Dialkylaminoethyl-functionalized *ansa*-zirconocene dichlorides: synthesis, structure, and polymerization properties

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Abstract

Donor substituted carbon- and silicon-bridged zirconocene dichlorides of the type $[\eta^5\text{-}C_{13}H_8\text{-}CMe_2\text{-}\eta^5\text{-}C_5H_3(CH_2CH_2NR_2)]ZrCl_2$ (R = Me (**2a**), Et (**2b**), ^{i}Pr (**2c**)) and $[\eta^5\text{-}C_{13}H_8\text{–}SiMe_2\text{-}\eta^5\text{-}C_5H_3(CH_2CH_2NR_2)]ZrCl_2$ (R = Me (**4a**), Et, (**4b**), ^{i}Pr (**4c**)) have been prepared. Activation of **2a–c** and **4a–c** with excess methylalumoxane results in the formation of catalytically active species for the polymerization of ethylene and propylene. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Metallocene dichlorides of titanium (IV) and zirconium (IV) have attracted considerable attention during the last decades; in combination with methylalumoxane (MAO) or certain borate-activators these compounds are effective catalysts in the homogeneous polymerization of olefins. The Group 4 metallocene systems have well defined catalytically active sites which is a prerequisite for the production of polymers with specific microstructures and narrow molecular weight distributions [1].

Group 4 metallocene derivatives with donor-functionalities in the side-chain, such as –PR$_2$, –SR, –OR, or –NR$_2$ groups, have also been reported in the literature and are currently explored by several research groups [2]. Generally, a donor substituent can result in dramatic changes in chemical as well as physical properties of the corresponding compounds; for example intramolecularly coordinated donor groups are capable of stabilizing highly reactive, unsaturated species as well as modifying the reactivity of metal centers towards certain substrates. In the non-coordinated fashion the 'spectator-ligand' provides the possibility of enhancing the solubility in polar solvents or of coordinating intermolecularly to other metal fragments rather than the central metal atom. In this context we have recently shown that the cocatalyst MAO plays an important role in the polymerization catalysis with dialkylaminoethyl-substituted Group 4 metallocene derivatives; the Lewis-basic amino-group is able to coordinate to Lewis-acidic aluminium centers of $[Me\text{-}Al(R)O\text{–}]_n$ units. This donor-acceptor-linkage is hemilabile [2a,3] under certain conditions, leading to the formation of two different catalytically active species in the polymerization process. Once activated by MAO, dialkylaminoethyl-substituted *ansa*-zirconocene derivatives turned out to be suitable catalysts for the production of polyethylene with different molecular weight distributions [4].

Because the synthesis of aminofunctionalized metallocene dichlorides has yet remained quite rare, we now wish to report on the preparation, characterization, and polymerization properties of *ansa*-zirconocene dichlorides with dialkylaminoethyl groups anchored to the cyclopentadienyl (Cp) moiety [2b]. We have focussed on the synthesis of stereorigid carbon- and silicon-bridged systems in which the donor-group is fixed nearby the metal center. This situation allows an influence of the dialkylaminoethyl-substituent on metallocene-based polymerization catalysis.

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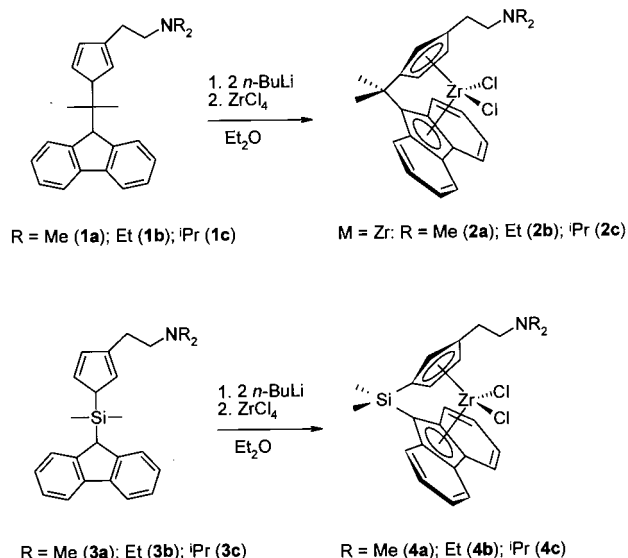
Scheme 1.

Table 1
Crystal data and structure refinement for **2a**

Empirical formula	$C_{25}H_{27}Cl_2NZr + 0.5C_7H_8$
Formula weight	549.66
Color	Red
Crystal size (mm)	$1.00 \times 0.60 \times 0.40$
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Unit cell dimensions	
a (Å)	13.87(2)
b (Å)	9.164(7)
c (Å)	20.55(2)
α (°)	90
β (°)	108.74(8)
γ (°)	90
Volume (Å³)	2474(4)
Z, calc. density (Mg m^{-3})	4, 1.476
Absorption coefficient (mm^{-1})	0.678
θ range (°)	1.5–27.0
Index ranges	$0 \leq h \leq 17$, $0 \leq k \leq 11$, $-26 \leq l \leq 24$
No. reflections collected	5625
No. of data/restraints/parameters	5397/1/303
Abs. correction	Semi-empirical from Ψ-scans
Goodness-of-fit on F^2	1.121
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0687$, $wR_2 = 0.1483$ [3744]
R indices (all data)	$R_1 = 0.1125$, $wR_2 = 0.1777$
Largest difference peak and hole (e Å^{-3})	0.6 and -0.7
Diffractometer used	Siemens P2(1) diffractometer
Programme used	Siemens SHELXTL plus/SHELXL-93
Refinement method	Full-matrix least-squares on F^2

Table 2
Selected bond lengths (Å) and bond angles (°) for **2a**

Bond lengths

Zr(1)–C(13)	2.405(6)	Zr(1)–C(7)	2.661(6)
Zr(1)–Cl(2)	2.420(3)	N(1)–C(23)	1.444(8)
Zr(1)–Cl(1)	2.422(3)	N(1)–C(24)	1.448(9)
Zr(1)–C(17)	2.424(6)	N(1)–C(25)	1.459(9)
Zr(1)–C(18)	2.448(6)	C(13)–C(14)	1.563(8)
Zr(1)–C(21)	2.469(7)	C(14)–C(16)	1.520(9)
Zr(1)–C(1)	2.501(6)	C(14)–C(17)	1.532(8)
Zr(1)–C(19)	2.543(6)	C(14)–C(15)	1.549(8)
Zr(1)–C(12)	2.544(6)	C(20)–C(22)	1.512(9)
Zr(1)–C(20)	2.585(6)	C(22)–C(23)	1.529(9)
Zr(1)–C(6)	2.639(6)		

Bond angles

Cl(2)–Zr(1)–Cl(1)	96.30(11)	C(16)–C(14)–C(15)	107.8(5)
C(23)–N(1)–C(24)	112.3(6)	C(17)–C(14)–C(13)	98.7(5)
C(23)–N(1)–C(25)	109.4(6)	C(20)–C(22)–C(23)	113.2(6)
C(24)–N(1)–C(25)	108.5(6)	N(1)–C(23)–C(22)	112.3(6)

2. Results and discussion

2.1. Preparation and characterization of dialkylaminoethyl-functionalized ansa-zirconocene dichlorides

We have recently reported on the regioselective synthesis of the carbon- and silicon- bridged 2-(*N,N*-dialkylamino)ethyl-substituted cyclopentadienes **1a**–**c** and **3a**–**c** [5]. These compounds are suitable precursors for the preparation of donor-substituted *ansa*-zirconocene dichlorides; the synthesis of such complexes is illustrated in Scheme 1. Reaction of the cyclopentadienes with two equivalents of *n*-BuLi in diethylether and subsequent addition of ZrCl$_4$ gave the *ansa*-complexes **2a**–**c** and **4a**–**c** as air- and moisture-sensitive, red or orange solids which were characterized by ^{1}H-, ^{13}C- and ^{29}Si-NMR spectroscopy, mass spectrometry and elemental analysis. The –CH$_2$–CH$_2$– protons of the dialkylaminoethyl-substituents appear as two multiplets. These resonances are shifted upfield compared to transition metal Cp-complexes with intramolecularly coordinated donor-groups [6]; this phenomenon indicates that the dialkylaminoethyl-group in **2a**–**c** as well as in **4a**–**c** is not coordinated to the metal center in solution.[1]

Compound **2a** was further characterized by single crystal X-ray diffraction studies; crystallographic data are presented in Table 1, selected bond lenghts and bond angles are listed in Table 2. The molecular struc-

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[1] The coordination of a donor-group to a metal center in neutral Group 4 metallocene dichlorides has only been rarely observed [7a]. The synthesis of $[\eta^5\text{-}C_5H_3(CH_2CH_2NMe_2)CMe_2\text{-}\eta^5\text{-}C_{13}H_8]ZrCH_3^+ B(C_6F_5)_4^-$ has been recently reported. In this compound, the donor-group is intramolecularly coordinated to the 14-VE-zirconium-atom [7b].

ture is illustrated in Fig. 1.[2] The structural analysis confirms the ^{1}H-NMR data and unambiguously reveals the absence of any bonding interaction between the -NMe$_2$ group and the zirconium center. Both Cp and Fluorenyl (Flu) ligands are η^5-coordinated to the metal center. The distances Zr–Cp (cent.) and Zr–Flu (cent.) are 2.185 Å and 2.237 Å, respectively. The Cp(cent.)–Zr–Flu(cent.) angle is 119.1°. Similar parameters were found in the parent compound [η^5-C$_{13}$H$_8$–CMe$_2$-η^5-C$_5$H$_4$]ZrCl$_2$, reported by Ewen and Razavi [8].

2.2. Polymerization of ethylene and propylene with MAO-activated dialkylaminoethyl-functionalized ansa-zirconocene dichlorides

When combined with large excess methylalumoxane (MAO) (Zr:Al = 1:1000) active species for the polymer-

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[2] A crystal of **2a** suitable for X-ray diffraction was obtained by recrystallization from toluene. Half of a disordered molecule of toluene was found in the unit cell and is omitted in Fig. 1 for clarity.
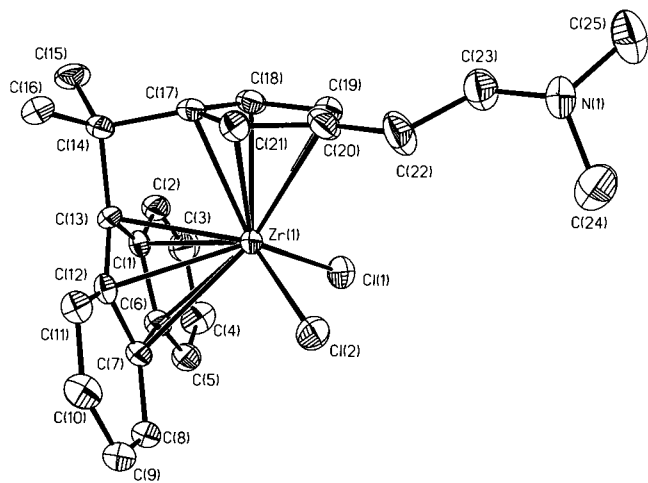

Fig. 1. Molecular structure of [η^5-C$_{13}$H$_8$-CMe$_2$-η^5-C$_5$H$_3$(CH$_2$CH$_2$NMe$_2$)]ZrCl$_2$ (**2a**) (ORTEP diagram; 50% probability ellipsoids).

Table 3
Polymerization results [a]

Compound	µmol	Time (min)	Activity [b]
2a	30	60	58.7
2b	30	60	84.3
2c	30	60	9.0
4a	14	5	754.0
4b	14	5	832.0
4c	14	30	226.0
5	10	6	760.0
6	10	6	4000.0

[a] Polymerization conditions: Zr:Al = 1:1000; V = 200 ml (toluene); polymerization temperature: T = 50°C.
[b] In kg PE (mol Zr·h·bar)$^{-1}$.

ization of ethylene are generated from the precatalysts **2a**–**c** and **4a**–**c**. Since metallocene-based polymerization activities depend on various factors, such as MAO quality, polymerization temperature, monomer pressure and monomer quality we also polymerized ethylene with the MAO-activated parent compounds [η^5-C$_{13}$H$_8$–CMe$_2$-η^5-C$_5$H$_4$]ZrCl$_2$ (**5**) [8] and [η^5-C$_{13}$H$_8$–SiMe$_2$-η^5-C$_5$H$_4$]ZrCl$_2$ (**6**) [9] under the same conditions. Table 3 summarizes the polymerization results of **2a**–**c**/MAO and **4a**–**c**/MAO as well as of the non-donor-substituted catalysts **5**/MAO and **6**/MAO. The silicon-bridged systems are much more active than the carbon-bridged compounds. This phenomenon has often been observed in the polymerization catalysis of olefins with carbon- or silicon-bridged metallocene derivatives [1b,10]. We have additionally found that the donor substitutent at the Cp-moiety substantially decreases access of the monomer to the catalytically active metal center; Table 3 shows the reduced activities of the side-chain functionalized systems in comparison to the corresponding parent zirconocene-complexes; the catalysts **2c**/MAO and **4c**/MAO containing the bulky diisopropyl-aminoethyl-substitutent show the lowest activities in the polymerization of ethylene while the dimethylamino- and diethylamino-derivatives have comparable rates in the production of polyethylene.

Using propylene in the polymerization catalysis the access of the larger monomer to the Zr-center is much more sensitive to substituents at the metallocene core compared to ethylene. We have observed low activities of **2a**,**b**/MAO and **4a**–**c**/MAO, while **2c**/MAO (diisopropylaminoethyl-substituent) does not polymerize propylene at all.[3] Nevertheless, these catalysts are suitable systems for the production of polypropylenes with temperature-dependent molecular weight distributions [4,11]. Furthermore, ^{13}C-NMR spectroscopic investigations reveal that the polymers obtained with **2a**,**b**/MAO are of hemiisotactical nature, while **4a**–**c**/MAO produce polypropylenes with mainly atactic microstructures [10,12].

3. Experimental

3.1. General

All manipulations were carried out under purified argon atmosphere using standard Schlenk techniques. The solvents were commercially available, purified by conventional means and distilled immediately prior to use. The melting point determination was performed using a Büchi 510 melting point apparatus. The elemental analyses were performed by the Microanalytical

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[3] Catalyst activities in kg PP (mol Zr·h·bar)$^{-1}$: **2a**: 0.7; **2b**: 8.4; **4a**: 9.3; **4b**: 8.0; **4c**: 8.0.

Laboratory of the Universiät Bielefeld. The NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer (^{1}H 500.1 MHz; ^{13}C{^{1}H} 125.8 MHz; ^{29}Si{^{1}H} 99.4 MHz). Chemical shifts are reported in ppm and are referenced to the solvent as internal standard.

3.2. Isopropylidene[3-(N,N-dialkylaminoethyl)-cyclopentadienyl-fluoren-9-yl]-zirconocenedichlorides (2a–c)

3.2.1. Compound 2a

n-BuLi (30.00 ml, 48.00 mmol in hexane) was slowly added to a solution of 2-[3-(2-(*N,N*-dimethylamino)ethyl)cyclopentadienyl]-2-fluoren-9-yl-propane (**1a**) (8.14 g, 24.00 mmol) in diethylether (120 ml) at −78°C. The reaction mixture was warmed up to room temperature (r.t.) and stirring was continued for 18 h. After cooling to −78°C ZrCl$_4$ (5.60 g, 24.00 mmol) was added to the red solution of the dilithium-salt in Et$_2$O and the suspension was allowed to warm to r.t. Stirring was continued for overnight. Subsequently the solvent was removed in vacuo and the residue was extracted with toluene (350 ml). After filtration the solution of **2a** in toluene was concentrated in vacuo to 100 ml and stored at −60°C. **2a** was obtained as an air and moisture sensitive, red solid after decanting the supernatant and evaporating of the solvent. Yield: 8.30 g (16.50 mmol, 69%). M.p.: 191°C. ^{1}H-NMR (C$_6$D$_6$): δ 1.79 (s, 6 H, C−CH$_3$), 1.97 (s, 6 H, N−CH$_3$), 2.19–2.21 (m, 1 H, Cp−CH$_2$−), 2.29–2.31 (m, 1 H, Cp−CH$_2$−), 2.51–2.53 (m, 2 H, Cp−CH$_2$−CH$_2$−), 5.17 (pt, *J*(H,H) = 2.5 Hz, 1 H, Cp−H), 5.28 (pt, *J*(H,H) = 3.2 Hz, 1 H, Cp−H), 6.00 (pt, *J*(H,H) = 2.5 Hz, 1 H, Cp−H), 6.92–6.97 (m, 2 H, fluorenyl-H), 7.23–7.29 (m, 2 H, fluorenyl-H), 7.34–7.39 (2 × d, ^{3}*J*(H,H) = 8.8 Hz, 2 H, fluorenyl-H), 7.75–7.77 (2 × d, ^{3}*J*(H,H) = 8.2 Hz, fluorenyl-H). Toluene: δ 2.10 (s, C$_6$H$_5$−CH$_3$), 7.00, 7.12 (2 × m, C$_6$H$_5$−CH$_3$). ^{13}C-NMR (C$_6$D$_6$): δ 21.4 (C$_6$H$_5$−CH$_3$), 28.4 (C−CH$_3$, Cp−CH$_2$−), 40.3 (*C*−CH$_3$), 45.3 (N−CH$_3$), 59.7 (Cp−CH$_2$−CH$_2$−), 79.1, 103.0, 103.4, 114.2, 117.9, 123.3, 123.4, 123.5, 123.6, 124.9, 125.0, 125.1, 128.3, 128.5, 128.8, 128.9, 129.3, 134.2 (Cp−C, fluorenyl-C). Toluene: δ 125.2 (C$_6$H$_5$−CH$_3$), 128.5, 129.3, 137.8 (C$_6$H$_5$−CH$_3$). MS (CI, isobutane): *m/z* (%): 503 (22) [*M*$^+$], 338 (14) [*M*$^+$−C$_{13}$H$_9$], 165 (12) [C$_{13}$H$_9^+$], 58 (100) [(CH$_3$)$_2$NCH$_2^+$]. Anal. Calc. for C$_{25}$H$_{27}$Cl$_2$NZr + 0.5C$_7$H$_8$ (549.66 g mol$^{−1}$): C, 62.28; H, 5.68; N, 2.55. Found: C, 61.87; H, 5.83; N, 2.76%.

3.2.2. Compound 2b

In the same manner as above compound **2b** (6.10 g, 11.50 mmol) was prepared from **1b** (8.68 g, 23.40 mmol) in 49% yield as an orange-red, air and moisture sensitive solid. M.p.: 158°C. ^{1}H-NMR (C$_6$D$_6$): δ 0.87 (t, ^{3}*J*(H,H) = 7.2 Hz, 6 H, −CH$_2$−CH$_3$), 1.81, (2 × s, 6 H, C−CH$_3$), 2.32 (m, 4 H, −CH$_2$−CH$_3$), 2.54, 2.62 (2 × m,

2 × 2 H, −CH$_2$−CH$_2$−), 5.29 (pt, ^{3,4}*J*(H,H) = 2.6 Hz, 1 H, Cp−H), 5.36 (pt, ^{4}*J* = 3.1 Hz, 1 H, Cp−H), 6.11 (pt, ^{3,4}*J*(H,H) = 2.6 Hz, 1 H, Cp−H), 6.99 (m, 2 H, fluorenyl-H), 7.33 (m, 2 H, fluorenyl-H), 7.44 (2 × d, ^{3}*J*(H,H) = 8.9 Hz, 2 × 1 H, fluorenyl-H), 7.85 (2 × d, ^{3}*J*(H,H) = 4.7 Hz, 2 × 1 H, fluorenyl-H). ^{13}C-NMR (C$_6$D$_6$): δ 12,4 (N−CH$_2$−CH$_3$), 28.2 (Cp−CH$_2$−), 28.4 (C−CH$_3$), 40.3 (C^q), 47.1 (N−CH$_2$−CH$_3$), 53.1 (Cp−CH$_2$−CH$_2$−), 79.1, 103.0, 103.4, 114.1, 117.7, 122.9, 123.0, 123.3, 123.4, 123.5, 124.9, 125.0, 125.1, 125.2, 128.8, 128.9, 134.5 (Cp−C, fluorenyl-C). MS (CI, methane): *m/z* (%): 165 (94) [C$_{13}$H$_9^+$], 86 (100) [(C$_2$H$_5$)$_2$NCH$_2^+$]. Anal. Calc. for C$_{27}$H$_{31}$Cl$_2$NZr (531.766 g mol$^{−1}$): C, 60.98; H, 5.88; N, 2.63. Found: C, 60.97; H, 5.67; N, 2.60%.

3.2.3. Compound 2c

Following the procedure described for **2a,b** compound **2c** (5.00 g, 8.90 mmol) was obtained from **1c** (7.82 g, 19.57 mmol) as an orange, air and moisture sensitive solid in 46% yield. M.p.: 247–249°C. ^{1}H-NMR (C$_6$D$_6$): δ 0.84 (d, ^{3}*J*(H,H) = 6.6 Hz, 6 H, CH−CH$_3$), 0.86 (d, ^{3}*J*(H,H) = 6.5 Hz, 6 H, CH−C*H$_3$*), 1.84, 1.85 (2 × s, 2 × 6 H, C−CH$_3$), 2.52–2.54 (m, 2 H, Cp−CH$_2$−), 2.59–2.62 (m, 2 H, Cp−CH$_2$−CH$_2$−), 2.82–2.84 (sept. ^{3}*J*(H,H) = 6.6 Hz, 2 H, C*H*−CH$_3$), 5.34 (d, ^{3}*J*(H,H) = 3.0 Hz, 1 H, Cp−H), 5.38 (d, ^{3}*J*(H,H) = 3.0 Hz, 1 H, Cp−H), 6.09 (s, 1 H, Cp−H), 6.99–7.15 (m, 2 H, fluorenyl-H), 7.29–7.36 (m, 2 H, fluorenyl-H), 7.43–7.49 (2 × d, ^{3}*J*(H,H) = 8.9 Hz, 2 H, fluorenyl-H), 7.84–7.87 (2 × d, ^{3}*J*(H,H) = 4.3 Hz, 2 H, fluorenyl-H). ^{13}C-NMR (C$_6$D$_6$): δ 20.8, 21.0 (CH−CH$_3$), 28.5 (C−CH$_3$), 31.7 (Cp−CH$_2$−), 40.3 (*C*−CH$_3$), 45.2 (Cp−CH$_2$−CH$_2$−), 47.9 (*C*H−CH$_3$), 79.1 (fluorenyl-Cq), 102.9, 103.6, 117.8 (Cp−C), 114.1 (Cp−C^q), 122.9, 123.0, 123.3, 123.4, 123.5, 123.6, 124.9, 125.0, 125.1, 125.2, 128.5, 128.8, 128.9 (fluorenyl-C), 134.7 (Cp−C^q). MS (CI, isobutane): *m/z* (%): 559 (13) [*M*$^+$], 544 (3) [*M*$^+$−C$_{13}$H$_9$], 165 (3) [C$_{13}$H$_9^+$], 114 (100) [(C$_3$H$_7$)$_2$NCH$_2^+$]. Anal. Calc. for C$_{29}$H$_{35}$Cl$_2$NZr (559.75 g mol$^{−1}$): C, 62.22; H, 6.30; N, 2.50. Found: C, 62.13; H, 6.37; N, 2.18%.

3.3. Dimethylsilanediyl[3-(N,N-dialkylaminoethyl)-cyclopentadienyl-fluoren-9-yl]-zirconocenedichlorides (4a–c)

3.3.1. Compound 4a

In a similar manner as described above **4a** was obtained by adding *n*-BuLi (11.50 ml, 18.40 mmol) to a solution of [(3-(2-(*N,N*-Dimethylamino)ethyl)cyclopentadienyl)(fluoren-9-yl)]dimethylsilane (**3a**) (3.25 g, 9.00 mmol) in Et$_2$O (50 ml) at −10°C, followed by addition of ZrCl$_4$ (2.11 g, 9.00 mmol) at −60°C. The reaction mixture was allowed to warm to r.t. and

stirring was continued for 18 h. The solvent was removed in vacuo and the residue extracted with toluene (70 ml). LiCl was filtered off, the orange solution was concentrated to 40 ml and stored at $-30°C$, affording **4a** as an orange, air and moisture sensitive solid. Yield: 0.98 g (1.73 mmol, 19%). M.p.: 186°C. ^{1}H-NMR (C_6D_6): δ 0.59, 0.60 (2 s, 6 H, Si–CH_3), 1.98 (s, 6 H, N–CH_3), 2.24–2.28 (m, 1 H, Cp–CH$_2$–CH_2–), 2.32–2.36 (m, 1 H, Cp–CH$_2$–CH_2–), 2.68–2.74 (m, 2 H, Cp–CH_2–), 5.31 (pt, $^{3,4}J$(H,H) = 2.3 Hz, 1 H, Cp–H), 5.48 (t, ^4J(H,H) = 2.8 Hz, 1 H, Cp–H), 6.42 (pt, $^{3,4}J$(H,H) = 2.5 HZ, 1 H, Cp–H), 7.06–7.12 (m, 2 H, fluorenyl-H), 7.29–7.33 ($2 \times$ d, ^3J(H,H) = 13.9 Hz, 2 H, fluorenyl-H), 7.39–7.46 (m, 2 H, fluorenyl-H), 7.89–7.92 ($2 \times$ d, ^3J(H,H) = 8.3 Hz, 2 H, fluorenyl-H). ^{13}C-NMR (C_6D_6): δ –1.3 (Si–CH_3), 28.8 (Cp–CH_2–), 45.3 (N–CH_3), 59.8 (Cp–CH$_2$–CH_2–), 66.6 (Cp–C), 102.8, 11.9, 112.1 (Cp–C), 123.9, 124.0, 124.7, 125.3, 125.4, 125.6, 126.5, 126.6, 128.3, 128.5, 128.7, 129.3, 129.4 (fluorenyl-C), 139.7 (Cp–C).). ^{29}Si-NMR (C_6D_6): δ –13.8. MS (CI, isobutane) m/z (%): 520 (7) [M^+], 484 (11) [M^+–HCl], 165 (10) [$C_{13}H_9^+$], 58 (100) [(CH$_3$)$_2$NCH$_2^+$]. Anal. Calc. for $C_{24}H_{27}SiNZrCl_2$ (519.79 g mol^{-1}): C, 55.46; H: 5.24; N, 2.69. Found: C, 56.13; H, 5.61; N, 2.22%.

3.3.2. Compound **4b**

In the same manner as above **4b** was synthesized from **3b** (3.85 g, 9.90 mmol) and was isolated as an orange, air and moisture sensitive solid. Yield: 0.90 g (1.64 mmol, 16.6%). M.p.: 122°C. ^{1}H-NMR (C_6D_6): δ 0.60, 0.61 ($2 \times$ s, $2 \times$ 3 H, Si–CH_3), 0.85 (t, ^3J(H,H) = 7.1 Hz, 6 H, –CH$_3$), 2.31 (m, 4 H, –CH_2–CH$_3$), 2.49, 2.71, ($2 \times$ m, 2×2 H, –CH$_2$–CH$_2$–), 5.34 (pt, $^{3,4}J$(H,H) = 2.3 Hz, 1 H, Cp–H), 5.45 (pt, $^{3,4}J$(H,H) = 2.8 Hz, 1 H, Cp–H), 6.41 (pt, $^{3,4}J$(H,H) = 2.5 Hz, 1 H, Cp–H), 7.06 (m, 2 H, fluorenyl-H), 7.31 ($2 \times$ d, 2×1 H, ^3J(H,H) = 8.4, 8.7 Hz, fluorenyl-H), 7.43 (m, 2 H, fluorenyl-H), 7.90 ($2 \times$ d, 2×1 H, ^3J(H,H) = 4.3 Hz, fluorenyl-H). ^{13}C-NMR (C_6D_6): δ –3.6 (Si–CH$_3$), 12.4 (N–CH$_2$–CH$_3$), 28.6 (Cp–CH_2–), 47.1 (N–CH_2–CH$_3$), 53.3 (Cp–CH_2–CH$_2$–), 66.6, 102.8, 109.8, 111.9, 112.1, 120.0, 120.1, 123.9, 124.0, 125.5, 125.4, 126.5, 126.6, 128.3, 128.4, 128.6, 128.7, 139.8 (Cp–C, fluorenyl-C). ^{29}Si-NMR (C_6D_6): δ –13.8. MS (EI) m/z (%): 547 (5) [M^+], 165 (100) [$C_{13}H_9^+$]. Anal. Calc. for $C_{26}H_{31}NSiZrCl_2$ (547.82 g mol^{-1}): C, 57.01; H, 5.70; N, 2.56. Found: C, 56.90; H, 5.69; N, 2.46%.

3.3.3. Compound **4c**

Compound **4c** was synthesized from **3c** (3.20 g, 7.70 mmol) following the procedure described above and was obtained as an orange, air and moisture sensitive solid. Yield: 0.75 g (1.3 mmol, 17%). M.p.: 179°C. ^{1}H-NMR (C_6D_6): δ 0.62 (s, 3 H, Si–CH$_3$), 0.64 (s, 3 H, Si–CH$_3$), 0.82 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH–

CH_3), 0.83 (d, ^3J(H,H) = 6.7 Hz, 6 H, CH–CH_3), 2.50–2.53 (m, 2 H, Cp–CH$_2$–), 2.68–2.71 (m, 2 H, CH–CH$_3$), 2.79–2.82 (m, 2 H, Cp–CH$_2$–CH$_2$–), 5.39 (pt, 1 H, H$_G$), 5.52 (t, ^4J(H,H) = 2.8 Hz, 1 H, Cp–H), 6.41 (pt, 1 H, Cp–H), 7.09–7.12 (m, 2 H, fluorenyl-H), 7.31–7.36 ($2 \times$ d, ^3J(H,H) = 8.4 Hz, 2 H, fluorenyl-H), 7.39–7.46 (m, 2 H, fluorenyl-H), 7.89–7.92 ($2 \times$ d, ^3J(H,H) = 5.8 Hz, fluorenyl-H). ^{13}C-NMR (C_6D_6): δ –1.3 (Si–CH_3), 20.8, 20.9 (CH–CH_3), 32.1 (Cp–CH_2–), 45.4 (Cp–CH$_2$–CH_2–), 47.9 (CH–CH$_3$), 66.5 (Cp–C), 102.7, 11.9, 112.3 (Cp–C), 123.9, 124.0, 124.8, 125.4, 126.5, 126.6, 128.4, 128.5, 128.6, 128.7, 129.2, 129.3, 129.4 (fluorenyl-C), 140.2 (Cp–C). ^{29}Si-NMR (C_6D_6): δ –13.9. MS (CI, isobutane) m/z (%): 576 (1) [M^+], 165 (23) [$C_{13}H_9^+$], 114 (90) [(C$_3$H$_7$)$_2$NCH$_2^+$]. Anal. Calc. for $C_{28}H_{35}NSiZrCl_2$ (575.80 g mol^{-1}): C, 58.41; H, 6.13; N, 2.43. Found: C, 58.58; H, 6.53; N, 2.32%.

3.4. General procedure for the polymerization of ethylene and propylene

A 1 l-Büchi autoclave, equipped with mass-flow and pressure-controller was filled under argon with toluene and 2.0 ml of MAO-solution (4.9% aluminum, $\rho \sim 0.9$ g ml^{-1}, 1 mmol Al = 0.6 ml). The interior was pressurized with ethylene (propylene) (5 bar) and thermostated to the desired temperature. The monomer pressure was kept constant during the polymerization process. The precatalysts were preactivated for 10 min with the remaining amount of MAO-solution. Subsequently the magenta catalyst-solutions were injected into the autoclave. The polymerization process was terminated by injecting 20 ml of isopropanol. Afterwards the content, containing the polymer, was poured into 200 ml of methanol/HCl (5:1) and stirred for 18 h. The polyethylenes were filtered off, washed with water and acetone and dried to constant mass. The toluene-soluble polypropylenes were isolated by removing the solvent in vacuum. The residue was washed with water and acetone and also dried to constant mass.

4. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 150286. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

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