresponding homopolymers, these copolymers exhibit different melting temperatures, crystallinities and mechanical and optical characteristics. LLDPE shows short chain branches, lower melting points and lower crystallinities compared to 'high density polyethylene' (HDPE) and 'low den-

* Corresponding author. E-mail address: helmut.alt@uni-bayreuth.de (H.G. Alt). sity polyethylene' (LDPE) [13–16]. Because of its excellent properties, LLDPE is one of the most attractive polyolefins. Zirconium complexes with substituted indenyl ligands are excellent candidates for the copolymerisation of ethylene and 1-hexene. Bridged derivatives usually incorporate higher amounts of an α olefin compared to the unbridged ones [17–19]. In the literature the described routes for the synthesis of such complexes are cumbersome. Therefore it is essential to find better routes for the synthesis of new 2-substituted indenyl complexes that give similar or better copolymerisation results compared to the already existing complexes. In this paper pathways to new 2-substituted indenyl complexes are presented.

2. Results and discussion

2.1. Synthesis of 2-bromoindene

An important starting compound for the preparation of 2-substituted indenes is 2-bromoindene (**2**) [20,21]. It was obtained in a two step reaction from indene and N-bromosuccinimide (NBS) in dimethylsulfoxide via a halohydrine reaction. The hydroxy group of the obtained 1-hydroxy-2-bromoindane (**1**) was removed in toluene under reflux catalysed by p-toluene sulfonic acid (p-TosOH) to give 2-bromoindene (**2**) (Scheme 1). 2-Bromoindene was then transferred to the Grignard compound **3** (Scheme 2).





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Scheme 1. Synthesis of 2-bromoindene (2) [20,21].



Scheme 2. Synthesis of 2-indenyl magnesium bromide (3).

2.2. Synthesis of 2-substituted indene compounds via Kumada reactions

In Kumada reactions, Grignard compounds and alkyl halides are coupled in the presence of nickel catalysts like 1,3-bisdiphenylphosphino-propane nickel dichloride [22,23]. 2-Bromoindene (**2**) was reacted with allyl magnesium bromide to give 2allylindene (**4**) (Scheme 3). The reaction of **3** and allyl bromide also gave **4** but in a much lower yield.

The Kumada reaction only worked smoothly with alkyl and alkenyl magnesium halides, not with aryl Grignard compounds giving side products.

2.3. Palladium catalysed synthesis of 2-substituted indene compounds

Indene was reacted with bromobenzene in the presence of a palladium catalyst. The desired 2-phenylindene (**5**) was obtained in a one step reaction after stirring for six hours at 100 °C (see Scheme 4).

The reaction was not successful for allyl bromide or cyclohexyl bromide; the yields were very low. Therefore, this route is only partially useful to obtain 2-substituted indene compounds.

2.4. Synthesis of 2-substituted indene compounds from 2-indanone

Another method to obtain the desired 2-indene compounds is the reaction of 2-indanone with Grignard reagents [25,26]. The resulting alcohols need to be dehydrated in a second step.

Experiments showed that such Grignard reactions give several side products, but their amounts can be minimized introducing an intermediate step, where the Grignard compound was treated with cerium trichloride before 2-indanone was added (Scheme 5) [27–29]. Cerium trichloride is an oxophilic salt which can activate carbonyl compounds by coordination. It also lowers the strong base character of the Grignard compounds. This is most likely

the main driving force of this reaction [27]. The alcohols **6–8** were dehydrogenated with sulfuric acid (Scheme 6).

Different from the 12-hour period necessary for the dehydration of the indanols with para-toluene sulfonic acid, this method only takes thirty minutes under reflux [30]. No noteworthy side reactions were observed.

2.5. Synthesis of dissymmetric unbridged indenyl zirconium complexes

2-Substituted indene compounds and their corresponding symmetric group (IV) metal indenyl complexes are well described in the literature [17,18]. Therefore, the goal was to obtain dissymmetric di- and trisubstituted indenyl complexes. Two approaches will be presented here: Either one substituted indenyl compound is reacted with indenyl zirconium trichloride or two indenyl ligands with different substituents are coordinated to a zirconium metal centre (see Scheme 7).

Substituents $\mathbb{R}^1 - \mathbb{R}^5$ can be alkyl, alkenyl, aryl or alkylaryl groups.

2.5.1. Multisubstituted indenyl compounds

More substituents can be introduced in positions one and three of 2-substituted indenes. The 2-substituted indene derivatives were deprotonated with *n*-butyl lithium and then reacted with methyliodide respectively allylbromide. The reaction conditions are very important to obtain the desired compounds. A reaction period of twelve hours afforded 1,2,3-substituted indenes. To gain the 1,2-substituted indene derivatives, the reaction time had to be reduced to four hours and, additionally, the lithium salt, which was produced in the first reaction step, had to be removed to get rid of traces of unreacted n-butyl lithium. Since the degree of alkylation can be controlled by choosing the appropriate reaction conditions, both 1,2- and 1,2,3-substituted indene derivatives were synthesised (see Schemes 8 and 9).

2.5.2. Synthesis of the dissymmetric bis(indenyl) zirconium complexes **15** and **16**

The synthesis of complexes **15** and **16** was carried out by deprotonation of the respective starting compound with n-butyl lithium and reaction with indenyl zirconium trichloride. The substituted indene compound was dissolved in diethylether and *n*-butyl lithium was added. After stirring for 20 h, indenyl zirconium trichloride was added resulting in the formation of light orange



Scheme 3. Synthesis of 2-allylindene (4) [24] via Kumada coupling.



Scheme 4. Synthesis of 2-phenylindene (5).



Scheme 5. Synthesis of 2-substituted indene compounds from Grignard reactions.



Scheme 6. Elimination of hydroxy groups of 2-indanols with sulfuric acid [31].



Scheme 7. Unsymmetrical bis(indenyl) zirconium complex.

dissymmetric bis(indenyl) zirconium complexes. The complexes could be isolated in yields up to 50% (see Scheme 10).

2.5.3. Dissymmetric bis(indenyl) zirconium complexes from 2substituted indenyl zirconium trichloride and substituted indene derivatives

In the above described route multisubstituted indene derivatives were reacted with indenyl zirconium trichloride. 2-Substituted indenyl zirconium trichloride half sandwich complexes are obtained in a two step reaction from 2-substituted indene derivatives treated with tributyl tin chloride followed by addition of zirconium tetrachloride [32] (see Scheme 11).

These half sandwich complexes can then be reacted with differently substituted indene compounds like 4,7-disubstituted indene derivatives. Those indene derivatives are obtained by reacting potassium tert-butylate with 2,5-diketones [33] and cyclopentadiene in methanol [34] (see Scheme 12). The half sandwich complexes and the 4,7-disubstituted indene derivatives can then be prepared following the previously described route (Section 2.5.2.). For olefin polymerisation reactions, the dissymmetric bis(indenyl) zirconium complex **17** was used as catalyst precursor (see Scheme 13).

Complexes **15–17** were characterized by ¹H and ¹³C NMR spectroscopy, mass spectrometry and elemental analysis. Schemes 14 and 15 show the ¹H and ¹³C NMR spectra of complex **17**.

The ¹H NMR spectrum of complex **17** shows a signal for the methyl group (14) at $\delta = 2.31$ ppm. At $\delta = 1.96$ ppm and at $\delta = 2.59-2.96$ ppm the signals of the methylene protons 7, 8, 20, 21 and 22 are located. The aromatic CH protons in the five membered indenyl ring give signals at $\delta = 5.71$, 5.77, 5.86, 6.14 and 6.20 ppm. The protons 5 and 6 give two signals because of rac and meso isomers. The signals for the remaining protons of the indenyl and phenyl rings appear between $\delta = 6.92$ bis 7.62 ppm.

In the ¹³C NMR spectrum, the methyl group 18 is visible at $\delta = 18.9$ ppm. The five carbon atoms of the CH₂ groups 10, 11, 28, 29 and 30 give signals at $\delta = 30.4$, 32.2, 33.7, 35.7 and 36.2 ppm. The aromatic methine carbon atoms of the phenyl and indenyl rings (1–4, 13–17, 20, 21 und 32–36) are found between $\delta = 125.3$ and 128.5 ppm. The aromatic methine carbon atoms of the five membered indenyl rings (6, 8 und 24–26) appear between $\delta = 103.0$ and 115.6 ppm. The nine quarternary carbon atoms give signals in the range between $\delta = 125.2$ and 143.5 ppm.

The mass spectrum of complex **15** (Scheme 16) shows the molecular ion at m/z = 508. The loss of an allyl group and both chloro ligands results in the formation of a fragment with m/z = 393. The peak at m/z = 355 arises from the loss of the unsubstituted indenyl group and a chloro ligand. Further elimination of the allyl group and the second chloro ligand results in the peak at m/z = 277. The peak at m/z = 232 arises from the loss of the fragment indenyl-Zr(Cl₂). The base peak at m/z = 191 can be assigned to a 2-phenylindenyl moiety (see Scheme 17).



Scheme 8. Synthesis of 1,2-disubstituted indene compounds.



Scheme 9. Synthesis of 1,2,3-trisubstituted indene compounds.



15: R^1 = Ph, R^2 = Allyl, R^3 = H **16**: R^1 = PhCH₂, R^2 = Me, R^3 = Me

Scheme 10. Synthesis of dissymmetric bis(indenyl) zirconium complexes.



R = aliphatic, aromatic, alkylaryl

Scheme 11. General synthesis of indenyl zirconium trichloride half sandwich complexes.



R = aliphatic, aromatic, alkylaryl

Scheme 12. General synthesis of 4,7-disubstituted indene compounds [34].



Scheme 13. Complex 17 as catalyst precursor for olefin polymerisation.

2.6. Results of homogeneous ethylene polymerisation and ethylene/1hexene copolymerisation with complexes **15–17/**MAO

In the past 25 years metallocene dichloride complexes with group IV metals in combination with methylaluminoxane (MAO) have proven as excellent catalysts for olefin polymerization [11,35, and references therein]. All synthesised bis(indenyl) zirco-nium complexes were used as catalyst precursors for homogeneous ethylene polymerisation and ethylene/1-hexene copolymerisation reactions.

For ethylene homopolymerisation experiments the complexes were activated with methylaluminoxane (MAO) applying a ratio Zr:Al = 1:2500. The polymerisation runs were routinely performed at a temperature of 60 °C over 1 h employing an ethylene pressure of 10 bar. As a solvent *n*-pentane was used. The polymerisation results, viscosity molecular weight and DSC data are given in Table 1.

For homogeneous ethylene/1-hexene copolymerisation reactions the complexes were activated with methylaluminoxane (MAO) applying a ratio Zr:Al = 1:2500. The polymerisation runs were routinely performed at a temperature of 60 °C over 1 h employing an ethylene pressure of 10 bar. The addition of 1-hexene was set to 20 g/h. As solvent *n*-pentane was used. The polymerisation results and the DSC data are given in Table 2.

The activities of the three bis(indenyl) zirconium complexes in copolymerisation reactions are in general lower than in ethylene



Scheme 15. ¹³C NMR spectrum of complex 17 in chloroform-d.

homopolymerisation experiments. The bulkyness of the indenyl substituents rises from **15** to **17**, which hinders the incorporation of the comonomer 1-hexene and the growth of the polymer chain. Complex **15**/MAO shows the lowest activity in both polymerisation types. It is likely, that the allyl substituent interacts with the active centre and hinders the coordination of 1-hexene.

2.7. Examination of the chain structure of the ethylene/1-hexene copolymers obtained with complexes **15–17**/MAO using ¹³C NMR spectroscopy

The chain structures of the copolymers were determined with ¹³C NMR analysis. Each signal in the spectrum can be assigned to

a certain sequence in the polymer chain [36]. The nomenclature of the different carbon groups was taken from Carman et. al. [37]. The labelling $\alpha\delta$ + means for example, that one methylene group has one methine group as direct neighbour, but the second methine group is at least four more methyl groups away.

All ¹³C NMR spectra show the typical spectrum for ethylene/1-hexene copolymers (Scheme 18).

The values from the ¹³C NMR spectra were compared with the data given in Table 3. The signals at δ = 38.8, 34.2 and 33.8 ppm (region B and C) are assigned for "EHE"- respectively "EHEE"- units where one 1-hexene unit (H) is located between two or more ethylene units (E). Long ethylene chains in the copolymer show signals at δ = 30.4 and 30.0 ppm. There, a 1-hexene unit is



Scheme 16. Mass spectrum of complex 15.



Scheme 17. Comparison of the polymerisation activities of the bis(indenyl) zirconium complexes 15–17/MAO in ethylene homopolymerisation and ethylene/1-hexene copolymerisation reactions.

Table 1

Ethylene homopolymerisation with the dissymmetric bis(indenyl) zirconium complexes **15–17**. Polymerisation conditions: solvent: 250 ml *n*-pentane, activator: MAO, Zr: Al = 1:2500, 60 °C, 10 bar ethylene, 1 h.

Compound	Activity (kg/molZr h)	M_{η} (g/mol)	<i>T</i> _m [°C]	$\Delta H_{\rm m}$ [J/g]	α [%]
15	4260	167500	136.50	144.51	50
16	13160	43000	132.14	205.33	71
17	19910	175200	136.81	160.27	55

Table 2

Ethylene/1-hexene copolymerisation with the dissymmetric bis(indenyl) zirconium complexes **15–17**. Polymerisation conditions: solvent: 250 ml n-pentane, activator: MAO (Zr: Al = 1:2500), 60 °C, 10 bar ethylene, 1 h, flow rate (1-hexene): 20 g/h.

Compound	Activity (kg/molZr h)	<i>T</i> _m [°C]	$\Delta H_{\rm m}$ [J/g]	α [%]
15	2990	125.39	91.57	32
16	5760	125.41	102.47	35
17	4210	127.34	28.74	10

followed by several ethylene units (HEEE) or only ethylene units can be found ((EEE)_n). The region G and H signals contain no specific sequence information. 1-Hexene units surrounded by ethylene units or more 1-hexene units next to each other are possible. The signal at δ = 27.1 ppm (region E) can be assigned to "HHEE"-units and signal δ = 29.3 ppm to "HHE"-units. Comparing the amount of signals that can be assigned to units where 1-hexene is surrounded by ethylene to other units leads to the conclusion that the incorporated 1-hexene units are mainly separated by at least two ethylene units in the obtained copolymers. Blocks with more 1-hexene units incorporated next to each other do not

exist (region A). The same is true for units, where the 1-hexene units are only separated by one ethylene unit (region F) (see Scheme 19).

2.8. Comparison of the properties of the polyethylenes and 1-hexene/ ethylene copolymers obtained with complexes **15–17**/MAO

The viscosity molecular weights M_{η} of the polymers obtained with the complexes **15–17**/MAO show a similar trend as the activities of the catalysts. The molecular weight of the homopolymer from complex **16**/MAO (43,000 g/mol) represents the lowest value



 Table 3

 Correlation of the signals of the ¹³C NMR spectrum to the sequences in the polymer chain [32] (E = ethylene unit, H = 1-hexene unit).

Region	С	Sequence	$\delta_{\text{theor.}}$ [ppm]	15 δ _{exp.} [ppm]	16 δ _{exp.} [ppm]	17 δ _{exp.} [ppm]
A	a a a a	НННН НННЕ ЕННЕ	41.4 40.9 40.2			
В	СН	EHE	38.1	37.8	37.8	37.8
С	CH 4B αγ αγ αδ ⁺ 4B	нне ннн ннен енен ннее нне	35.9 35.4 35.0 34.9			
	α δ+ 4B CH	EHEE EHE HHH	34.5 34.1 33.5	34.2 33.8	34.2 33.8	34.2 33.8
D	γγ γδ+ δ+ δ+ 3B 3B 3B	HEEH HEEE (EEE) n EHE HHE HHH	30.9 30.5 30.0 29.5 29.3 29.2	30.4 30.0 29.3	30.4 30.0 29.3	30.4 30.0 29.3
E	βδ⁺ βδ⁺	EHEE HHEE	27.3 27.1	27.1	27.1	27.1
F	β β β β β β	ЕНЕНЕ ННЕНЕ ННЕНН	24.5 24.4 24.3			
G	2B	EHE + HHE + HHH	23.4	23.4	23.4	23.4
Н	1B	EHE + HHE + HHH	14.1		14.2	14.2

On the basis of the integrals in the ¹H NMR spectra, the incorporation of 1-hexene in mol% was calculated (Table 4).

among the tested catalysts. The molecular weights of the other two homopolymers were determined as 167,500 g/mol und 175,200 g/mol. Since the molecular weights were calculated by viscosimetry measurements, it is not possible to compare the molecular weights of the homopolymers and the copolymers because the viscosimetry measurements reflect a too low value for the copolymers (see Table 4).

DSC analyses showed clear differences in the polymer properties. The homopolymers exhibit melting points between 132 and 137 °C, the copolymers are about 10 °C lower (see Scheme 20).

The melting point of the homopolymer obtained from **15**/MAO at 132 °C is lower than the ones of the other two polymers. The melting points of the copolymers from **15**/MAO and **17**/MAO are at 125 °C. The copolymer obtained with **17**/MAO shows two melt-

ing peaks in the melting curve. The higher one is at T_m = 127.5 °C and the lower one at T_m = 112 °C. Obviously the copolymer consists of different polyethylene types (see Scheme 21).

The crystallinities α were calculated from the melting enthalpies of the polymers. The values of the copolymers were again lower than those of the homopolymers (Scheme 22).

For the copolymer obtained with **17**/MAO, the crystallinity α was calculated as 10% corresponding to a mainly amorphous structure. This polymer is best for further processing. The crystallinities of the other two copolymers were distinctively higher (32% und 34%). The crystallinities of the ethylene homopolymers obtained from **15**/MAO and **17**/MAO were determined as 50%. The highest crystallinity was found for the polymer obtained with **16**/MAO (70%).



Scheme 19. Comparison of the molecular weight M_{η} of the polymers obtained with **15–17**/MAO.

Table 4

Incorporation of 1-hexene into the copolymers obtained with the complexes 15–17/ MAO.

Copolymer of complex	Incorporation [%]		
	1-hexene	Ethylene	
15/MAO	33.3	66.7	
16/MAO	16.7	83.3	
17 /MAO	12.5	87.5	

3. Experimental

3.1. NMR spectroscopy

The spectrometers Bruker ARX 250 and Varian (Inova 400) were available for the recording of the NMR spectra. The samples were prepared under inert atmosphere (argon) and routinely recorded at 25 °C. The chemical shifts in the ¹H NMR spectra are referred to the residual proton signal of the solvent (δ = 7.24 ppm for CDcl₃; δ = 5.32 ppm for CD₂Cl₂, δ = 7.15 ppm for C₆D₆) and in ¹³C NMR spectra to the solvent signal (δ = 77.0 ppm for CDcl₃; δ = 53.5 ppm for CD₂Cl₂; δ = 128.0 ppm for C₆D₆).

3.2. GC/MS spectroscopy

GC/MS spectra were recorded with a Thermo Focus gas chromatograph in combination with a Thermo DSQ mass detector. A 30 m HP-5MS fused silica column (film 0.25 μ m, flow 75 ml/min, split ratio 50:1), helium (4.6) was applied as the carrier gas. Using a 30 m column, the routinely performed temperature program started at 50 °C (2 min). After a heating phase of 24 min (10 K/



Scheme 21. Melting curve of the copolymer obtained with 17/MAO.

min, final temperature 290 $^{\circ}$ C) the end temperature was held for 15 min (plateau phase).

At the Zentrale Analytik of the University of Bayreuth GC/MS spectra were routinely recorded with a HP5890 gas chromatograph in combination with MAT 95 mass detector.

3.3. Mass spectrometry

Mass spectra were routinely recorded at the Zentrale Analytik of the University of Bayreuth with a VARIAN MAT CH-7 instrument (direct inlet, EI, E = 70 EV) and a VARIAN MAT 8500 spectrometer.

3.4. Elemental analysis

The analyses were performed with a VarioEI III CHN instrument. The raw values of the carbon, hydrogen and nitrogen contents



Scheme 20. Comparison of the melting points of the ethylene homopolymers and the ethylene/1-hexene copolymers of complexes 15-17/MAO.



Scheme 22. Crystallinities α of the homo- and copolymers produced with the complexes 15–17/MAO.

were multiplied with calibration factors (calibration compound: acetamide).

3.5. Differential scanning calorimetry (DSC)

The thermal attributes of the polymer samples were examined in a Diamond DSC instrument (Perkin-Elmer). After drying the polymer samples, an amount of 4–7 mg was weighed into a standard aluminium pan. The sealed pan was then introduced into the instrument. The measurements were performed with the following temperature program:

- Heating phase (10 K/min) from 50 °C to 160 °C; 1. cooling phase (-10 K/min) to 50 °C.
- (2) Heating phase (10 K/min) from 50 °C to 160 °C; 2. cooling phase (-10 K/min) to 50 °C.

The temperature was corrected linearly to indium (mp = 156.6 °C), for calibration the melting enthalpy of indium was used ($\Delta H_{\rm m}$ = 28.45 J/g).

For polyethylene, the maxima of the second heating cycle were used. For the calculation of the crystallinity, the correlation $\alpha = \frac{\Delta H_{\rm m}}{\Delta H_{\rm m}^0}$ was used. $\Delta H_{\rm m}$ was obtained from the second heating cycle of the DSC, for $\Delta H_{\rm m}^0$ as the melting enthalpy extrapolated for 100% crystalline polyethylene a value of 290 J/g [38] was used.

3.6. Viscosimetry

The molecular weight M_{η} was determined with an Ubbelohde precision capillary viscosimeter (0C, Schott-Geräte) in cis/trans decaline at 135 ± 0.1 °C. The heating bath used was a CT 1450 instrument and the measurement unit an AVS 310. The samples were weighed into Erlenmeyer vessels and dissolved in the corresponding amount of decaline during 3–4 h at 140–150 °C. Insolvable parts were filtered off with glass wool. For the determination of M_{η} , reference sheets were available. To reduce errors, each polymer sample was weighed and measured twice. The possible error in the molecular weight calculation is ±10%.

3.7. Synthesis

3.7.1. Synthesis of 2-bromoindene (2)

To a solution of freshly distilled indene (42.61 mmol) in 200 ml of dimethyl sulfoxide and water (82.2 mmol), N-bromosuccinimide (43.29 mmol) was added. After stirring for 12 h, water was added slowly to the reaction mixture. The organic layer was extracted with diethylether four times, dried over sodium sulfate and the sol-

vent was evaporated. 1-Hydroxy-2-bromoindane (1) was obtained quantitatively as a mixture of diastereomers.

1-Hydroxy-2-bromoindane (42.61 mmol) was then dissolved in 300 ml of toluene, and a catalytic amount of para-toluene sulfonic acid was added. After stirring the reaction mixture for 3 days under reflux with a Dean-Stark trap, the toluene was evaporated and *n*-pentane was added. The suspension was filtered over silica and the solvent removed. The product was obtained as yellow needles after recrystallisation. Yield: 60–90%. ¹H NMR: 7.35 d (1H, Ar-H), 7.29 d (1H, Ar-H), 7.23 t (1H, Ar-H), 7.16 dt (1H, Ar-H), 6.91 s (1H, Ar-H), 3.58 s (2H, Ind-CH₂). ¹³C NMR: 144.0, 142.6, 124.9 (C_q), 132.9, 126.7, 124.8, 123.2, 120.2 (Ar-CH), 45.5 (Ind-CH₂). MS: *m/z* 196 M^{+.} (8), 115 M – Br (100).

3.7.2. Synthesis of 2-allylindene (4)

Allyl magnesium bromide (5 mmol) in 25 ml diethylether was slowly added to a solution of 2-bromoindene (5 mmol) and Ni (dppp)Cl₂ (0.05 mmol), dissolved in 25 ml diethylether and stirred over night at room temperature. Diluted hydrochloric acid was used for the following hydrolysis. The organic layer was separated and dried over sodium sulfate. The evaporation of the solvent and recrystallization from n-pentane yielded compound **4**. Yield: 55%. ¹H NMR: 7.12–7.39 m (4H, Ar-H), 6.55 s (1H, Ar-H), 5.85 m (1H,= CH), 5.03 m (2H,=CH₂), 3.35 s (2H, Ind-CH₂), 3.23 d (2H, CH₂). ¹³C NMR: 145.1, 144.6, 142.7 (C_q), 135.2 (=CH), 131.7, 129.6, 128.4, 126.6, 125.9 (Ar-CH), 115.9 (=CH₂), 38.1 (Ind-CH₂), 34.9 (CH₂). MS: *m/z* 156 M^{+.} (55), 141 M – CH₃ (42), 128 M – C₂H₄ (68), 115 Indenyl (100).

3.7.3. Synthesis of 2-phenylindene (5)

To a solution of bromobenzene (6.54 mmol), indene (15 mmol) and triethylamine (25.9 mmol) in 30 ml of dimethylformamide, bis-(tri-o-tolyl-phosphine)-palladium dichloride (0.14 mmol) was added. The reaction mixture was stirred at 100 °C for six hours, then evaporated and the residue dissolved in a mixture of n-pentane and dichloromethane (100:3). The solution was then filtered over silica, the solvent removed and the product recrystallized from n-pentane. Yield: 37%. ¹H NMR: 7.62 d (2H, Ar-H), 7.42–7.50 q (1H, Ar-H), 7.34–7.40 m (3H, Ar-H), 7.21–7.28 m (3H, Ar-H), 7.15–7.19 m (1H, Ar-H), 3.78 s (2H, Ind-CH₂). ¹³C NMR: 146.3, 145.3, 143.1, 136.1 (C_q), 128.7 (2C), 127.6, 126.6, 126.4, 125.7 (2C), 124.7, 123.7, 120.9 (Ar-CH), 39.0 (Ind-CH₂). MS: m/z 192 M⁺. (100), 115 M – C₆H₅ (10).

3.7.4. Synthesis of the 2-substituted indene compounds 5, 9 und 10

Cerium trichloride (45 mmol) was quickly and finely ground to a powder in a mortar and placed in a 30 ml two-necked flask. The flask was immersed in an oil bath and heated gradually to 135–

140 °C and evacuated (ca. 0.1 torr). After maintenance of the cerium chloride at a constant temperature for 1 h, a magnetic stirring bar was placed in the flask and the cerium chloride was completely dried in vacuo by stirring at the same temperature for an additional 1 h. The hot flask was filled with argon gas and then cooled in an ice bath. THF (5 ml) was added all at once with vigorous stirring. The ice bath was removed and the suspension was stirred overnight under argon at room temperature. Meanwhile the Grignard reagent was prepared. To magnesium powder (75 mmol, 50 mesh) 50 ml tetrahydrofuran and a small piece of iodine was added. Then 10 ml of the corresponding bromo compound (45 mmol) in 100 ml of tetrahydrofuran was added. After the iodine colour disappeared, the remaining bromide solution was added with a dropping funnel and the solution was stirred over night. The cerium trichloride suspension was again immersed in an ice bath and the Grignard reagent was added after filtration. After stirring for 1.5 h at 0 °C, 2-indanone (30 mmol), dissolved in tetrahydrofurane (50 ml), was added and the stirring was continued for 120 minutes. The reaction mixture was treated with 10 ml of a 10% aqueous acetic acid. The product was extracted into ether, and combined extracts were washed with brine and NaHCO₃ solution and brine and dried with sodium sulfate. The solvent was evaporated and the alcohols 6-8 were obtained and dehydrogenated without further characterisation.

In a second step, the hydroxyl groups of the alcohols were removed by addition of 25 ml of 9 M sulfuric acid and stirring for 30 minutes at 110 °C. For neutralisation, a 20% sodium hydroxide solution was added. The mixture was washed with dichloromethane twice, filtered over sodium sulfate and the solvent was removed to obtain the product. Yield: 70–75%. (**9**) ¹H NMR: 7.12–7.39 m (9H, Ar-H), 6.54 s (1H, Ar-H), 3.84 s (2H, Ind-CH₂), 3.30 s (2H, CH₂). GC/MS: m/z 206 M^{+.} (35), 129 M – C₆H₅ (21), 115 M – C₇H₇ (23), 91 benzyl (100).

(10) ¹H NMR: 7.10–7.36 m (9H, Ar-H), 6.54 s (1H, Ar-H), 3.32 s (2H, Ind-CH₂), 2.78–2.97 m (4H, CH₂). GC/MS: m/z 220 M⁺. (15), 129 M – C₇H₇ (100).

3.7.5. Synthesis of 1- and 2-disubstituted indene compounds **11** and **12**

A 2-substituted indene compound (5 mmol) was dissolved in diethylether (100 ml), and then n-butyl lithium (5 mmol, 2.5 M in hexane) was added. After stirring for four hours at room temperature, the lithium salt was filtered and washed to remove traces of unreacted n-butyl lithium. The salt was then diluted in diethylether and allylbromide respectively methyliodide (6 mmol) was added. The mixture was then stirred for four hours. The solvent diethylether was evaporated, toluene was added and the solution was filtered over sodium sulfate. The solvent was again removed. Yield: 45%. (11) ¹H NMR: 7.55 d (2H, Ar-H), 7.44 t (2H, Ar-H), 7.39 d (2H, Ar-H), 7.25-7.31 m (2H, Ar-H), 7.19-7.24 m (1H, Ar-H), 7.09 s (1H, Ar-H), 3.93 q (1H, Ind-H), 1.35 dd (3H, CH₃). ¹³C NMR: 152.5, 149.5, 143.5, 135.4 (Cq), 128.6 (2C), 127.3, 126.8 (2C), 126.7, 125.8, 124.8, 122.8, 121.0 (Ar-CH), 44.0 (Ind-CH), 17.2 (CH₃). MS: m/z 206 M^{+.} (100), 191 M - CH₃ (77), 129 M -C₆H₅ (18).

(**12**) GC/MS: *m*/*z* 232 M⁺ (30), 191 M – C₃H₅ (100).

3.7.6. Synthesis of 1-, 2- and 3-trisubstituted indene compounds 13 and 14

A 2-substituted indene compound (5 mmol) was dissolved in diethylether (100 ml), and then treated with n-butyl lithium (5 mmol, 2.5 M in hexane). After stirring over night at room temperature, allylbromide respectively methyliodide (6 mmol) was added and the mixture was again stirred for four hours. The solvent was evaporated. Toluene was added and the solution was filtered

over sodium sulfate. The solvent was again removed. Yield: 58%. (**13**) ¹H NMR: 7.29–7.04 m (9H, Ar-H), 4.26 q (1H, Ind-H), 2.12 s (2H, CH₂), 1.54 d (3H, CH₂), 1.53 s (3H, CH₃). GC/MS: m/z 234 M⁺. (21), 219 M – CH₃ (10), 204 M – 2 CH₃ (11), 129 M – CH₃ – C₇H₇ (15), 115 Indenyl (8), 105 M – 2 CH₃ – C₁₀H₁₂ (100).

(14) GC/MS: $m/z 286 \text{ M}^+$ (4), 245 M – C₃H₅ (100), 217 M – C₃H₅ – C₂H₄ (52), 203 M – 2 C₃H₅ (90), 167 M – C₃H₅ – C₆H₅ (24), 141 M – C₃H₅ – C₂H₄ – C₆H₅ (87).

3.7.7. Synthesis of the bis(indenyl) zirconium complexes 15 and 16

To the indenyl derivatives 12 respectively 13 (5.44 mmol), dissolved in 50 ml diethylether, n-butyllithium (5.44 mmol, 2.5 M in hexane) was added at -78 °C. The reaction mixture was stirred over night at room temperature. Then indenyl zirconium trichloride (5.44 mmol) was added at -78 °C. The mixture was stirred for four more hours and then the solvent was removed. The residue was extracted with toluene and filtered over sodium sulfate. The filtrate was evaporated and complexes 15 and 16 were obtained after crystallization at -25 °C. Yield: 36-42%. (15) ¹H NMR: 7.54-7.63 m (2H, Ar-H), 7.51 d (1H, Ar-H), 7.37-7.47 m (5H, Ar-H), 7.32-7.36 m (1H, Ar-H), 7.22-7.30 m (2H, Ar-H), 7.12-7.21 m (2H, Ar-H), 7.02-7.11 m (1H, Ar-H), 6.38 s (1H, Ar-H), 6.26 t (1H, Ar-H), 6.14-6.19 m (1H, Ar-H), 5.72-5.83 m (1H, -CH=), 4.73-4.92 dd (2H,=CH₂), 3.76-3.81 m (1H, Ind-CH-Allyl), 1.48-1.90 m (2H, CH₂). ¹³C NMR: 134.2, 133.9, 129.3, 126.8, 123.8, 119.2 (C_q), 116.0 (=CH₂), 135.2, 128.8, 128.5, 128.2, 126.5, 126.4, 126.3, 126.2, 125.9, 125.4, 125.0, 124.4, 124.3, 120.8, 104.9, 104.2, 104.1 (Ar-CH), 99.9 (=CH), 30.9 (CH₂). MS: m/z 508 M⁺ (2), 393 M - 2 Cl - C₃H₅ (25), 355 M - Ind - Cl (6), 277 M - Ind - C₃H₅ - 2 Cl (15), 232 M – IndZrCl₂ (45), 191 M – IndZrCl₂ – C₃H₅ (100). Elemental analyses: Found: C, 63.3; H, 3.85. Calc: C, 63.8; H, 4.38.

(**16**) ¹H NMR: 7.54–7.58 dd (1H, Ar-H), 7.43–7.49 dd (1H, Ar-H), 7.32–7.41 m (2H, Ar-H), 7.18–7.24 m (4H, Ar-H), 7.10–7.15 m (3H, Ar-H), 7.02–7.08 m (2H, Ar-H), 6.89–6.98 m (2H, Ar-H), 6.78–6.84 m (1H, Ar-H), 2.87 s (2H, CH₂), 0.82 s (3H, CH₃), 0.79 s (3H, CH₃). ¹³C NMR: 149.9, 146.1, 145.4, 145.1, 142.8, 141.7, 126.8, 114.7 (C_q), 134.1, 128.5, 128.4, 128.3, 126.3, 126.1, 126.5, 125.8, 125.4, 125.0, 124.6, 124.0, 122.2, 120.9, 118.4, 104.1 (Ar-CH), 29.7 (CH₂), 14.1 (2C) (CH₃). MS: m/z 512 M⁺ (0), 437 M – 2 Cl (5), 397 M – Ind (6), 345 M – Ind – Cl – CH₃ (4), 308 M – Ind – 2 Cl – CH₃ (8), 233 M – IndZrCl₂ (32), 218 M – IndZrCl₂ – CH₃ (100), 203 M – IndZrCl₂ – 2 CH₃ (26), 127 M – IndZrCl₂ – C₇H₇ – CH₃ (18). Elemental analyses: Found: C, 63.9; H, 4.49. Calc: C, 63.5; H, 4.74.

3.7.8. NMR and elemental analysis data for complex 17

To 4-methyl-7-(2-phenylpropylyl)-indene, dissolved in 50 ml diethylether, an equivalent of n-butyllithium was added at -78 °C. The reaction mixture was stirred over night at room temperature. Then an equivalent of 2-(2-phenylethyl)-indenyl zirconium trichloride was added at -78 °C. The mixture was stirred for four more hours and then the solvent was removed. The residue was extracted with toluene and filtered over sodium sulfate. The filtrate was evaporated and the complexes **15** and **16** were obtained after crystallization at -25 °C.

¹H NMR: 7.62 t (2H, Ar-H), 7.20–7.33 m (9H, Ar-H), 7.09 d (3H, Ar-H), 6.92 s (2H, Ar-H), 6.20 s (1H, Ar-H), 6.14 s (1H, Ar-H), 5.86 d (1H, Ar-H), 5.77 d (1H, Ar-H), 5.71 d (1H, Ar-H), 2.90–2.96 m (2H, CH₂), 2.79–2.85 m (2H, CH₂), 2.59–2.74 m (4H, CH₂), 2.31 s (3H, CH₃), 1.96 s (2H, CH₂). ¹³C NMR: 143.5, 142.2, 141.1, 135.6, 132.1, 129.2, 129.2, 125.2, 125.2 (C_q), 128.5 (2C), 128.4 (2C), 128.33, 128.26 (4C), 126.2, 126.0, 125.7, 125.31 (2C), 125.27 (2C), 115.6, 105.6, 103.8, 103.3, 103.0 (Ar-CH), 36.2, 35.7, 33.7, 32.2, 30.4 (CH₂), 18.9 (CH₃). Elemental analyses: Found: C, 69.5; H, 5.68. Calc: C, 68.8; H, 5.45.

3.7.9. Polymerisation of ethylene with the bis(indenyl) zirconium complexes **15–17**

The corresponding zirconium complex (1-5 mg) was dissolved in 5 ml of toluene. Then methylaluminoxane (MAO, 30% in toluene, Zr:Al ratio = 1:2500) was added to the solution and filled into a flask with 250 ml of n-pentane. A 1l autoclave was evacuated and filled with argon several times and the catalyst mixture was added. The mixture was then stirred for 1 hour at 60 °C with an ethylene pressure of 10 bar. The ethylene pressure was released and after cooling to room temperature the polymer mixture was taken out of the reactor. The obtained polymer was washed with hydrochloric acid, water and acetone and it was finally dried in vacuo.

3.7.10. Copolymerisation of ethylene and 1-hexene with the bis (indenyl) zirconium complexes **15–17**

The corresponding zirconium complex (1-5 mg) was dissolved in 5 ml of toluene. Then methylaluminoxane (MAO, 30% in toluene) was added to the solution to obtain an Zr:Al ratio of 1:2500. The mixture was filled into a flask containing 250 ml of *n*-pentane. The 1 l autoclave was evacuated and filled with argon several times and the catalyst mixture was added. At the same time, the feed of 1-hexene was opened. 1-Hexene was added with a constant flow of 20 g/h – regulated by an electromagnetic valve. The mixture was then stirred for 1 h at 60 °C under an ethylene pressure of 10 bar. After stopping the reaction, the remaining ethylene pressure was released and the polymer mixture was removed from the reactor. The obtained polymer was washed with hydrochloric acid, water and acetone and dried in vacuo.

4. Conclusions

The goal of this work was the synthesis of new metallocene complexes and to test their behaviour in ethylene/1-hexene copolymerisation reactions. Three different routes for the preparation of 2-substituted indenyl compounds have been investigated. The modified Grignard reaction applying cerium trichloride to obtain tri-substituted indene derivatives was the most successful synthesis route. Several ways for the synthesis of dissymmetric bis(indenyl) zirconium complexes were examined and the obtained complexes were active both in homogeneous ethylene polymerisation and ethylene/1-hexene copolymerisation. The comparison of the obtained homo- and copolymers showed clear differences of the polymer properties. The copolymers have lower crystallinities and lower melting points than the ethylene homopolymers and are therefore useful for industrial processing.

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