

Boryl-substituted Zirconocene Dichloride Complexes as Catalyst Precursors for Homogeneous Ethylene Polymerization

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Dedicated to Professor Helgard G. Raubenheimer on the occasion of his 65th birthday

The synthesis and characterization of 16 new boryl-substituted zirconocene dichloride complexes are reported. After activation with methyl aluminoxane (MAO) these complexes are catalysts for homogeneous ethylene polymerization. The combination of these complexes with nickel catalysts containing Lewis basic substituents produces polymers with bimodal molecular weight distributions.

Key words: Zirconium, Ethylene Polymerization, Donor-Acceptor Catalysts, Bimodal Molecular Weight Distributions

Introduction

Only few metallocene catalysts carrying boryl-substituted cyclopentadienyl derivatives are known in the literature [1, 2]. Complexes with boryl-substituted indenyl ligands are still unknown. The preparation of boryl-substituted metallocene complexes *via* hydroboration of allyl complexes has been considered very promising [3–6].

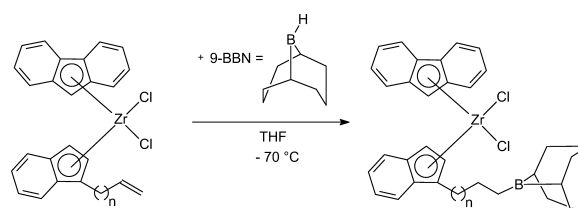
Cyclopentadienyl complexes with Lewis acidic boryl substituents are of growing interest as self-activating alkene polymerization catalysts [7, 8]. Further potential arises from the connection of Lewis acidic boryl-substituted metallocene complexes with catalyst compounds containing a Lewis base function like an (α -diimine)nickel complex. These nickel complexes have been known for a long time and were applied by Brookhart as polymerization catalysts [9–18].

Our aim was to produce polymers with bimodal molecular weight distributions based on the features of these two complex types. In the literature, related donor-acceptor-complexes are already known [19–23]. The idea was to prepare dinuclear complexes by donor-acceptor coupling.

Results and Discussion

Synthesis of the boryl-substituted zirconocene dichloride complexes 1–16

Boryl-substituted zirconocene complexes can be synthesized by the reaction of an ω -alkenyl zir-



Scheme 1. Hydroboration of ω -alkenyl-substituted zirconocene complexes.

conocene complex [24, 25] with 9-BBN (9-H-bora-bicyclo[3.3.1]nonane) at $-70\text{ }^{\circ}\text{C}$ in THF (Scheme 1). The obtained complexes were characterized by NMR spectroscopy (Table 1). Fig. 1 gives a survey of the synthesized zirconocene dichloride complexes.

Polymerization of ethylene

The synthesized complexes were activated with MAO (Al:Zr = 2 500:1) and used for the homogeneous polymerization of ethylene. The polymerization activity of the zirconocene complexes with boryl substituents showed a dependence on the distance between the ring systems and the 9-BBN group. The highest activity was observed with the cyclopentadienyl-indenyl systems. These complexes were substituted with one or two boryl moieties. Complex **6** was the most active one showing an activity of 68 300 [kg(prod)/mol(Zr) · h].

The metallocene complexes **9–11** show an increasing catalytic activity with an increasing number of carbon atoms between the 9-BBN group and the rings due

Table 1. NMR data of compounds **1** – **16**^a.

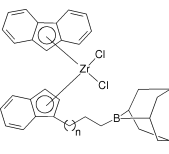
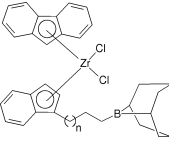
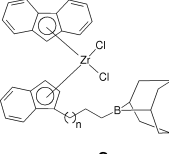
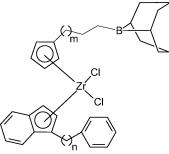
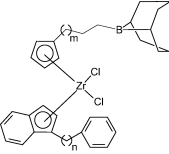
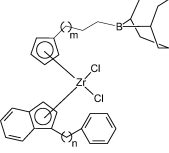
Compound	¹ H NMR [J(H,H) in Hz]	¹³ C NMR	¹¹ B NMR
 1 $n = 1$	7.81 (d, 2H, Flu-H) [8.3], 7.69 (d, 2H, Flu-H) [7.8], 7.33–7.19 (m, 4H, Ar-CH), 7.02 (m, 4H, Ar-CH), 5.55 (m, 1H, Ind-H ³), 5.05 (m, 1H, Ind-H ²), 1.77–1.25 (m, 20H; 9 CH ₂ , 2 CH ^{9-BBN})	C _q : 144.4, 143.5, 142.2, 142.1, 125.3; CH: 128.6, 128.2, 127.8, 127.1, 127.0, 127.0, 126.9, 120.6, 120.2, (Ar-CH), 99.6 (Ind-C ²²), 31.5 (B-CH, br); CH ₂ : 36.9, 33.4, 27.7, 23.6; 25.3 (B-CH ₂ , br)	88.7
 2 $n = 2$	7.70 (d, 2H, Flu-H) [6.1], 7.36–7.27 (m, 10H, Ar-CH), 6.81 (m, 1H, Ind-H ³), 6.50 (m, 1H, Ind-H ²), 1.90–1.17 (m, 22H; 10 CH ₂ , 2 CH ^{9-BBN})	C _q : 148.3, 144.8, 143.5, 142.1, 120.6; CH: 127.9, 127.0, 126.9, 126.8, 125.2, 125.1, 123.2, 121.4, 120.2 (Ar-CH), 30.8 (B-CH, br); CH ₂ : 36.9, 33.4, 31.7, 25.5, 23.6 25.6 (B-CH ₂ , br)	88.2
 3 $n = 3$	7.63 (d, 2H, Flu-H) [7.2], 7.26 (d, 2H, Flu-H) [7.2], 7.28–7.15 (m, 8H, Ar-CH), 6.43 (m, 1H, Ind-H ³), 6.21 (m, 1H, Ind-H ²), 2.14–1.19 (m, 24H; 11 CH ₂ , 2 CH ^{9-BBN})	C _q : 143.5, 142.2, 139.8, 139.3, 120.6; CH: 128.1, 127.8, 127.5, 127.4, 127.0, 126.9, 125.3, 120.2 (Ar-CH), 33.4 (B-CH, br); CH ₂ : 36.9, 34.5, 27.2, 21.4, 21.1, 20.7 25.8 (B-CH ₂ , br)	88.0
 4 $m = 1, n = 1$	7.50 (m, 2H, Ar-CH), 7.13–7.01 (m, 5H, Ar-CH), 6.86 (d, 2H, Ar-CH) [3.2], 6.34 (d, 2H, Cp) [3.2], 5.86–5.73 (m, 2H, Cp), 5.41 (m, 1H, Ind-H ³), 5.40 (m, 1H, Ind-H ²), 3.34 (m, 1H, CH ₂ -Phenyl), 3.12 (m, 1H, CH ₂ -Phenyl), 2.64 (m, 2H, CH ₂ -Cp), 1.80–1.29 (m, 18H; 8 CH ₂ , 2 CH ^{9-BBN})	C _q : 140.3, 139.0, 120.1; CH: 131.3, 129.3, 126.6, 125.9, 125.6, 125.4, 124.4, 124.0, 121.5, 116.9 (Ar-CH), 113.2 (Cp-CH), 112.8 (Cp-CH), 96.7, (Ind-C ²), 31.3 (B-CH, br); CH ₂ : 34.4, 33.5, 26.2, 23.6, 23.0; 25.7 (B-CH ₂ , br)	88.1
 5 $m = 1, n = 2$	7.34 (m, 2H), 7.23–6.91 (m, 7H), 6.42 (m, 1H, Cp), 6.38 (m, 1H, Cp), 6.29 (m, 1H, Cp), 6.07 (m, 1H, Cp), 5.96 (m, 1H, Ind-H ³), 5.93 (m, 1H, Ind-H ²), 3.25 (m, 2H, CH ₂ -Ind), 2.72 (m, 2H, CH ₂ -Phenyl), 1.83–1.44 (m, 20H)	C _q : 141.8, 137.7, 121.4; CH: 128.9, 126.3, 125.5, 124.9, 124.4, 124.2, 121.6, 119.1, 116.3 (Ar-CH), 113.7 (Cp-CH), 113.4 (Cp-CH), 97.5 (Ind-C ²), 30.8 (B-CH, br); CH ₂ : 33.7, 33.5, 30.4, 25.7, 23.5, 23.0; 28.0 (B-CH ₂ , br)	85.2
 6 $m = 2, n = 2$	7.36–7.33 (m, 2H, Ar-CH), 7.15–7.02 (m, 7H, Ar-CH), 6.58 (m, 1H, Cp), 6.36 (d, 1H, Cp) [3.3], 5.88 (m, 1H, Cp), 5.70 (d, 1H, Cp) [2.8], 5.49 (d, 1H, Ind-H ³) [2.8], 5.34 (d, 1H, Ind-H ²) [2.8], 3.28 (m, 2H, CH ₂ -Ind), 2.85 (m, 2H, CH ₂ -Phenyl), 2.64 (m, 2H, CH ₂ -Cp), 2.09–1.20 (m, 20H)	C _q : 141.8, 135.5, 121.1; CH: 128.9, 128.7, 126.3, 125.7, 125.5, 125.0, 124.5, 124.3, 117.9, 116.5 (Ar-CH), 113.5 (Cp-CH), 112.8 (Cp-CH), 96.8 (Ind-C ²), 31.3 (B-CH, br); CH ₂ : 36.3, 34.0, 33.6, 33.4, 30.5, 30.4, 24.6, 23.6 28.3 (B-CH ₂ , br)	87.2

Table 1 (continued).

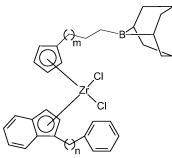
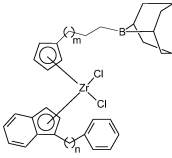
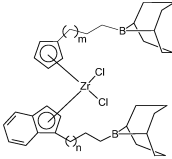
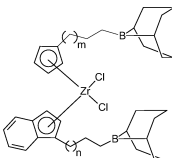
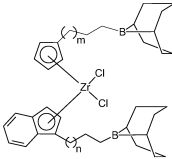
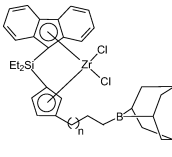
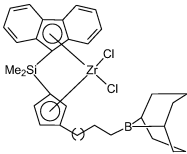
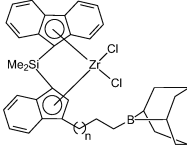
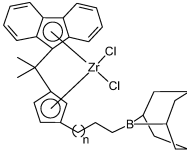
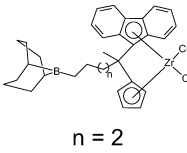
Compound	¹ H NMR [J(H,H) in Hz]	¹³ C NMR	¹¹ B NMR
 <p>7 m = 3, n = 1</p>	7.48 (m, 2H, Ar-CH), 7.15–6.85 (m, 7H, Ar-CH), 6.32 (d, 1H) [3.3], 5.88 (m, 1H), 5.81 (d, 1H) [3.3], 5.72 (m, 1H), 5.51 (m, 1H), 5.47 (m, 1H), 2.63 (m, 2H, CH ₂ -Phenyl), 1.86–1.32 (m, 22H)	C _q : 140.3, 135.4, 120.9; CH: 129.3, 128.6, 127.7, 125.9, 125.5, 125.4, 124.4, 117.6, 116.6 (Ar-CH), 113.2 (Cp-CH), 112.9 (Cp-CH), 111.9, 96.6 (Ind-C ²), 31.4 (B-CH, br); CH ₂ : 33.6, 33.3, 32.9, 30.9, 25.7, 24.6, 23.7; 27.7 (B-CH ₂ , br)	87.7
 <p>8 m = 3, n = 2</p>	7.30 (m, 2H, Ar-CH), 7.15–6.98 (m, 7H, Ar-CH), 6.85 (m, 1H), 6.34 (m, 1H), 5.84 (m, 1H), 5.46 (m, 1H), 5.34 (m, 1H), 5.33 (m, 1H), 3.23 (m, 2H, CH ₂ -Ind), 2.83 (m, 2H, CH ₂ -Phenyl), 2.48 (m, 2H, CH ₂ -Cp), 2.10 (m, 2H), 1.43–1.22 (m, 22H)	C _q : 141.8, 134.9, 124.9; CH: 128.9, 128.6, 126.3, 125.7, 125.0, 124.3, 121.1, 117.7, 116.4, 115.0 (Ar-CH), 113.6 (Cp-CH), 112.9 (Cp-CH), 96.8 (Ind-C ²), 30.3 (B-CH, br); CH ₂ : 36.3, 34.9, 31.9, 29.8, 29.7, 27.2, 25.6, 23.0, 33.4 (B-CH ₂ , br)	87.8
 <p>9 m = 1, n = 1</p>	7.67 (m, 2H, Ar-CH), 7.32–7.16 (m, 2H, Ar-CH), 6.98 (m, 1H, Ind-H ³), 6.70 (d, 1H, Ind-H ²) [3.4], 6.06 (m, 1H, Cp), 5.85 (m, 1H, Cp), 5.67 (m, 1H, Cp), 5.54 (m, 1H, Cp), 2.76 (m, 2H, CH ₂ -Cp), 2.15 (m, 2H), 1.99–1.31 (m, 36H)	C _q : 134.7, 122.1; CH: 127.1, 125.5, 125.1, 124.8, 124.4, 117.9, 116.7 (Ar-CH), 113.5 (Cp-CH), 112.9 (Cp-CH), 97.2 (Ind-C ²), 32.2 (B-CH, br); CH ₂ : 34.5, 33.6, 33.4, 27.3, 25.7, 24.8, 23.6; 27.7 (B-CH ₂ , br)	88.7
 <p>10 m = 2, n = 1</p>	7.53 (m, 2H, Ar-CH), 7.24–7.15 (m, 1H, Ar-CH), 6.89 (m, 1H), 6.56 (d, 1H, Ind-H ³) [3.2], 5.98 (d, 1H, Ind-H ²) [3.1], 5.91 (m, 1H, Cp), 5.71 (m, 1H, Cp), 5.56 (m, 1H, Cp), 5.44 (m, 1H, Cp), 3.08 (m, 2H, CH ₂ -Ind), 2.64 (m, 2H, CH ₂ -Cp), 2.08 (m, 2H), 1.82–1.16 (m, 34H)	C _q : 135.4, 122.2; CH: 125.6, 125.0, 124.7, 124.4, 122.1, 117.8, 116.4 (Ar-CH), 113.6 (Cp-CH), 112.9 (Cp-CH), 97.2 (Ind-C ²), 31.4 (B-CH, br); CH ₂ : 34.7, 34.0, 33.4, 30.5, 25.7, 24.6, 23.6, 23.0; 27.7 (B-CH ₂ , br)	87.7
 <p>11 m = 2, n = 2</p>	7.53 (d, 2H, Ar-CH) [8.8], 7.22–7.15 (m, 2H, Ar-CH), 6.88 (m, 1H), 6.56 (d, 1H) [3.3], 5.94 (m, 1H), 5.72 (d, 1H) [2.2], 5.54 (d, 1H) [2.2], 5.40 (d, 1H) [2.2], 3.08 (m, 2H, CH ₂ -Ind), 2.65 (m, 2H, CH ₂ -Cp), 1.86–1.19 (m, 40 H)	C _q : 135.4, 122.4; CH: 126.3, 125.6, 125.0, 124.6, 124.4, 122.4, 117.8, 116.5 (Ar-CH), 113.5 (Cp-CH), 112.8 (Cp-CH), 96.9 (Ind-C ²), 31.3 (B-CH, br); CH ₂ : 36.3, 34.0, 33.6, 33.4, 30.4, 24.6, 23.6; 28.3 (B-CH ₂ , br)	86.3
 <p>12 n = 1</p>	7.68 (m, 2H, Flu-H), 7.21–7.14 (m, 6H, Flu-H), 6.38 (m, 1H, Cp), 5.54 (m, 1H, Cp), 5.36 (m, 1H, Cp), 2.46 (m, 2H, CH ₂ -Cp), 1.87–1.16 (m, 18 H), 0.96 (t, 6H, CH ₃), 0.86 (m, 4H, Si-CH ₂)	C _q : 145.8, 141.6, 141.2, 141.1; CH: 129.4, 129.2, 128.8, 127.3, 127.0, 126.5, 124.8, 120.4, 120.3, 118.8, 111.1, 32.5 (B-CH, br); CH ₂ : 33.9, 27.3 (B-CH ₂ , br), 25.7, 24.8, 23.7, 3.8 (Si-CH ₂); CH ₃ : 6.2	87.1 ²⁹ Si NMR n. b.

Table 1 (continued).

Compound	^1H NMR [J(H,H) in Hz]	^{13}C NMR	^{11}B NMR
 13 $n = 3$	7.73 (d, 2H, Flu-H) [8.2], 7.30 (m, 6H, Flu-H), 6.49 (m, 1H, Cp), 6.15 (m, 1H, Cp), 5.82 (m, 1H, Cp), 2.13–1.26 (m, 24H), 0.71 (s, 3H, Si-CH ₃), 0.74 (s, 3H, Si-CH ₃)	C_q : 145.5, 145.3, 141.0, 140.9; CH : 126.2, 126.1, 126.0, 125.9, 125.9, 125.8, 125.7, 125.7, 125.6, 124.6, 120.1, 28.7 (B-CH, br); CH₂ : 33.6, 32.2, 31.4, 27.7 (B-CH ₂ , br), 25.6, 24.2, 23.6, 22.9; CH₃ : –0.8	89.8 ^{29}Si NMR –1.1
 14 $n = 2$	7.78 (d, 1H, Flu-H) [8.5], 7.31–7.48 (m, 2H), 7.15–7.29 (m, 9H), 6.05 (s, 1H, Ind-H ²), 2.63 (m, 2H, CH ₂ -Ind), 2.08–2.17 (m, 2H), 1.87–1.22 (m, 16H), 0.29 (s, 3H, Si-CH ₃), 0.08 (s, 3H, Si-CH ₃)	C_q : 145.9, 145.6, 145.5, 143.1, 141.1; CH : 129.1, 127.8, 127.8, 126.6, 126.5, 125.9, 125.3, 124.6, 124.5, 124.3, 123.4, 120.5, 119.7, 29.1 (B-CH, br); CH₂ : 34.4, 33.4, 32.3, 27.7 (B-CH ₂ , br), 25.7, 24.9, 23.6; CH₃ : –8.0, –9.9	88.8 ^{29}Si NMR 6.9
 15 $n = 1$	7.82 (m, 2H, Flu-H), 7.74–7.48 (m, 2H, Flu-H), 7.33–6.92 (m, 4H, Flu-H), 5.81 (m, 1H, Cp), 5.48 (m, 1H, Cp), 5.25 (m, 1H, Cp), 2.04–1.25 (m, 20H), 1.12 (s, 3H, CH ₃), 1.15 (s, 3H, CH ₃)	C_q : 142.6, 142.6, 41.8; CH : 128.3, 127.9, 127.3, 127.2, 127.1, 126.9, 119.6, 32.5 (B-CH, br); CH₂ : 33.6, 27.3 br, 26.9, 25.7, 24.8; CH₃ : 25.6	86.0
 16 $n = 2$	7.88 (d, 2H, Flu-H) [8.4], 7.52 (m, 2H, Flu-H), 7.39 (m, 2H, Flu-H), 7.37–7.11 (m, 2H, Flu-H), 6.21 (m, 1H, Cp), 5.95 (m, 1H, Cp), 5.55 (m, 1H, Cp), 5.46 (m, 1H, Cp), 2.12–1.25 (m, 22H), 1.99 (s, 3H, CH ₃)	C_q : 145.8, 145.2, 142.6, 142.4, 45.3 (bridge); CH : 128.4, 127.3, 126.5, 126.4, 126.3, 125.3, 125.2, 125.1, 123.6, 123.5, 122.4, 119.3, 27.7 (B-CH, br); CH₂ : 33.3, 31.4, 36.9, 23.9, 23.4; CH₃ : 25.4	88.4

^a All spectra in [D₆]benzene at 25 °C; δ (ppm) vs. internal solvent (^1H , ^{13}C), ext. BF₃–Et₂O (^{11}B), or ext. TMS (^{29}Si).

to the better access of ethylene to the catalytically active center. The polymerization results are summarized in Table 2.

Formation of di- or trinuclear complexes

The most active zirconocene dichloride complexes were combined with the (α -diimine)nickel complex **17** (Fig. 2). This nickel complex was synthesized from the corresponding diimine with (dimethoxyethane)nickel dibromide in THF. The paramagnetic complex was characterized by mass spectrometry. Its polymerization data are given in Table 2.

The nickel complexes contain Lewis base functions (NMe₂ groups), while the zirconocene complex carries a Lewis acidic boryl substituent. The combination of these two systems by a Lewis acid-base reaction (donor-acceptor principle) should result in di- or multinuclear complexes that can produce polymers with a bimodal or multimodal molecular weight distribution. Scheme 2 shows the proposed formation of a trinuclear complex with two different active centers, while Scheme 3 shows the different combination possibilities.

For polymerization reactions, the donor and the acceptor catalyst precursor were mixed together in equi-

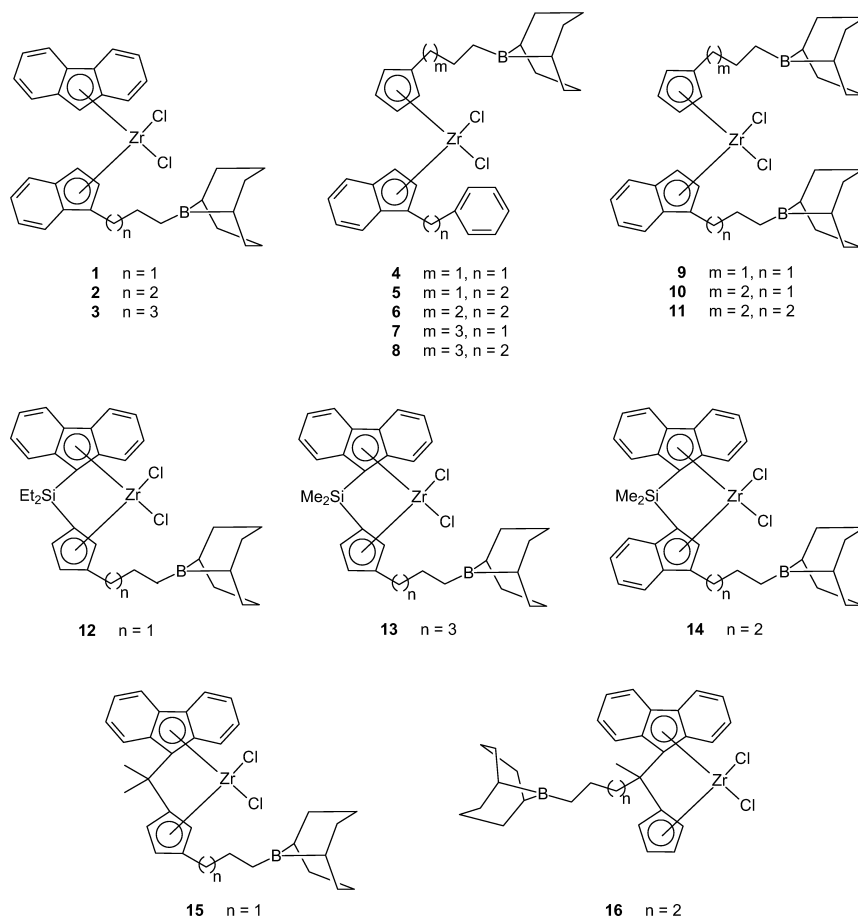
Table 2. Polymerization data of complexes **1**–**16**.

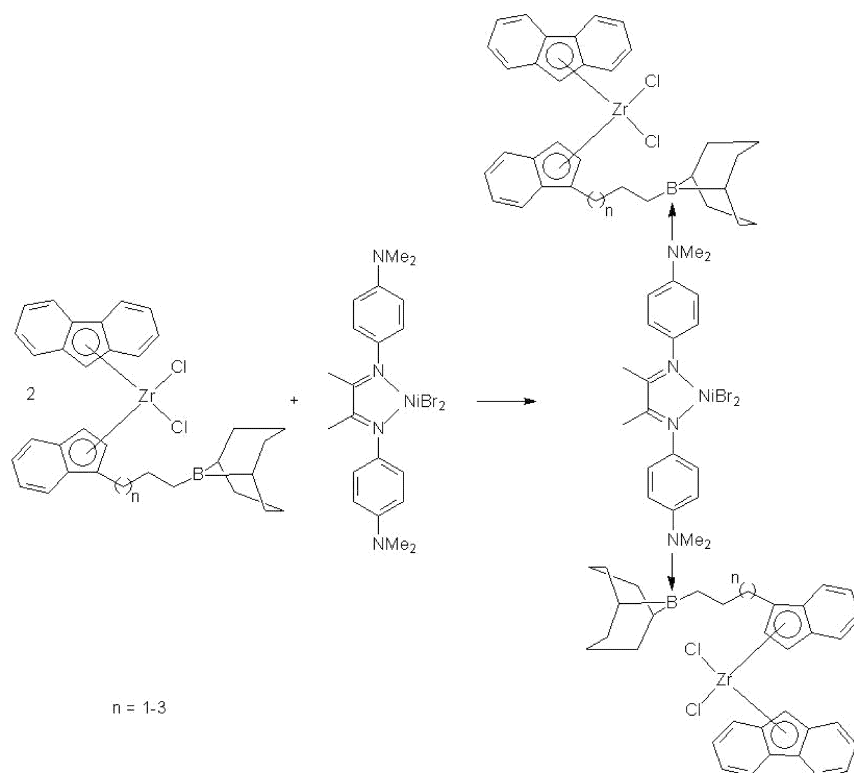
Complex	Activity [kg(PE)/mol(M)·h]	HT-GPC polymer share					
		M_n [g/mol]	M_w [g/mol]	M_z [g/mol]	M_{z+1} [g/mol]	MP [g/mol]	D (= M_w/M_n)
1	16 000	98 200	337 300	784 600	1 303 800	210 400	3.4
2	1 000	70 600	335 000	816 500	1 349 800	220 100	4.8
3	670	75 300	358 800	894 700	1 472 400	220 900	4.8
4	37 200	75 000	286 600	571 700	816 900	208 700	3.8
5	40 500	96 300	335 500	620 900	854 600	261 600	3.5
6	68 300	74 100	246 600	494 200	735 900	178 500	3.3
7	35 700	63 300	262 000	609 500	1 037 500	183 600	4.1
8	55 600	89 600	322 200	599 700	830 800	260 300	3.6
9	30 400	110 100	365 600	633 200	850 200	316 400	3.3
10	39 000	97 400	361 800	648 100	869 700	333 200	3.7
11	55 800	60 900	253 600	601 700	1 051 900	172 900	4.2
12	5 500	82 600	281 200	618 500	1 061 400	191 000	3.4
13	1 800	116 300	391 500	790 800	1 230 400	312 800	3.4
14	5 800	99 300	269 700	570 600	997 300	191 700	2.7
15	2 200	122 400	425 800	890 000	1 378 800	309 600	3.5
16	490	55 200	175 000	514 200	1 112 700	101 000	3.2
17	930	2 080	9 000	42 000	88 700	1 190	4.3

(polymer share 11 %)

 $\alpha = 0.83$ Polymerization conditions: Al:Zr = 2 500 : 1; polymerization in 250 mL of *n*-pentane, 60 °C, 1 L autoclave, 10 bar ethylene pressure, 60 min.

$$\alpha = \frac{k_B}{(k_B + k_C)} = \frac{\text{rate of propagation}}{\text{rate of propagation} + \text{rate of chain transfer}} \quad (\text{Schulz-Flory constant})$$

Fig. 1. Synthesized boryl-substituted zirconocene dichloride complexes **1**–**16**.

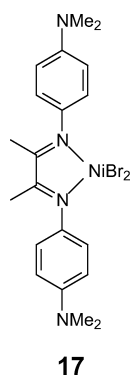


Scheme 2. Proposed formation of a trinuclear complex.

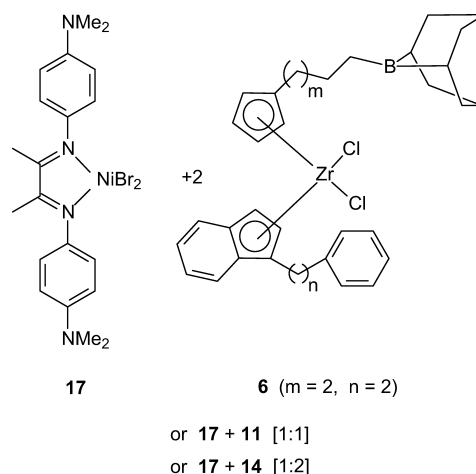
Table 3. Polymerization data of multinuclear complexes.

Complex	Activity [kg(prod)/mol (ZrNi)·h]	Polymer share [wt. %]	α
17/6	3 600	96.6	0.71
17/11	20 100	96.4	0.69
17/14	1 900	46.6	0.81

Polymerization conditions: Al:M = 2 500:1; polymerization in 250 mL of *n*-pentane, 60 °C, 1 L autoclave, 10 bar ethylene pressure, 60 min. Schulz-Flory constant α as in Table 2.

Fig. 2. (α -Diimine)nickel complex with *p*-dimethylaminophenyl groups.

valent amounts, and the mixture was stirred at r. t. for two hours. A precipitate was formed but it could not be dissolved in a non-coordinating solvent. Therefore



Scheme 3. Different combination possibilities of donor/acceptor catalyst precursors.

a characterization by NMR spectroscopy could not be performed. The precipitate was activated with a 2 500-fold molar excess of MAO and used for the homogeneous polymerization of ethylene. The obtained polymers were dried *in vacuo*. Table 3 shows the polymerization results.

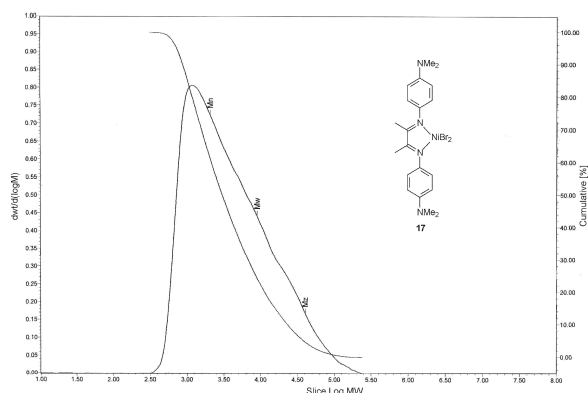


Fig. 3. GPC diagram of polyethylene produced with **17**/MAO.

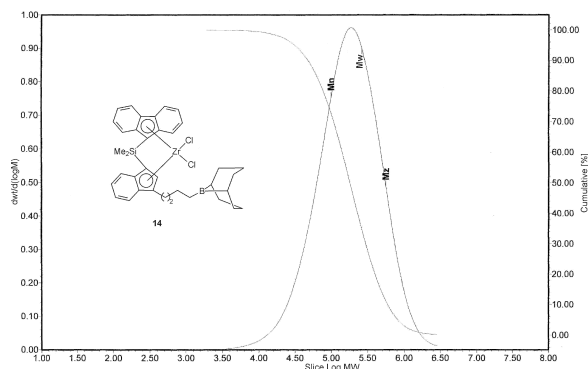


Fig. 4. GPC diagram of polyethylene produced with **14**/MAO.

The catalytic polymerization of ethylene with di- or trinuclear complexes produced polymers with a bimodal molecular weight distribution. The nickel complex produced polymers with a lower molecular weight than the individual zirconocene component (Figs. 3 and 4). The combination of the two systems resulted in a combination of both molecular weight distributions. The first maximum belongs to the polymer produced by the nickel complex and the second to that produced by the zirconocene complex (Fig. 5). The molecular weight distribution of the polymer produced by the metallocene catalyst is broader indicating some multimodal behavior.

When both complexes were applied in equimolar amounts (Fig. 6) the zirconocene component showed higher productivity than expected. The nickel complex produced a polymer together with an oligomer with a share of 55.3 % which has not been considered in the diagram.

For the system **17**/6/MAO the first maximum of molecular weight has increased (Fig. 7). The polymer

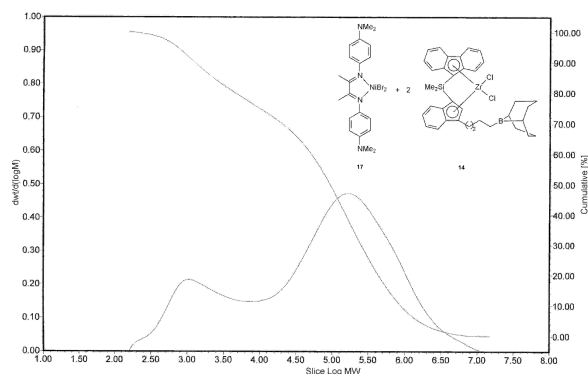


Fig. 5. GPC diagram of polyethylene produced with **17**/**14**/MAO.

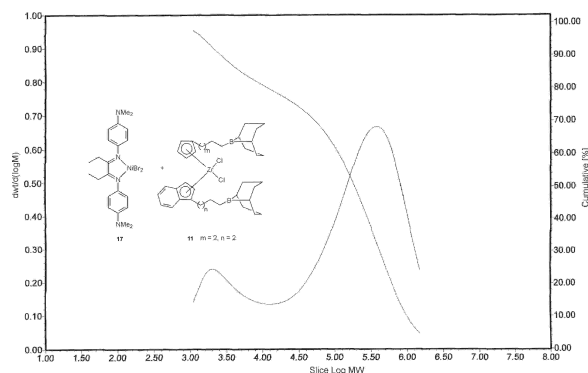


Fig. 6. GPC diagram of polyethylene produced with **17**/**11**/MAO.

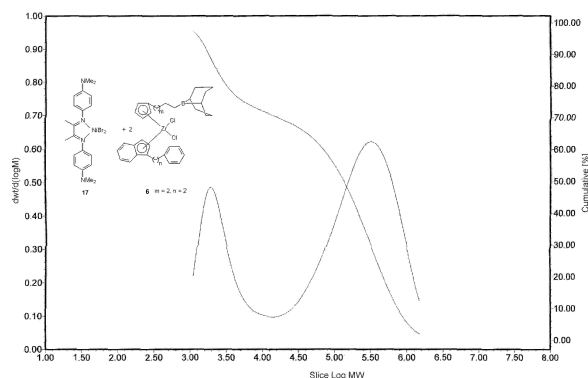


Fig. 7. GPC diagram of polyethylene produced with **17**/**6**/MAO.

share is 96.6 %. Only a small amount of oligomers was produced from the nickel center.

In all cases the activity of the di- or trinuclear complexes was lower than the sum of the single activities of the complexes. This was a hint for the formation of a new species with several catalytically active centers. Obviously, in these multinuclear complexes ac-

cess of olefin to the active centers is more complicated not only because of steric reasons but also because of the interactions of the cationic active centers with the MAO anions.

Experimental Section

NMR Spectroscopic investigations were performed with a Bruker ARX 250 instrument at 25 °C. CDCl₃ and C₆D₆ served as solvents. The chemical shifts (δ) in the NMR spectra are referenced to the (residual) signal of the solvent (¹H: δ = 7.24 ppm for chloroform; δ = 7.15 ppm for benzene, ¹³C: δ = 77.0 ppm for chloroform; δ = 128.0 ppm for benzene). Mass spectra were recorded with a VARIAN MAT CH7 mass spectrometer (direct inlet system, electron impact ionization, 70 eV). In addition, a Hewlett Packard 5971A mass spectrometer was routinely used in combination with a Hewlett Packard Series II 5890 gas chromatograph to record GC/MS spectra. Molecular weight determinations of the polyethylene samples were performed using HT-GPC equipment. Gas chromatograms were recorded using a Perkin Elmer Auto System gas chromatograph with flame ionization detector (FID) and helium as carrier gas (5.7 mL min⁻¹). The temperature program was as follows: starting phase: 3 min at 50 °C; heating phase: 4 °C min⁻¹ (15 min); plateau phase: 250 °C (37 min). Methylaluminoxane was supplied by Witco GmbH, Bergkamen, as a 30 % solution in toluene (average molecular weight 1100 g/mol, aluminum content: 13.1 %, 3.5 % as trimethylaluminum).

General procedure for the synthesis of the boryl-substituted complexes **1–16**

1 mmol of the corresponding zirconocene dichloride complex was dissolved in mL of THF. At –78 °C one or two equivalents of 9-H-borabicyclo[3.3.1]nonane were dissolved in 20 or 40 mL of THF, respectively. The two solutions were combined and the reaction mixture was stirred at –78 °C for 1 h and at r. t. for 2 h. After removing the solvent *in vacuo*, the residue was washed with *n*-hexane. The products remained as yellow or orange solids. Yields: 80–95 %.

All compounds were characterized by NMR spectroscopy (Table 1).

General procedure for the synthesis of the nickel complex **17**

0.7 mmol of the respective diimine ligand was dissolved in 50 mL of THF. Then 0.7 mmol of (dimethoxyethane)

nickel dibromide was added. The mixture was stirred for 12 h at r. t. For purification, the volume of the solvent was reduced *in vacuo* and the complexes were precipitated by adding *n*-pentane. After washing several times with *n*-pentane, the solvent remained colorless and the product was dried *in vacuo*. The complex was obtained as a brown powder. Yield: 85 %. The complex was identified by mass spectrometry: m/z = 541 [M]⁺; other fragments: m/z = 461, 322, 161, 120, 105, 77.

General procedure for the combination of donor and acceptor catalyst precursors

Equivalent amounts of the corresponding zirconocene dichloride and the nickel complex were dissolved in toluene and stirred at r. t. for 2 h. The solvent was removed *in vacuo* and the activated catalyst suspended in 50 mL of *n*-pentane.

General procedure for the activation of the complexes

An amount of 5–10 mg of the complex was suspended in toluene and activated with the corresponding amount of MAO (Al : Ni = 2 500 : 1). The solvent was removed *in vacuo* and the activated catalyst was suspended in 50 mL of *n*-pentane. The catalyst suspension was used for ethylene polymerization.

Homogeneous polymerization of ethylene

n-Pentane (250 mL) was placed in a 1 L Büchi laboratory autoclave, mixed with the catalyst solution and the autoclave thermostated at 60 °C. An ethylene pressure (99.98 % ethylene) of 10 bar was applied after an inside temperature of 50 °C was reached. The mixture was stirred for 1 h at 60(±2) °C, and subsequently the reaction was terminated by releasing the pressure in the reactor. For the separation of the oligomers and the polymers, the mixture was filtered and the remaining polymer was washed with half-concentrated hydrochloric acid in order to remove excess MAO. After that the polymer was dried *in vacuo* and weighed. The pentane of the oligomer solution was removed by distillation over a Vigreux column and the oligomers were analyzed by GC.

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