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Synthesis, characterization and polymerization potential of unbridged and bridged half-sandwich complexes of zirconium containing *N*-donor ligands

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Abstract

The synthesis of unbridged half-sandwich complexes of the type $(C_5H_5)Zr[N(SiMe_3)CH_2CH_2R]Cl_2$ (R = OMe, NMe_2) and bridged half-sandwich complexes of the type $(Cp^{\#}-SiMe_2-NCH_2CH_2R)ZrCl_2$ ($Cp^{\#} = C_5H_4$, C_9H_6, $C_{13}H_8$) including intramolecular *N*-donor ligands is described. The complexes were characterized by ^1H-, ^{13}C-, and ^{29}Si-NMR spectroscopy. The complexes $(C_5H_5)Zr[N(SiMe_3)CH_2CH_2NMe_2]Cl_2$ (**2**) and $(C_5H_4\text{-}SiMe_2\text{-}NCH_2CH_2NMe_2)ZrCl_2$ (**4**) were further characterized by X-ray crystal structure determinations. In the solid state the nitrogen atom of the dimethylamino group is coordinated to the zirconium atom. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium; Half-sandwich complexes; Indenyl; Fluorenyl; Ethylene; Polymerization

1. Introduction

Amido functionalized half-sandwich dichloride complexes with a group four metal [1–11] are coordinatively and electronically (14 electron complexes) unsaturated, because the amido ligand can function at most as a $4e^-$ donor. In combination with methyl aluminoxane (MAO) these complexes are suitable catalysts for olefin polymerization [1,2].The polymerization behavior of these 'single-site' catalysts (e.g. the activities or the micro structure of the corresponding polymers) is highly dependent on the surroundings of the catalytically active center. The catalytic activity of the metal center is also influenced by steric and electronic effects (e.g. type, structure and number of ligands). Intramolecular *N*-donor groups can further influence the Lewis acidity of coordinatively and electronically unsaturated metal centers of amido functionalized half-sandwich dichloride complexes. This can have a significant impact on the polymerization behavior of these complexes.

2. Results and discussion

2.1. Synthesis and characterization of unbridged half-sandwich complexes of zirconium

Amido functionalized cyclopentadienyl dichloride complexes of zirconium are obtained by the reaction of the half-sandwich trichloride complex $CpZrCl_3$ with the corresponding lithium amide $Li[N(SiMe_3)CH_2CH_2R]$ (R = OMe, NMe_2) [12]. In toluene the components react at −78°C with elimination of lithium chloride and formation of complexes **1** and **2** $[(C_5H_5)Zr[N(SiMe_3)CH_2CH_2R]Cl_2]$ (Scheme 1).

Temperature-dependent NMR spectra indicate that the interaction between the *N*-donor groups of the amido ligand and the central metal of the complex is a dynamic process. A 'closed' form with intramolecular

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coordination of the *N*-donor group to the zirconium atom and an 'open' form with a free *N*-donor group can be differentiated. Compared with the NMR time scale at room temperature, the intramolecular coordination and dissociation process between the *N*-donor group and the central metal of these *ansa*-half-sandwich complexes are very fast (see below).

The compounds **1** and **2** were characterized by their ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra (Table 1), and their mass spectra. The room temperature ^{1}H-NMR spectra of **1** and **2** show one singlet in the aromatic region at approximately $\delta = 6.50$ ppm for the five protons of the cyclopentadienyl ring. The splitting pattern of an AA′MM′ spin system is obtained for the methylene protons of the substituted ethyl group. This becomes evident by the roof effect of both virtual triplets in the region of $\delta = 3.40-3.00$ ppm. One singlet at approximately $\delta = 2.60$ ppm is attributed to the protons of the methoxy or the dimethyl amino group. The resonance for the nine protons of the trimethylsilyl group appears as a singlet at about $\delta = 0$ ppm.

In the ^{13}C-NMR spectra of complexes **1** and **2**, the signals of the magnetically equivalent carbon atoms of the cyclopentadienyl ring appear at about $\delta = 120$ ppm. At $\delta = 49.1$ ppm (**1**) and $\delta = 48.2$ ppm (**2**) the signals for the carbon atoms at the nitrogen are found. The signals at $\delta = 79.6$ ppm (**1**) and $\delta = 61.2$ ppm (**2**) are assigned to the methylene carbon atoms of the amino nitrogen or of the methoxy group. At approximately $\delta = 1.0$ ppm appears the signal for the carbon atoms of the trimethylsilyl group.

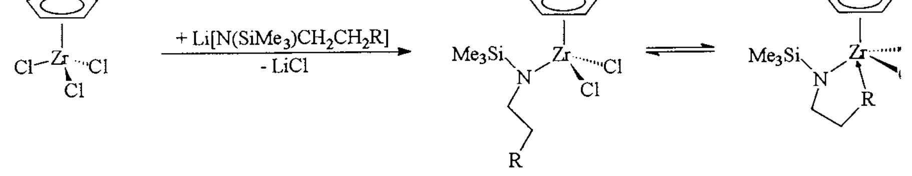
In the solid state the 'closed' form of the dimethyl amino substituted complex is observed (Fig. 1). This is confirmed by the X-ray structure analysis of compound **2**. The crystal structure shows disorder in the cyclopentadienyl ring and the coordinating dimethyl amino group of the amido ligand. The central metal of the complex is surrounded by its five ligands in almost a tetrahedral-pyramidal structure, wherein the center of the cyclopentadienyl ring occupies the top of the pyramid and the two chloro ligands, Cl(1) and Cl(2), and the two nitrogens, N(1) and N(2), of the amido ligand form the base of the pyramid.

The distance between the nitrogen atom N(1) of the dimethyl amino group to the metal is 244.5(4) pm (Table 2). This is approximately 40 pm longer than the bond between zirconium and the σ-bonded amido nitrogen N(2) that is known to possess partial double bond character [4,9,13]. The nitrogen atom N(2) of the zirconium complex is surrounded in a trigonal planar manner by the silicon atom, the amido carbon atom C(9) and the zirconium atom (angle sum = 358.8°). This indicates an interaction between the p_{π}-d_{π} zirconium orbitals and the p_z orbital (π-lone-pair electrons) of the nitrogen. In contrast to the amido nitrogen N(2), the amido nitrogen N(1) has a distorted tetrahedral structure. Nitrogen N(1) coordinates to the electrophilic transition metal center through the free electron pair. The bond length Zr–N(1) is 244 pm which is similar to the distance found for the *N*-donor–acceptor-bond between the amine nitrogen and the zirconium in the half-sandwich complex $[C_5H_4-SiMe_2-N^{t}Bu]ZrCl_2(NMe_2H)$ [14].

2.2. Synthesis and characterization of bridged half-sandwich complexes of zirconium

The analogous *ansa*-half-sandwich complexes are synthesized by the reaction of the dilithiated ligand precursor with zirconium tetrachloride [1–3]. Similar titanium complexes were synthesized by Okuda [11] in a different synthetic route. When the organolithium compound $Li_2[C_5H_4-SiMe_2-NCH_2CH_2R]$ is slowly added to a suspension of zirconium tetrachloride in toluene, the dimethylsilyl bridged, amido functionalized half-sandwich dichloride complexes $(C_5H_4-SiMe_2-NCH_2CH_2OMe)ZrCl_2$ (**3**) and $(C_5H_4-SiMe_2NCH_2CH_2NMe_2)ZrCl_2$ (**4**) are formed following LiCl salt elimination.

This result is unusual as the reaction of $ZrCl_4$ with the dilithiated ligand precursor $Li_2[C_5H_4-SiMe_2-N^{t}Bu]$, independent of the reaction conditions or the stoichiometry of either component, always produces the spiro zirconocene compound $[C_5H_4-SiMe_2N^{t}Bu]_2Zr$ as the main product [15] and not the desired *ansa*-dichlo-



R = OMe **1**
NMe$_2$ **2**

Scheme 1.

Table 1
^{1}H-, ^{13}C- and ^{29}Si-NMR data^a of compounds **1**–**6**

	^{1}H-NMR	^{13}C-NMR	^{29}Si-NMR
1	6.49 (s, 5H), 3.93 (m, 2H), 3.73 (s, 3H), 3.44 (m, 2H), 0.13 (s, 9H)	115.4 (CH), 79.6 (CH$_2$), 63.3 (CH$_3$), 49.1 (CH$_2$), 1.1 (CH$_3$)	7.1
2	6.48 (s, 5H), 3.37 (m, 2H), 3.08 (m, 2H), 2.64 (s, 6H), 0.15 (s, 9H)	115.7 (CH), 61.2 (CH$_2$), 48.7 (CH$_3$), 48.2 (CH$_2$), 0.8 (CH$_3$)	6.5
3	6.82 (m, 2H), 6.38 (m, 2H), 4.05 (m, 2H), 3.93 (s, 3H), 3.37 (m, 2H) 0.37 (s, 6H)	121.9 (CH), 119.1 (CH), 109.5 (C$_q$), 77.9 (CH$_2$), 62.6 (CH$_3$), 47.1 (CH$_2$), −2.8 (CH$_3$)	−17.4
4	6.84 (m, 2H), 6.22 (m, 2H), 3.28 (m, 2H), 2.99 (m, 2H), 2.59 (s, 6H), 0.37 (s, 6H)	123.5 (CH), 117.8 (CH), 110.6 (C$_q$), 62.2 (CH$_2$), 47.1 (CH$_2$), 47.1 (CH3), −2.6 (CH$_3$)	−14.7
5^b	7.68 (m, 2H), 7.11 (m, 1H), 7.08 (m, 1H), 6.99 (m, 1H), 6.61 (m, 1H), 3.95 (m, 1H), 3.74 (s, 3H), 3.40 (m, 2H), 0.49 (s, 3H), 0.48 (s, 3H)	132.1 (Cq), 131.9 (Cq), 127.0 (CH), 126.2 (CH), 125.1 (CH), 124.9 (CH), 123.7 (CH), 112.6 (CH), 95.1 (C$_q$), 77.6 (CH$_2$), 62.7 (CH$_3$), 47.3 (CH$_2$), −0.1 (CH$_3$), −1.8 (CH$_3$)	−15.8
6^b	8.06 (m, 2H), 7.81 (m, 2H), 7.47 (m, 2H), 7.41 (m, 2H), 3.84 (m, 2H), 3.61 (s, 3H), 3.45 (m, 2H), 0.83 (s, 6H)	133.8 (C$_q$), 128.8 (CH), 127.4 (C$_q$), 126.1 (CH), 125.6 (CH), 124.0 (CH), 77.5 (CH$_2$), 63.7 (CH$_3$), 47.6 (CH$_2$), 2.3 (CH$_3$)	n.o.

[a] In CDCl$_3$ (RT); n.o., not observed.
[b] In CD$_2$Cl$_2$.

ride complex $[C_5H_4{-}SiMe_2{-}N^tBu]ZrCl_2$. If the dilithiated ligand precursor has an organyl group with an *N*-donor ligand instead of the aliphatic amine group, the reaction with the metal tetrachloride produces the corresponding *ansa*-half-sandwich dichloride compounds **3** and **4** in ca. 75% yields (Scheme 2) and not the spiro zirconacycle.

The proton and carbon signals of complexes **3** and **4** appear in the same regions as signals of the analogous unbridged half-sandwich complexes **1** and **2**, with the difference that at room temperature the aromatic protons of the cyclopentadienyl ring appear as two virtual triplets of an AA′BB′ spin system due to the bridging SiMe$_2$ group.

With regard to the coordination behavior of the intramolecular *N*-donor group, the same conclusions can be drawn for the unbridged complexes **1** and **2** by evaluating the temperature-dependent NMR spectra. For example, compound **4** gives a coalescence temperature for the coordination process of the *N*-donor group in the ^{1}H-NMR spectra at −50°C (Fig. 2) and in the ^{13}C-NMR spectra at −30°C (Fig. 3).

In the solid state, the structure of the *ansa*-complex **4** exhibits, as for analogous compound **2**, a disorder in the coordination of the dimethyl amino group to the central metal atom (Fig. 4). The zirconium atom is surrounded by five ligands in a trigonal bipyramidal manner. The cyclopentadienyl ring and the amino nitrogen N(2) are positioned axially with both chloro ligands, Cl(1) and Cl(2), and the amido nitrogen N(1) in the equatorial plane.

The distance between the center metal atom and carbon atoms C(3) and C(4) is about 8 pm longer than the corresponding Zr–C(2) or Zr–C(5) bond lengths, 250 pm each (Table 3). The bond distance between the zirconium atom and the quaternary C(1) atom is about 4 pm shorter. In contrast to the penta hapticity of the cyclopentadienyl ring of the unbridged complex **2**, these bond distances are indicative of a η^3-bonding mode for the aromatic ligand. The cyclopentadienyl ring that is usually centrosymmetrically positioned above the zirconium atom for unbridged complexes, is pulled towards the amido nitrogen N(1) by the bridging SiMe$_2$ group.

The SiMe$_2$ bridge between the aromatic ligand and the amido nitrogen N(1) causes not only the hapticity change of the five-membered ring, but also a change in structure from the tetragonal pyramidal arrangement of the unbridged complex **2** ligands to the trigonal bipyramidal conformation of the ligands around the zirconium atom in *ansa*-complex **4**. The SiMe$_2$ group pulls the sterically demanding aromatic five-membered ring from the 'open' coordination sphere of both chloro ligands towards the amido nitrogen atom N(1). There-

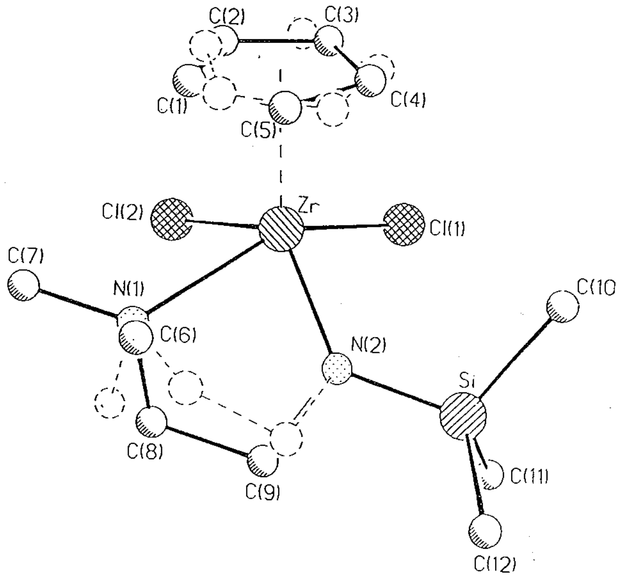


Fig. 1. Molecular structure of **2** in the solid state.

Table 2
Selected bond lengths (pm) and angles (°) of **2**

Bong lengths (pm)					
Zr–Cl(1)	245.5(2)	Zr–N(1)	244.5(4)	N(2)–Si	175.3(5)
Zr–Cl(2)	245.1(2)	Zr–N(2)	204.6(4)	Zr–C(1)	259.9(13)
Zr–C(2)	264.0(12)	Zr–C(3)	256.8(11)	Zr–C(4)	256.8(16)
Zr–C(5)	250.7(11)	N(1)–C(8)	142.4(10)	N(2)–C(9)	153.4(8)
Bong angles (°)					
Cl(1)–Zr–Cl(2)	87.1(1)	Zr–N(2)–Si	131.3(2)	Si–N(2)–C(9)	110.3(3)
Zr–N(2)–C(9)	117.2(4)	Zr–N(1)–C(8)	99.6(5)	Zr–N(1)–C(6)	114 3(6)

fore, the coordination sphere of the complex increases in size, which is shown by the 26° wider Cl(1)–Zr–Cl(2)-bond angle in comparison with the same angle in the unbridged half-sandwich complex **2**. Due to the increase in the angle to 113°, the sum of the angles for the three ligands Cl(1), Cl(2) and N(1) around the zirconium atom is 346.9°. Therefore, the central metal atom of the complex is almost trigonally planar surrounded by these three ligands. The amino nitrogen atom N(2) and the center of the five-membered ring are almost perpendicular to the plane of the other three ligands. The resulting distorted trigonal bipyramidal coordination of the ligands around the central metal atom for this half-sandwich complex is, except for the tetramethyl substituted derivative [C_5Me_4–$SiMe_2$–$NCH_2CH_2NMe_2$]$ZrCl_2$ [16], only observed in exceptional cases [17–19].

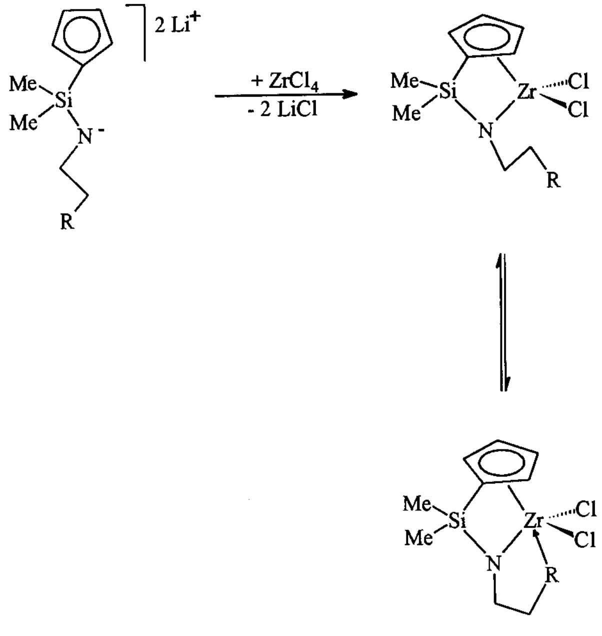
The Zr–N(1) and Zr–N(2) bond distances (206.2(3) and 246.5(3) pm) are close to the corresponding values found for the half-sandwich complex **2**. The amido nitrogen N(1) is also surrounded by a trigonal planar structure (sum of angles: 358.7°). The spatial environment and the 40 pm shorter bond length found for the Zr–N(1) bond compared with the Zr–N(2) bond reflects the interference of the free electron pair of N(1) positioned in a p_z orbital with orbitals of the transition metal.

The dimethylsilyl bridged half-sandwich complexes with a fluorenyl and an indenyl ligand (Scheme 3) instead of a cyclopentadienyl ligand can be synthesized in the same way. The corresponding ligand precursors are obtained as viscous, yellow oils by the reaction of the lithium amide Li[$NHCH_2CH_2OMe$] with 9-(chlorodimethylsilyl)fluorene or with 1-(chlorodimethylsilyl)indene. The lithiated ligand precursors after reaction with zirconium tetrachloride form the *ansa*-fluorenyl complex **5** and the *ansa*-indenyl complex **6**. The compounds **5** and **6** show a similar behavior in their temperature-dependent NMR spectra. The coalescence temperatures for the coordination process of the *N*-donor group to the zirconium atom are in a similar range as in **1**–**4**.

After activation with MAO the half-sandwich complexes **1**–**6** form catalysts that are suitable for homogeneous ethylene polymerization.

The ethylene polymerization activities (Table 4) of the unbridged half-sandwich complexes **1** and **2** are almost the same as those for the corresponding *ansa*-complexes **3** and **4**. The melting point of the polyethylene made with the NMe_2-substituted *ansa*-complex **4** is approximately 3.7°C higher than for the corresponding polymer made with the unbridged complex **2**. Likewise, the melting point of the polyethylene produced with the bridged methoxy-substituted complex **3** is 5.9°C higher than that of analogous polymers made with the unbridged complex **1**.

The activities and molecular weights for polymers of the methoxy substituted *ansa*-complexes **4**–**6** are given in Table 4. The activity of the indenyl complex **5** is significantly higher than the activities of the other half-sandwich complexes. The same is valid for the intrinsic viscosities of the corresponding polyethylenes. Among the *N*-donor substituted complexes, the activated com-



R = OMe **3**
NMe_2 **4**

Scheme 2.

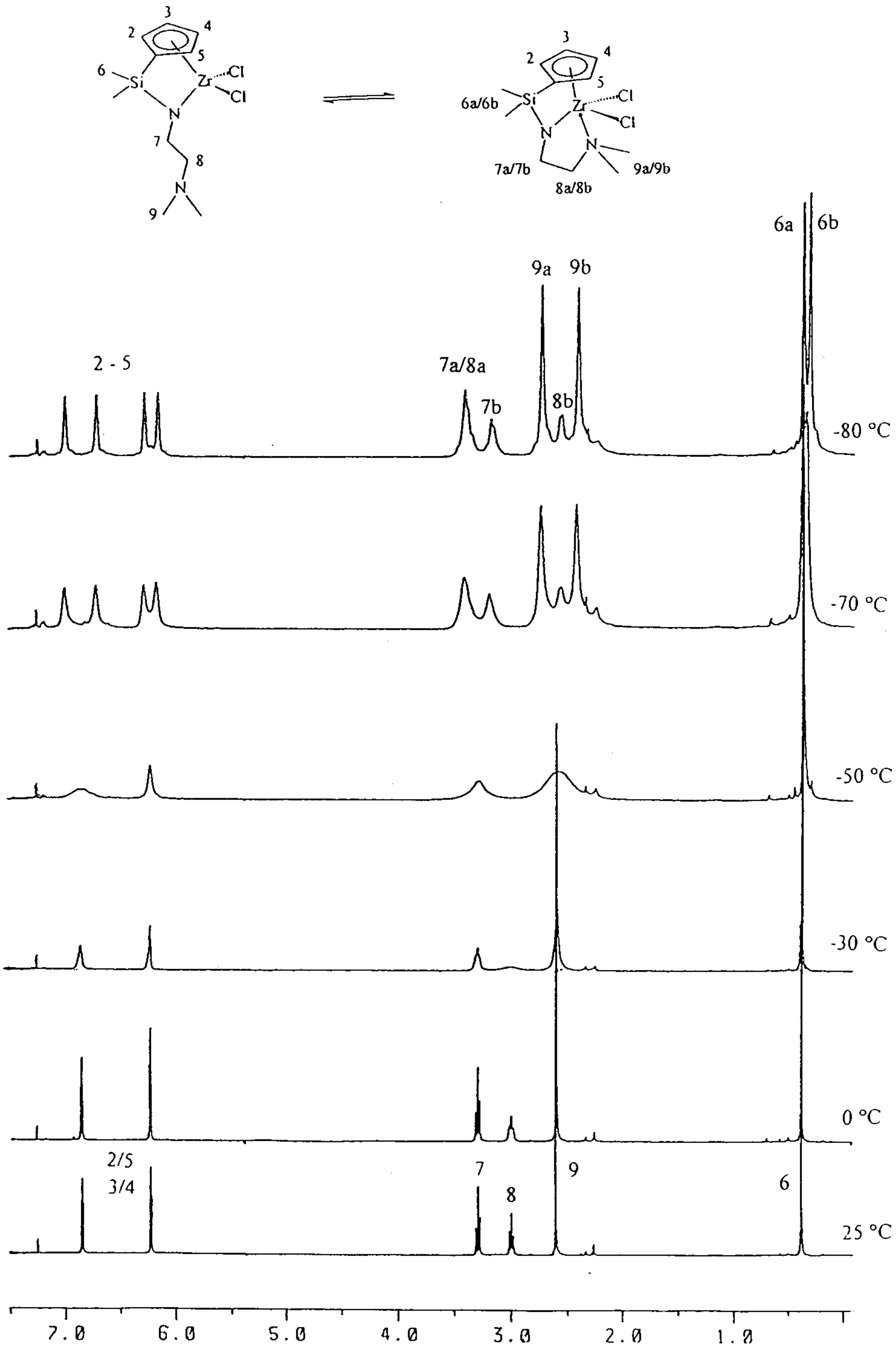


Fig. 2. 300.13 MHz ^{1}H-NMR spectra of compound **4**.

plex **5** produces polyethylene with the highest molecular weight.

3. Experimental

All operations were carried out using the Schlenk technique to exclude air and moisture. Purified and dried argon was used as inert gas (BTS catalyst, molecular sieves). The solvents used were dried over Na/K alloy (diethylether, toluene, *n*-pentane) or over P_2O_5 and subsequently over CaH_2 (CH_2Cl_2).

The Me_2SiCl substituted 9-fluorene, 1-indene and cyclopentadiene derivatives were synthesized according to literature procedures [20].

The NMR spectra were recorded in deuterated solvents at 25°C using a Bruker ARX 250 spectrometer. In the ^{1}H-NMR spectra, the chemical shifts refer to the residual proton signal of the solvent ($\delta = 7.24$ ppm for chloroform), in ^{13}C-NMR spectra to the solvent signal ($\delta = 77.0$ ppm for chloroform-d_1) and in ^{29}Si-NMR spectra to the resonance of external TMS ($\delta = 0.0$ ppm).

EI mass spectra were recorded using a Varian MAT CH7 mass spectrometer (direct inlet, EI = 70 eV).

Ethylene (dried over Alox) was polymerized in a 1-l metal Büchi autoclave (model 280 BEP). The complexes were activated by adding a 1000-fold molar excess of MAO (30 wt% in toluene; Witco). The autoclave was filled with 500 ml pentane and 3 ml MAO and stirred for 10 min to dry the pentane. After adding the activated complex (ca. 1 mg), the polymerizations were carried out under an ethylene pressure of 10 bar and at a temperature of 60°C over a period of 1 h. The polymer samples were subsequently washed with MeOH/HCl and dried under high vacuum.

Molecular weight determinations of the polyethylene samples were carried out using an Ubbelohde precision capillary viscometer in *cis*/*trans* decalin at 135 ± 0.1°C. Calibration curves for three different polymer concentrations were available ($c = 0.03$, 0.1 and 3.0 g dl^{-1}) for determination of $\bar{M}_\eta$.

A Netzsch DSC 200 apparatus was available for the determination of thermal characteristics of the polyethylene samples. Approximately 5 mg PE each

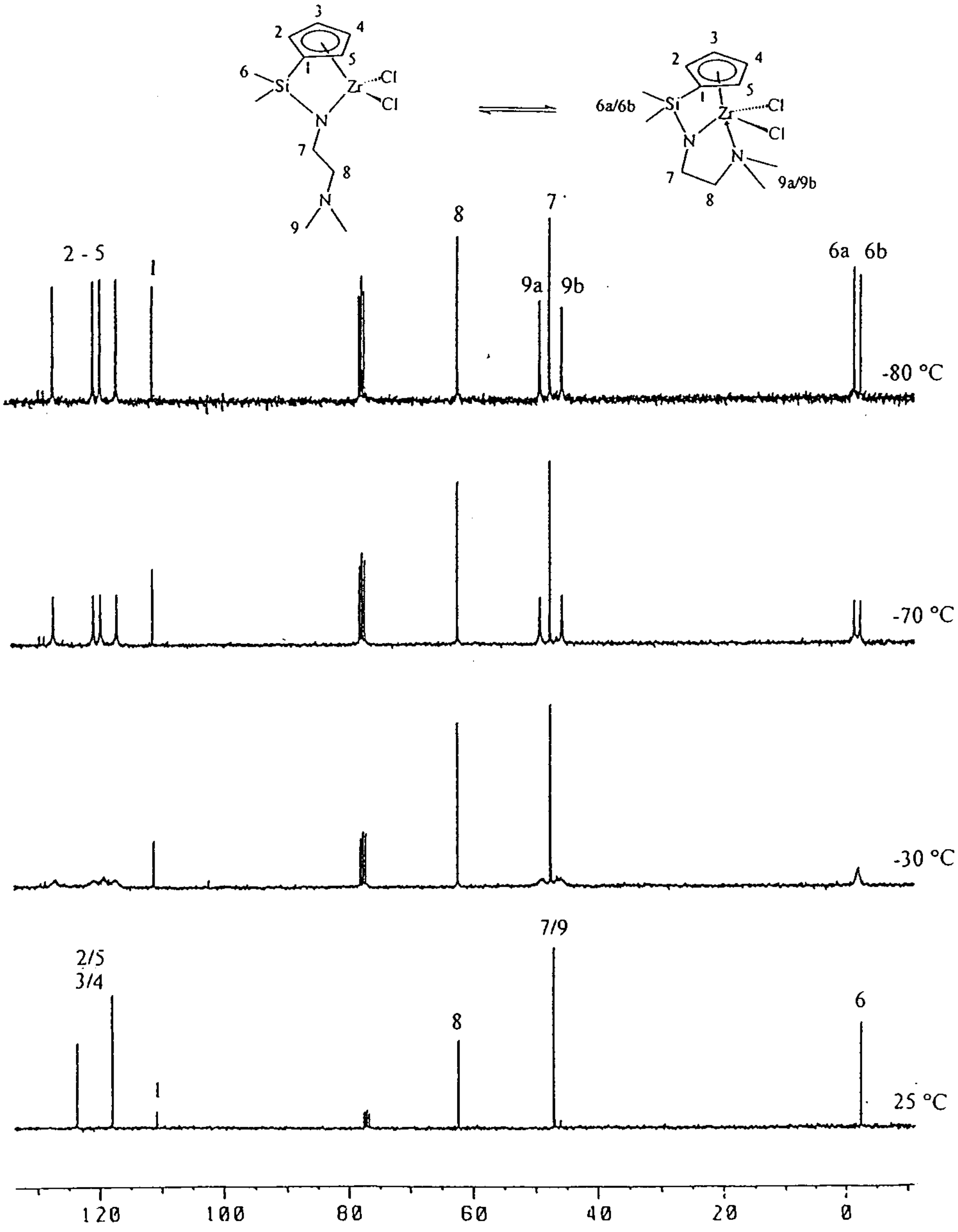


Fig. 3. 75.5 MHz ^{13}C-NMR spectra of compound **4**.

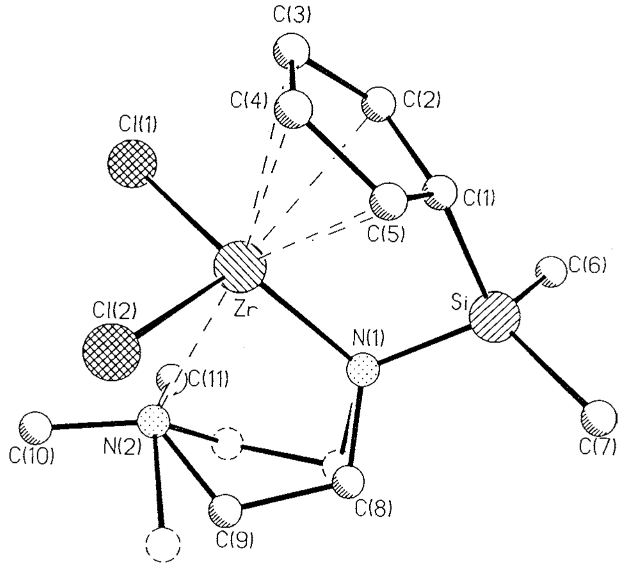


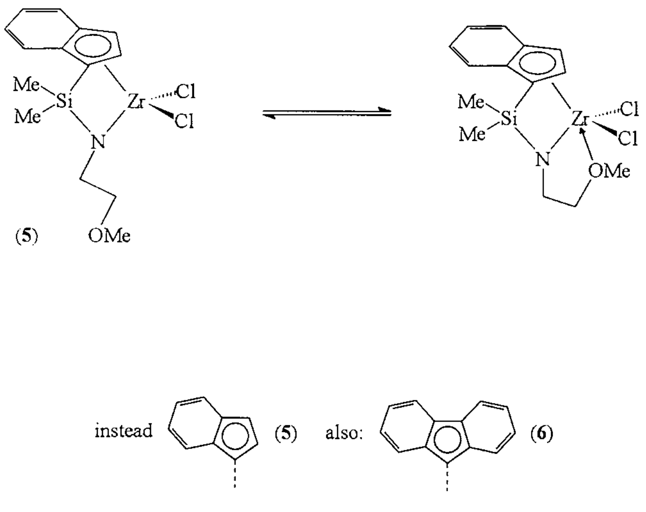
Fig. 4. Molecular structure of **4** in the solid state.

were fused in standard aluminum pans and measured using the following temperature program: 1. Heating phase (20°C min^{-1}) from 40 to 200°C, isothermal phase (3 min) at 200°C, cooling phase (-20°C min^{-1}) to 40°C; 2. heating phase (20°C min^{-1}) from 40 to 200°C. The melting points were measured during the second heating phase.

Crystal structure analyses were carried out on a Siemens P4 diffractometer, wherein a Mo–K_{α} radiation with a wavelength of 0.71073 Å was used (graphite monochromator). The software package Siemens SHELXTL PLUS (VMS) was used to resolve the structure.

3.1. Synthesis procedure for ligand precursors of the type $Cp^{\#}HSiMe_2NHCH_2CH_2NR_2$ and $Me_3SiNHCH_2CH_2R$

A total of 10 mmol of the corresponding amine are dissolved in 50 ml Et_2O and lithiated at 0°C by adding dropwise 10 mmol BuLi (1.6 M in hexane). After 6 h the suspension is reduced in volume and at 0°C added in portions to 10 mmol of the corresponding $Cp^{\#}HSiMe_2Cl$ ligand precursor, or to 10 mmol Me_3SiCl, dissolved in 100 ml Et_2O. After the addition is completed the mixture is stirred for an additional 12 h, filtered over Na_2SO_4, reduced in volume in vacuo and distiled. $Me_3SiNHCH_2CH_2OMe$: Bp., 58°C. EI-MS, $m/e = 147$ (M^+); yield, 87%. $Me_3SiNHCH_2CH_2NMe_2$: Bp., 82°C. EI-MS, $m/e = 160$ (M^+); yield, 71%. $C_5H_5SiMe_2NHCH_2CH_2NHOMe$: Bp., 43°C (membrane vacuum), EI-MS, $m/e = 197$ (M^+); yield, 68%. $C_5H_5SiMe_2NHCH_2CH_2NHNMe_2$: Bp., 62°C (membrane vacuum), EI-MS, $m/e = 210$ (M^+); yield, 60%. $C_9H_7SiMe_2NHCH_2CH_2NHOMe$: Bp., 119°C (high vacuum). EI-MS, $m/e = 247$ (M^+); yield, 85%. $C_{13}H_9SiMe_2NHCH_2CH_2NHOMe$: Bp., 208°C (high vacuum). EI-MS, $m/e = 297$ (M^+); yield, 55%.



Scheme 3.

3.2. Synthesis procedure for half-sandwich complexes of the type $(C_5H_5)Zr[N(SiMe_3)CH_2CH_2R]Cl_2$

A total of 5 mmol of the corresponding $Me_3SiNHCH_2CH_2R$ ligand precursor are dissolved in 30 ml Et_2O and lithiated at -78°C by adding 5 mmol BuLi (1.6 M in hexane) dropwise. After 12 h the suspension is reduced in volume and at -78°C added in portions to 5 mmol $(C_5H_5)ZrCl_3$, suspended in 30 ml

Table 3
Selected bond lengths (pm) and angles (°) of compound **4**

Bond lengths (pm)					
Zr–Cl(1)	246.1(1)	Zr–N(1)	206.2(3)	N(1)–Si	172.5(3)
Zr–Cl(2)	245.4(1)	Zr–N(2)	246.5(3)	C(1)–Si	186.8(3)
Zr–C(1)	248.4(3)	Zr–C(2)	250.3(3)	Zr–C(3)	257.9(3)
Zr–C(4)	257.3(3)	Zr–C(5)	249.9(3)		
Bond angles					
Cl(1)–Zr–Cl(2)	113.0(1)	Cl(2)–Zr–N(1)	116.4(1)	Cl(1)–Zr–N(1)	117.5(1)
Si–N–C(8)	109.8(1)	Zr–N(1)–Si	109.8(1)	Zr–N(1)–C(8)	122 8(3)
Cl(1)–Zr–N(2)	81.1(1)	Cl(2)–Zr–N(2)	81 6(1)		

toluene. After the addition is completed the mixture is stirred for an additional 24 h, filtered over Na_2SO_4, concentrated and crystallized at −30°C.

3.2.1. $(C_5H_5)Zr[N(SiMe_3)CH_2CH_2OMe]Cl_2$ (**1**)

EI-MS, $m/e = 371$ (M^+, 2%); yield, 67%.

3.2.2. $(C_5H_5)Zr[N(SiMe_3)CH_2CH_2NMe_2]Cl_2$ (**2**)

EI-MS, $m/e = 384$ (M^+, 6%); yield, 70%. Elemental analysis: found C, 37.16; H, 6.35. $C_{11}H_{24}Cl_2N_2SiZr$ calculated C, 37.29; H, 6.26. X-ray structure analysis: yellow prisms (from toluene) in the dimension $0.25 \times 0.20 \times 0.18$ mm^3, monoclinic; space group $P2_1/n$; $a = 9.909(2)$ Å, $b = 13.394(3)$ Å and $c = 13.488(3)$ Å; $\beta = 98.31(3)°$; $V = 1771.3(7)$ Å^3; $Z = 4$, $M = 386.5$ g mol^{-1}, $D_{calc.} = 1.449$ mg m^{-3}, absorption coefficient: 0.977 mm^{-1}, F(000) = 792, measuring temperature: 296 K, measuring range: $3.0° \leq 2\theta \leq 55.0°$, measured reflections: 5365, independent reflections: 4062 ($R_{int} = 2.22\%$), observed reflections: 2972 ($F > 3.0\ \sigma\ (F)$), refined parameters: 185, absorption correction: semi-empirical (Ψ-scans), minimum transmission 0.4609, maximum transmission 0.5122, goodness-of-fit: 1.58, R-value: $R = 5.57\%$, wR-value ($w^{-1} = \sigma^2$(F)): 4.02%, maximum of the residual electron density: 0.70 e Å^{-3}, minimum of the residual electron density −0.45 e Å^{-3}.

Further details of the crystal structure analyses are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-408528 (**2**) and CSD-408527 (**4**), the names of the authors and the journal citation.

3.3. Synthesis procedure for ansa-half-sandwich complexes of the type $(Cp^{\#}{-}SiMe_2{-}NCH_2CH_2R)ZrCl_2$

5 mmol of the corresponding $Cp^{\#}HSiMe_2NHCH_2CH_2R$ ligand precursor are dissolved in 30 ml Et_2O and lithiated dropwise at −78°C by adding 10 mmol BuLi (1.6 M in hexane). After 6 h the suspension is reduced in volume and at −78°C added in portions to 5 mmol $ZrCl_4$, suspended in 40 ml toluene. After the addition is completed the mixture is stirred for an additional 48 h, filtered over Na_2SO_4, reduced in volume and crystallized at −30°C.

Table 4
Polymerization experiments and analytical results for the polymers

Complex	Activity[a] (kg PE mmol^{-1} [M] h)	$\bar{M}_\eta$[b] (kg mol^{-1})	T_m^c (°C)
1	3.9	300	134.2
2	2.1	240	137.2
3	4.3	360	140.1
4	2.9	280	140.9
5	12.5	500	140.6
6	0.1	260	138.0

[a] $T_p = 60°C$; solvent, 500 ml pentane; $p(C_2H_4) = 10$ bar; [M]/[Al] = 1:5000.

[b] Average molecular weight determined by viscosimetry.

[c] Maximum of the melting peak during second heating course (DSC).

3.3.1. $(C_5H_4{-}SiMe_2{-}NCH_2CH_2OMe)ZrCl_2$ (**3**)

EI-MS, $m/e = 355$ (M^+, 5%); yield, 73%.

3.3.2. $(C_5H_4{-}SiMe_2{-}NCH_2CH_2NMe_2)ZrCl_2$ (**4**)

EI-MS, $m/e = 368$ (M^+, 8%); yield, 81%. Elemental analysis: found C, 36.16; H, 5.54. $C_{11}H_{20}Cl_2N_2SiZr$ calculated C, 35.66; H, 5.44. X-ray structure analysis: irregular, colorless crystals (from toluene) in the dimension $0.35 \times 0.25 \times 0.20$ mm^3, monoclinic; space group $P2_1/n$; $a = 8.050(2)$ Å, $b = 12.839(2)$ Å and $c = 14.945(2)$ Å; $\beta = 90.59(2)°$; $V = 1544.6(5)$ Å^3; $Z = 4$, $M = 371.5$ g mol^{-1}, $D_{calc.} = 1.598$ mg m^{-3}, absorption coefficient: 1.117 mm^{-1}, F(000) = 756, measuring temperature: 173 K, measuring range: $3.0° \leq 2\theta \leq 55.0°$, measured reflections: 4887, independent reflections: 3558 ($R_{int} = 1.86\%$), observed reflections: 3176 ($F > 3.0\ \sigma\ (F)$), refined parameters: 165, absorption correction: N/A, goodness-of-fit: 1.99, R-value: $R = 3.78\%$, wR-value ($w^{-1} = \sigma^2(F)$): 3.22%, maximum of the residual electron density: 1.62 e Å^{-3}, minimum of the residual electron density −1.15 e Å^{-3}.

3.3.3. $(C_9H_6{-}SiMe_2{-}NCH_2CH_2OMe)ZrCl_2$ (**5**)

EI-MS, $m/e = 405$ (M^+, 1%); yield, 65%.

3.3.4. $(C_{13}H_8{-}SiMe_2{-}NCH_2CH_2OMe)ZrCl_2$ (**6**)

EI-MS, $m/e = 455$ (M^+, 1%); yield, 57%.

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