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ω-Phenylalkyl substituted amido functionalized *ansa* half-sandwich complexes of titanium and zirconium and metallacycles thereof as catalyst precursors for homogeneous ethylene polymerization

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Abstract

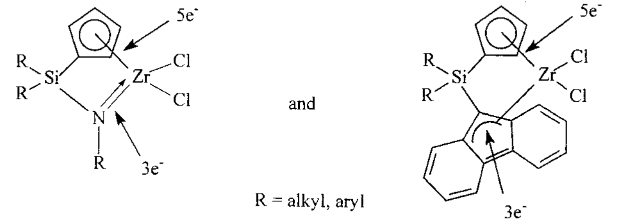
The preparation and characterization of ω-phenylalkyl substituted *ansa* half-sandwich dichloride complexes of titanium and zirconium is described. These complexes react with butyllithium to give metallacycles via a CH activation reaction on the *ortho* position of the phenyl group. All complexes were used as catalyst precursors for homogeneous ethylene polymerization. The effect of the catalyst structure on the polyethylene properties is discussed.

Keywords: Group 4 metals; *ansa* Half-sandwich complexes; Metallacycles; Ethylene polymerization; Homogeneous polymerization

1. Introduction

The electron balance of amido functionalized *ansa* half-sandwich complexes of Group 4 metals can be compared with the electron balance of metallocene complexes if one of the aromatic ligands of the metallocene complex is able to undergo a ring slippage reaction from η^5 to η^3 [1,2].

For instance:



Because of this situation the class of half-sandwich complexes is gaining increasing interest as catalyst precursors for catalytic olefin polymerization [3–21]. Since the preparation of the first bridged amido functionalized half-sandwich complex [22] carbon linked derivatives have also been reported [23–25].

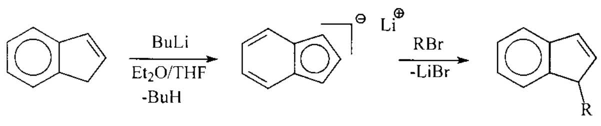
Metallocene complexes with ω-phenyl functionalized alkyl substituents have proven to be excellent catalyst precursors [26–28]. Upon reaction with butyllithium they can form metallacycles via C,H activation reactions and increase their catalytic activity [29,30].

Because of this background our intention was to prepare *ansa* half-sandwich complexes with ω-phenylalkyl substituents in order to investigate their reactivity with butyllithium and to test their catalytic potential for the polymerization of ethylene.

2. Results and discussion

2.1. Synthesis of the ligand precursors

The functionalization of the aromatic system with an ω-phenylalkyl group is conducted as a salt elimination



1 (R = CH_2Ph)
2 (R = $(CH_2)_2Ph$)
3 (R = $(CH_2)_3Ph$)

Scheme 1. Substitution of indene with $(CH_2)_nPh$ groups ($n = 1–3$).

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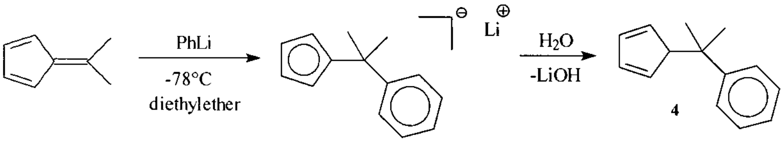
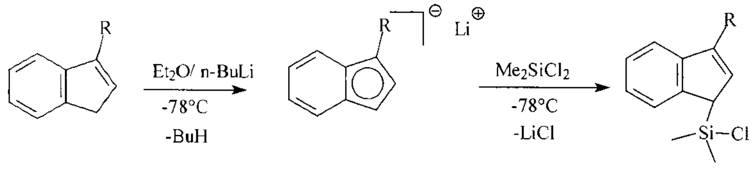


Scheme 2. Preparation of a cyclopentadiene derivative with a CMe_2Ph substituent. The corresponding indene derivative **5** was prepared in an analogous manner.



6 ($R = CH_2Ph$)
7 ($R = (CH_2)_2Ph$)
8 ($R = (CH_2)_3Ph$)
9 ($R = CMe_2Ph$)
10 ($C_5H_4(CMe_2Ph)SiMe_2Cl$)

Scheme 3. Synthesis of functionalized chlorodimethylsilane derivatives.

reaction [31–35] (Scheme 1). For a CMe_2Ph substituent a fulvene reaction is advantageous (Scheme 2).

Different from literature procedures, the linking of the silyl substituent to the functionalized cyclopentadiene or indene system is not conducted in non-polar solvents but in diethyl ether [36] because of higher yields (Scheme 3).

In general, there are two methods to synthesize alkylamine(dialkylsilyl) substituted 1-indene- and 1-cyclopentadiene derivatives.

If the path of the conventional method is pursued [37], the desired ligand precursor is obtained by the reaction of the chlorosilane compound with the lithium salt of the corresponding amine. Here the chlorosilane compound is mixed with an excess of amine in a polar solvent (Scheme 4).

*2.2. Synthesis of the ansa half-sandwich complexes **16–23***

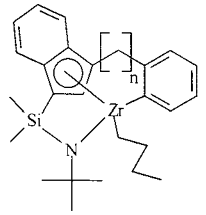
Amido functionalized *ansa* half-sandwich complexes of titanium were synthesized in very high yields using the method described in Scheme 5. In the first step the ligand precursor is reacted with two equivalents of *n*-butyllithium to form the dianion. Subsequently, $TiCl_3 \cdot 3THF$ is added and then $PbCl_2$ is added as a mild oxidation agent. Compared to the reaction of the dilithiated ligand precursor with titanium tetrachloride [38] this path prevents the formation of a sandwich complex and gives higher yields [39,40].

The synthesis of the zirconium complexes proceeds in the conventional manner [41]. The dilithiated ligand precursor is reacted with the corresponding metal tetrachloride. Hereby the yields are lower compared with the corresponding titanium complexes (Scheme 5).

*2.3. Synthesis of the metallacycles **24–26***

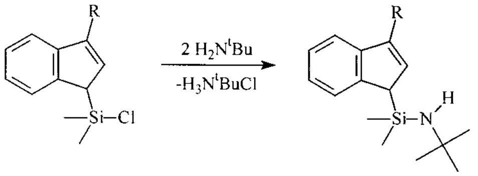
The ω-phenylalkyl functionalized *ansa* half-sandwich complexes react with butyllithium to yield metallacycles via a C,H activation reaction (Scheme 6).

The metallacycles **25** and **26** were obtained in the same way:



25 (n = 2)
26 (n = 3)

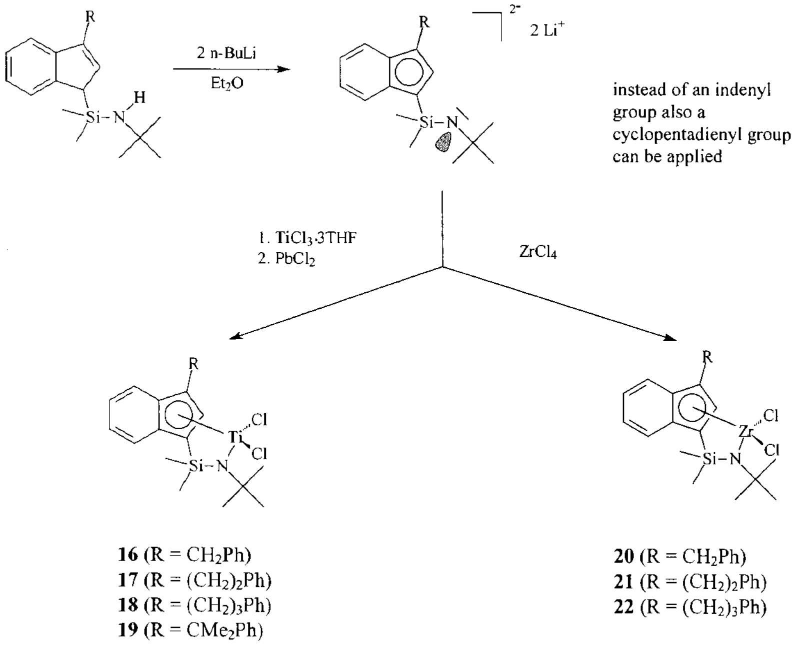
No metallacycle was obtained from compound **20**. It is assumed that one methylene group as a spacer unit is not sufficient for the required ring closure to the metal. The titanacycle **24** was formed despite the C_1 spacer. Presumably both space-demanding methyl groups in *exo* position reduce the angle between the cyclopentadienyl ring and the phenyl ring so far that a bond from



11 ($R = CH_2Ph$)
12 ($R = (CH_2)_2Ph$)
13 ($R = (CH_2)_3Ph$)
14 ($R = CMe_2Ph$)

15 ($C_5H_4(CMe_2Ph)SiMe_2NH^tBu$)

Scheme 4. Synthesis of the ligand precursors.



16 ($R = CH_2Ph$)
17 ($R = (CH_2)_2Ph$)
18 ($R = (CH_2)_3Ph$)
19 ($R = CMe_2Ph$)

20 ($R = CH_2Ph$)
21 ($R = (CH_2)_2Ph$)
22 ($R = (CH_2)_3Ph$)

23 ($C_5H_3(CMe_2Ph)SiMe_2N^tBuTiCl_2$)

Scheme 5. Synthesis of the amido functionalized ansa half-sandwich complexes **16**–**23**.

the metal to the carbon atom in *ortho* position of the phenyl ring can be established without major ring strain. Titanacycles with indenyl ligands were only obtained in product mixtures with the corresponding dichloride complexes.

2.4. Characterization of the complexes

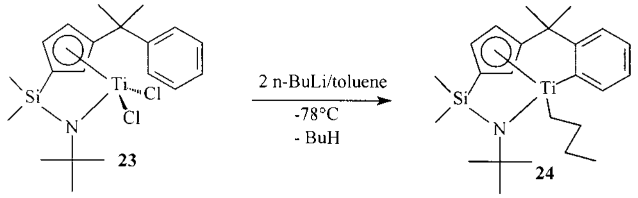
^{1}H-, ^{13}C- and ^{29}Si-NMR spectroscopy were used to characterize the *ansa* amido half-sandwich complexes and the metallacycles. The data are listed in Section 3. The ^{1}H- and ^{13}C-NMR spectra of two examples (**23** and **24**) are discussed.

In the ^{1}H-NMR spectrum of compound **23** (Fig. 1) the signals for the phenyl protons are detected at $\delta = 7.21–7.08$ ppm. At $\delta = 6.70$, 6.40 and 6.15 ppm the three virtual triplets appear that can be assigned to the AMX spin system of the 1,3-substituted cyclopentadienyl ring. The aliphatic region is marked with two singlets for the diastereotopic methyl groups of the C_1 spacer ($\delta = 1.78$ and 1.76 ppm) and of the bridging silicon atom spacer ($\delta = 0.27$ and 0.24 ppm). The three methyl groups of the *tert*-butyl group are homotopic and form one singlet with a signal intensity of nine protons at $\delta = 1.47$ ppm.

In the *J*-modulated ^{13}C-NMR spectrum of **23** all five resonance signals with negative phase are attributed to the quaternary carbon atoms 3, 10, 11, 14 and 17. The CH resonances in the aryl area (positive phase) correspond to the ring carbon atoms of the cyclopentadienyl and the phenyl ring. The aliphatic area exhibits at $\delta = 32.1$ ppm the singlet signal for the three homotopic methyl carbon atoms of the *tert*-butyl group. The diastereotopic carbon atoms 12 and 13 appear at $\delta = 28.6$ and 27.9 ppm, respectively, the carbon atoms of the methyl groups 1 and 2 at $\delta = 0.0$ and -0.5 ppm, respectively (Fig. 2).

In the following the resonance signals of both the metallacycle **24** and the corresponding complex **23** are compared.

The metallacycle exhibits significant changes in the ^{1}H-NMR spectrum compared to the parent dichloride compound. The relatively simple spin system for the phenyl ring in **23** changes into an ABCD-spin system for **24**. Hereby both doublet signals for protons 10 and 13 are found at $\delta = 8.15$ and 7.42 ppm, respectively. The three virtual triplets of the cyclopentadienyl ring appear at higher field; they are widely spread. The shift difference of both diastereotopic methyl protons on the C_1-bridge to the phenyl ring is very small and the resonances overlap with the signal of the nine methyl protons 4 (confirmed by ^{1}H-,^{13}C 2D correlation NMR



Scheme 6. Synthesis of amido half-sandwich metallacycles.

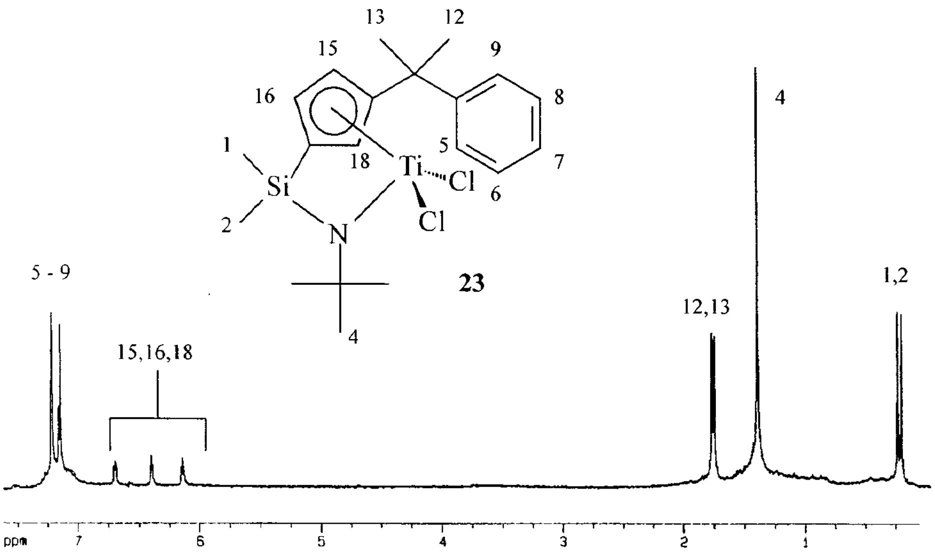


Fig. 1. 300.13 MHz ^{1}H-NMR spectrum of **23** (25°C, C_6D_6).

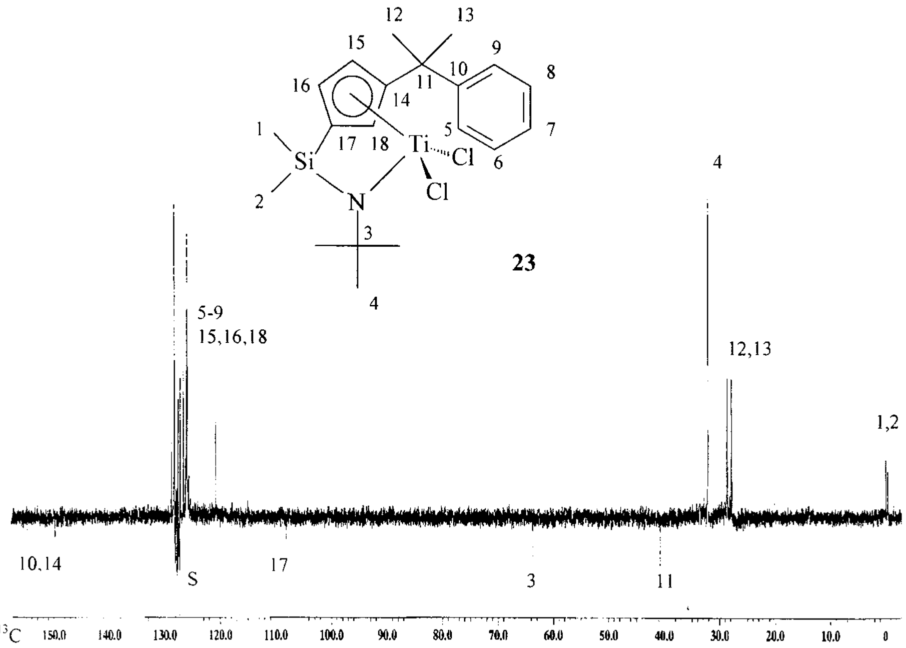


Fig. 2. 67.94 MHz J-modulated ^{13}C-NMR spectrum of **23** (25°C, C_6D_6); S = C_6D_6.

experiment). The signals for the three methylene protons 5–7 can be observed in the region of $\delta = 1.92$–0.99 ppm, the triplet for the terminal methyl group 8 at $\delta = 0.83$ ppm. The least-affected signals are the singlet signals for the diastereotopic methyl groups on the silicon atom. They are recorded at $\delta = 0.34$ and 0.30 ppm (Fig. 3).

A closer examination of the J-modulated ^{13}C-NMR spectrum of metallacycle **24** (Fig. 4) reveals significant differences when compared with the spectrum of the dichloride compound **23**. The signal of an additional quaternary carbon atom is observed at $\delta = 191.1$ ppm which is attributed to the ring carbon 9. The neighboring quaternary carbon atom 14 is shifted downfield by about 17 ppm to $\delta = 171.6$ ppm. The signals for the methylene groups of the butyl ligand exhibit their resonances at $\delta = 86.7$, 35.9 and 26.3 ppm. The resonance for methyl group 8 is detected at $\delta = 30.2$ ppm. The two diastereotopic methyl groups 16 and 17 appear at $\delta = 29.1$ and 14.1 ppm, respectively. The chemical shifts for the methyl groups of the *tert*-butyl group (4) and the silicon atom (1,2) are hardly affected.

2.5. Polymerization of ethylene

The *ansa* half-sandwich complexes **16**–**23** and the metallacycles **24**–**26** can be activated with methylalumoxane (MAO) and then be used for homogeneous ethylene polymerization. Fig. 5 and Table 1 show the activities of these catalysts and the molecular weights, melting points, melting enthalpies and crystallinities of the produced polyethylenes.

2.6. The effect of the catalyst structure on the polyethylene properties (structure–properties relationship)

The effect of various substituents in *ansa* half-sandwich complexes [43–45] on the activity of these catalysts has not been studied to the same extent as in the case of metallocene complexes [46]. From Fig. 5 it becomes obvious that alkyl substituents with a terminal

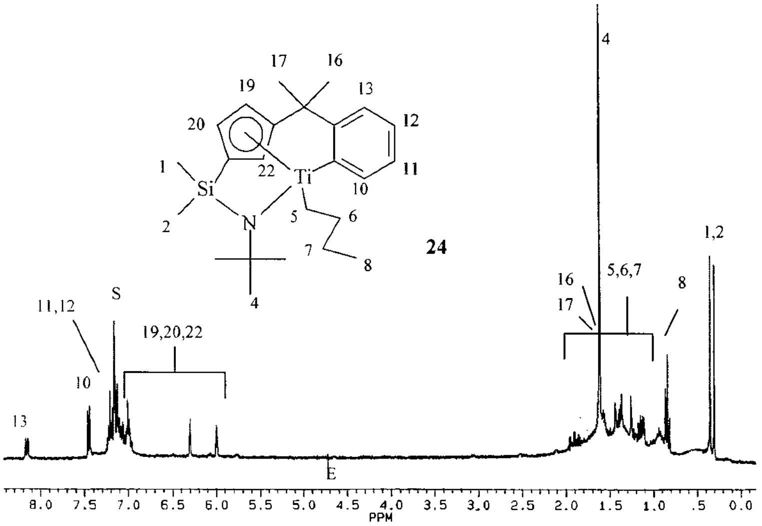


Fig. 3. 300.13 MHz ^{1}H-NMR spectrum of **24** (25°C, C_6D_6); S = C_6H_6, E = spike.

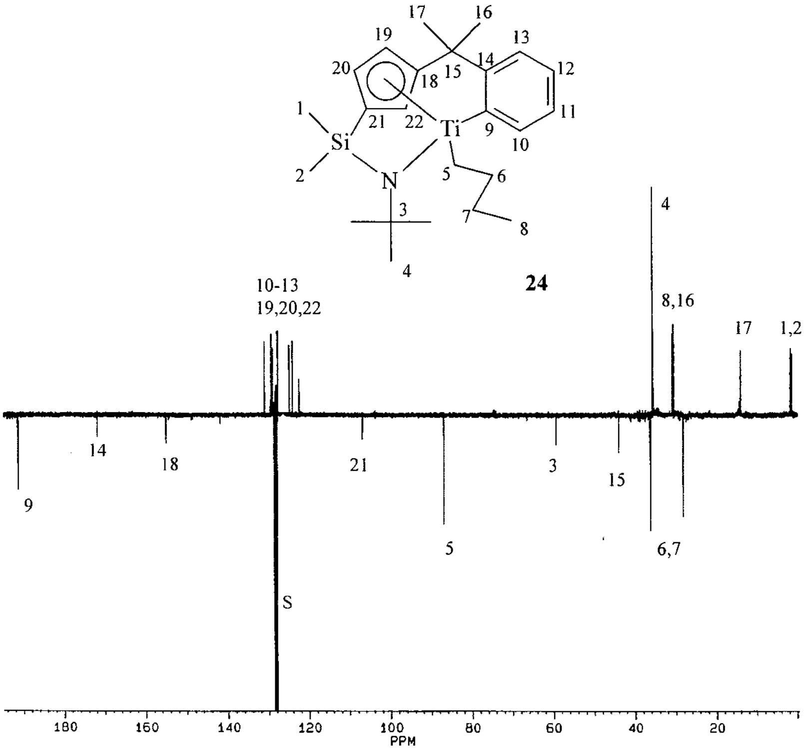


Fig. 4. 75.47 MHz *J*-modulated ^{13}C-NMR spectrum of **24** (25°C, C_6D_6). The signal for the quaternary carbon atom 9 at 191.1 ppm is characteristic; S = C_6D_6.

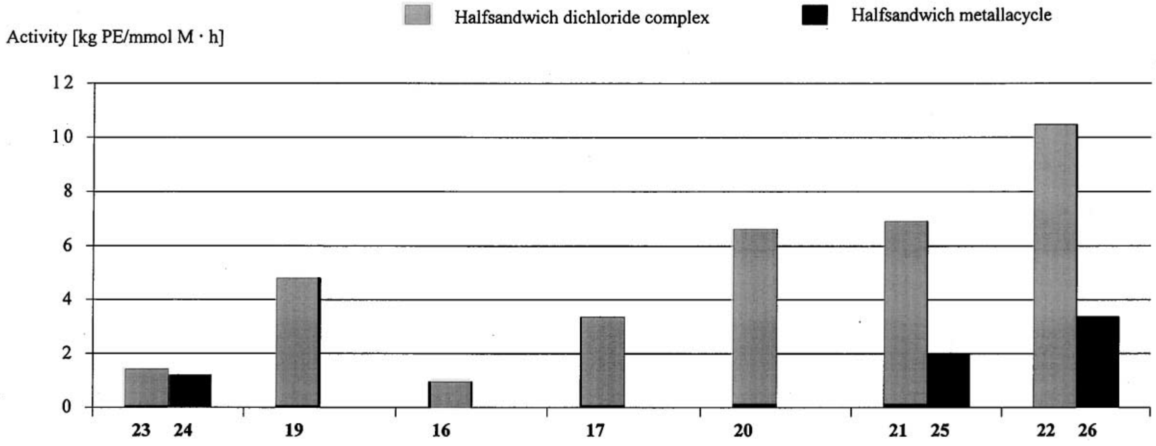


Fig. 5. Activities of the ω-phenylalkyl substituted half-sandwich complexes in homogeneous ethylene polymerization.

Table 1
Polymerization data

Complex	Activity (g) PE/(mmol) M h	GPC			DSC		
		$\bar{M}_w$ (g mol^{-1})	$\bar{M}_n$ (g mol^{-1})	HI	M.p. [a] (°C)	$\Delta\bar{H}_m$ (J g^{-1})	α [b]
16	958	766 800	178 000	4.31	134.3	93.7	32.3
17	3353	647 400	161 900	4.00	142.6	166.5	57.4
18	ND [c]	ND [c]			ND [c]		
19	4790	1 184 000	55 130	21.47	142.0	90.2	31.1
20	6823	1 211 000	195 400	6.20	142.8	138.7	47.8
21	6841	669 000	195 400	3.42	142.1	156.2	53.9
22	10 490	521 600	149 900	3.48	142.0	158.5	54.6
23	1485	752 100	22 070	34.07	133.7	51.4	17.7
24	1203	$\bar{M}_w > 1\ 100\ 000$ [d]			136.1	63.4	21.9
25	2006	1 003 000	336 500	2.98	141.0	141.1	48.7
26	3374	863 300	242 100	3.56	141.1	149.0	51.4

[a] Maximum of the melting peak during the second heating course of the DSC.

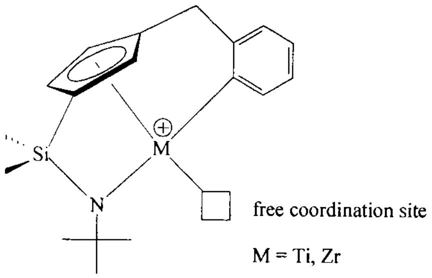
[b] $\alpha = \Delta H_m / \Delta H_m^\circ$ with $\Delta H_m^\circ = 290$ J g^{-1} [42].

[c] Not determined.

[d] New styra gel HT6E-GPC-column; molecular weight too high.

phenyl group increase the activity of the catalyst. This could be due to a spacer effect that separates the bulky MAO anion from the catalyst cation during the polymerization process. This effect has been studied with *ansa* bis(fluorenyl) complexes [47]. The flexibility and the volume of the spacers increase with the length of these substituents.

Zirconium complexes with indenylidene ligands (**20**–**22**) are more active than the analogous titanium derivatives (**16** and **17**). The reason for this behavior could be the longer lifetime of zirconium derivatives at elevated temperatures. Surprisingly, the metallacycles **24**–**26** show a lower activity than the parent half-sandwich dichloride complexes. In the corresponding metallocene series the opposite behavior was observed [29,30]. It can be speculated that the hypothetic cationic catalyst molecule is too stable to allow fast ethylene insertion reactions into the M–C$_{\text{phenylene}}$ bond during the polymerization process.



Principally one should keep in mind that a whole series of parameters like ion–ion interactions, solvent, temperature, cocatalyst, ethylene pressure contribute to the kinetics of the polymerization reaction and thus determine the activity. The individual influence of each parameter, however, is unknown.

The polyethylenes obtained from the various homogeneous polymerization reactions all show high molecular weights and in some cases (**19** and **23**) high polydispersities (21.47 and 34.07). The high molecular weight distributions indicate various active sites generated during the course of the polymerization. This could be due to changes of the catalyst, interactions (catalyst–cocatalyst) or generation of different heterogeneous active sites.

A high molecular weight of the obtained polyethylene is not automatically accompanied by a high melting point. Short- and long-chain branching can reduce the viscosity of such a resin [48]. Further investigations of these aspects are in progress.

3. Experimental

All experimental work was routinely carried out with Schlenk technique. Dried and purified Ar was used as inert gas. The solvents $C_6H_5CH_3$, C_5H_{12}, Et_2O and THF were purified by distillation over Na–K alloy. Et_2O was additionally distilled over lithium aluminum hydride. CH_2Cl_2 was dried with CaH_2. Deuterated solvents such as $CDCl_3$ and C_6D_6 were dried over molecular sieves (300 pm), degassed and stored under inert gas atmosphere.

Prior to use commercial indene was distilled and stored at −30°C. Cyclopentadiene was freshly distilled from the dimer. Methylaluminoxane (MAO) was supplied by Witco Company, Bergkamen, as 30% solution in $C_6H_5CH_3$. All the other starting materials were commercially available and were used without further purification.

3.1. NMR spectroscopy

The spectrometers JEOL FX 90Q and JNM-EX 270 E, and Bruker ARX 250, AC 300 and DRX 500 used for recording the NMR spectra. The organometallic compounds were prepared under Ar and measured at 25°C. The chemical shifts in ^{1}H-NMR spectra are referred to the residual proton signal of the solvent ($\delta = 7.24$ ppm for $CDCl_3$, $\delta = 7.15$ ppm for benzene) and in ^{13}C-NMR spectra to the solvent signal ($\delta = 77.0$ ppm for $CDCl_3$, $\delta = 128.0$ ppm for C_6D_6). Me_4Si ($\delta = 0.0$) was used as an external standard for ^{29}Si-NMR spectra.

3.2. Mass spectroscopy

The mass spectra were recorded with a Varian MAT CH7 instrument, GC–MS with a Varian 3700 gas chromatograph in combination with a Varian MAT 312 mass spectrometer.

3.3. Gas chromatography

Gas chromatograms were recorded using a Perkin–Elmer auto system gas chromatograph with a flame ionization detector (FID) and He as carrier gas (1 ml min^{-1}).

Temperature program:
starting phase, 3 min at 50°C;
heating phase, 5°C min^{-1} (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 instrument. In a typical run 3–5 mg each of the dried polymer was fused into standard aluminum pans and measured using the following temperature program: first heating phase (20 K min^{-1}) from 320 to 470 K, cooling phase (−50 K min^{-1}) to 320 K, second heating phase (10 K min^{-1}) from 320 to 470 K. The peak maximum of the second heating curve was indicated as the melting point.

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

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

3.6. Synthesis procedure for 1-(7,7-dimethylbenzyl)cyclopentadiene

6,6-Dimethylfulvene (or 6,6-dimethylbenzofulvene) (20.0 mmol) was dissolved in 150 ml Et_2O, mixed with 10.0 ml (20.0 mmol) phenyllithium (2 M solution in cyclohexane–Et_2O 70:30 wt%) at −78°C and the white suspension was stirred for 4 h at room temperature (r.t.). After filtration over Na_2SO_4 and removal of the solvent the product was obtained in 90% yields.

3.7. General procedure for the synthesis of the substituted cyclopentadienyl alkenyl methyl chlorosilane derivatives

At −78°C, 41.5 mmol (26.0 ml) *n*-butyllithium was added slowly to 41.5 mmol substituted cyclopentadiene in 150 ml Et_2O. The reaction mixture was stirred for 8 h. Subsequently the solvent was removed in vacuo (10 Torr). The lithium salt was added in portions to 83 mmol alkenylmethyldichlorosilane in 200 ml Et_2O at

− 78°C within 30 min. The mixture was stirred for 12 h. The suspension was filtered over Na_2SO_4, the solvent was evaporated and the remaining yellow liquid was distilled in vacuo. Yields: 59–80%.

*3.8. General procedure for the synthesis of the organyl substituted indene derivatives **1–5***

Indene (86 mmol) was dissolved in a mixture of 180 ml Et_2O and 18 ml THF and cooled to − 78°C. *n*-Butyllithium (86 mmol) was added using a syringe and the reaction mixture was stirred for 4 h at r.t. Subsequently 86 mmol of the corresponding bromide was added dropwise at − 78°C and stirred for 10 h. The reaction mixture was hydrolyzed with 50 ml water, the organic layer was filtered over Na_2SO_4 and the solvent was evaporated. The crude product was distilled in vacuo. The products were obtained in 85–90% yields.

*3.9. General procedure for the synthesis of the substituted indenylchlorosilane derivatives **6–9***

The corresponding indene derivative (80 mmol) was dissolved in 150 ml Et_2O and cooled to − 78°C. The equimolar amount of *n*-butyllithium was added slowly and the mixture was stirred for 4 h at r.t. Subsequently, the lithium salt was added to the equimolar amount of the dichlorodimethylsilane in 100 ml Et_2O at − 78°C and the mixture was stirred for 12 h. The suspension was filtered over Na_2SO_4 and the solvent was evaporated. The product was obtained in 80–96% yields (see Table 2 for NMR data).

*3.10. Procedure for the synthesis of the cyclopentadienyl ligand precursor **10***

The corresponding substituted cyclopentadienyl(ω-phenylalkyl)methylchlorosilane (39.2 mmol) in 200 ml C_5H_{10} was mixed at 0°C with 98 mmol (10.3 ml) *tert*-butylamine (2.5-fold excess). The solution was stirred for 12 h. The hydrogen chloride was eliminated by excess amine and precipitated as ammonium hydrochloride. The suspension was filtered, the solvent was evaporated and the residue was distilled (see Table 3 for NMR data).

*3.11. General procedure for the synthesis of the indenyl ligand precursors **11–15***

The corresponding indenylchlorosilane compound (80 mmol) was dissolved in 200 ml CH_2Cl_2 and 200 mmol *tert*-butylamine was added quickly. After stirring for 12 h the hydrogen chloride was eliminated by excess amine and precipitated as ammonium hydrochloride. The solvent was removed and the residue was dissolved in 200 ml C_5H_{12}. The suspension was filtered over Na_2SO_4 and the solvent was reduced in volume. The ligand precursors were obtained quantitatively as yellow to light red oils (see Table 3 for NMR data).

*3.12. General procedure for the synthesis of the amido functionalized ansa half-sandwich titanium complexes **16–19** and **23***

The corresponding ligand precursor (18 mmol) in Et_2O was added 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 r.t. The equimolar amount of the dilithium salt solution of the ligand was added slowly to 18 mmol (6.64 g) $TiCl_3{\cdot}3THF$ in 100 ml Et_2O at − 78°C. The mixture was stirred for 10 h. For oxidation, the titanium(III) compound was mixed with 18 mmol (4.99 g) $PbCl_2$ at r.t. and the reaction mixture was stirred for 30 min. The precipi-

Table 2
NMR data of the chlorosilane compounds **6**–**9** [a]

Compound	^1H-NMR	^{13}C-NMR	^{29}Si-NMR
6	7.60 (d, 1H) [7.5], 7.40 (d, 1H) [7.5], 7.3 (m), 6.32 (s, 1H), 4.00 (s, 1H), 0.25 (s, 3H), 0.22 (s, 3H)	C_q: 144.5, 143.8, 143.2, 139.6; CH: 129.7, 128.9, 128.5, 126.3, 125.7, 124.6, 123.6, 119.9, 45.8; CH_2: 34.6; CH_3: 0.3, −0.4	27.8
7	7.73 (d, 1H) [7.5], 7.60 (d, 1H) [7.5], 7.44 (m), 6.46 (s, 1H), 3.76 (s, 1H), 3.13 (m, 4H), 0.31 (s, 3H), 0.29 (s, 3H)	C_q: 144.8, 143.8, 142.1; CH: 128.6, 128.5, 128.1, 128.0, 126.2, 125.9, 124.7, 123.7, 119.5, 45.8; CH_2: 34.9, 29.7; CH_3: 0.3, −0.2	27.7
8	7.79 (d, 1H) [7.5], 7.62 (d, 1H) [7.5], 7.51 (m), 6.56 (s, 1H), 3.85 (s, 1H), 2,92 (m, 4H), 2.26 (m, 2H), 0.46 (s, 3H), 0.41 (s, 3H)	C_q: 145.0, 144.1, 143.8, 142.4; CH: 128.7, 128.6, 127.8, 126.0, 125.8, 124.6, 123.6, 119.5, 45.7; CH_2: 36.0, 30.5, 27.5; CH_3: 0.3, 0.0	27.7
9	7.74 (d, 1H) [7.5], 7.55 (d, 1H) [7.5], 7.49 (m), 7.40 (m), 6.76 (s, 1H), 3.83 (s, 1H), 1.87 (s, 3H), 1.86 (s, 3H), 0.40 (s, 3H), 0.36 (s, 3H)	ND [b]	28.1

[a] In $CDCl_3$ at 25°C.

[b] Not determined.

Table 3
NMR data of the ligand precursors **11**–**15** [a]

Compound	^{1}H-NMR	^{13}C-NMR	^{29}Si-NMR
11	7.65 (d, 1H) [7.4], 7.49 (d, 1H) [7.4], 7.46 (m), 7.37 (m), 6.50 (s, 1H), 4.19 (s, 1H), 3.69 (s, 1H), 1.39 (s, 9H), 0.18 (s, 3H), 0.10 (s, 3H)	C_q: 146.2, 144.4, 140.3, 140.1, 49.1; CH: 132.8, 131.1, 130.0, 128.9, 128.3, 126.0, 124.5, 123.8, 123.6, 123.1, 119.4, 49.6; CH_2: 34.5; CH_3: 33.9, 0.2, −0.7	−1.6
12	(d, 1H) [7.3], 7.36 (d, 1H) [7.3], 7.25 (m), 7.20 (m), 6.30 (s, 1H) 2.94 (m, 2H), 1.59 (m, 2H), 1.09 (s, 9H), 0.1 (s, 3H), −0.17 (s, 3H)	C_q: 145.0, 143.2, 141.1, 139.2, 65.8; CH: 130.8, 128.4, 128.2, 125.9, 124.4, 124.6, 123.7, 118.8, 46.8; CH_2: 35.0, 29.7; CH_3: 32.4, −0.2, −0.9	−2.0
13	7.84 (d, 1H) [7.7], 7.66 (d, 1H) [7.7], 7.55 (m), 7.48 (m), 6.67 (s, 1H), 3.79 (s, 1H), 2,99 (m, 4H), 2.34 (m, 2H), 1.50 (s, 9H), 0.28 (s, 3H), 0.22 (s, 3H)	C_q: 146.3, 144.9, 142.7, 141.5, 49.8. CH: 130.9, 128.8, 128.6, 126.0, 124.7, 124.0, 123.7, 123.4, 119.2, 49.8; CH_2: 36.2, 30.8, 27.6;CH_3: 0.3, −0.5	−1.8
14	7.67 (d, 1H) [7.4], 7.52 (d, 1H) [7.4], 7.48 (m), 7.33 (m), 6.57 (s, 1H), 3.23 (s, 3H), 3.10 (s, 3H), 1.34 (s, 9H), 0.17 (s, 3H), 0.08 (s, 3H)	ND [b]	−1.5
15	7.74 (d, 1H) [7.5], 7.47 (m), 7.40 (m), 7.30 (m), 7.26 (m), 6.56 (s, 1H), 6.45 (s), 6.43 (s), 6.34 (m), 3.52 (s, 1H), 1.71 (s, 3H), 1.34 (s, 9H), 1.21 (s, 3H), 1.02 (s, 3H), 0.31 (s, 3H), 0.19 (s, 3H), 0.13 (s, 3H)	C_q: 154.3, 149.7, 60.3, 49.5; CH: 134.3, 131.3, 128.8, 128.0, 126.4, 125.8, 125.552.5; CH_2: 40.0; CH_3: 33.7, 30.0, 29.8, 1.6, 0.9, 0.5, 0.2	−3.0, −14.0, −14.1

[a] In $CDCl_3$ at 25°C.
[b] Not determined.

tated elemental Pb and $PbCl_2$ settled in the reaction solution after stirring was stopped, the liquid was separated using a cannula. The solvent was evaporated in vacuo, the residue was dissolved in C_5H_{12} and the precipitated lithium salt was separated over a frit. After removing the solvent, the complex was obtained as a deep red to black solid. Yields: 65–95%. The complexes were characterized by NMR spectroscopy (Table 4).

*3.13. General procedure for the synthesis of the amido functionalized ansa half-sandwich zirconium complexes **20**–**22***

The corresponding ligand precursor (18 mmol) in Et_2O was added 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 r.t. The equimolar amount of $ZrCl_4$ (4.19 g) was added and the reaction solution was stirred for an additional 12 h. The precipitated lithium chloride was filtered, Et_2O was evaporated in vacuo and the residue was dissolved in pentane. The precipitating solid was filtered, the solvent was reduced in volume to almost dryness and the solution was stored at −78°C for 24 h. The complex precipitated as a yellow–white solid and could be dried in vacuo. Yields: 19–30%. The complexes were characterized by NMR spectroscopy (Table 4).

*3.14. General procedure for the synthesis of the amido functionalized ansa half-sandwich metallacycles **24**–**26***

The corresponding alkylaryl substituted amido functionalized *ansa* half-sandwich complex (3 mmol) was dissolved in 100 ml $C_6H_5CH_3$ and mixed with 3.75 ml (6.00 mmol) *n*-butyllithium at −78°C. The reaction mixture was defrosted to r.t. within 6 h and stirred for an additional 14 h. Subsequently, the reaction solution was filtered over Na_2SO_4 and the solvent was evaporated. The amido functionalized *ansa* half-sandwich metallacycles were obtained as yellow to brown oils in 90% yields (see Table 4 for NMR data).

3.15. Polymerization reactions

The corresponding complex (10–15 mg) was dissolved in 50 ml $C_6H_5CH_3$. A solution containing 1–3 mg complex was activated with MAO (30% in $C_6H_5CH_3$) (metal–Al = 1:2500). The catalyst solution was dissolved in 250 ml C_5H_{12}, 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 presented in Table 1.

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Table 4
NMR data of the dichloride complexes and the metallacycles **16**–**26** [a]

Complex	^{1}H-NMR	^{13}C-NMR	^{29}Si-NMR
16	7.64 (d, 1H) [8.5], 7.44 (d, 1H) [8.5], 7.17 (m), 7.11 (m), 7.09 (m), 7.06 (m), 6.35 (s, 1H), 5.53 (d, 1H) [14.3], 4.29 (d, 1H) [14.3], 1.42 (s, 9H), 0.64 (s, 3H), 0.39 (s, 3H)	C_q: 139.7, 136.2, 135.9, 135.1, 97.0, 62.7; CH: 128.8, 128.5, 128.0, 128.1, 127.8, 127.4, 126.5, 124.6; CH_2: 35.2; CH_3: 32.2, 2.9, 0.6	−19.9
17	7.65 (d, 1H) [8.5], 7.32 (d, 1H) [8.5], 7.22 (t, 1H) [8.5], 7.21 (m, 2H), 7.06 (t, 1H) [8.5], 7.04 (m, 3H), 6.23 (s, 1H), 3.32 (m, 2H), 2.93 (m, 2H), 1.41 (s, 9H), 0.64 (s, 3H), 0.42 (s, 3H)	C_q: 141.0, 137.1, 135.8, 135.0, 96.1, 62.6; CH: 128.6, 128.5, 128.1, 127.8, 127.7, 127.3, 126.2, 124.6; CH_2: 35.9, 31.1; CH_3: 32.2, 2.9, 0.6	−20.1
18	7.56 (d, 1H) [8.5], 7.48 (d, 1H) [8.5], 7.29 (m), 7.11 (m), 6.93 (m), 6.13 (s, 1H), 3.07 (m, 2H), 2.52 (m, 2H), 1.87 (m, 2H), 1.33 (s, 9H), 0.57 (s, 3H), 0.37 (s, 3H)	C_q: 141.8, 139.1, 137.2, 132.8, 97.8, 62.1; CH: 128.8, 128.3, 127.7, 127.2, 126.2, 126.0, 124.8, 116.1; CH_2: 36.1, 31.8, 29.1; CH_3: 32.5, 3.2, 0.9	−20.1
19	7.69 (d, 1H) [8.5], 7.49 (d, 1H), [8.5], 7.27 (t, 1H), 7.24 (m), 7.07 (m), 6.87 (s, 1H), 1.40 (s, 9H), 0.69 (s, 3H), 0.52 (s, 3H), 0.11 (s, 3H), 0.04 (s, 3H)	C_q: 154.8, 149.7, 140.3, 127.7, 108.3, 80.0, 63.7; CH: 137.1, 132.1, 128.1, 127.4, 127.2, 127.0, 126.3, 125.9, 120.8; CH_3: 32.1, 28.9, 27.8, −0.1, −0.5	−21.3
20	7.77 (d, 1H) [8.5], 7.54 (d, 1H) [8.5], 7.34 (m, 1H), 7.23 (m, 1H), 7.16 (m, 5H), 6.50 (s, 1H), 4.50 [15.9], 4.35 (s, 1H) [15.9], 1.47 (s, 9H), 0.77 (s, 3H), 0.51 (s, 3H)	C_q: 140.1, 134.2, 131.9, 127.1, 91.6, 57.1; CH: 128.8, 128.6, 128.3, 127.9, 127.3, 126.8, 125.9, 124.1; CH_2: 34.4; CH_3: 33.1, 3.9, 1.8	−20.2
21	7.69 (d, 1H) [8.5], 7.32 (d, 1H) [8.5], 7.21 (m), 7.19 (m), 7.09 (m), 7.04 (m), 6.30 (s, 1H), 3.25 (m, 2H), 2.84 (m), 1.34 (s, 9H), 0.68 (s, 3H), 0.46 (s, 3H)	C_q: 141.0, 138.4, 134.0, 131.6, 128.0, 56.8; CH: 128.6, 128.4, 127.7, 127.5, 127.1, 126.1, 125.7, 123.7; CH_2: 36.2, 30.1; CH_3: 33.5, 3.6, 1.6	−20.5
22	7.70 (d, 1H) [8.5], 7.42 (d, 1H) [8.5], 7.25 (m, 2H), 7.20 (m, 5H), 6.36 (s, 1H), 2.91 (m, 2H), 2.57 (m, 2H), 1.93 (m, 2H), 1.33 (s, 9H), 0.69 (s, 3H), 0.48 (s, 3H)	C_q: 141.7, 134.1, 131.6, 128.8, 90.7, 56.8; CH: 128.4, 128.1, 127.7, 127.6, 126.0, 125.7, 125.4, 123.8; CH_2: 35.7, 31.8, 27.7; CH_3: 32.8, 3.7, 1.7	−20.5
23	7.21 (d, 1H) [7.0], 7.19 (m, 1H), 7.17 (m, 1H), 7.12 (m, 2H), 7.09 (m, 2H), 7.01 (m, 1H), 6.70 (t, 1H), 6.40 (t, 1H), 6.15 (t, 1H), 1.78 (s, 3H), 1.76 (s, 3H), 1.47 (s, 9H), 0.27 (s, 3H), 0.24 (s, 3H)	C_q: 155.1, 149.4, 109.3, 64.0, 38.4; CH: 128.5, 128.3, 126.8, 126.3, 126.2, 121.1; CH_3: 32.1, 28.6, 27.9, 0.0, −0.5	−20.5
24	8.15 (d, 1H) [8.5], 7.42 (d, 1H) [8.5], 7.19 (m), 7.04 (m), 6.97 (m, 1H), 6.29 (m, 1H), 5.97 (m, 1H), 2.10 (s, 3H), 1.99 (m), 1.60 (s, 9H), 1.54 (m), 0.99 (m), 0.83 (s, 3H), 0.34 (s, 3H), 0.30 (s, 3H)	C_q: 191.1, 171.6, 154.8, 106.6, 59.0, 43.7; CH: 132.3, 130.7, 129.3, 129.0, 126.5, 124.6, 123.8; CH_2: 86.7, 35.9, 26.3; CH_3: 30.5, 30.2, 29.1, 14.1, 1.4, 1.2	−19.3
25	8.21 (d, 1H) [8.5], 7.81 (d, 1H) [8.5], 7.29 (m, 6H), 6.20 (s, 1H), 3.09 (m, 4H), 2.65 (m, 2H), 1.55 (s, 9H), 1.39 (m, 2H), 1.21 (m, 2H), 1.67 (t, 3H), 0,80 (s, 3H), 0.51 (s, 3H)	C_q: 184.1, 182.3, 148.4, 140.8, 135.1, 89.9, 64.1; CH: 130.9, 129.6, 128.6, 126.3, 125.4, 124.8 124.1, 123.1, 119.2; CH_2: 56.3, 49.1, 28.7, 26.7, 25.4; CH_3: 34.1, 13.9, 4.6, 2.7	21.1
26	7.72 (d, 1H) [8.4], 7.41 (d, 1H) [8.4], 7.24 (m, 6H), 6.43 (s, 1H), 2.95 (t, 2H), 2.66 (m, 2H), 1.92 (m, 2H), 1.46 (s, 9H), 1.28 (m, 2H), 1.17 (m, 4H), 1.14 (t, 3H), 0.81 (s, 3H), 0.62 (s, 3H)	C_q: 187.4, 184.0, 144.9, 138.4, 135.1, 90.2, 63.1; CH: 129.1, 126.0, 125.5, 124.9, 124.3, 124.1, 123.8, 121.9, 119.2; CH_2: 86.9, 60.1, 54.3, 35.4, 28.9, 26.3; CH_3: 34.5, 13.9, 4.7, 2.6	−22.5

[a] In C_6D_6 at 25°C.

References

[1] H.G. Alt, M. Jung, G. Kehr, J. Organomet. Chem. 562 (1998) 153.

[2] H.G. Alt, M. Jung, J. Organomet. Chem. 562 (1998) 229.

[3] J.A.M. Canich, US Patent 5,026,798, 1991.

[4] J.A.M. Canich, G.F. Licciardi, US Patent 5,057,475, 1991.

[5] J.A.M. Canich, Eur. Pat. Appl. 0 420 436 A1, 1991.

[6] 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. 0 416 815, 1991.

[7] J.C. Stevens, D.R. Neithammer, Eur. Pat. Appl. 0 418 044 A2, 1991.

[8] R.B. Pannell, J.A.M. Canich, G.G. Hlatky, PCT Int. Appl. WO 94/005000, 1994.

[9] J.A.M. Canich, US Patent 5,096,867, 1992.

[10] P. Brant, J.A.M. Canich, PCT Int. Appl. WO 93/12151, 1991.

[11] P. Brant, J.A.M. Canich, N.A. Merril, PCT Int. Appl. WO 93/21242, 1993.

[12] P. Brant, J.A.M. Canich, A.J. Dias, R.L. Bamberger, G.F. Liccardi, P.M. Henrichs, PCT Int. Appl. 94/07930, 1994.

[13] J.A.M. Canich, PCT Int. Appl. WO 96/00244, 1996.

[14] R.E. LaPointe, R.K. Rosen, P.N. Nickias, Eur. Pat. Appl. 0 495 375 A2, 1992.
[15] R.E. LaPointe, J.C. Stevens, P.N. Nickias, M.H. McAdon, Eur. Pat. Appl. 0 520 732 A1, 1992.
[16] S.Y. Lai, J.R. Wilson, G.W. Knight, J.C. Stevens, PCT Int. Appl. WO 93/08221, 1993.
[17] R.K. Rosen, P.N. Nickias, D.D. Devore, J.C. Stevens, F.J. Timmers, US Patent 5,374,696, 1994.
[18] D.D. Devore, L.H. Crawford, J.C. Stevens, F.J. Timmers, R.D. Russel, D.R. Wilson, R.K. Rosen, PCT Int. Appl. WO 95/00526, 1995.
[19] P.N. Nickias, M.H. McAdon, J.T. Patton, PCT Int. Appl. WO 97/15583, 1997.
[20] B.A. Harrington, PCT Int. Appl. WO 96/40806, 1996.
[21] B.A. Harrington, G.G. Hlatky, J.A.M. Canich, N.A. Merril, US Patent 5,635,573, 1997.
[22] J. Okuda, Chem. Ber. 123 (1990) 1649.
[23] P.-J. Sinnema, L. van der Veen, A.L. Spek, N. Veldman, J.H. Teuben, Organometallics 16 (1997) 4245.
[24] P.T. Gomes, M.L.H. Green, A.M. Martins, P. Mountford, J. Organomet. Chem. 541 (1997) 121.
[25] B. Peifer, W. Milius, H.G. Alt, J. Organomet. Chem. 553 (1998) 205.
[26] H.G. Alt, M. Jung, W. Milius, J. Organomet. Chem. 558 (1998) 111.
[27] J. Saßmannshausen, A.K. Powell, C.E. Anson, S. Wocadlo, M. Bochmann, J. Organomet. Chem. 592 (1999) 84.
[28] E.H. Licht, H.G. Alt, M.M. Karim, J. Organomet. Chem. 599 (2000) 275.
[29] E.H. Licht, H.G. Alt, M.M. Karim, J. Organomet. Chem. 599 (2000) 261.
[30] E.H. Licht, H.G. Alt, J. Mol. Catal. A 154 (2000) 65.
[31] W.S. Murphy, C.R. Hauser, J. Org. Chem. 31 (1966) 85.
[32] O. Meth-Cohn, S. Gronowitz, J. Chem. Soc. Chem. Commun. (1996) 81.
[33] Z. Liu, G. Rong, Synth. Commun. 16 (1986) 871.
[34] J. Quéré, E. Maréchal, Bull. Soc. Chim. Fr. (1969) 4087.
[35] E.J. Greenhow, E.N. White, D. McNeil, J. Chem. Soc. (1951) 2848.
[36] K. Patsidis, H.G. Alt, W. Milius, S.J. Palackal, J. Organomet. Chem. 509 (1996) 63.
[37] J. Okuda, F.J. Schattenmann, S. Wocadlo, W. Massa, Organometallics 14 (1995) 789.
[38] A.K. Hughes, A. Meetsma, J.H. Teuben, Organometallics 12 (1993) 1996.
[39] F. Amor, J. Okuda, J. Organomet. Chem. 520 (1996) 247.
[40] K.E. du Plooy, U. Moll, S. Wocadlo, W. Massa, J. Okuda, Organometallics 14 (1995) 3130.
[41] H.G. Alt, S.J. Palackal, J. Organomet. Chem. 472 (1994) 113.
[42] G. Luft, M. Dorn, Angew. Macromol. Chem. 188 (1991) 177.
[43] Y.-X. Chen, T.J. Marks, Organometallics 16 (1997) 3649.
[44] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. 111 (1999) 448; Angew. Chem. Int. Ed. Engl. 38 (1999) 428.
[45] H.G. Alt, A. Reb, W. Milius, A. Weis, J. Organomet. Chem. 628 (2001) 169.
[46] H.G. Alt, A. Köppl, Chem. Rev. 100 (2000) 1205.
[47] P. Schertl, H.G. Alt, J. Organomet. Chem. 582 (1999) 328.
[48] G.M. Benedikt, B.L. Goodall (Eds.), Metallocene-Catalyzed Polymers, Plastics Design Library, Norwich, NY, 1998.