

# Amido functionalized *ansa* half-sandwich dichloride complexes of titanium, zirconium and hafnium with alkyl and $\omega$ -alkenyl substituents as homogeneous and self-immobilizing catalyst precursors for ethylene polymerization

Helmut G. Alt \*, Alexander Reb, Wolfgang Milius, Annette Weis

Laboratorium für Anorganische Chemie der Universität Bayreuth, Postfach 10 12 51, D-95440 Bayreuth, Germany

Received 15 December 2000; received in revised form 26 February 2001; accepted 6 March 2001

Dedicated to Professor Max Herberhold on the occasion of his 65th birthday (August 2, 2001)

## Abstract

A total of 24 amido functionalized *ansa* half-sandwich dichloride complexes of titanium, zirconium and hafnium with cyclopentadienyl or indenyl ligands have been prepared, characterized and used for catalytic ethylene polymerization. Alkyl and  $\omega$ -alkenyl substituents on the aromatic system influence the polymerization activity of the catalysts and the properties of the produced polyethylene. After activation with methylalumoxane the  $\omega$ -alkenyl substituted catalysts show self-immobilization in ethylene polymerization. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Group 4 metals; *ansa* Half-sandwich complexes; Ethylene polymerization; Self-immobilization

## 1. Introduction

Since the first publication about amido functionalized *ansa* half-sandwich complexes in 1990 [1] these compounds enjoy increasing interest as catalysts for olefin polymerization in research and industry [2–10]. Due to their sterically open metal center they are excellent candidates for the copolymerization of ethylene and styrene, 1-hexene or 1-octene [11,12]. In order to investigate the effect of the catalyst structure on the polymerization parameters and polymer properties we functionalized the aromatic system with alkyl or  $\omega$ -alkenyl groups to compare the activities of the various catalysts. We were interested especially in the influence of the chain length of the  $\omega$ -alkenyl substituents for self-immobilization [13–15] since such amido functionalized *ansa* half-sandwich complexes have not yet been applied as heterogeneous catalysts.

## 2. Results and discussion

### 2.1. Synthesis of substituted cyclopentadienyl and indenyl derivatives

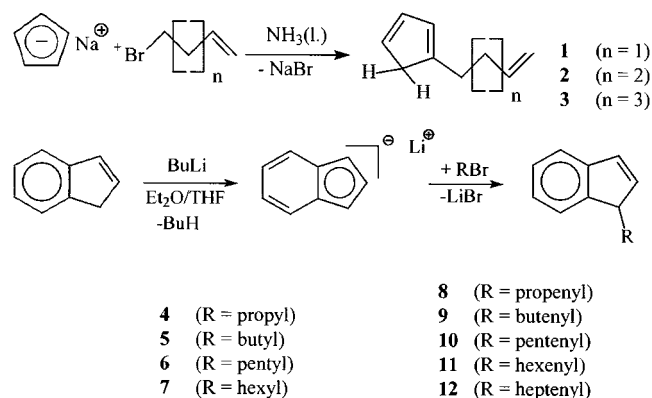
In order to functionalize the ring system of cyclopentadienyl compounds with alkyl or alkenyl groups the corresponding sodium salt was treated with an alkenyl bromide [16] in liquid ammonia [17]. Substituted indenyl derivatives were obtained by dissolving indene in a mixture of diethylether and THF [18]. After addition of one equivalent BuLi the alkyl or alkenyl bromide was added (Scheme 1).

### 2.2. Synthesis of the chlorosilane derivatives $Cp'SiMe_2Cl$ and $Ind'SiMe_2Cl$ ( $Cp' = \omega$ -alkenyl substituted Cp; $Ind' = \omega$ -alkenyl or alkyl substituted Ind)

To establish the silyl substituent on the functionalized cyclopentadiene or indene the reaction was not carried out in a non-polar solvent as described in

\* Corresponding author. Tel.: +49-921-552555; fax: +49-921-552157.

E-mail address: helmut.alt@uni-bayreuth.de (H.G. Alt).



Scheme 1. Synthesis of the cyclopentadienyl and indenyl derivatives **1–12**.

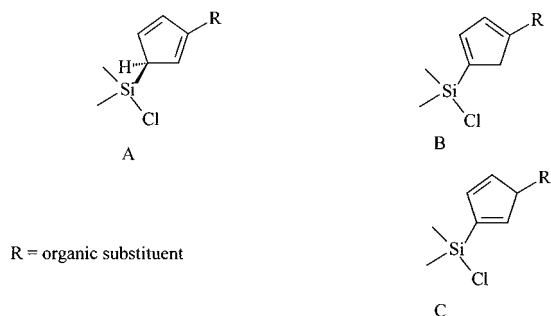


Fig. 1. Possible isomers of 1,3-disubstituted cyclopentadiene derivatives.

common procedures [19] instead of in diethylether. This path allows a quantitative reaction.

The  $^{29}\text{Si}$ -NMR spectroscopy plays an important role in controlling these reactions. Every isomer of the cyclopentadienyl derivatives shows one signal in the  $^{29}\text{Si}$ -NMR spectrum (Fig. 1). The signals of isomers B and C have almost the same chemical shifts because the

silicon atom is connected with an  $\text{sp}^2$  hybridized carbon atom [20].

The corresponding indene derivatives show a signal for only one of the two possible isomers in the  $^{29}\text{Si}$ -NMR spectrum (Fig. 2). It is possible that the steric influence of the substituent R forces the silyl substituent to occupy the position at the  $\text{sp}^3$  hybridized carbon atom.

### 2.3. Synthesis of the ligand precursors

The synthesized chlorosilane derivatives react with a threefold molar excess of *tert*-butylamine in dichloromethane to give the products **25–36\*** (Scheme 2 and Fig. 3). In pentane this reaction is not efficient, because the chlorosilane derivatives of indene do not dissolve completely.  $^{29}\text{Si}$ -NMR spectroscopy is a good tool to control the progress of the reaction.

### 2.4. Synthesis of the amido functionalized *ansa* half-sandwich complexes

The amido functionalized *ansa* half-sandwich complexes were obtained by treating the ligand precursors with two equivalents of BuLi and then the dianion formed with  $\text{TiCl}_3 \cdot 3\text{THF}$  (Fig. 4). Subsequently,  $\text{PbCl}_2$  was added as an oxidant in order to obtain the Ti(+IV) species [21] (Scheme 3).

### 2.5. Characterization by NMR spectroscopy

The amido functionalized *ansa* half-sandwich complexes were characterized by  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{29}\text{Si}$ -NMR spectroscopy. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra of **45** are presented in Fig. 5. The  $^1\text{H}$ -NMR spectrum shows two doublets at  $\delta = 7.82$  and  $7.74$  ppm for the two protons 15 and 18. The signals at  $\delta = 7.56$  and  $7.41$  ppm are

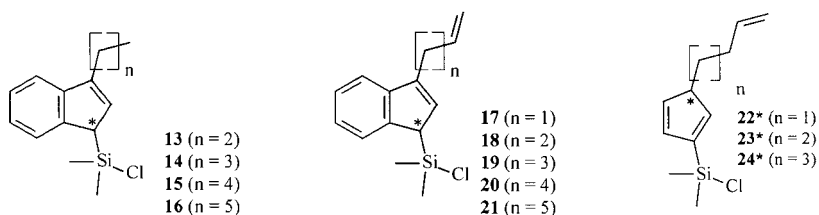
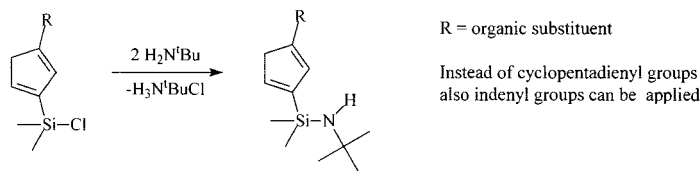


Fig. 2. Synthesized chlorosilane derivatives **13–24\***.



Scheme 2. Synthesis of the ligand precursors.

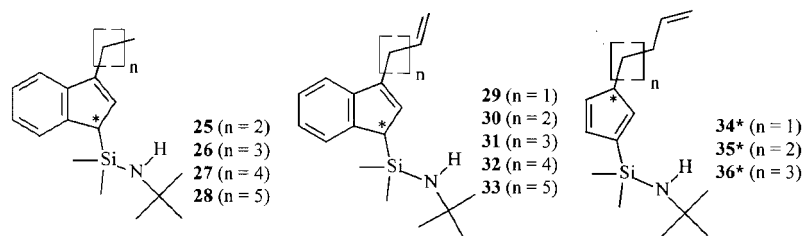
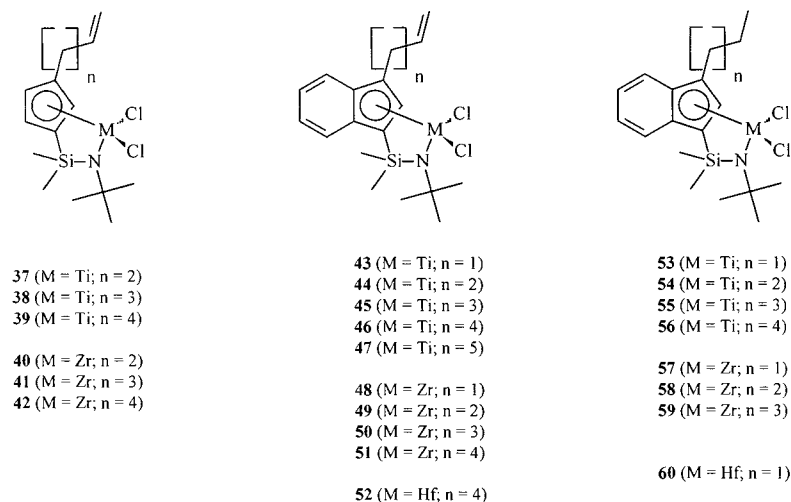
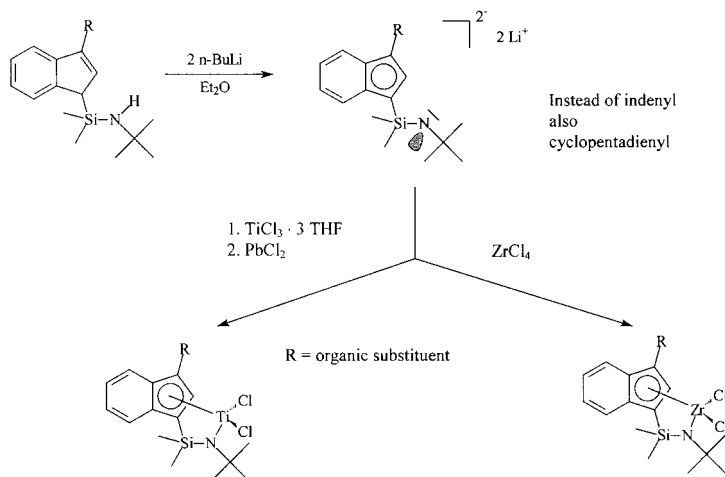


Fig. 3. Synthesized ligand precursors 25–36\*.

Fig. 4. Synthesized amido functionalized *ansa* half-sandwich complexes 37–60.Scheme 3. Synthesis of amido functionalized *ansa* half-sandwich complexes.

assigned to the protons 16 and 17. These aromatic protons have a <sup>3</sup>*J*-*ortho* coupling of 8.1 Hz. The lone proton 6 shows a singlet at  $\delta = 6.44$  ppm. The unsaturated double bond is an ABMX<sub>2</sub> spin system. The M part (11) shows a multiplet at  $\delta = 5.91$  ppm and also the AB part (11 and 12) at  $\delta = 5.11$  ppm. The three aliphatic methylene groups 8, 9 and 10 give signals at  $\delta = 3.16$ , 1.93 and 2.23 ppm, respectively. This order was confirmed by a 2D <sup>1</sup>H,<sup>1</sup>H-COSY NMR experi-

ment. The singlet at  $\delta = 1.49$  ppm belongs to the nine homotopic protons of the *tert*-butyl group. The two diastereotopic methyl groups show their signals at  $\delta = 0.76$  and 0.66 ppm.

The *J*-modulated <sup>13</sup>C-NMR spectrum of **45** shows the quaternary carbon atoms at  $\delta = 138.5$ , 135.8, 135.0 and 96.5 ppm for the aromatic indenylidene system. The double bond of the substituent gives signals at  $\delta = 137.5$  (positive phase) and at  $\delta = 115.2$  ppm (nega-

tive phase). The three methylene groups are assigned to the resonances at  $\delta = 33.4(10)$ ,  $29.1(9)$  and  $28.4$  ppm (8). The methyl groups of the *tert*-butyl group and the silicon atom show their signals at  $\delta = 33.1$ ,  $3.3$  and  $1.0$  ppm.

## 2.6. X-ray analyses of the crystal structures of **50** and **60**

The molecular structure of the hafnium complex **60** (Fig. 6) reveals that this amido functionalized *ansa* half-sandwich complex exists as two enantiomers.

Every unit cell consists of six molecules: three pairs of enantiomers. The inversion center is in the middle of the elemental cell. The bond between the nitrogen atom and the metal is  $203.1$  pm and therefore it has double bond character. Recent crystal structures of similar complexes show similar results [21–24]. The sum of the bond angles around the nitrogen atom is  $359.75^\circ$ . This confirms its trigonal planar surrounding; nitrogen donates three electrons to the metal (Table 1).

The preliminary molecular structure of **50** is shown in Fig. 7. Because of thermic factors the *R* value of  $5.4\%$  could not be improved.

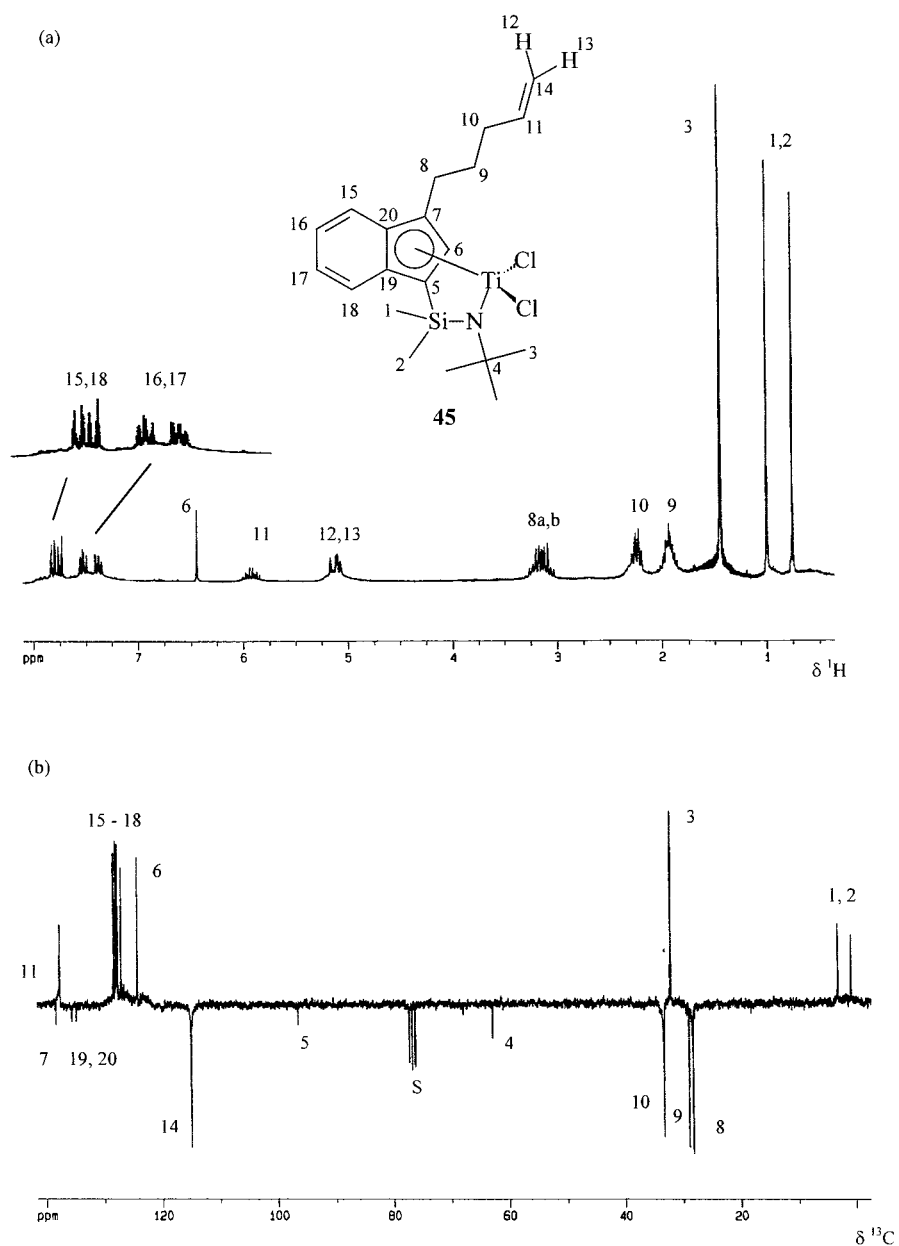
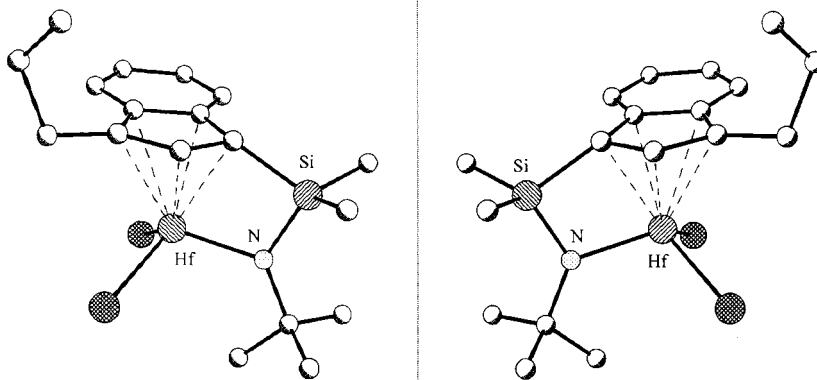


Fig. 5. (a) 250.13 MHz <sup>1</sup>H-NMR spectrum of **45** (CDCl<sub>3</sub>, 25°C); (b) 62.9 MHz *J*-modulated <sup>13</sup>C{<sup>1</sup>H}-NMR spectrum of **45** (CDCl<sub>3</sub>, 25°C). Quaternary and CH<sub>2</sub> carbon atoms (negative phase), CH and CH<sub>3</sub> carbon atoms (positive phase) are in phase; S = CDCl<sub>3</sub>.

Fig. 6. X-ray structure of **60**. Both enantiomers are shown.Table 1  
Important bond lengths and bond angles of **60**

Hf–N	203.1(3)	Hf–C(2)	242.2(4)	Hf–Si	300.0(13)
Hf–Cl(2)	237.3(13)	Hf–C(3)	238.1(4)	Si–N	175.1(4)
Hf–Cl(1)	237.4(14)	Hf–C(4)	248.5(4)	Si–C(3)	186.5(4)
Hf–C(1)	253.8(4)	Hf–C(9)	259.2(4)	N–C(15)	149.4(6)
Cl(2)–Hf–Cl(1)	105.6(5)	Hf–N–Si	104.8(17)	N–Si–C(3)	93.4(18)
N–Si–C(13)	114.8(2)	N–Si–C(14)	115.4(2)	Cl(2)–Hf–N	109.9(11)

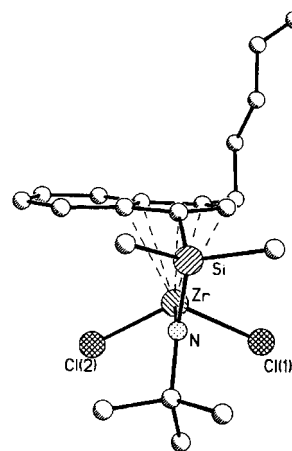
### 2.7. Homogeneous ethylene polymerization

All synthesized complexes were tested for ethylene polymerization after activation with methylalumoxane (MAO). Fig. 8 gives an overview of the polymerization activities of  $\omega$ -alkenyl substituted catalysts. Indenylidene complexes have much higher activities than the corresponding cyclopentadienylidene compounds. This could be due to a weaker  $\pi$ -donor effect of the indenyl system increasing the Lewis acidity at the central metal. With the  $\omega$ -alkenyl substituted complexes of titanium the activity increases with longer chain lengths of the unsaturated group. A similar result has been observed with  $\omega$ -alkenyl functionalized metallocene complexes [15,25] and interpreted with the restricted mobility of the catalyst molecule that is fixed on the backbone of the polymer chain. Indenyl complexes of titanium and cyclopentadienyl complexes of zirconium show the opposite trend. The activities decrease with longer  $\omega$ -alkenyl chain lengths. At this point it is hard to predict trends because small differences in the structure of a catalyst, together with the reaction parameters, can induce a strong impact on the kinetics of the polymerization process. Hafnium catalysts of the amido functionalized half-sandwich type generally show lower activities in ethylene polymerization than analogous titanium and zirconium catalysts.

In Fig. 9 the melting points ( $T_m$ ) and the melting enthalpies ( $\Delta\bar{H}_m$ ) of some of the obtained polyethylenes

are given. In general the titanium catalysts produce a polymer with a lower melting point and with a lower melting enthalpy. The only exception is the polyethylene obtained from the titanium complex **45** ( $R = C_5^-$ ) that has a higher melting point and a higher melting enthalpy than the corresponding zirconium complex.

The data dealing with homogeneous ethylene polymerization of all synthesized complexes are shown in Table 2.

Fig. 7. Preliminary X-ray structure of **50**.

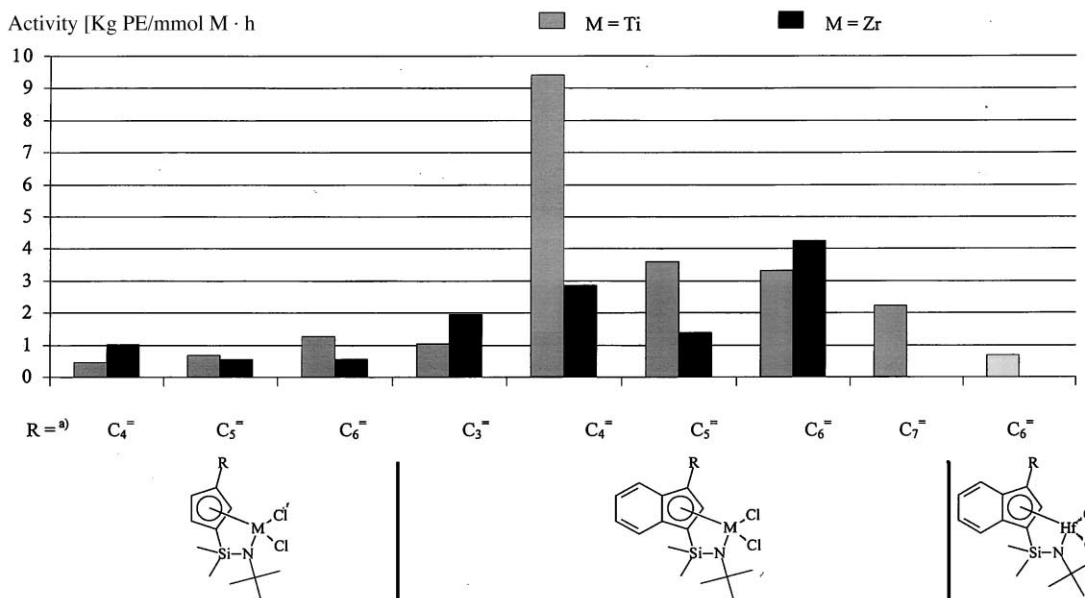


Fig. 8. Catalyst activities in homogeneous ethylene polymerization.

### 2.8. Heterogeneous ethylene polymerization with self-immobilized catalysts

The heterogeneous polymerization of ethylene was tested with complexes **44–47**. All four complexes are substituted with an  $\omega$ -alkenyl chain at the indenylidene ligand. We assume that after activation with MAO the double bond of the  $\omega$ -alkenyl substituent is copolymerized with ethylene in the polymer chain during the prepolymerization step. This self-immobilization allows the heterogenization of the catalyst system [13–15]. The activities of the prepolymerized catalysts are given in Fig. 10. For complex **45** an activity improvement by a factor of 13 can be observed compared to the homogeneous polymerization of ethylene. Complex **46** showed also an increase compared to the homogeneous catalysis (factor of 11). Complexes **44** and **47** have lower activities. Their  $\omega$ -alkenyl chain is too short or too long for an efficient incorporation into the polymer chain during prepolymerization. The complete data of the polymerization of ethylene with the prepolymerized catalysts are shown in Table 3.

### 3. Experimental

All operations were carried out using Schlenk technique. Purified and dried Ar was used as inert gas (BTS catalyst, molecular sieve). The solvents were dried over Na–K alloy (Et<sub>2</sub>O, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, *n*-C<sub>5</sub>H<sub>12</sub>) and/or over P<sub>2</sub>O<sub>5</sub> and CaH<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>).

The NMR spectra were recorded in deuterated solvents at 25°C using a Bruker ARX 250 spectrometer. In

<sup>1</sup>H-NMR spectra the chemical shifts refer to the residual proton signal of the solvent ( $\delta = 7.24$  ppm for CHCl<sub>3</sub>-*d*<sub>1</sub>,  $\delta = 7.15$  ppm for C<sub>6</sub>H<sub>6</sub>-*d*<sub>6</sub>), in <sup>13</sup>C-NMR spectra to the solvent signal ( $\delta = 77.0$  ppm for CHCl<sub>3</sub>-*d*<sub>1</sub>,  $\delta = 128.0$  ppm for C<sub>6</sub>H<sub>6</sub>-*d*<sub>6</sub>) and in <sup>29</sup>Si-NMR spectra to the resonance of Me<sub>4</sub>Si (external reference,  $\delta = 0.0$  ppm).

**Prepolymerizations.** The complexes (10 mg) were dissolved in 75 ml C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> and activated by adding a 250-fold molar excess of MAO (30 wt% in C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>; Witco). Then 2 g of dried silica was added (water < 1 wt%). The prepolymerization took 30 min at 0.4 bar ethylene pressure.

**Homogeneous polymerizations.** The complexes were activated by adding a 2500-fold molar excess of MAO (30 wt%, Witco). After adding the activated complex (ca. 2 mg) to the 1-l metal autoclave (Büchi), filled with 250 ml *n*-C<sub>5</sub>H<sub>12</sub>, the polymerizations were performed under an ethylene pressure of 10 bar and at a temperature of 60°C over a period of 1 h.

**Heterogeneous polymerizations.** A slurry of the catalyst and 250 ml *n*-C<sub>5</sub>H<sub>12</sub> was added to the 1-l metal autoclave (Büchi). The polymerizations were performed under an ethylene pressure of 10 bar and at a temperature of 60°C over a period of 1 h.

**Polymer characterization.** Molecular weight determinations of the polyethylene (PE) samples were performed using a Millipore Waters 150 C HT-GPC with refractometric detection (RI Waters 401). The polymer samples were dissolved in 1,2,4-trichlorobenzene (flow rate, 1 ml min<sup>-1</sup>) and measured at 150°C.

A Netzsch DSC 200 was available to determine the thermal characteristics of the PE samples. PE (5 mg)

was fused in standard aluminum pans and measured using the following temperature program: (1) heating phase ( $20^{\circ}\text{C min}^{-1}$ ) from 50 to  $170^{\circ}\text{C}$ , isothermal phase (3 min) at  $170^{\circ}\text{C}$ , cooling phase ( $-20^{\circ}\text{C min}^{-1}$ ) to  $50^{\circ}\text{C}$ ; (2) heating phase ( $20^{\circ}\text{C min}^{-1}$ ) from 50 to  $170^{\circ}\text{C}$ . The melting points were measured during the second heating phase.

### 3.1. Preparation of substituted cyclopentadiene derivatives

In a Schlenk tube with 14.0 g (159.1 mmol) cyclopentadienyl sodium, 150 ml liquid  $\text{NH}_3$  was condensed.  $\omega$ -Alkenyl bromide (120.0 mmol) in 60 ml  $n\text{-C}_5\text{H}_{12}$  was added dropwise within 30 min. The reaction mixture was stirred for 3 h. After evaporation of the  $\text{NH}_3$ , the dark brown slurry was filtered over

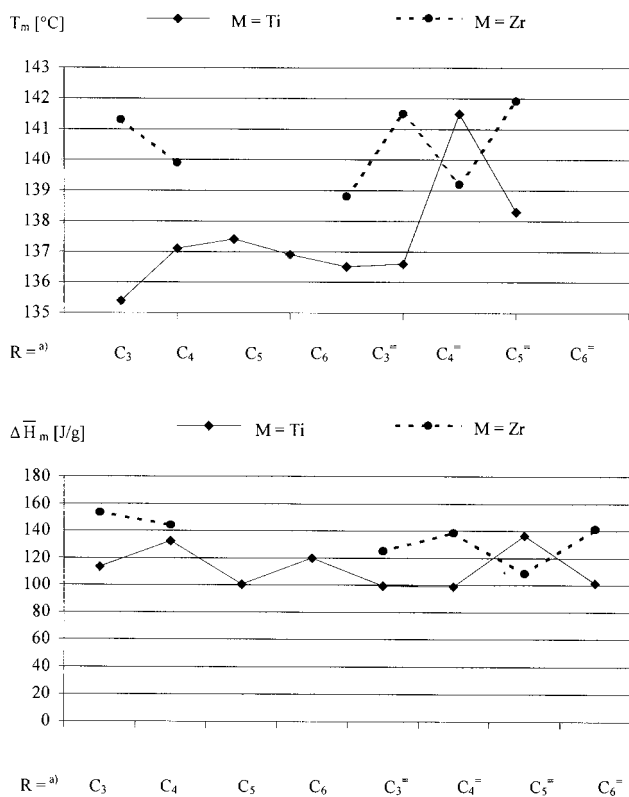
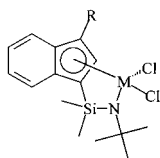


Fig. 9. Melting points and melting enthalpies of polyethylenes of indenylidene amido functionalized half-sandwich complexes from homogeneous polymerization.  $\text{C}_n$ , alkyl substituent with a chainlength of  $n$ ;  $\text{C}_n''$ ,  $\omega$ -alkenyl substituent with a chainlength of  $n$ .

$\text{Na}_2\text{SO}_4$  and silica and the residual solvent was removed in vacuo. Yields: 85–90%.

### 3.2. Preparation of the substituted indene derivatives

Indene (86 mmol) was dissolved in a mixture of 180 ml  $\text{Et}_2\text{O}$  and 18 ml THF and cooled to  $-78^{\circ}\text{C}$ .  $n$ -Butyllithium (86 mmol) was added with a syringe. The solution was allowed to warm up to room temperature (r.t.) and stirred for 4 h. The corresponding  $\omega$ -alkenyl bromide (86 mmol) was added dropwise at  $-78^{\circ}\text{C}$  and the reaction mixture was stirred for 10 h. The mixture was hydrolyzed with 50 ml of water, filtered over  $\text{Na}_2\text{SO}_4$  and silica and the solvent was removed. Yields: 85–90%.

### 3.3. Preparation of 7-bromo-1-heptene

In a three-necked flask with dropping funnel, liquid condenser and bubbler, 5 g Mg (206 mmol) in 100 ml  $\text{Et}_2\text{O}$  was placed and 24.9 g (206 mmol) allylbromide in 50 ml  $\text{Et}_2\text{O}$  was added dropwise at  $0^{\circ}\text{C}$ . After stirring for 3 h the allylmagnesiumbromide was added to 44.5 g (206 mmol) 1,4-dibromobutane in 100 ml  $\text{Et}_2\text{O}$  with a dropping funnel within 30 min. After stirring for 4 h the solution was hydrolyzed with 50 ml water and the organic phase was dried over  $\text{Na}_2\text{SO}_4$ . After distillation a mixture of 1,4-dibromobutane and 7-bromo-1-heptene was obtained. The mixture was dissolved in 70 ml  $n\text{-C}_5\text{H}_{12}$  and crystallized at  $-78^{\circ}\text{C}$ . The 1,4-dibromobutane was precipitated and the 7-bromo-1-heptene was collected. After removing the solvent the product resulted in 30% yield.

### 3.4. General procedure for the preparation of the substituted indene and cyclopentadiene dimethylchlorosilane derivatives 13–24\*

The corresponding substituted indene or cyclopentadiene derivatives (80 mmol) were dissolved in 150 ml  $\text{Et}_2\text{O}$  and the solution was cooled to  $-78^{\circ}\text{C}$ .  $n$ -Butyl-

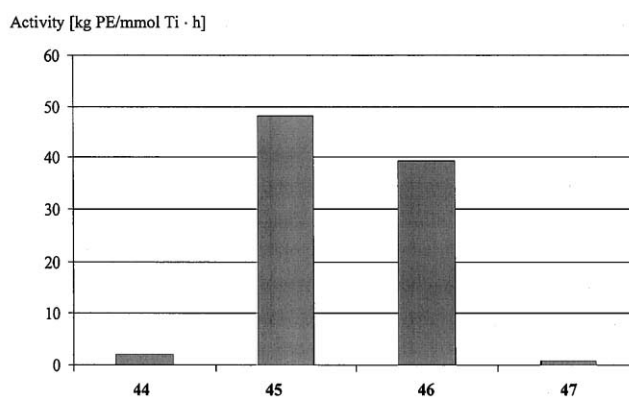


Fig. 10. Activities of prepolymerized catalysts.

Table 2

Overview of the polymerization experiments and the polymer analyses of the homogeneous ethylene polymerizations

Complex	Activity (g) PE/(mmol) M h	GPC			DSC		
		$\overline{M}_w$ (g mol <sup>-1</sup> )	$\overline{M}_n$ (g mol <sup>-1</sup> )	HI	$T_m^a$ (°C)	$\Delta\overline{H}_m$ (J g <sup>-1</sup> )	$\alpha^b$
37	451	1 461 000	101 600	14.38	127.3	153.1	53
38	695	$\overline{M}_w > 1\,100\,000^c$			127.6	154.7	53
39	1747	1 877 000	167 700	11.19	121.4	175.0	60
40	1021	1 780 000	337 700	5.27	127.7	130.1	45
41	566	2 198 000	143 100	15.36	129.2	147.3	51
42	547	1 508 000	335 700	4.49	129.1	167.1	58
43	1046	$\overline{M}_w > 1\,100\,000^c$			136.5	99.2	34.2
44	9421	$\overline{M}_w > 1\,100\,000^c$			136.6	98.7	34.0
45	3607	695 300	n.c. <sup>d</sup>	n.c. <sup>d</sup>	141.5	126.5	43.6
46	3324	573 000	71 500	8.01	138.3	101.1	34.9
47	2246	1 207 000	203 500	5.93	n.m. <sup>e</sup>		
48	1961	875 800	228 800	3.29	138.8	125.3	43.2
49	2864	$\overline{M}_w > 1\,100\,000^c$			141.5	138.5	47.6
50	1396	$\overline{M}_w > 1\,100\,000^c$			139.2	108.5	37.4
51	4260	1 179 000	189 600	6.22	141.9	141.1	48.7
52	685	605 700	27 890	21.71	136.7	23.5	8.1
53	1542	360 000	89 850	4.01	137.5	124.0	42.8
54	3504	458 000	153 200	2.99	137.1	132.2	45.6
55	1536	7 857 000	180 700	43.49	137.4	100.5	34.6
56	2083	314 300	127 400	2.47	136.9	119.8	41.3
57	6384	675 900	116 200	5.8	141.3	153.2	52.8
58	3813	992 700	176 700	5.62	139.9	144.2	49.7
59	1 530	$\overline{M}_w > 1\,100\,000^c$			n.m. <sup>e</sup>		
60	623	644 500	97 850	6.59	139.0	88.5	30.5

<sup>a</sup> The maximum of the melting peak at the second heating course of the DSC was selected as melting point.<sup>b</sup>  $\alpha = \Delta H_m / \Delta H_m^0$  with  $\Delta H_m^0 = 290 \text{ J g}^{-1}$  [26].<sup>c</sup> New Styragel HT6E-GPC-column; molecular weight too high.<sup>d</sup> n.m., not measured.<sup>e</sup> n.c., not clear (presumably multimodal resin).

lithium, 80 mmol (50 ml) (1.6 M in hexane) was added with a syringe and the solution was stirred for 4 h and then warmed up to r.t. The lithium salt was added to the equimolar amount of Me<sub>2</sub>Cl<sub>2</sub>Si in 100 ml Et<sub>2</sub>O at -78°C and stirred for 12 h. The reaction mixture was filtered over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed. Yields: 80–96%.

The compounds were characterized by NMR spectroscopy (see Table 4).

### 3.5. General procedure for the preparation of the ligand precursors 25–36\*

The respective substituted indenyl or cyclopentadienyl dimethylchlorosilane derivatives (80 mmol) were dissolved in 200 ml CH<sub>2</sub>Cl<sub>2</sub> and 200 mmol *tert*-butylamine was added quickly. After stirring for 4 h the solvent was removed, the residue was dissolved in 200 ml *n*-C<sub>5</sub>H<sub>12</sub> and the reaction mixture was filtered over

Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent the ligand precursors resulted in yields between 98 and 100%.

The compounds were characterized by NMR spectroscopy (see Table 5).

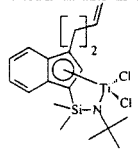
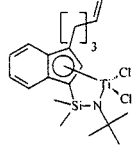
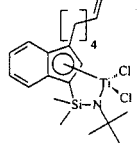
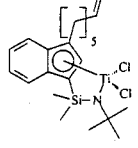
### 3.6. General procedure for the preparation of the amido functionalized ansa half-sandwich titanium complexes 37–39, 43–47, 53–56

The respective ligand precursors (18 mmol) were dissolved in 200 ml Et<sub>2</sub>O at -78°C and 22.5 ml (36 mmol) *n*-butyllithium (1.6 M in hexane) was added with a syringe. The reaction mixture was stirred for 6 h. The dilithium salt was added to 6.64 g TiCl<sub>3</sub>·3THF in 100 ml Et<sub>2</sub>O and the solution was stirred for 10 h. The resulting titanium(III) complex was treated with 18 mmol (4.99 g) PbCl<sub>2</sub> and the slurry was stirred for 30 min. The solvent was removed, the residue was dissolved in 200 ml *n*-C<sub>5</sub>H<sub>12</sub> and the solution was filtered



Table 3

Overview of the polymerization experiments and the polymer analyses of the heterogeneous ethylene polymerizations with prepolymerized catalysts

Complex	Activity [g] PE/[mmol] M · h	GPC		DSC		
		$\overline{M}_w$ [g/mol]	$\overline{M}_n$ [g/mol]	$T_m^a$ [°C]	$\Delta\overline{H}_m$ [J/g]	$\alpha^b$
44 	2 000	$\overline{M}_w > 1\,100\,000^c$		138.4	161.9	55.8
45 	48 000	2 234 000	896 200	149.1	73.6	25.4
46 	39 360	2 745 000	727 000	137.2	103.6	35.7
47 	800	1 078 000	194 300	n.m.		

<sup>a)</sup> The maximum of the melting peak of the second heating course of the DSC was selected as melting point;

<sup>b)</sup>  $\alpha = \Delta H_m / \Delta H_m^\circ$  with  $\Delta H_m^\circ = 290$  J/g [22];

<sup>c)</sup> New Styragel HT6E-GPC-column; molecular weight too high. n.m. = not measured.

over  $\text{Na}_2\text{SO}_4$ . The pentane was removed until a 50 ml volume was left. The complex was crystallized at  $-78^\circ\text{C}$ . Yield: 65–95%.

The complexes were characterized by NMR spectroscopy (see Table 6).

### 3.7. General procedure for the preparation of the amido functionalized half-sandwich complexes of zirconium and hafnium 39–42, 48–52, 57–60

The respective ligand precursors (18 mmol) were dissolved in 200 ml  $\text{Et}_2\text{O}$  at  $-78^\circ\text{C}$  and 22.5 ml (36 mmol) *n*-butyllithium (1.6 M in hexane) was added with a syringe. The reaction mixture was stirred for 6 h. The dilithium salt was added to 18 mmol (4.19 g)  $\text{ZrCl}_4$  (or 5.72 g  $\text{HfCl}_4$ ) in 100 ml  $\text{Et}_2\text{O}$  and the slurry was stirred for 10 h. The solvent was removed, the residue

was dissolved in 200 ml *n*- $\text{C}_5\text{H}_{12}$  and the reaction mixture was filtered over  $\text{Na}_2\text{SO}_4$ . The pentane was removed until a 50 ml volume was left. The complex was crystallized at  $-78^\circ\text{C}$ . Yield: 25–30%.

All complexes were characterized by NMR spectroscopy (see Table 6).

### 3.8. Preparation of $\text{TiCl}_3 \cdot 3\text{THF}$

THF (200 ml) and 10.0 g  $\text{TiCl}_3$  were refluxed in a 500 ml Schlenk flask for 22 h. After cooling to r.t. the blue crystals precipitated were filtered and washed three times with pentane. The washing was given to the mother liquor and stored at  $-18^\circ\text{C}$  for 24 h. The product precipitated again in small amounts. Overall yield: 21.96 g (92%).

Table 4  
NMR data of the chlorosilane derivatives **13–24**\*<sup>a</sup>

Compound	<sup>1</sup> H-NMR <sup>b</sup>	<sup>13</sup> C-NMR	<sup>29</sup> Si-NMR
<b>13</b>	7.45 (m), 7.32 (m), 7.22 (m), 6.59 (s, 1H), 6.26 (s, 1H), 3.43 (s, 1H), 1.86 (m, 2H), 1.56 (m, 2H), 0.52 (s, 3H), 0.43 (s, 3H), 0.39 (s, 3H)	C <sub>q</sub> : 144.4, 144.1, 138.9; CH: 133.3, 132.2, 128.0, 127.5, 126.1, 125.3, 123.9, 51.6, 29.9; CH <sub>2</sub> : 17.5, 15.3; CH <sub>3</sub> : 0.7, 0.6	27.5
<b>14</b>	7.61 (d, 1H) [7.3], 7.47 (d, 1H) [7.3], 7.32 (t, 2H) [7.3], 7.28 (t, 2H) [7.3], 6.35 (s, 1H), 3.66 (s, 1H), 2.67 (t, 2H) [7.5], 1.73 (m), 1.47 (sx, 2H) [7.35], 1.02 (t, 3H) [7.25] 0.25 (s, 3H), 0.22 (s, 3H)	C <sub>q</sub> : 145.0, 144.6, 143.7; CH: 127.3, 125.6, 124.4, 123.5, 119.4, 45.5; CH <sub>2</sub> : 30.9, 27.6, 22.9; CH <sub>3</sub> : 14.1, 0.2, -0.2	27.6
<b>15</b>	7.66 (d, 1H) [7.5], 7.52 (d, 1H) [7.5], 7.44 (t, 1H) [7.5], 7.27 (t, 1H) [7.5], 6.84 (s, 1H), 3.85 (s, 1H), 2.81 (m), 1.82 (m), 1.57 (m), 1.10 (m), 0.58 (s, 3H), 0.31 (s, 3H)	C <sub>q</sub> : n.b.; CH: 126.3, 126.1, 124.2, 123.3, 120.5, 48.7; CH <sub>2</sub> : 32.0, 31.8, 29.4, 22.9; CH <sub>3</sub> : 1.4, -0.4	27.6
<b>16</b>	7.66 (d, 1H) [7.5], 7.52 (d, 1H) [7.5], 7.44 (t, 1H) [7.5], 7.27 (t, 1H) [7.5], 6.84 (s, 1H), 3.85 (s, 1H), 2.81 (m), 1.82 (m), 1.57 (m), 1.10 (m), 0.58 (s, 3H), 0.31 (s, 3H)	C <sub>q</sub> : 146.2, 143.7, 142.5; CH: 126.5, 126.2, 123.5, 123.1, 120.1, 48.9; CH <sub>2</sub> : 32.9, 31.2, 29.4, 26.0, 21.9; CH <sub>3</sub> : 1.5, -0.6	27.7
<b>17</b>	8.22 (d, 1H) [7.3], 8.08 (d, 1H) [7.3], 7.96 (t, 1H) [7.3], 7.88 (t, 1H) [7.3], 7.01 (s, 1H), 6.65 (m, 1H), 5.53 (d, 1H) [17.5], 5.77 (d, 1H) [12.5], 4.30 (s, 1H), 4.06 (m, 2H), 0.86 (s, 3H), 0.84 (s, 3H)	C <sub>q</sub> : 144.4, 143.6, 142.0; CH: 135.6, 128.5, 125.5, 124.1, 123.4, 119.6, 45.6; CH <sub>2</sub> : 116.2, 32.4; CH <sub>3</sub> : 0.0, -0.3	27.7
<b>18</b>	7.61 (d, 1H) [7.5], 7.48 (d, 1H) [7.5], 7.35 (t, 1H) [7.5], 7.27 (t, 1H) [7.5], 6.38 (s, 1H), 5.96 (m, 1H), 5.15 (d, 1H) [12.5], 5.07 (d, 1H) [10], 3.67 (s, 1H), 2.77 (t, 2H) [7.3], 2.53 (t, 2H) [7.3], 0.24 (s, 3H), 0.22 (s, 3H)	C <sub>q</sub> : 145.2, 143.9, 143.8; CH: 138.6, 128.0, 125.9, 124.8, 123.8, 119.6, 45.9; CH <sub>2</sub> : 115.4, 33.0, 27.5; CH <sub>3</sub> : 0.4, 0.0	27.6
<b>19</b>	7.59 (d, 1H) [7.5], 7.44 (d, 1H) [7.5], 7.30 (t, 1H) [7.5], 7.22 (t, 1H) [7.5], 6.3 (s, 1H), 5.85 (m, 1H), 5.04 (d, 1H) [12.5], 5.00 (d, 1H) [10.0], 3.62 (s, 1H), 2.61 (t, 2H) [7.5], 2.17 (m, 2H), 1.79 (m, 2H), 0.21 (s, 3H), 0.16 (s, 3H)	C <sub>q</sub> : 145.0, 144.5, 144.2; CH: 139.3, 127.9, 125.7, 124.3, 123.3, 118.6, 45.2; CH <sub>2</sub> : 114.1, 33.3, 29.0, 28.1, 26.8; CH <sub>3</sub> : 0.4, 0.1	27.5
<b>20</b>	7.55 (d, 1H) [7.4], 7.41 (d, 1H) [7.5], 7.28 (t, 1H) [7.5], 7.20 (t, 1H) [7.5], 6.28 (s, 1H), 5.81 (m, 1H), 5.01 (d, 1H) [12.5], 4.94 (d, 1H) [10.0], 3.60 (s, 1H), 2.60 (t, 2H) [7.5], 2.08 (m, 2H), 1.70 (m, 2H), 1.47 (m, 2H), 0.19 (s, 3H), 0.16 (s, 3H)	C <sub>q</sub> : 145.1, 144.6, 143.9; CH: 139.1, 127.6, 125.8, 124.6, 123.7, 119.6, 45.8; CH <sub>2</sub> : 114.8, 33.9, 29.2, 28.3, 27.9; CH <sub>3</sub> : 0.3, 0.0	27.6
<b>21</b>	7.56 (d, 1H) [7.5], 7.44 (d, 1H) [7.5], 7.32 (t, 1H) [7.5], 7.23 (t, 1H) [7.5], 6.31 (s, 1H), 5.82 (m, 1H), 4.98 (m, 2H), 3.64 (s, 1H), 2.61 (t, 2H), 2.08 (m, 2H), 1.71 (m, 2H), 1.46 (m, 4H), 0.22 (s, 3H), 0.19 (s, 3H)	C <sub>q</sub> : 145.6, 144.3, 142.8; CH: 139.0, 127.2, 125.4, 124.2, 123.4, 119.3, 45.4; CH <sub>2</sub> : 114.3, 33.7, 29.1, 28.7, 28.3, 27.6; CH <sub>3</sub> : 0.0, -0.3	27.6
<b>22*</b>	6.75 (m, 1H), 6.71 (m), 6.61 (m), 6.52 (m), 5.82 (m, 1H), 3.22 (m, 2H), 2.57 (m, 2H), 0.83 (s, 3H), 0.65 (m, 2H)	C <sub>q</sub> : 139.3, 134.7, 114.5; CH: 132.7, 127.6, 127.3, 114.6, 59.5, 49.4; CH <sub>2</sub> : 46.2, 33.9, 29.2; CH <sub>3</sub> : 2.3, 1.1, 0.2	28.0, 17.9, 17.2
<b>23*</b>	6.89 (m, 1H), 6.77 (m), 6.60 (m), 5.84 (m, 1H), 3.23 (m, 2H), 3.09 (m, 2H), 2.67 (m, 2H), 0.91 (s, 3H), 0.60 (s, 3H)	C <sub>q</sub> : 140.0, 135.8, 114.5; CH: 132.9, 126.8, 126.3, 114.0, 57.3, 48.9, 46.8; CH <sub>2</sub> : 34.1, 29.9, 26.6, 24.8; CH <sub>3</sub> : 2.1, 1.8, 0.5, -0.1	27.9, 17.3, 16.8
<b>24*</b>	6.81 (m, 1H), 6.75 (m), 6.42 (m), 5.67 (m, 1H), 3.65 (m, 2H), 3.34 (m, 2H), 2.87 (m, 2H), 2.77 (m, 2H), 0.75 (s, 3H), 0.45 (s, 3H)	C <sub>q</sub> : 145.4, 135.5, 112.7; CH: 131.7, 124.8, 124.1, 120.3, 111.9, 59.3, 49.1; CH <sub>2</sub> : 36.9, 32.7, 29.5, 27.5, 24.2, 22.1, 19.5; CH <sub>3</sub> : 2.6, 1.9, 0.7, -0.4	28.2, 17.5, 17.0

<sup>a</sup> In CDCl<sub>3</sub>, at 25°C; only one isomer shown.

<sup>b</sup> Because of overlapping, the signals are not assigned to the isomers.

### 3.9. X-ray analysis

A Siemens P4 diffractometer (Mo-K<sub>α</sub> radiation; λ = 0.71073 Å) with a graphite monochromator was used for the measurement of the reflection intensities. The structure calculation was performed with Siemens SHELXTL PLUS (VMS).

*C*<sub>16</sub>*H*<sub>21</sub>*SiNHfCl*<sub>2</sub> (**60**). A yellow prism crystallized in pentane of dimension 0.20 × 0.16 × 0.13 mm<sup>3</sup>; monoclinic; space group *P*2<sub>1</sub>/*c*; *a* = 14.916 (14), *b* = 11.760 (9), *c* = 13.051 (13) Å, β = 112.29 (7)°; *V* = 2118.2 (3) Å<sup>3</sup>; *Z* = 4; *d*<sub>calc</sub> = 1.583 Mg m<sup>-3</sup>; absorption coefficient, 5.228 mm<sup>-1</sup>; *F*(000) = 976; measured reflections, 4656; independent reflections, 3706; goodness-of-fit, 1.026; *R* = 2.5%.

Table 5  
NMR data of the ligand precursors **25–36\***<sup>a</sup>

Compound	<sup>1</sup> H-NMR <sup>b</sup>	<sup>13</sup> C-NMR	<sup>29</sup> Si-NMR
<b>25</b>	7.50 (d, 1H) [7.5], 7.37 (d, 1H) [7.5], 7.23 (t, 1H) [7.5], 7.15 (t, 1H) [7.5], 6.32 (s, 1H), 3.45 (s, 1H), 2.58 (t, 2H) [7.6], 1.71 (m, 2H), 1.17 (s, 9H), 1.00 (s, 3H) [7.6], 0.04 (s, 3H), –0.05 (s, 3H)	C <sub>q</sub> : 146.1, 144.8, 141.6, 49.6; CH: 130.5, 124.4, 123.7, 123.3, 118.9, 46.7; CH <sub>2</sub> : 30.0, 22.0; CH <sub>3</sub> : 33.8, 14.3, 0.0, –0.9	–1.9
<b>26</b>	7.59 (d, 1H) [7.2], 7.48 (d, 1H) [7.2], 7.32 (t, 1H) [7.2], 7.3 (t, 1H) [7.2], 6.40 (s, 1H), 3.53 (s, 1H), 2.69 (t, 2H) [7.4], 1.76 (m, 2H), 1.54 (m, 2H), 1.27 (s, 9H), 1.05 (t, 3H) [7.3], 0.05 (s, 3H), –0.03 (s, 3H)	C <sub>q</sub> : 146.2, 144.9, 141.8, 49.6; CH: 130.4, 124.5, 123.8, 123.4, 123.2, 119.0; CH <sub>2</sub> : 31.1, 27.6, 22.9; CH <sub>3</sub> : 34.0, 14.1, 0.1, –0.7	–1.9
<b>27</b>	7.59 (d, 1H) [7.5], 7.48 (d, 1H) [7.5], 7.32 (t, 1H) [7.5], 7.23 (t, 1H) [7.5], 6.40 (s, 1H), 3.53 (s, 1H), 2.69 (t, 2H) [7.4], 1.76 (m, 2H), 1.54 (m, 2H), 1.05 (t, 3H) [7.4], 0.05 (s, 3H), –0.03 (s, 3H)	C <sub>q</sub> : 146.2, 144.9, 141.8, 49.6; CH: 130.4, 124.4, 123.8, 123.4, 123.2, 119.0, 46.7; CH <sub>2</sub> : 31.1, 27.6, 22.9; CH <sub>3</sub> : 34.0, 14.1, 0.1, –0.7	–1.9
<b>28</b>	7.49 (d, 1H) [7.3], 7.36 (d, 1H) [7.3], 7.21 (t, 1H) [7.3], 7.16 (t, 1H) [7.3], 6.30 (s, 1H), 3.44 (s, 1H), 2.58 (t, 2H) [7.4], 1.66 (m, 2H), 1.32 (m, 4H), 1.17 (s, 9H), 0.88 (m, 2H), –0.08 (s, 3H), –0.15 (s, 3H)	C <sub>q</sub> : 145.1, 144.2, 141.8, 46.7; CH: 130.3, 124.4, 123.7, 123.3, 123.1, 118.9; CH <sub>2</sub> : 31.8, 29.5, 28.8, 27.8, 22.7; CH <sub>3</sub> : 33.8, 14.2, 0.0, –0.9	–2.0
<b>29</b>	8.19 (d, 1H) [7.5], 8.07 (d, 1H) [7.5], 7.92 (t, 1H) [7.5], 7.85 (t, 1H) [7.5], 7.05 (s, 1H), 6.70 (m, 1H), 5.78 (m, 2H), 4.17 (s, 1H), 4.05 (d, 2H) [5.3], 1.87 (s, 9H), 0.64 (s, 3H), 0.58 (s, 3H)	C <sub>q</sub> : 146.3, 143.1, 139.5, 49.8; CH: 136.6, 131.9, 124.6, 123.7, 123.3, 119.4, 47.2; CH <sub>2</sub> : 116.0, 32.8; CH <sub>3</sub> : 34.1, 0.2, –0.6	–1.9
<b>30</b>	7.73 (d, 1H) [7.3], 7.60 (d, 1H) [7.3], 7.46 (t, 1H) [7.3], 7.8 (t, 1H) [7.3], 6.57 (s, 1H), 6.14 (ddt, 1H), 5.31 (dd, 1H), 5.25 (dd, 1H), 3.67 (s, 1H), 2.93 (m, 2H), 2.70 (m, 2H), 1.39 (s, 9H), 0.19 (s, 3H), 0.12 (s, 3H)	C <sub>q</sub> : 146.5, 145.1, 141.3, 50.0; CH: 139.0, 131.0, 125.0, 124.0, 123.6, 119.3, 47.2; CH <sub>2</sub> : 115.2, 33.4, 27.8; CH <sub>3</sub> : 34.3, 0.6, –0.3	–1.9 [ <sup>1</sup> J( <sup>29</sup> Si, <sup>13</sup> C) = 12 Hz]
<b>31</b>	7.59 (d, 1H) [7.3], 7.46 (d, 1H) [7.3], 7.29 (t, 1H) [7.3], 7.24 (t, 1H) [7.3], 6.41 (s, 1H), 5.94 (ddt, 1H), 5.09 (dd, 1H), 5.05 (dd, 1H), 3.55 (s, 1H), 2.70 (t, 2H) [7.5], 2.24 (m, 2H), 1.86 (m, 2H), 1.27 (s, 9H), 0.87 (s, 3H), 0.79 (s, 3H)	C <sub>q</sub> : 146.0, 144.1, 141.3, 50.1; CH: 138.7, 130.5, 124.3, 123.4, 123.0, 118.8, 46.7; CH <sub>2</sub> : 114.7, 33.7, 28.0, 27.1; CH <sub>3</sub> : 33.8, 0.0, –0.9	–2.0
<b>32</b>	7.59 (d, 1H) [7.3], 7.46 (d, 1H) [7.3], 7.31 (t, 1H), [7.3], 7.23 (t, 1H) [7.3], 6.41 (s, 1H), 5.95 (ddt, 1H), 5.09 (dd, 1H), 5.03 (dd, 1H), 3.53 (s, 1H), 2.69 (t, 2H) [7.6], 2.20 (m, 2H), 1.76 (m, 2H), 1.61 (m, 2H), 1.27 (s, 9H), 0.05 (s, 3H), –0.04 (s, 3H)	C <sub>q</sub> : n. b. (DEPT); CH: 145.0, 137.1, 131.0, 129.8, 128.6, 124.9, 52.7; CH <sub>2</sub> : 121.1, 39.9, 36.0, 35.0, 34.1; CH <sub>3</sub> : 40.1, 3.0, 2.6	–1.9
<b>33</b>	7.53 (d, 1H) [7.7], 7.40 (d, 1H) [7.7], 7.26 (t, 1H) [7.7], 7.18 (t, 1H) [7.7], 6.34 (s, 1H), 6.87 (m, 1H), 4.98 (m, 2H), 3.48 (s, 1H), 2.62 (m, 2H), 2.10 (m, 2H), 1.71 (m, 2H), 1.45 (m, 4H), 1.24 (s, 9H), –0.02 (s, 3H), –0.10 (s, 3H)	C <sub>q</sub> : 146.0, 144.7, 141.6, 49.3; CH: 141.6, 130.3, 124.3, 123.3, 123.0, 118.8, 46.6; CH <sub>2</sub> : 33.8, 29.2, 28.8, 28.6, 27.7; CH <sub>3</sub> : 33.8, –0.1, –1.0	–2.0
<b>34*</b>	7.34 (m), 6.72 (m), 6.68 (m), 6.31 (m), 5.60 (m), 2.97 (m), 1.93 (m), 1.79 (m), 1.03 (s), 0.76 (s), 0.62 (s)	C <sub>q</sub> : 149.5, 144.4, 141.8, 139.5, 54.7, 49.7, 43.2; CH: 136.9, 135.7, 132.5, 127.9, 124.5, 123.9, 120.5, 116.7; CH <sub>2</sub> : 113.1, 34.6, 28.9, 26.7, 23.5; CH <sub>3</sub> : 30.7, 3.6, –0.1	–3.7, –14.3, –14.5
<b>35*</b>	7.41 (m), 6.82 (m), 6.75 (m), 6.35 (m), 5.63 (m), 3.06 (m), 2.73 (m), 1.88 (s), 1.83 (s), 0.91 (s), 0.78 (s), 0.66 (s)	C <sub>q</sub> : 154.5, 149.8, 145.7, 53.2, 49.3, 44.6; CH: 138.4, 138.1, 133.7, 130.3, 127.3, 126.8, 125.9, 114.6, 114.4; CH <sub>2</sub> : 114.5, 33.8, 32.8, 29.1, 27.2, 26.5; CH <sub>3</sub> : 30.3, 3.5, –0.2	–3.6, –14.2, –14.7
<b>36*</b>	7.43 (m), 7.01 (m), 6.76 (m), 6.27 (m), 5.44 (m), 2.89 (m), 2.23 (m), 1.95 (m), 1.76 (m), 1.54 (m), 0.98 (s), 0.76 (s), 0.69 (s)	C <sub>q</sub> : 145.9, 145.0, 142.9, 139.3, 53.6, 49.9, 45.1; CH: 134.7, 132.7, 131.9, 130.8, 127.9, 127.8, 125.3, 114.9; CH <sub>2</sub> : 114.8, 34.2, 29.2; CH <sub>3</sub> : 30.1, 2.1, 0.4	–3.5, –14.4, –15.0

<sup>a</sup> In CDCl<sub>3</sub> at 25°C; only one isomer shown.

<sup>b</sup> Because of overlapping, the signals are not assigned to the isomers.

Table 6  
NMR data of the amido functionalized *ansa* half-sandwich complexes 37–60<sup>a</sup>

Complex	<sup>1</sup> H-NMR	<sup>13</sup> C-NMR	<sup>29</sup> Si-NMR
37	6.53 (m, 1H), 6.10 (m, 1H), 5.93 (m, 1H), 5.66 (m, 2H), 4.95 (m, 1H), 2.67 (m, 2H), 2.15 (m, 2H), 1.38 (s, 9H), 0.25 (s, 3H), 0.23 (s, 3H)	C <sub>q</sub> : 146.5, 108.7, 64.1; CH: 137.9, 125.8, 125.6, 125.1; CH <sub>2</sub> : 115.9, 34.2, 30.3; CH <sub>3</sub> : 32.6, 0.2, 0.0	–19.4
38	6.80 (m, 1H), 6.38 (m, 1H), 6.22 (m, 1H), 5.93 (m, 2H), 5.23 (m, 1H), 2.84 (m, 2H), 2.15 (m, 2H), 1.73 (m, 2H), 1.66 (s, 9H), 0.50 (s, 3H), 0.49 (s, 3H)	C <sub>q</sub> : 145.7, 109.1, 63.2; CH: 137.8, 126.2, 125.0, 124.9; CH <sub>2</sub> : 114.8, 33.4, 29.8; CH <sub>3</sub> : 32.0, 0.2, 0.0	–19.7
39	6.56 (m, 1H), 6.12 (m, 1H), 5.98 (m, 1H), 5.68 (m, 2H), 4.95 (m, 1H), 2.59 (m, 2H), 1.90 (m, 2H), 1.56 (m, 2H), 1.43 (m, 2H), 1.27 (s, 9H), 0.25 (s, 3H), 0.22 (s, 3H)	C <sub>q</sub> : 145.6, 110.0, 63.8; CH: 126.8, 125.8, 125.5; CH <sub>2</sub> : 137.8, 114.8, 33.4, 29.8; CH <sub>3</sub> : 32.0, 0.2, 0.0	–19.5
40	6.38 (m, 1H), 6.13 (m, 1H), 5.98 (m, 1H), 5.66 (m, 2H), 4.95 (m, 1H), 2.64 (m, 2H), 2.16 (m, 2H), 1.30 (s, 9H), 0.29 (s, 3H), 0.27 (s, 3H)	C <sub>q</sub> : 140.1, 108.8, 57.8; CH: 122.4, 121.8, 120.1; CH <sub>2</sub> : 137.5, 115.8, 108.8, 34.6, 29.2; CH <sub>3</sub> : 32.7, 0.9, 0.7	–20.3
41	6.36 (m, 1H), 6.32 (m, 1H), 6.26 (m, 1H), 5.98 (m, 2H), 5.14 (m, 1H), 2.81 (m, 2H), 2.12 (m, 2H), 1.81 (m, 2H), 1.63 (s, 9H), 0.42 (s, 3H), 0.45 (s, 3H)	C <sub>q</sub> : 145.3, 108.5, 63.7; CH: 125.8, 125.3, 123.7; CH <sub>2</sub> : 136.9, 114.8, 33.8, 29.8, 28.9; CH <sub>3</sub> : 32.0, 1.2, 0.5	–20.4
42	6.33 (m, 1H), 6.16 (m, 1H), 6.02 (m, 1H), 5.69 (m, 2H), 4.97 (m, 1H), 2.52 (m, 2H), 1.90 (m, 2H), 1.57 (m, 2H), 1.37 (m, 2H), 1.32 (s, 9H), 0.30 (s, 3H), 0.28 (s, 3H)	C <sub>q</sub> : 145.1, 109.0, 57.8; CH: 122.6, 121.8, 120.3; CH <sub>2</sub> : 138.9, 115.0, 33.9, 30.4, 29.9, 29.4; CH <sub>3</sub> : 33.0, 1.1, 0.9	–20.4
43	7.23 (d, 1H) [8.5], 7.13 (d, 1H) [8.5], 7.01 (t, 1H) [8.5], 6.87 (t, 1H) [8.5], 6.22 (s, 1H), 5.67 (m, 1H), 4.78 (m, 2H), 3.75 (m, 2H), 1.27 (s, 9H), 0.87 (s, 3H), 0.43 (s, 3H)	C <sub>q</sub> : 136.1, 134.4, 132.1, 97.5, 62.5; CH: 135.4, 128.6, 128.1, 127.4, 124.7; CH <sub>2</sub> : 116.6, 33.6; CH <sub>3</sub> : 32.2, 2.9, 0.6	–20.0
44	7.61 (d, 1H) [8.5], 7.74 (d, 1H) [8.5], 7.08 (t, 1H) [8.5], 7.01 (t, 1H) [8.5], 6.26 (s, 1H), 5.69 (m, 1H), 4.95 (m, 2H), 2.92 (m, 2H), 2.26 (m, 2H), 1.23 (s, 9H), 0.60 (s, 3H), 0.40 (s, 3H)	C <sub>q</sub> : 137.5, 136.0, 135.2, 96.7, 62.8; CH: 137.5, 128.8, 124.8, 125.6, 122.9; CH <sub>2</sub> : 115.4, 34.6, 28.8; CH <sub>3</sub> : 32.8, 3.2, 0.8	–19.9
45	7.82 (d, 1H) [8.1], 7.74 (d, 1H) [8.1], 7.56 (t, 1H) [8.1], 7.41 (t, 1H) [8.1], 6.44 (s, 1H), 5.91 (m, 1H), 5.11 (m, 2H), 3.19 (m, 2H), 2.23 (m, 2H), 1.93 (m, 2H), 1.49 (s, 9H), 0.76 (s, 3H), 0.66 (s, 3H)	C <sub>q</sub> : 138.5, 135.8, 135.0, 115.2, 63; CH: 137.9, 128.6, 128.1, 127.5, 126.9, 123.2; CH <sub>2</sub> : 115.2, 33.4, 29.1, 28.4; CH <sub>3</sub> : 33.1, 3.3, 1.0	–20.4
46	7.60 (d, 1H) [8.5], 7.36 (d, 1H) [8.5], 7.15 (t, 1H) [8.5], 6.98 (t, 1H) [8.5], 6.24 (s, 1H), 5.69 (m, 1H), 4.96 (m, 2H), 2.89 (m, 2H), 1.89 (m, 2H), 1.55 (m, 2H), 1.32 (m, 2H), 1.31 (s, 9H), 0.56 (s, 3H), 0.37 (s, 3H)	C <sub>q</sub> : 136.7, 135.7, 131.3, 92.6, 63.1; CH: 138.7, 128.8, 128.4, 127.6, 125.7, 124.9; CH <sub>2</sub> : 114.8, 33.8, 29.8, 29.3, 29.0; CH <sub>3</sub> : 32.5, 3.3, 0.9	–20.2
47	7.66 (d, 1H) [8.5], 7.45 (d, 1H) [8.5], 7.22 (t, 1H) [8.5], 7.07 (t, 1H) [8.5], 6.34 (s, 1H), 5.79 (m, 1H), 5.06 (m, 2H), 3.03 (m, 2H), 1.98 (m, 2H), 1.52 (m, 2H), 1.40 (m, 2H), 1.36 (s, 9H), 1.31 (m, 2H), 0.59 (s, 3H), 0.46 (s, 3H)	C <sub>q</sub> : 138.5, 135.8, 135.0, 96.4, 62.5; CH: 138.6, 128.5, 127.3, 126.9, 125.7, 124.6; CH <sub>2</sub> : 114.4, 33.7, 29.8, 29.1, 28.9, 28.6; CH <sub>3</sub> : 32.2, 3.0, 0.6	–20.2
48	7.36 (d, 1H) [8.5], 7.41 (d, 1H) [8.5], 7.03 (t, 1H) [8.5], 6.97 (t, 1H) [8.5], 6.28 (s, 1H), 5.97 (m, 1H), 4.98 (m, 2H), 3.68 (m, 2H), 1.22 (s, 9H), 0.59 (s, 3H), 0.37 (s, 3H)	C <sub>q</sub> : 136.1, 134.2, 132.5, 90.9, 57.4; CH: 135.5, 127.6, 126.0, 125.6, 124.0; CH <sub>2</sub> : 116.4, 32.8; CH <sub>3</sub> : 32.4, 3.6, 1.6	–20.4
49	7.61 (d, 1H) [8.5], 7.74 (d, 1H) [8.5], 7.08 (t, 1H) [8.5], 7.01 (t, 1H) [8.5], 6.26 (s, 1H), 5.69 (m, 1H), 4.95 (m, 2H), 2.92 (m, 2H), 2.26 (m, 2H), 1.23 (s, 9H), 0.60 (s, 3H), 0.40 (s, 3H)	C <sub>q</sub> : 136.3, 134.2, 131.8, 90.6, 57.0; CH: 137.5, 127.6, 127.3, 125.6, 124.1; CH <sub>2</sub> : 115.7, 34.4, 27.7; CH <sub>3</sub> : 33.0, 3.9, 1.8	–20.5
50	7.64 (d, 1H) [8.5], 7.35 (d, 1H) [8.5], 7.06 (t, 1H) [8.5], 6.98 (t, 1H) [8.5], 6.28 (s, 1H), 5.89 (m, 1H), 5.00 (m, 2H), 2.78 (m, 2H), 1.94 (m, 2H), 1.57 (m, 2H), 1.23 (s, 9H), 0.60 (s, 3H), 0.39 (s, 3H)	C <sub>q</sub> : 136.2, 134.3, 131.1, 95.6, 57.3; CH: 138.2, 127.9, 127.4, 125.9, 124.1, 124.0; CH <sub>2</sub> : 115.3, 33.7, 29.7, 27.7; CH <sub>3</sub> : 33.0, 3.9, 1.8	–20.5
51	7.48 (d, 1H) [8.5], 7.26 (d, 1H) [8.5], 6.94 (t, 1H) [8.5], 6.84 (t, 1H) [8.5], 6.17 (s, 1H), 5.69 (m, 1H), 4.83 (m, 2H), 2.74 (m, 2H), 1.78 (m, 2H), 1.38 (m, 2H), 1.14 (m, 2H), 1.10 (s, 9H), 0.46 (s, 3H), 0.25 (s, 3H)	C <sub>q</sub> : 136.2, 134.7, 131.9, 92.6, 62.3; CH: 138.6, 127.9, 127.7, 126.0, 125.7, 124.0; CH <sub>2</sub> : 114.8, 33.7, 29.9, 28.9, 28.1; CH <sub>3</sub> : 33.1, 4.0, 1.9	–20.5

Table 6 (Continued)

Complex	<sup>1</sup> H-NMR	<sup>13</sup> C-NMR	<sup>29</sup> Si-NMR
52	7.63 (d, 1H) [8.5], 7.36 (d, 1H) [8.5], 7.07 (t, 1H) [8.5], 6.96 (t, 1H) [8.5], 6.20 (s, 1H), 5.70 (m, 1H), 4.96 (m, 2H), 2.91 (m, 2H), 1.92 (m, 2H), 1.30 (m, 2H), 1.24 (m, 2H), 1.22 (s, 9H), 0.64 (s, 3H), 0.43 (s, 3H)	C <sub>q</sub> : 137.8, 126.6, 126.0, 91.3, 58.9; CH: 137.8, 126.6, 127.7, 126.0, 125.7, 124.0; CH <sub>2</sub> : 114.1, 32.4, 27.4, 28.2, 27.4; CH <sub>3</sub> : 33.5, 4.9, 1.8	–20.8
53	7.57 (d, 1H) [8.5], 7.33 (d, 1H), [8.5], 7.12 (t, 1H) [8.5], 7.02 (t, 1H) [8.5], 6.21 (s, 1H), 2.99 (m, 2H), 1.52 (t, 2H) [7.5], 1.31 (s, 9H), 0.89 (t, 3H) [7.5], 0.57 (s, 3H), 0.38 (s, 3H)	C <sub>q</sub> : 138.9, 137.3, 127.3, 97.0, 58.6; CH: 128.5, 127.4, 124.9, 124.6, 123.7; CH <sub>2</sub> : 31.1, 22.7; CH <sub>3</sub> : 32.2, 14.0, 3.0, 0.7	–20.2
54	7.60 (d, 1H) [8.5], 7.36 (d, 1H) [8.5], 7.15 (t, 1H) [8.5], 7.05 (t, 1H) [8.5], 6.24 (s, 1H), 3.02 (m, 2H), 1.49 (m, 2H), 1.31 (s, 9H), 1.21 (m, 2H), 0.81 (t, 3H) [7.3], 0.58 (s, 3H), 0.39 (s, 3H)	C <sub>q</sub> : 138.8, 137.1, 135.4, 99.9, 63.1; CH: 128.1, 127.2, 126.2, 125.0, 118.1; CH <sub>2</sub> : 33.4, 29.9, 23.3; CH <sub>3</sub> : 33.2, 14.2, 4.1, 2.1	–20.2
55	7.65 (d, 1H) [8.5], 7.43 (d, 1H) [8.5], 7.22 (t, 1H) [8.5], 7.09 (t, 1H) [8.5], 6.31 (s, 1H), 3.30 (m, 2H), 3.08 (m, 2H), 1.56 (m, 2H), 1.38 (s, 9H), 1.12 (m, 2H), 0.90 (t, 3H) [7.3], 0.64 (s, 3H), 0.45 (s, 3H)	C <sub>q</sub> : 138.5, 136.7, 134.8, 100.3, 62.2; CH: 128.7, 126.8, 126.1, 124.6, 113.9; CH <sub>2</sub> : 33.4, 29.9, 25.4, 23.3; CH <sub>3</sub> : 33.7, 12.3, 3.7, 2.4	–20.2
56	7.69 (d, 1H) [8.5], 7.34 (d, 1H) [8.5], 7.11 (t, 1H) [8.5], 7.09 (t, 1H) [8.5], 6.22 (s, 1H), 3.33 (m, 2H), 3.18 (m, 2H), 2.88 (m, 2H), 1.59 (m, 2H), 1.43 (s, 9H), 1.11 (m, 2H), 0.88 (t, 3H) [7.3], 0.58 (s, 3H), 0.39 (s, 3H)	C <sub>q</sub> : 137.6, 136.7, 135.8, 98.9, 64.1; CH: 128.6, 126.2, 125.4, 123.1, 114.3; CH <sub>2</sub> : 32.9, 28.7, 24.2, 22.9, 21.3; CH <sub>3</sub> : 33.1, 11.7, 3.3, 2.1	–20.2
57	7.70 (d, 1H) [8.5], 7.41 (d, 1H), [8.5], 7.10 (t, 1H) [8.5], 7.01 (t, 1H) [8.5], 6.30 (s, 1H), 2.99 (m, 2H), 1.60 (t, 2H) [7.5], 1.31 (s, 9H), 0.90 (t, 3H) [7.5], 0.75 (s, 3H), 0.52 (s, 3H)	C <sub>q</sub> : 139.1, 134.9, 128.9, 92.0, 56.8; CH: 128.2, 127.3, 125.6, 125.5, 123.9; CH <sub>2</sub> : 30.0, 23.5; CH <sub>3</sub> : 32.8, 13.8, 3.7, 1.6	–20.5
58	7.56 (d, 1H) [8.5], 7.28 (d, 1H) [8.5], 7.13 (t, 1H) [8.5], 6.98 (t, 1H) [8.5], 6.21 (s, 1H), 2.98 (m, 2H), 1.42 (m, 2H), 1.41 (s, 9H), 1.26 (m, 2H), 0.87 (t, 3H) [7.3], 0.67 (s, 3H), 0.29 (s, 3H)	C <sub>q</sub> : 142.2, 139.6, 135.8, 100.7, 59.5; CH: 127.1, 126.8, 126.2, 124.7, 117.9; CH <sub>2</sub> : 32.6, 28.9, 23.1; CH <sub>3</sub> : 32.6, 13.9, 3.8, 2.0	–20.5
59	7.67 (d, 1H) [8.5], 7.55 (d, 1H) [8.5], 7.14 (t, 1H) [8.5], 7.02 (t, 1H) [8.5], 6.43 (s, 1H), 2.70 (m, 2H), 3.12 (m, 2H), 1.55 (m, 2H), 1.27 (s, 9H), 1.12 (m, 2H), 0.94 (t, 3H) [7.3], 0.45 (s, 3H), 0.21 (s, 3H)	C <sub>q</sub> : 142.1, 141.7, 140.2, 89.9, 55.2; CH: 127.9, 127.1, 125.1, 123.8, 119.3; CH <sub>2</sub> : 33.1, 29.2, 24.2, 22.7; CH <sub>3</sub> : 33.8, 14.2, 4.0, 1.9	–20.5
60	7.74 (d, 1H) [8.5], 7.45 (d, 1H) [8.5], 7.17 (t, 1H) [8.5], 7.10 (t, 1H) [8.5], 6.31 (s, 1H), 2.93 (m, 2H), 1.64 (t, 2H) [7.5], 1.34 (s, 9H), 0.93 (t, 3H) [7.5], 0.75 (s, 3H), 0.54 (s, 3H)	C <sub>q</sub> : 139.9, 133.6, 127.0, 89.8, 55.3; CH: 127.3, 126.8, 125.6, 124.5, 123.7; CH <sub>2</sub> : 29.8, 23.7; CH <sub>3</sub> : 33.6, 13.8, 4.0, 1.9	–20.8

<sup>a</sup> In C<sub>6</sub>H<sub>6</sub>-d<sub>6</sub> at 25°C.

## Acknowledgements

We thank Phillips Petroleum Company (Bartlesville, OK, USA) for the financial support and Witco Company for a donation of methylaluminoxane.

## References

- [1] P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, *Organometallics* 9 (1990) 867.
- [2] J. Okuda, *Chem. Ber.* 123 (1990) 1649.
- [3] A.K. Hughes, A. Meetsma, J.H. Teuben, *Organometallics* 12 (1993) 1996.
- [4] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem.* 111 (1999) 448; *Angew. Chem. Int. Ed. Engl.* 38 (1999) 428, and references therein.
- [5] Exxon Chemical Co., US Patent 5,026,798, 1991.
- [6] T.E. Ready, R.O. Day, J.C.W. Chien, M.D. Rausch, *Macromolecules* 26 (1993) 5822.
- [7a] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* 19 (1986) 2464.
- [7b] N. Ishihara, M. Kuramoto, M. Uoi, *Macromolecules* 21 (1988) 3356.
- [8] J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, N.P. Nickias, R.K. Rosen, W. Knight, S.Y. Lai, Dow Chemical Co., *Eur. Pat. Appl. EP 0416815*, 1991; *Chem. Abstr.* 115 (1991) 93163.
- [9] Dow Chemical Company Co., *Eur. Pat. Appl. 416815*, 1991.
- [10] J.A. Canich, US Patent 4,168,15, 1992.
- [11] C. Pellecchia, A. Proto, A. Zambelli, *Macromolecules* 25 (1992) 4490.
- [12] P. Aaltonen, J. Seppälä, *Eur. Polym. J.* 10 (1991) 310.
- [13] B. Peifer, W. Milius, H.G. Alt, *J. Organomet. Chem.* 553 (1998) 205.

- [14] H.G. Alt, M. Jung, *J. Organomet. Chem.* 580 (1999) 1.
- [15] H.G. Alt, *J. Chem. Soc. Dalton Trans.* (1999) 1703, and references therein.
- [16] W. Kaminsky, F. Renner, *Makromol. Chem. Rapid. Commun.* 14 (1993) 239.
- [17] K. Ziegler, H. Froitzheim-Kühlhorn, K. Hafner, *Chem. Ber.* 89 (1956) 434.
- [18] J. Quéré, E. Maréchal, *Bull. Soc. Chim. Fr.* (1969) 4087.
- [19] K. Patsidis, H.G. Alt, W. Milius, S.J. Palackal, *J. Organomet. Chem.* 509 (1996) 63.
- [20] P. Diehl, E. Fluck, R. Kosfeld, *NMR Basic Principles and Progress*, Springer, Berlin, 1981 (p. 154).
- [21] G.A. Luinstra, J.H. Teuben, *J. Chem. Soc. Chem. Commun.* (1990) 1470.
- [22] T.K. Woo, F.L. Ziegler, *Organometallics* 13 (1994) 2252.
- [23] J. Okuda, F.J. Schattenmann, S. Wocadlo, W. Massa, *Organometallics* 14 (1995) 789.
- [24] K.E. du Plooy, U. Moll, S. Wocadlo, W. Massa, J. Okuda, *Organometallics* 14 (1995) 3129.
- [25] H.G. Alt, M. Jung, *J. Organomet. Chem.* 562 (1998) 229.
- [26] G. Luft, M. Dorn, *Angew. Macromol. Chem.* 188 (1991) 177.