Diastereomeric amido functionalized *ansa* half-sandwich complexes of titanium and zirconium as catalyst precursors for ethylene polymerization to give resins with bimodal molecular weight distributions

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Abstract

A total of 20 diastereomeric amido functionalized *ansa* half-sandwich dichloride complexes of titanium and zirconium have been prepared and characterized. All complexes were used as catalyst precursors for ethylene polymerization. Since such catalysts consist of diastereomers they have the potential to produce resins with a bimodal molecular weight distribution. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Group IV metal; *Ansa* half-sandwich complexes; Ethylene polymerization; Homogeneous polymerization; Bimodal polyethylene

1. Introduction

Since the discovery of amido functionalized *ansa* half-sandwich complexes of titanium in 1990 [1] these compounds gained widespread importance as catalysts for the polymerization of olefins. Due to their good copolymerization properties [2–6] and their ability to produce high molecular weight linear low density polyethylene [7] (LLDPE) the commercial value of *ansa*-amido catalysts increases [8–28]
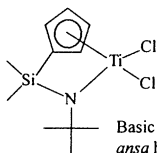
Basic structure of amido
ansa half-sandwich **complexes**

So far all published *ansa* half-sandwich complexes possess a dimethylsilylene unit as a bridge between the nitrogen atom and the aromatic ligand. It was the intention to substitute one methyl substituent at the silicon atom in order to generate a center of chirality. The activation of such catalyst precursors with methylaluminoxane (MAO) should produce diastereomers with individual catalytic properties. The results of such investigations are reported.

2. Results and discussion

2.1. Preparation of the complexes

The desired mono substituted cyclopentadienyl and indenyl complexes were prepared according to the following reaction Scheme 1.

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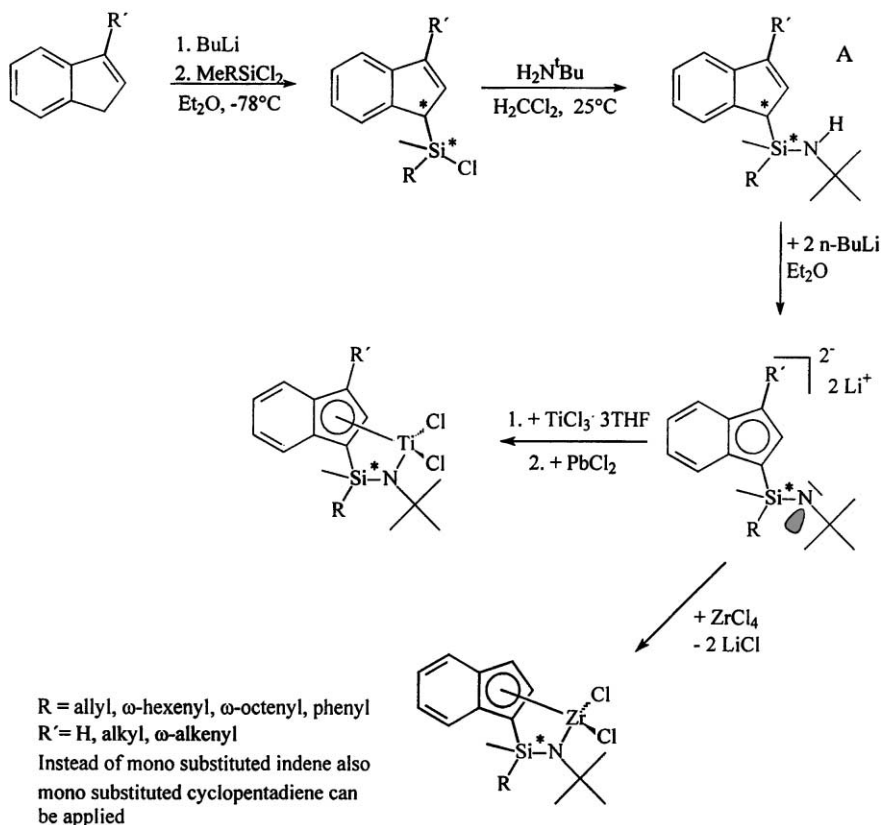
Scheme 1. Synthesis of diastereomeric amido functionalized *ansa* half-sandwich complexes.

The following complexes (diastereomers) were synthesized according to this method:

Ligand precursors containing four different substituents on the bridging silicon atom possess two neighbouring chiral centers and consist of two diastereomers. During the complexation step, two diastereomeric half-sandwich compounds are formed (Figs. 1 and 2).

In the indenyl series the *Z*-form is present when the substituent *R'* is in the spatial proximity of the six-membered ring of the indenyl structure. The *E*-form exists when the substituent points away from the six-membered ring. *Z*- and *E*-form possess a mirror image each with different sense of rotation of the substituents on the silicon atom. The structure with clockwise decreasing priority of the substituents is described as *R*-form, the one with increasing priority as *S*-form [29]. Both mirror images do not coincide. Therefore, they are enantiomers. Despite the fact that

only one optically active center is present (Si atom), four different stereoisomers can be distinguished. Due to the existence of these four stereoisomeric amido half-sandwich complexes that are formed "automatically" in the complexation step, four different catalysts for olefin polymerization are obtained after the activation with MAO.

Two isomers produce the same polyolefin since the *R*-form is the mirror image of the corresponding *S*-form. The *E*- and *Z*-forms, however, exhibit completely different orientations of both equatorial substituents on the silicon atom. Therefore, they are different catalysts and the *E*- and *Z*-forms produce individual polyethylenes that are different from each other. Thus, the *E*-(*R*)-form would produce exactly the same polyethylene as the *E*-(*S*)-form and the *Z*-(*R*)-form the same polyolefin as the *Z*-(*S*)-form. Consequently, such a catalyst is expected to produce a bimodal polymer.
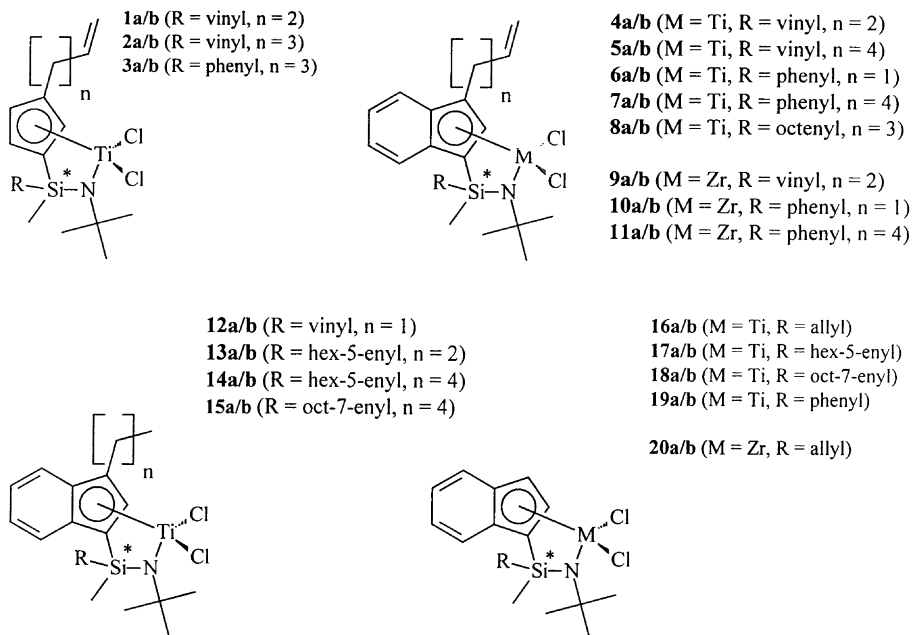
1a/b (R = vinyl, n = 2)
2a/b (R = vinyl, n = 3)
3a/b (R = phenyl, n = 3)

4a/b (M = Ti, R = vinyl, n = 2)
5a/b (M = Ti, R = vinyl, n = 4)
6a/b (M = Ti, R = phenyl, n = 1)
7a/b (M = Ti, R = phenyl, n = 4)
8a/b (M = Ti, R = octenyl, n = 3)

9a/b (M = Zr, R = vinyl, n = 2)
10a/b (M = Zr, R = phenyl, n = 1)
11a/b (M = Zr, R = phenyl, n = 4)

12a/b (R = vinyl, n = 1)
13a/b (R = hex-5-enyl, n = 2)
14a/b (R = hex-5-enyl, n = 4)
15a/b (R = oct-7-enyl, n = 4)

16a/b (M = Ti, R = allyl)
17a/b (M = Ti, R = hex-5-enyl)
18a/b (M = Ti, R = oct-7-enyl)
19a/b (M = Ti, R = phenyl)

20a/b (M = Zr, R = allyl)

Fig. 1. Overview of the diastereomeric amido functionalized *ansa* half-sandwich complexes. Only one isomer of the diastereomers is shown.

E-(S)-form   **E-(R)**-form

Z-(R)-form   **Z-(S)**-form

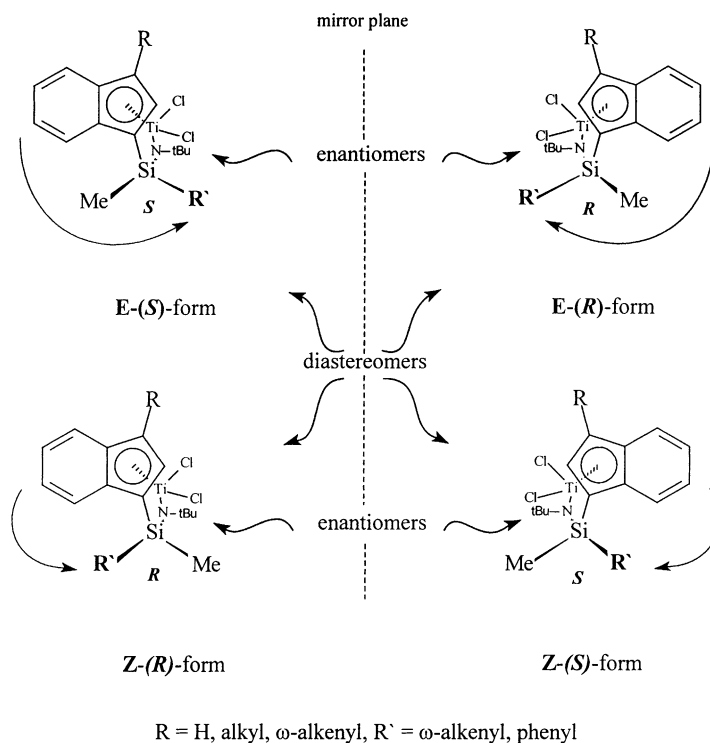R = H, alkyl, ω-alkenyl, R` = ω-alkenyl, phenyl

Fig. 2. Amido functionalized *ansa* half-sandwich complexes with four different substituents on the silicon atom consist of four stereoisomers.

2.2. NMR spectroscopic characterization of 5a/b

In the ^{1}H NMR spectrum of complex **5a/b** (Fig. 3), two sets of signal groups reveal the existence of two isomers. The best separation of the signals for the protons of both diastereomers is achieved when they are in a different environment as the methyl groups on the silicon atoms ($\delta = 0.84$ and 0.66 ppm). The aromatic proton 9 gives a singlet for each diastereomer ($\delta = 6.56$ and 6.44 ppm). The two signal sets of the vinyl group are in the region of $\delta = 6.69$–6.03 ppm. They appear as overlapping resonance signals of two ABX-spin systems. The effect of the asymmetric center on neighbouring atoms is obvious for protons 20 and 23. While the doublet of the protons 20 for both diastereomers overlap at $\delta = 7.54$ ppm (the signal has the double intensity), proton 23 exhibits separated resonances at $\delta = 7.92$ and 7.76 ppm due to the different spatial influence of the vinyl group for both diastereomers. The signals of the hex-5-enyl group exhibit for the E- and Z-form only marginal differences in their chemical shifts. However, they are visible as overlapping coupling pattern.

In the J-modulated ^{13}C NMR spectrum of compound **5a/b** (Fig. 4) almost all signals appear doubled. Especially the signals for the methyl group 1 on the silicon atom and the signals for the CH-groups of both vinyl groups 2 show two resonances each. A closer examination of the sections for the methyl groups 12, 13 and 14 from the J-modulated 75.47 MHz ^{13}C NMR spectrum proves that even those signals are represented twice. The resonance signals for the quaternary carbon atoms of the indenylidene ring also appear as a double set.

According to the signal intensities from the ^{1}H and ^{13}C NMR spectra, both diastereomers exist in the same ratio.

A 2D ^{13}C, ^{1}H correlation spectrum [HXCOBI] of complex **5a/b** (Fig. 5) confirms the assignment of the signals made from the one-dimensional ^{1}H and ^{13}C NMR spectra. The F1 projection is the positive, internal representation of the 2D spectrum. The F2 projection is the external projection from the one-dimensional ^{1}H NMR spectrum. Since the splitting pattern is so complex, an additional internal, positive projection from the 2D NMR spectrum (low

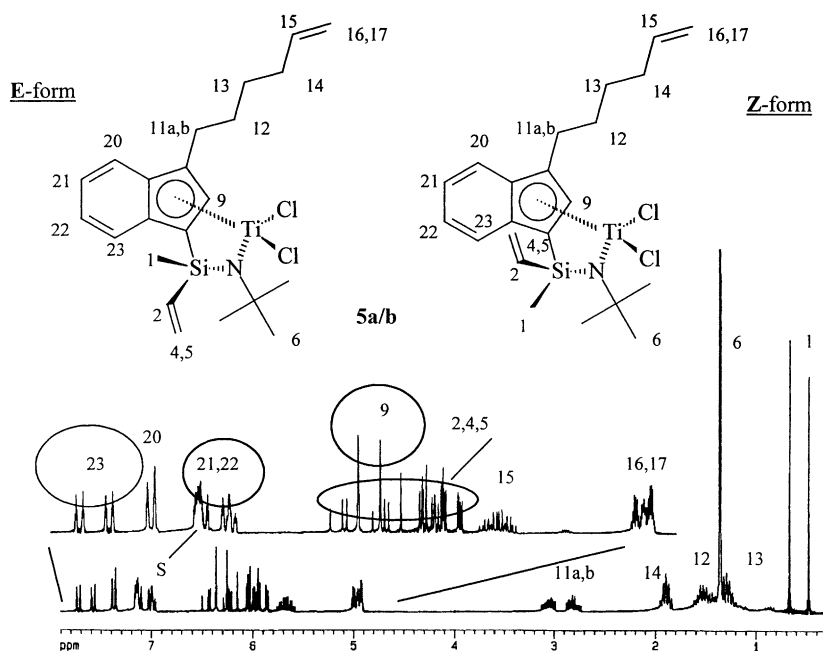Fig. 3. ^{1}H NMR spectrum of **5a/b** (25°C, C_6D_6). The aryl area becomes very complex due to overlapping of the signals of both diastereomers. The methyl groups (1) give clearly separated signals. S: C_6D_6.
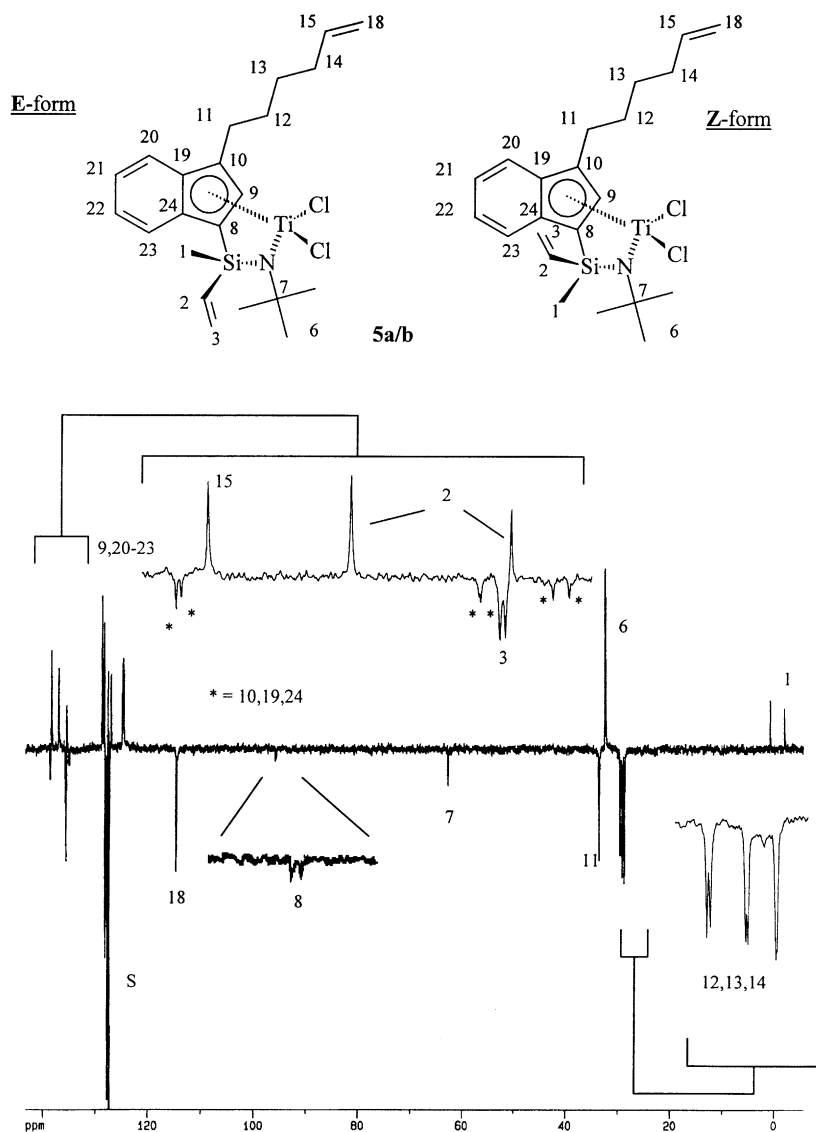
Fig. 4. *J*-modulated 62.69 MHz $^{13}C\{^1H\}$ NMR spectrum of **5a/b** (25°C, C_6D_6). Almost all signals appear doubled due to two diastereomers. The enlarged partial spectra are derived from sections of the *J*-modulated 75.47 MHz ^{13}C NMR spectrum (25°C, C_6D_6). S: C_6D_6.

resolution ^1H $\{^1H\}$ NMR spectrum) is shown for better assignment of the centers of the signals on the F2 axis to the cross signals.

Three resonance groups are found of which group I is formed by two signal groups with four cross signals each that are attributed to the aromatic CH-groups of the six-membered ring of both diastereomers.

Group II also consists of a double set of signals corresponding to the CH-correlations in the vinyl groups of the *E*- and *Z*-form.

Group III confirms the assignment of both strongest signals in the vinyl group area of the ^1H NMR spectrum to the corresponding carbons 9 of both diastereomers.
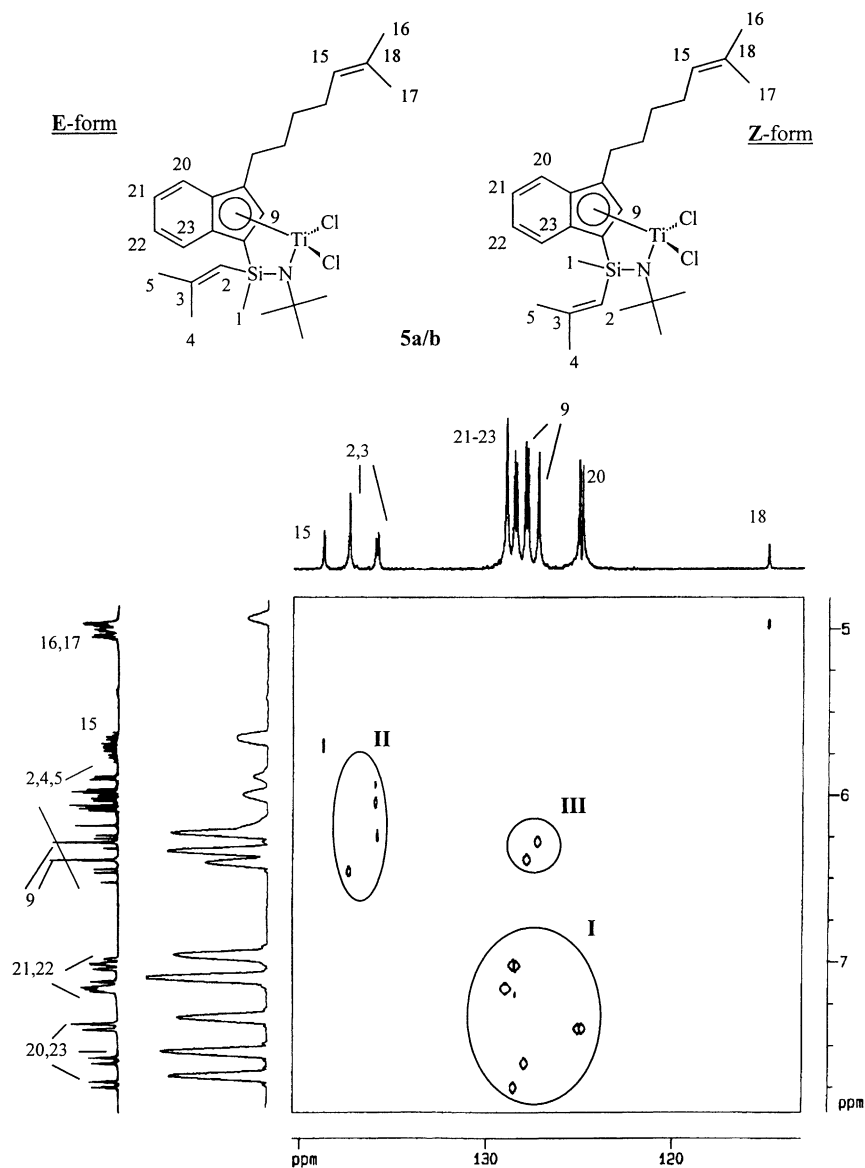
Fig. 5. 2D ^{1}H, ^{13}C NMR correlation spectrum of **5a/b**. The four cross signals for both diastereotop vinyl groups and the cross signals for the six-membered ring of the indenylidene ligand are well resolved.

The ^{29}Si and the ^{15}N NMR spectrum also show differences in the chemical shifts of both diastereomers. These nuclei were recorded using an INEPTRD-pulse sequence. $^2J(^{29}Si,^1H) = 7.5\,Hz$ was selected as exciting coupling for the polarization transfer of [29]Si and $^3J(^{15}N,^1H) = 2.5\,Hz$ for [15]N.

2.3. ^{29}Si NMR spectroscopy as a probe for the reaction control

The ^{29}Si NMR spectroscopy plays a decisive role for the characterization of the amido functionalized *ansa* half-sandwich complexes as probe for

the reaction control. The chemical shift of the ^{29}Si NMR signal is dependent on two essential factors. On one hand, the silicon shift is influenced by the angles formed by the substituents surrounding the silicon atom. However, these angles remain almost constant in amido functionalized *ansa* half-sandwich complexes as it is described in previous publications [30–33]. Therefore, the chemical shift of the ^{29}Si NMR signal does not vary significantly within this compound type. The substituents on the silicon atom, however, have a substantial impact on the chemical shift of the ^{29}Si NMR signal due to their shielding or deshielding effect.

For compounds containing two methyl groups on the bridging silicon atom, the ^{29}Si NMR signal appears at $\delta = -20$ ppm (± 1 ppm) for all synthesized half-sandwich complexes. If one of the methyl groups is substituted by a vinyl group, the ^{29}Si NMR Signal is shifted to lower field by 11 ppm. The phenyl group has less shielding effect (9 ppm to lower field). The chemical shift moves to lower field by about 16 ppm when finally both methyl groups are substituted by two phenyl groups. In contrast, the ^{29}Si NMR signal of the synthesized complexes is neither influenced by the substituents on the aromatic system, nor by the aromatic system itself (cyclopentadienylidene-, indenylidene-, fluorenylidene ligand) nor by the substituent on the nitrogen atom as long as the transition metal compounds of group IV are used. Hence, the chemical shift of the ^{29}Si NMR signal is predictable for each amido functionalized *ansa* half-sandwich complex as long as both substituents of the silicon atom are known. Therefore, besides ^{1}H NMR spectroscopy, the ^{29}Si NMR spectroscopy serves as an important tool for the reaction control during the synthesis of these compounds.

2.4. Homogeneous ethylene polymerization

All complexes were activated with MAO and tested for homogeneous ethylene polymerization. The high temperature gel permeation showed a bimodal molecular weight distribution for all resins. Only the resins obtained from the cyclopentadienyl catalysts were monomodal but had a broad molecular weight distribution.

The diastereomeric complex **13a/b** produces bimodal polyethylene under homogeneous catalysis conditions. The four-fold differently substituted silicon atom and the asymmetric indenylidene ring (the indenylidene ring does not contain a plane of symmetry) are the reason for the existence of two diastereomers. Each of the diastereomers produces a specific polymer. The molecular weight distribution for both components of the polymer is indicated by dotted Gauss curves in Figs. 6–9. The low molecular component of the polymer mixture has a molecular
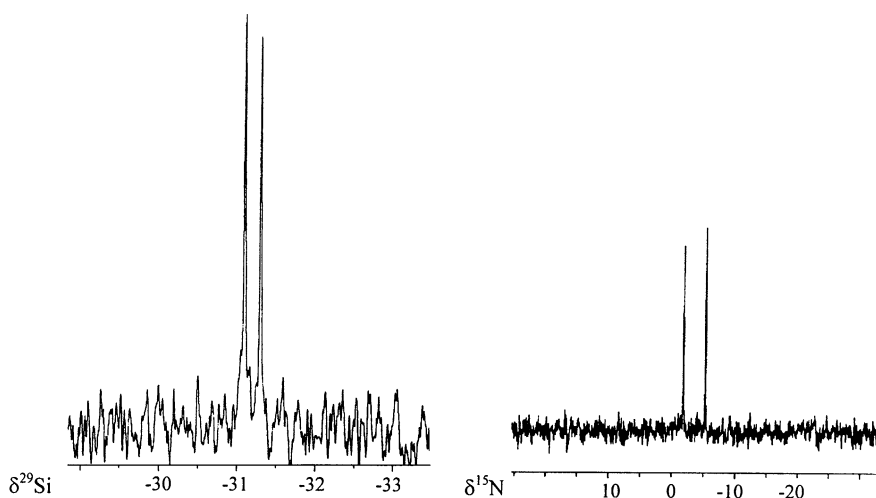

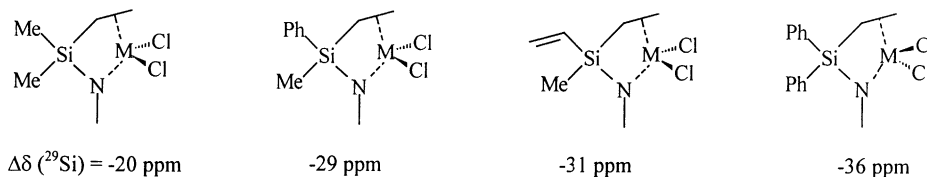Fig. 6. 49.69 MHz ^{29}Si INEPTRD NMR spectrum and 25.35 MHz ^{15}N INEPTRD NMR spectrum of **5a/b**.

Fig. 7. Impact of the substituents on the bridging atom on the chemical shift of the ^{29}Si NMR signal. M: group IV metal.

weight $\bar{M}_w$ of ca. 570,000 g/mol. The number average of the high molecular portion is found at $\bar{M}_w \approx 1,600,000$ g/mol. The HT-GPC diagram is shown in Fig. 8.

Compound **l7a/b** only differs from **13a/b** by a missing propyl substituent in position 1 of the indenylidene ligand. A substituent on the indenylidene ring is not required for the asymmetry of the complex since the indenylidene ligand itself is asymmetric (does not exhibit a plane of symmetry). For the same reasons as for complex **l3a/b** the compound consists of two diastereomers. Again, the asymmetric indenylidene ligand in combination with the four-fold differently substituted

silicon atom that forms a chiral center is responsible for this effect.

3. Experimental

3.1. General working techniques

All the work was routinely carried out using Schlenk technique. Dried and purified argon was used as inert gas. The solvents used (toluene, *n*-pentane, diethylether, THF) were purified in reflux distills under argon atmosphere with Na/K alloy. Ether was additionally distilled over lithium aluminum
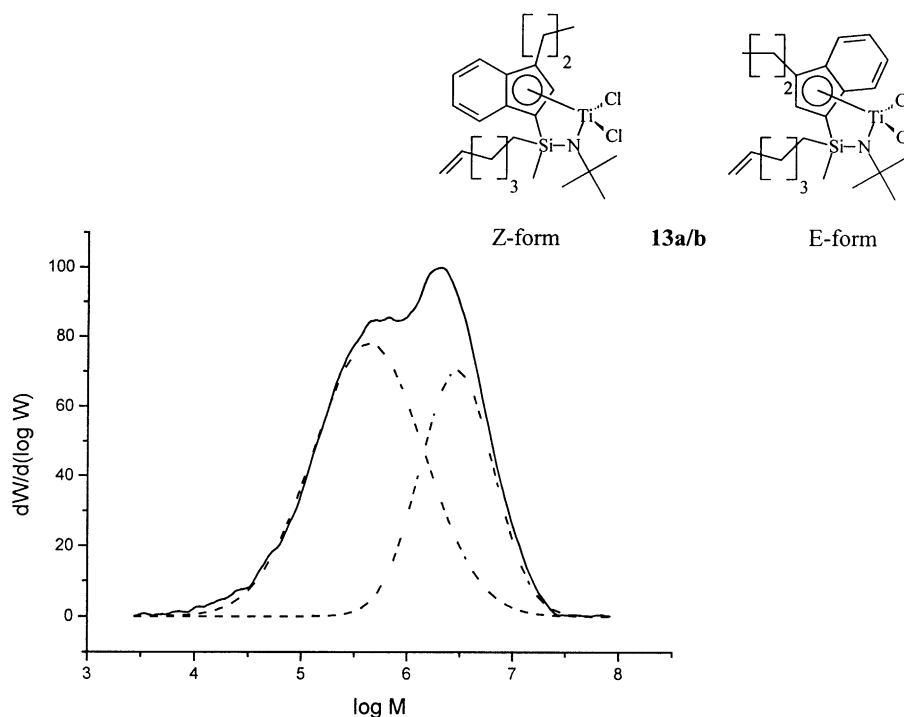

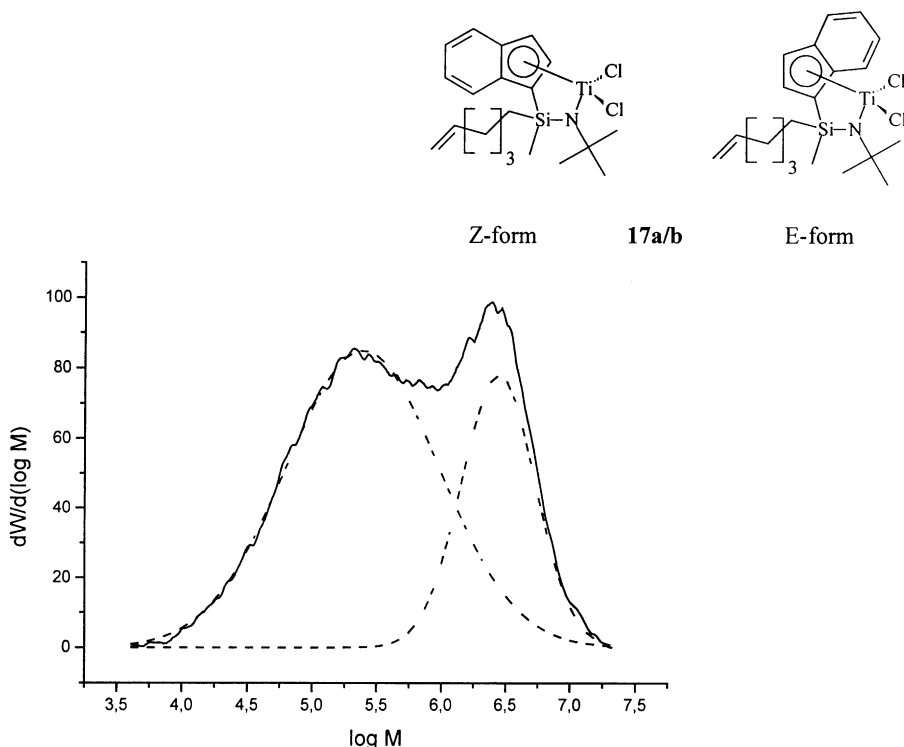Fig. 8. HT-GPC diagram of the polyethylene obtained from **l3a/b**.

Z-form   **17a/b**   E-form

Fig. 9. HT-GPC diagram of the polyethylene obtained from **17a/b**.

hydride. Methylene chloride was dried with CaH_2. Deuterated solvents, such as deuterochloroform-d_1 and benzene-d_6 were dried over molecular sieves (300 pm), degassed and stored under inert gas atmosphere. Dry ice/isopropanol cooling mixtures ($-78°C$) were used to cool the reactions.

Prior to use commercial indene was distilled and stored at $-30°C$. Cyclopentadiene was freshly obtained by distillation of the dimer. MAO was supplied by Witco Company, Bergkamen, as 30% solution in toluene. All other starting materials are commercially available and were used without further purification.

3.2. NMR spectroscopy

The spectrometers Jeol FX 90Q, Jeol JNM-EX 270 E, Bruker ARX 250, Bruker AC 300 and Bruker DRX 500 were available for the recording of NMR spectra. The organometallic compounds were filled under argon and measured at $25°C$. The chemical shifts in ^1H NMR spectra are referred to the residual proton sig-

nal of the solvent ($\delta = 7.24$ ppm for chloroform, $\delta = 7.15$ ppm for benzene) and in ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for chloroform-d_1, $\delta = 128.0$ ppm for benzene-d_6). Tetramethylsilane ($\delta = 0.0$) was used for ^{29}Si NMR spectra and $MeNO_2$ ($\delta = 0.0$) for ^{15}N NMR spectra as external standard.

3.3. Gas chromatography

Gas chromatograms were recorded using a Perkin–Elmer Auto System gas chromatograph with flame ionization detector (FID) and helium as carrier gas (1 ml/min).

Temperature program.

Starting phase: 3 min at $50°C$.
Heating phase: $5°C$/min (15 min).
Plateau phase: $310°C$ (15 min).

3.4. Differential scanning calorimetry (DSC)

The melting points of the polymer samples were determined using a Perkin–Elmer DSC-200 instru-

ment. Therefore, 3–5 mg each of the dried polymer were fused into standard aluminum pans and measured using the following temperature program, first heating phase (20 K/min) from 320 to 470 K, cooling phase (−50 K/min) to 320 K, second heating phase (10 K/min) from 320 to 470 K. The peak maximum of the second heating curve was indicated as melting point.

3.5. High temperature gel permeation chromatography (HAT-GPC)

The polymers were measured with a HT-GPC 15°C apparatus of Millipore Waters Company. Four successive columns filled with cross-linked polystyrene were used for separation. The pore diameter of the individual columns was 500, 1000, 10,000 and 100,000 Å. The detection was refractometric, using a RI Waters 401 refractometer. Degassed 1,2,4-trichlorobenzene was used as eluent (flow rate 1 ml/min). The polymer samples were dissolved in boiling 1,2,4-trichlorobenzene. The measurements were conducted at 150°C. The apparatus was calibrated using a polystyrene standard.

3.6. General synthesis procedure for ω-alkenylmethyldichlorosilane derivatives

0.5 mol of the corresponding 1,ω-alkadiene was charged into a three necked flask equipped with reflux condenser, thermometer and dropping funnel at room temperature. 300 mg bis-[(2-Phenylethyn-l-yl)-methylphenylcarbinol]platinu (0) [34] were dissolved. About 31.09 ml (0.3 mol) recondensed dichloromethylsilane were added dropwise under slight reflux. The addition of methyl dichlorosilane was controlled in a way that the temperature did not exceed 45°C. After the addition was finished, the mixture was stirred for another 60 min at room temperature. The subsequent distillation produced the respective product in 50–60% yields.

3.7. Synthesis procedure for allylmethyldichlorosilane

In a three necked flask, cooled to 0°C, equipped with a dropping funnel, reflux condenser and pres-

sure relief valve, 5 g (206 mmol) magnesium turnings were slurried in 100 ml diethylether. Then 24.9 g (206 mmol) allylbromide in 50 ml diethylether were added dropwise. The reaction mixture was stirred for 3 h at room temperature. At 0°C, the generated allylmagnesiumbromide was added dropwise to 32.0 ml (300 mmol) methyltrichiorosilane using a dropping funnel and stirred for 3 h. Allylmethyldichlorosilane was directly distilled from the reaction solution.

3.8. General synthesis procedure for substituted cyclopentadienyl alkenyl methyl chlorosilane derivatives

At −78°C, 41.5 mmol (26.0 ml) *n*-butyllithium were added dropwise to 41.5 mmol substituted cyclcopentadiene in 150 ml diethylether. The solution was stirred for 8 h. The solvent was removed in vacuo.

The lithium salt was added in portions to 83 mmol alkenylmethyldichlorosilane in 200 ml diethylether at −78°C within 30 min. The solution was stirred for another 12 h. The suspension was filtered over sodium sulfate, the solvent was evaporated and the obtained yellow liquid was distilled in vacuo. Yields 59–80%.

3.9. General synthesis procedure for substituted indenylchlorosilane derivatives

80 mmol of the corresponding indene derivative was dissolved in 150 ml diethylether and cooled to −78°C. The equimolar amount of *n*-butyllithium was added dropwise using a syringe and stirred for 4 h at room temperature. The lithium salt was added to the equimolar amount of the corresponding dichlorosilane compound in 100 ml diethylether at −78°C and the solution was stirred for 12 h. The reaction solution was filtered over sodium sulfate and the solvent was removed. The product was obtained in 80–96% yields.

3.10. General synthesis procedure for cyclopentadienyl ligand precursors

39.2 mmol of the corresponding substituted cyclopentadienyl alkylmethylchlorosilane in 200 ml pentane was mixed at 0°C with 98 mmol (10.3 ml)

Table 1
NMR data of complexes 1–20[a]

Complex	^{1}H NMR	^{13}C NMR	^{29}Si NMR
la/b	6.47 (m), 5.98 (m), 5.86 (m), 5.66 (m), 5.52 (m), 4.88 (m), 2.47 (m), 1.81(m), 1.32 (s, 9H), 1.33 (s, 9H), 0.76 (m), 0.25 (s, 3H), 0.23 (s, 3H)	C_q: 145.6, 109.9, 63.8; CH: 137.4, 134.9, 134.8, 127.0, 126.6, 126.0, 125.6, 125.5, 125.4; CH_2: 135.9, 115.7, 34.0, 30.1; CH_3: 32.7, −2.3, −2.5	−30.6
2a/b	6.40 (m), 5.93 (m), 5.87 (m), 5.45 (m), 4.56 (m), 2.45 (m), 1.77 (m), 1.30 (s, 9H), 1.35 (s, 9H), 1.21 (m), 0.45 (m), 0.20 (s, 3H), 0.15 (s, 3H)	C_q: 146.2, 108.0, 3.8; CH: 138.2, 134.9, 134.8, 127.1, 126.6, 125.9, 125.4, 125.3; CH_2: 135.9, 115.2, 33.6, 30.2, 26.9; CH_3: 32.7, 32.6, −2.3, −3.0	−30.6
3a/b	6.60 (m), 5.99 (m), 5.86 (m), 5.44 (m), 5.18 (m), 4.62 (m), 3.99 (m), 1.56 (m), 0.94 (m), 0.91 (s, 9H), 0.76 (m), 0.23 (s, 3H), 0.19 (s, 3H)	C_q: 146.1, 135.1, 103.4, 62.1; CH: 138.1, 135.1, 130.8, 128.5, 126.8, 126.5, 126.1; CH_2: 115.1, 33.6, 30.1, 29.6; CH_3: 32.8, −1.9, −2.8	−28.9, −29.9
4a/b	7.75 (d, 1H) [8.5], 7.61 (d, 1H) [8.5], 7.35 (m, 2H), 7.11 (m, 2H), 7.04 (m, 2H), 6.38 (s, 1H), 6.26 (s, 1H), 6.01 (m, 2H), 5.96 (m, 2H), 5.81 (m, 2H), 4.98 (m, 4H), 3.01 (m, 4H), 2.29 (m, 4H), 1.41 (s, 9H), 1.39 (m, 9H), 0.70 (s, 3H), 0.52 (s, 3H)	C_q: 146.2, 1.36.7, 135.1, 104.2, 60.2; CH: 137.4, 137.2, 135.8, 135.7, 128.9, 127.3, 124.9, 124.8; CH_2: 135.9, 115.8, 34.1, 28.8; CH_3: 33.0, 5.1, 2.1	⁻31.0, −31.2
5a/b	7.92 (d, 1H), 7.76 (d, 1H), 7.54 (d, 2H), 7.15 (m), 6.99 (m), 6.56 (s, 1H), 6.50 (m), 6.44 (s, 1H), 6.10 (m), 6.68 (m, 2H), 4.95 (m, 4H), 291 (m, 4H), 1.89 (m, 4H), 1.53 (m, 4H), 1.36 (s, 18H), 0.84 (s, 3H), 0.66 (s, 3H)	C_q: 138.9, 138.7, 135.9, 135.8, 135.4, 95.8, 95.5, 62.2; CH: 138.3, 137.0, 135.8, 128.6, 128.2, 127.5, 126.9, 124.7, 124.5; CH_2: 135.7, 114.5, 33.4, 29.4, 29.0, 28.6; CH_3: 32.3, 0.6, −2.1	−31.0, −31.3
6a/b	7.82 (m, 2H), 7.72 (d, 1H), [8.4] 7.48 (d, 1H) [8.4], 7.32 (m), 7.10 (m), 6.37 (s, 1H), 5.91 (m, 2H), 4.93 (m, 4H), 3.62 (m, 4H), 1.42 (s, 9H), 1.31 (s, 9H), 1.08 (s, 3H), 1.03 (s, 3H)	C_q: 136.l, 135.7, 134.7, 134.4, 94.6, 63.6; CH: 135.6, 135.2, 130.5, 128.7, 128.3, 128.0, 127.6, 127.5, 125.1; CH_2: 116.5, 25.1, 25.4; CH_3: 32.8, 32.5, 0.6	−29.2 (br)
7a/b	7.85 (d, 2H), 7.79 (d, 1H) [8.5], 7.50 (d, 1H) [8.5], 7.42 (m), 7.27 (m), 6.47 (s, 1H), 6.43 (m, 1H), 5.83 (m, 2H), 5.04 (m, 4H), 3.05 (m, 4H), 2.04 (m, 4H), 2.01 (m, 4H), 1.52 (s, 9H), 1.35 (s, 9H), 1.27 (m, 4H), 0.97 (s, 3H), 0.87 (s, 3H)	C_q:l37.l, 136.8, 132.0, 131.3, 93.0, 58.6; CH: 138.1, 135.4, 134.3, 130.4, 128.7, 126.1, 123.4, 123.1, 121.3; CH_2: 114.0, 113.2, 30.0, 29.1, 26.7, 25.1; CH_3: 33.1, 32.2, 1.0, −0.9	−29.3, −30.0
8a/b	7.79 (d, 1H) [8.5], 7.69 (d, 1H) [8.5], 7.39 (m), 7.29 (m), 6.43 (s, 1H), 6.32 (s, 1H), 5.87 (m, 2H), 5.07 (m, 4H), 3.09 (m, 4H), 2.05 (m), 1.50 (m), 1.42 (m), 1.26 (s, 9H), 1.12 (s, 9H), 0.49 (s, 3H), 0.44 (s, 3H)	C_q: 145.3, 145.2, 138.6, 138.4, 133.1, 96.5, 62.3; CH: 138.8, 138.6, 138.5, 137.8, 133.9, 128.7, 128.5, 127.6, 124.5, 123.4; CH_2: 117.7, 114.3, 114.2, 36.0, 35.7, 34.2, 33.6, 33.3, 29.8, 25.6, 24.4, 24.0, 17.8, 17.0, 13.7, 12.6;CH_3: 35.3, 32.3, −1.0, −1.5	−19.3, −19.8
9a/b	7.90 (d, 1H) [7.6], 7.74 (d, 1H) [7.6], 7.49 (d, 2H), 7.17 (m), 6.95 (m), 6.53 (s, 1H), 6.41 (s, 1H), 6.45 (m), 5.62 (m, 2H), 4.98 (m, 4H), 2.96 (m, 2H), 1.92 (m, 4H), 1.52 (m, 4H), 1.37 (s, 18H), 1.31 (m, 4H), 0.86 (s, 3H), 0.67 (s, 3H)	C_q: 138.5, 138.3, 135.5, 135.6, 135.2 95.5, 95.3, 62.0; CH: 138.1, 137.0, 135.3, 128.4, 128.0, 127.3, 126.7, 124.4, 124.3; CH_2: 135.8, 114.6, 33.2, 29.2, 29.1, 28.4; CH_3: 32.2, 0.5, −2.2	−31.0, −31.3
l0a/b	8.12 (m, 2H), 7.98 (d, 1H) [8.4], 7.78 (d, 1H) [8.4], 7.53 (m), 7.21 (m), 6.48 (s, 1H), 6.03 (m, 2H), 4.99 (m, 4H), 3.69 (m, 4H), 1.41 (s, 9H), 1.36 (s, 9H), 0.78 (s, 3H), 0.69 (s, 3H)	C_q: 138.1, 136.8, 135.3, 134.4, 94.9, 59.1; CH: 135.4, 134.7, 130.4, 128.1, 127.8, 126.7, 125.5, 127.5, 123.4; CH_2: 116.4, 32.6; CH_3: 33.5, 33.1, −0.4	−29.1, −29.8

Table 1 (*Continued*)

Complex	^{1}H NMR	^{13}C NMR	^{29}Si NMR
11a/b	7.95 (d, 2H), 7.85 (d, 1H) [8.5], 7.49 (d, 1H) [8.5], 7.40 (m), 7.24 (m), 6.52 (s, 1H), 6.49 (m, 1H), 5.86 (m, 2H), 5.14 (m, 4H), 3.41 (m, 4H), 2.93 (m, 4H), 2.03 (m, 4H), 1.52 (m, 4H), 1.47 (s, 9H), 1.43 (s, 9H), 1.10 (s, 3H), 0.87 (s, 3H)	C_q: 137.9, 137.1, 132.3, 131.2, 93.5, 59.1; CH: 138.4, 135.7, 134.1, 130.0, 128.2, 126.3, 124.1, 123.5, 122.4; CH_2: 114.2, 114.0, 30.0, 29.0, 27.8, 27.1; CH_3: 33.4, 32.9, 1.6, 0.0	−29.2, −29.8
12a/b	7.83 (d, 1H) [8.5], 7.63 (d, 1H) [8.5], 7.42 (d, 2H), 7.20 (m), 7.09 (m), 6.48 (s, 1H), 6.32 (s, 1H), 6.21 (m), 5.98 (s, 1H), 2.98 (m, 4H), 1.49 (s, 9H), 0.79 (s, 3H), 0.61 (s, 3H)	C_q: 137.3, 136.3, 134.5, 131.2, 84.2, 62.3; CH: 137.1, 128.2, 128.1, 127.7, 124.6, 124.5, 123.9; CH_2: 135.6, 135.5, 22.3; CH_3: 32.3, 13.7, 0.7, −4.1	−31.1, −30.6
13a/b	7.62 (m, 2H), 7.35 (d, 1H), 7.13 (m), 7.04 (m), 6.31 (s, 1H), 6.26 (s, 1H), 5.78 (m, 1H), 5.43 (m, 3H), 5.02 (m, 2H), 2.91 (m, 4H), 2.19 (m), 1.56 (m), 1.36 (s, 9H), 1.35 (s, 9H), 0.80 (m), 0.61 (s, 3H), 0.41 (s, 3H)	C_q: 138.8, 136.6, 135.5, 135.2, 95.9, 62.1; CH: 138.6, 130.8, 130.1, 129.9, 128.2, 127.1, 127.4, 124.8; CH_2: 114.8, 36.1, 33.5, 32.3, 32.3, 32.2, 31.0, 23.4; CH_3: 32.3, 13.9, 1.1, −0.6	−19.3, −19.8
14a/b	7.72 (m), 7.22 (m), 7.07 (m), 6.40 (s, 1H), 6.35 (s, 1H), 5.89 (m), 5.50 (m), 5.07 (m), 3.47 (m), 3.07 (m), 2.07 (m), 1.62 (m), 1.41 (s), 1.26 (m), 0.87 (m), 0.67 (s, 3H), 0.49 (s, 3H)	C_q: 139.0, 138.9, 136.4, 135.7, 135.4, 135.2, 114.8, 96.0, 62.5; CH: 139.1, 130.9, 128.7, 127.9, 127.5, 125.7, 124.7, 114.8; CH_2: 114.8, 33.6, 32.7, 32.4, 30.5, 30.0, 29.9, 28.0, 27.1, 23.7, 22.9, 22.6, 18.8, 18.0, 17.0; CH_3: 32.7, 32.4, 1.3, −1.4	−22.4, −23.7
15a/b	n.d.	n.d.	−19.3, −19.8
16a/b	7.68 (d, 1H) [8.4], 7.57 (d, 1H) [8.4], 7.33 (m), 7.10 (m), 6.99 (m), 6.41 (s, 1H), 6.30 (s, 1H), 5.89 (m, 2H), 5.11, (m, 4H), 3.59 (m, 4H), 1.45 (s, 9H), 1.40 (s, 9H), 0.62 (s, 3H), 0.41 (s, 3H)	C_q: 136.3, 136.0, 135.2, 14.4, 97.7, 97.5, 62.6; CH: 132.7, 132.1, 129.2, 128.6, 128.5, 127.8, 127.7, 126.5, 119.4; CH_2: 116.7, 116.1, 26.3, 24.8; CH_3: 32.3, 32.2, 0.8, −1.7	−22.6, −23.0
17a/b	7.62 (m), 7.52 (m), 7.37 (m), 7.23 (m), 7.04 (m), 6.38 (s, 1H), 5.83 (m), 5.07 (m), 3.66 (m), 2.07 (m), 1.50 (m), 1.39, (s), 1.15 (m), 0.93 (m), 0.65 (s, 3H), 0.42 (s, 3H)	C_q: 144.1, 135.9, 135.1, 134.2, 97.2, 96.3, 62.5; CH: 138.8, 138.5, 128.9, 128.4, 128.1, 127.7, 126.2, 124.6; CH_2: 114.6, 114.2, 33.7, 33.4, 32.5, 25.6, 25.4, 22.8, 22.6, 16.7; CH_3: 32.1, 1.1, −1.6	−18.7, −19.1
18a/b	7.60 (m), 7.50 (m), 7.33 (m), 7.19 (m), 7.06 (m), 6.40 (s, 1H), 5.84 (m), 5.09, (m), 3.62 (m), 3.12 (m), 2.12 (m), 1.52, (m), 1.52 (s), 1.16 (m), 0.94 (m), 0.68, (s, 3H), 0.41 (s, 3H)	C_q: 144 0, 136.3, 133.5, 134.1, 97.2, 96.7, 62.0; CH: 138.6, 138.3, 129.3, 128.1, 128.0, 127.4, 126.0, 124.5; CH_2: 114.3, 114.1, 33.8, 33.2, 32.4, 30.1, 29.8, 25.3, 25.2, 22.9, 22.7, 16.6; CH_3: 32.0, 0.8, −2.2	−18.6, −19.2
19a/b	7.76 (m), 7.33 (m), 7.30 (m), 7.25 (m), 7.06 (m), 6.43 (s, 1H), 6.00 (s, 1H), 1.46 (s, 9H), 1.42 (s, 9H), 1.36 (s, 3H), 0.72 (s, 3H)	n.d.	−28.7, −29.7
20a/b	7.84 (Am), 7.22 (m), 7.16 (m), 6.93 (m), 6.91 (m), 6.85 (m), 6.09 (m, 2H), 5.07, (m, 4H), 4.02 (m, 4H), 1.39 (s, 9H), 1.31 (s, 9H), 0.81 (s, 3H), 0.77 (s, 3H)	C_q: 136.6, 136.1, 135.7, 14.0, 101.2, 97.7, 62.8; CH: 132.1, 132.4, 129.7, 128.7, 128.1, 127.2, 127.0, 126.8, 119.0; CH_2: 116.1, 115.6, 26.2, 24.2; CH_3: 32.0, 31.5, 0.6, −1.2	−24.7, −25.2

[a] In C_6D_6 at 25°C only one isomer illustrated the signals from the ^{1}H NMR and the ^{13}C NMR were not assigned to the isomers. A more detailed assignment was not performed due to strong resonance overlapping in the ^{1}H NMR spectrum; n.d.: not determined.

Table 2
Polymerization data

Complex	Activity ([g]PE/[mmol] M h)	GPC ($\bar{M}_w$)[g/mol]); ($\bar{M}_n$ [g/mol]); (HI)	DSC (Mp. [°C]); ($\Delta \bar{H}_m$ [J/g]); ($\alpha^{a,b}$)
1a/b		1024000	n.d.
	2529	37530	n.d.
		27.28	n.d.
2a/b		1516000	n.d.
	2654	182900	n.d.
		8.29	n.d.
3a/b		1310000	133.6
	291	300800	69.4
		4.36	23.9
4a/b		>1100000[c]	138.4
	1964		115.9
			40.0
5a/b		1322000	137.5
	3504	256600	124.0
		5.15	42.8
6a/b		955000	135.8
	1006	70420	102.4
		13.53	35.3
7a/b		>1100000[c]	134.9
	9139		89.8
			31.0
8a/b		>1100000[c]	137.2
	2657		93.8
			32.3
9a/b		>1100000[c]	138.8
	1049		126.5
			43.6
10a/b		788300	135.6
	2308	168700	103.4
		4.67	35.7
11a/b		610100	139.1
	3959	19820	144.8
		30.8	50.0
12a/b		990000	142.8
	1054	142000	138.7
		6.94	47.8
13a/b		2065000	140.0
	4790	254000	104.2
		8.13	35.9
14a/b		813600	138.9
	2395	33180	111.4
		24.52	38.4
15a/b		1043000	135.8
	3164	404600	96.5
		25.77	33.3
16a/b		1415000	140.4
	1245	142700	143.7
		9.92	49.6
17a/b		1463000	138.7
	2060	152000	114.4
		9.62	39.4

Table 2 (*Continued*)

Complex	Activity ([g]PE/[mmol] M h)	GPC ($\bar{M}_w$)[g/mol]); ($\bar{M}_n$ [g/mol]); (HI)	DSC (Mp. [°C]); ($\Delta \bar{H}_m$ [J/g]); ($\alpha^{a,b}$)
18a/b		>1100000[c]	135.2
	345		38.5
			13.3
19a/b		>1100000[c]	138.3
	1624		122.9
			42.4
20a/b		333100	139.2
	2171	12070	64.4
		27.59	22.2

[a] Maximum of the melting peak during the second heating course of the DSC.
[b] $\alpha = \Delta H_m / \Delta H_m{}^\circ$ with $\Delta H_m{}^\circ = 290$ J/g [34].
[c] New styra gel HT6E-GPC-column, molecular weight too high; n.d.: not determined.

t-butylamine (2.5-fold excess). The solution was stirred for 12 h. The white *t*-butylammoniumchloride was separated in a frit over sodium sulfate, the solvent was evaporated and the residue was distilled. Yields 65–80%.

3.11. General synthesis procedure for indenyl ligand precursors

80 mmol of the corresponding indenyl chlorosilane compound was dissolved in 200 ml methylene chloride and 200 mmol *t*-butylamine was added quickly. After stirring for 12 h the solvent was removed, the residue was dissolved in 200 ml pentane and the suspension was filtered over sodium sulfate. The solvent was reduced in volume. The ligand precursors were obtained quantitatively as yellow to light red oils.

3.12. General synthesis procedure for amido functionalized ansa half-sandwich complexes of titanium

18 mmol of the respective ligand precursor in diethyl ether was charged to a flask at −78°C and 22.5 ml (36 mmol) *n*-butyllithium was added with a syringe. The reaction mixture was stirred for 8 h at room temperature. The equimolar amount of the dilithium salt solution of the ligand was added slowly to 18 mmol (6.64 g) TiCl₃·3THF in 100 ml diethylether at −78°C. The mixture was stirred for 10 h. For oxidation, the titanium(III) compound was mixed

with 18 mmol (4.99 g) PbCl₂ at room temperature and the reaction mixture was stirred for 30 min. The precipitated elemental lead and lead dichloride settled in the reaction solution after stop stirring, the liquid was separated using a cannula. The solvent was evaporated in vacuo, the residue was dissolved in pentane and the precipitated lithium salt was separated over a frit. After removing the solvent, the complex was obtained as deep red to black solid. Yields 65–95%. The complexes were characterized by NMR spectroscopy (Table 1).

3.13. General synthesis procedure for amido functionalized ansa half-sandwich complexes of zirconium

About 18 mmol of the respective ligand precursor in diethylether was charged to a cooled flask (−78°C) and mixed with 22.5 ml (36 mmol) *n*-butyllithium. The reaction mixture was stirred for 8 h at room temperature. The equimolar amount of zirconium tetrachloride (4.19 g) was added and the reaction solution was stirred for additional 12 h. The precipitating lithiumchloride was filtered, ether was evaporated in vacuo and the residue was dissolved in pentane. The precipitating solid was filtered again, the solvent was reduced in volume to almost dryness and the solution was stored at −78°C for 24 h. The complex precipitated as yellow-white solid and could be dried in vacuo. Yields 19–30%. The complexes were characterized by NMR spectroscopy (Table 1).

4. Polymerization of ethylene

10–15 mg of the corresponding complex were dissolved in 50 ml toluene. A solution containing 1–3 mg complex was taken and activated with MAO (30% in toluene) (metal:Al = 1:2500). The catalyst solution was dissolved in 250 ml pentane, charged to a 1 L Büchi laboratory autoclave and thermostated at 60°C. After the inside temperature was calibrated to 60°C an ethylene pressure of 10 bar was applied and the mixture was stirred for 1 h at 60 (±2)°C. The obtained polymer was dried in vacuo. The polymerization results and the physical data of the polymers are shown in Table 2.

Acknowledgements

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