

Substituted 1-(2-pyridyl)-2-azaethene-(*N,N*)-nickel dibromide complexes as catalyst precursors for homogeneous and heterogeneous ethylene polymerization

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Abstract

The complex 1-(2-pyridyl)-2-azaethene-(*N,N*)-nickel dibromide and its derivatives can be used for the catalytic polymerization of ethylene after activation with methylaluminoxane (MAO). The polyethylenes made with these catalysts have a high degree of short-chain-branching with up to 240 branches per 1000 carbon atoms. Homogeneous ethylene polymerization reactions produce highly viscous oligomers with low molecular weights. Polymers with significantly higher molecular weights and lower amounts of branching are obtained when the ethylene polymerization reactions with these catalyst systems are carried out as heterogeneous reactions. The activities of these paramagnetic complexes are significantly lower than the activities of metallocene catalysts. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Nickel; Pyridine; Catalysis; Polymerization; Branched polyethylene

1. Introduction

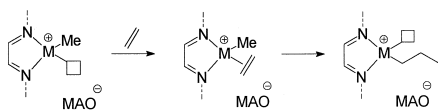
The development of polyolefin technology started in the thirties with the discovery of high-pressure radical polymerization of ethylene by Imperial. Due to the extreme reaction conditions of this polyolefin synthesis, only high molecular weight low density polyethylenes containing both long and short chain branches (LDPE: low density polyethylene) were produced. Ethylene homopolymers, made for the

first time in the fifties with Ziegler–Natta catalysts [1–7], were extraordinarily linear along the polymer chain, with no short or long chain branching. More recently, Johnson et al. [8,9] and Brookhart et al. [10] have succeeded in activating diazadiene nickel and palladium complexes with MAO or other weakly coordinating counter ions and used them for α -olefin polymerization reactions (Scheme 1).

Unlike the earlier resins, the polyethylene homopolymers, produced with these new catalysts, are relatively low in molecular weight and contain both short and long chain branching depending on reactor conditions, e.g., monomer pressure and reactor temperature. Polar mono-

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Scheme 1. Metal(II) catalysts (M = Ni, Pd) for the synthesis of branched polyethylenes [8–10].

mers can also be polymerized with these new catalyst systems [8–10]. For instance, α -olefin-acrylate copolymers can be prepared in the absence of MAO.

Here, we report about new nickel catalyst precursors that produce, in combination with MAO, highly branched polymers with new microstructures.

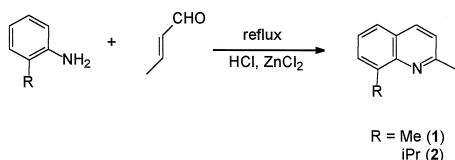
2. Results and discussion

The new nickel(II) catalysts are diazadiene nickel dibromide complexes with bulky substituents in the ligand sphere that can be activated with MAO. The synthesis of the ligands and the corresponding nickel complexes follows the reaction schemes below.

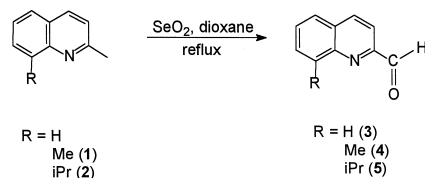
2.1. Synthesis of catalyst precursors

2.1.1. Synthesis of the 2-methylquinoline derivatives

Using the Doebner–Miller synthesis, quinoline derivatives can be obtained from an aniline derivative and crotonaldehyde in the presence of the complexing agent zinc chloride in approximately 50% yields [11]. For example, 2,8-dimethylquinoline is synthesized by a condensation reaction of *o*-toluidine with crotonaldehyde in the presence of concentrated hydrochloric acid and aqueous zinc chloride (Scheme 2).



Scheme 2. Synthesis of the 2-methylquinoline derivatives **1** and **2**.



Scheme 3. Synthesis of the 2-carbaldehyde quinoline derivatives **3–5**.

2.1.2. Synthesis of 2-carbaldehyde quinoline derivatives

2-Carbaldehyde quinoline derivatives are produced by heating the quinoline derivatives synthesized in Section 2.1.1 with selenium dioxide in aqueous dioxane suspension [12] (Scheme 3).

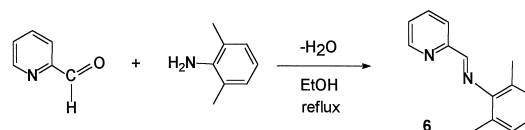
2.1.3. Synthesis of diazadiene ligands

Diazadiene ligands are synthesized by the condensation of pyridine-2-carbaldehyde or quinoline-2-carbaldehyde derivatives with an equimolar amount of the aniline derivative in ethanol [13]. If the corresponding acetyl compound is used instead of the aldehyde, the condensation reaction occurs in toluene with toluenesulfonic acid as catalyst. The synthesis of 1-(2-pyridyl)-2-(2,6-dimethylphenyl)-2-azaethene (**6**) is illustrated in Scheme 4 as an example.

Several diazadiene ligands were synthesized, using a reaction scheme (Scheme 5) similar to that above, and characterized by ^1H and ^{13}C NMR spectroscopy. The corresponding NMR data are summarized in Table 1.

2.1.4. Synthesis of the diazadiene nickel dibromide complexes **21–35**

The diazadiene nickel dibromide complexes were synthesized according to known proce-



Scheme 4. Synthesis of 1-(2-pyridyl)-2-(2,6-dimethylphenyl)-2-azaethene **6**.

Table 1
¹H and ¹³C NMR data of compounds 2, 6–20

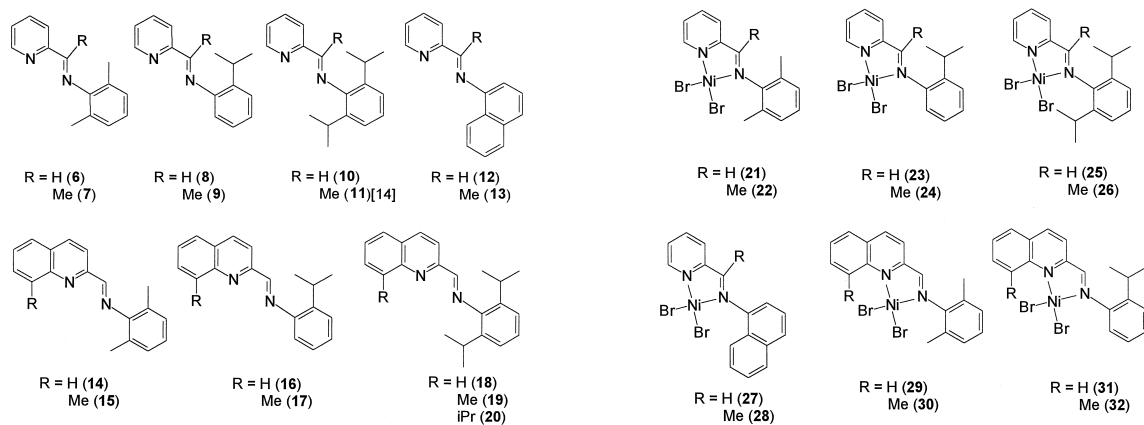
No.	¹ H NMR ^a	¹³ C NMR ^b
2	8.03 (d, 1H), 7.86–7.63 (m, 3H), 7.28 (d, 1H), 4.83 (qi, 1H), 2.95 (s, 3H), 1.73 (d, 6H)	157.1 (C _q), 146.6 (C _q), 145.6 (C _q), 135.9 (CH), 126.3 (C _q), 125.3 (CH), 125.0 (CH), 124.8 (CH), 121.1 (CH), 26.9 (CH ₃), 25.4 (CH), 23.5 (CH ₃)
6	8.66 (d, 1H), 8.37 (s, 1H), 8.27 (d, 1H), 7.71 (dt, 1H), 7.31–7.25 (m, 1H), 7.07–6.91 (m, 3H), 2.16 (s, 1H)	163.1 (CH), 154.0 (C _q), 150.0 (C _q), 149.2 (CH), 136.2 (CH), 127.6 (CH), 126.4 (C _q), 124.9 (CH), 123.7 (CH), 120.8 (CH), 17.9 (CH ₃)
7	8.47 (d, 1H), 8.24 (d, 1H), 7.5 (t, 1H), 7.09–7.05 (m, 1H), 6.99 (d, 2H), 6.79–6.74 (m, 1H), 2.05 (s, 3H), 1.90–1.88 (m, 6H)	166.6 (C _q), 155.9 (C _q), 148.2 (CH), 135.8 (CH), 127.8 (C _q), 127.5 (CH), 124.7 (CH), 124.7 (C _q), 122.6 (CH), 120.7 (CH), 17.5 (CH ₃), 16.1 (CH ₃)
8	8.52–8.49 (m, 2H), 8.11 (d, 1H), 7.43 (t, 1H), 7.18–6.85 (m, 5H), 4.47 (qi, 1H), 1.17–1.13 (m, 6H)	162.9 (CH), 154.2 (C _q), 149.5 (CH), 148.3 (C _q), 137.0 (C _q), 136.5 (CH), 125.1 (CH), 124.4 (CH), 122.9 (CH), 121.1 (CH), 27.8 (CH), 23.3 (CH ₃)
9	8.99 (d, 1H), 8.71 (d, 1H), 8.03 (t, 1H), 7.69–7.43 (m, 4H), 6.99 (d, 1H), 3.40 (qi, 1H), 2.72 (s, 3H), 1.55 (d, 6H)	166.1 (C _q), 156.4 (C _q), 148.2 (CH), 137.7 (C _q), 135.9 (CH), 125.8 (CH), 125.3 (CH), 124.3 (C _q), 123.7 (CH), 121.0 (CH), 118.0 (CH), 28.1 (CH), 22.5 (CH ₃), 16.2 (CH ₃)
10	8.73–8.71 (m, 1H), 8.37 (s, 1H), 8.30 (d, 1H), 7.79 (t, 1H), 7.38–7.33 (m, 1H), 7.23–7.15 (m, 3H), 3.02 (qi, 2H) 1.20 (d, 12H)	162.9 (CH), 154.2 (C _q), 149.5 (CH), 148.3 (C _q), 137.0 (C _q), 136.5 (CH), 125.1 (CH), 124.1 (CH), 122.9 (CH), 121.1 (CH), 27.8 (CH), 23.3 (CH ₃)
11	8.76 (d, 1H), 8.47 (d, 1H), 7.89 (t, 1H), 7.50–7.45 (m, 1H), 7.35–7.12 (m, 3H), 2.87 (qi, 2H), 2.31 (s, 3H), 1.24 (d, 12H)	166.9 (C _q), 156.4 (C _q), 148.5 (CH), 146.4 (C _q), 136.4 (C _q), 135.7 (CH), 124.5 (CH), 123.5 (CH), 122.9 (CH), 121.2 (CH), 28.2 (CH), 22.8 (CH ₃), 17.2 (CH ₃)
12	8.67 (s, 1H), 8.51–8.43 (m, 2H), 8.16 (d, 1H), 7.69 (d, 1H), 7.57 (d, 1H), 7.45–7.23 (m, 4H), 7.00 (d, 1H), 6.92–6.88 (m, 1H)	160.7 (CH), 154.4 (C _q), 149.3 (CH), 147.9 (C _q), 136.1 (CH), 133.8 (C _q), 128.8 (C _q), 127.6 (CH), 126.5 (CH), 126.3 (CH), 125.9 (CH), 125.7 (CH), 124.8 (CH), 123.9 (CH), 121.5 (CH), 112.7 (CH)
13	8.48 (d, 1H), 8.32 (d, 1H), 8.23 (d, 1H), 7.76 (d, 1H), 7.57 (t, 2H), 7.54–6.96 (m, 3H), 6.59 (d, 2H), 2.47 (s, 3H)	167.8 (CH), 156.0 (C _q), 148.1 (CH), 147.2 (C _q), 135.9 (CH), 133.7 (CH), 127.6 (CH), 126.5 (CH), 124.5 (CH), 125.4 (CH), 123.1 (CH), 121.0 (CH), 108.9 (CH), 16.2 (CH ₃)
14	8.63 (s, 1H), 8.50 (d, 1H), 8.28–8.24 (m, 2H), 7.90–7.77 (m, 2H), 7.63 (t, 1H), 7.19–7.00 (m, 3H), 2.30 (s, 6H)	163.7 (CH), 154.4 (C _q), 150.1 (C _q), 147.7 (C _q), 136.4 (CH), 129.7 (CH), 129.6 (CH), 128.8 (C _q), 128.0 (CH), 127.6 (CH), 126.5 (CH), 124.0 (CH), 121.3 (C _q), 117.9 (CH), 18.2 (CH ₃)
15	8.69 (s, 1H), 8.29–8.22 (m, 2H), 8.01–7.88 (m, 2H), 7.61 (t, 1H), 7.32–7.01 (m, 3H), 2.96 (s, 3H), 2.34 (s, 6H)	161.1 (CH), 155.2 (C _q), 151.2 (C _q), 147.9 (C _q), 142.2 (C _q), 128.9 (CH), 128.3 (CH), 128.0 (C _q), 127.5 (CH), 127.1 (CH), 126.2 (CH), 124.1 (CH), 121.6 (C _q), 117.3 (CH), 20.2 (CH ₃)
16	8.78 (s, 1H), 8.39 (d, 1H), 8.17 (dd, 2H), 7.76–7.66 (m, 2H), 7.50 (t, 1H), 7.39–7.09 (m, 4H), 3.72 (qi, 1H), 1.34 (d, 6H)	159.7 (CH), 154.8 (C _q), 148.5 (C _q), 147.7 (C _q), 142.6 (C _q), 136.2 (CH), 129.5 (CH), 129.5 (CH), 128.5 (C _q), 127.4 (CH), 127.3 (CH), 126.8 (CH), 126.4 (CH), 125.4 (CH), 118.3 (CH), 117.4 (CH), 28.1 (CH), 23.0 (CH ₃)
17	8.87 (s, 1H), 8.49 (d, 1H), 8.23 (d, 1H), 7.72–7.10 (m, 5H), 6.90 (t, 1H), 6.74 (d, 1H), 3.82–3.74 (m, 1H), 2.97 (s, 3H), 1.39 (dd, 6H)	160.5 (CH), 153.7 (C _q), 149.0 (C _q), 142.1 (C _q), 137.7 (C _q), 136.3 (CH), 129.6 (CH), 128.2 (C _q), 127.1 (CH), 126.3 (CH), 126.1 (C _q), 125.3 (CH), 118.6 (CH), 117.9 (CH), 117.5 (CH), 115.5 (CH), 28.0 (CH), 22.9 (CH ₃), 17.6 (CH ₃)
18	8.63 (s, 1H), 8.53 (d, 1H), 8.33–8.27 (m, 2H), 7.93–7.77 (m, 2H), 7.67–7.61 (m, 1H), 7.32–7.11 (m, 3H), 3.15 (qi, 1H), 2.99 (qi, 1H), 1.37–1.28 (m, 12H)	163.3 (CH), 154.4 (C _q), 148.3 (C _q), 147.9 (C _q), 140.1 (C _q), 137.0 (CH), 136.6 (CH), 132.2 (C _q), 129.7 (CH), 128.9 (C _q), 127.7 (CH), 124.5 (CH), 123.0 (CH), 122.6 (CH), 118.1 (CH), 27.9 (CH), 23.3 (CH ₃)
19	8.76 (s, 1H), 8.52 (d, 1H), 8.22 (d, 1H), 7.62–7.11 (m, 4H), 6.88 (t, 1H), 6.72 (d, 1H), 3.92–3.85 (m, 1H), 2.92 (s, 3H), 1.32–1.24 (m, 12H)	162.5 (CH), 153.1 (C _q), 147.0 (C _q), 142.8 (C _q), 137.3 (C _q), 134.2 (CH), 129.3 (CH), 127.2 (C _q), 126.1 (CH), 125.2 (C _q), 125.0 (CH), 118.8 (CH), 117.5 (CH), 117.1 (CH), 115.2 (CH), 28.0 (CH), 20.9 (CH ₃), 17.1 (CH ₃)
20	8.88 (s, 1H), 8.32 (d, 1H), 8.19 (d, 1H), 7.22–7.01 (m, 4H), 6.79 (t, 1H), 6.65 (d, 1H), 3.92–3.55 (m, 3H), 2.92 (s, 6H), 1.32–1.24 (m, 12H)	162.5 (CH), 153.1 (C _q), 147.0 (C _q), 142.8 (C _q), 137.3 (C _q), 134.2 (CH), 129.3 (CH), 127.2 (C _q), 126.1 (CH), 125.2 (C _q), 125.0 (CH), 118.8 (CH), 117.5 (CH), 117.1 (CH), 115.2 (CH), 28.0 (CH), 20.9 (CH ₃), 17.1 (CH ₃)

^a25°C, in chloroform-*d*₁, δ [ppm] rel. chloroform (7.24).

^b25°C, in chloroform-*d*₁, δ [ppm] rel. chloroform (77.0).

dures [14,15]. The diazadiene derivative is dissolved in tetrahydrofuran and reacted with an

equimolar amount of dimethoxyethane nickel dibromide [16]. The diazadiene nickel dibro-

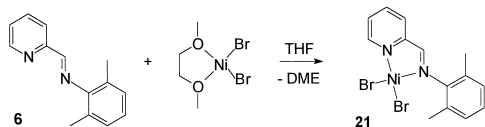
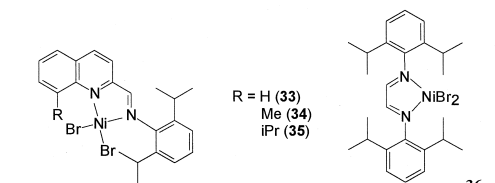


Scheme 5. Synthesized diazadiene ligands 6–20.

mid complexes precipitate almost quantitatively from the reaction mixture. The synthesis of 1-(2-pyridyl)-2-(2,6-dimethylphenyl)-2-azaethene-(*N,N*)-nickel dibromide (**21**) is illustrated in Scheme 6 as an example.

The diazadiene nickel dibromide complexes **21–35** synthesized above are summarized in Scheme 7. The NMR spectroscopic characterization of complexes **21–35** could not be performed due to the paramagnetic nature of this class of compound. Except for complexes **22** and **24**, the mass spectra did not reveal the expected signals for the molecule ion. Fragments with the loss of one or both bromine atoms were observed instead.

Complex **25** was published very recently [17] and the X-ray structure revealed a dinuclear species in the solid state. The analogous Pd complex, however, is monomeric. It has not been cleared yet, whether complexes **21–36** are monomeric or dimeric in solution. For catalytic application, however, this question is not essential because the activated species is monomeric in solution [8–10].

Scheme 6. Synthesis of 1-(2-pyridyl)-2-(2,6-dimethylphenyl)-2-azaethene nickel dibromide (**21**).Scheme 7. Diazadiene nickel dibromide complexes **21–36** (can be dimers in the solid state [17]).

2.1.5. Activation of catalyst precursors with the heterogeneous cocatalyst silica gel–PHT (PHT = partially hydrolyzed trimethylaluminum (TMA))

The catalyst precursors **25**, **26** and **36** [8–10] were activated with the cocatalyst system silica gel–PHT [18] to give a heterogeneous catalyst. The catalyst was synthesized by first reacting calcined silica gel with TMA in toluene. Subsequently, water was added to produce an aluminoxane structure. After the catalyst precursor was added to the cocatalyst suspension, the catalyst was isolated (Scheme 8).

2.2. Polymerization of ethylene with nickel(II) complexes **21–35**

The diazadiene nickel dibromide complexes synthesized above were tested for the homoge-

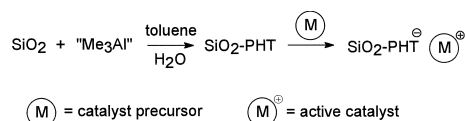
Scheme 8. Synthesis of the immobilized SiO₂–PHT catalyst.

Table 2

Catalyst activities for the homogeneous ethylene polymerization with the diazadiene nickel dibromide complexes (**21–35**)

Catalyst precursor	Activity [g PE/g Ni · h] ^a
21	4300
22	3100
23	1400
24	900
25	4100
26	4000
27	0
28	1300
29	0
30	0
31	0
32	0
33	0
34	0
35	1100

^aPolymerization conditions: activation with 30 wt.% methylaluminumoxane in toluene (Al:Ni = 2500:1; polymerization in 50 ml toluene, 25°C, 380 ml pressure Schlenk tube, 5.0 bar ethylene pressure, 5 min).

neous ethylene polymerization (Table 2) with MAO as cocatalyst. Significant differences in activities were observed for the different complexes. Some of the complexes formed no active catalysts. The diazadiene nickel dibromide complexes **25** [17] and **26**, active during the homogeneous testing, were activated and heterogenized using the silica gel–PHT cocatalyst [18] to determine the catalytic properties for heterogeneous ethylene polymerization reactions with these complexes. Similarly, the catalyst precursor **36** [8–10] was also activated with

silica gel–PHT [18] and tested for ethylene polymerization. The results are summarized in Table 3.

The results of the homogeneous tests show that complexes with quinoline fragments in the ligand structure are not suited for ethylene polymerization. An exception is compound **35**, which possesses three bulky isopropyl groups in the ligand sphere. The catalyst precursors **23**, **24** and **28** with only one bulky substituent on the phenyl group, also exhibit low catalyst activities.

In contrast, complexes, in which the phenyl group is symmetrically substituted, are found to have better catalytic potential. Compared to the diimine nickel dibromide complex **36**, the activities of **25** and **26** are lower by a factor of 10 for both homogeneous and heterogeneous ethylene polymerization reactions. The lower polymerization activities of complexes **25** and **26** could be due to the very high degree of branching of the resulting polymers. During homogeneous polymerization with MAO, as well as during heterogeneous polymerization with silica gel–PHT, complexes **25** and **26** produce polymers with two to three times more branching than found for resins made with complex **36** [8–10]. The branching results from the so-called “chain-running” mechanism in which the active catalyst moves along the polymer chain by continuous elimination and coordination steps [8–10]. This “chain-running” mechanism seems to occur more readily for complexes **25** and **26**

Table 3

Polymerization results for the diazadiene nickel dibromide complexes activated with silica gel–PHT and methylaluminumoxane

Catalyst precursor	Cocatalyst	Activity [kg PE/g Ni · h]	M_n [kg/mol]	T_m [°C]	ΔH_m [J/g]	Branches per 1000 C ^a
25	SiO ₂ –PHT	1.3	20	118.1	11.1	87
25	MAO	2.1	0.30 ^b	–	–	116
26	SiO ₂ –PHT	1.1	21	119.8	10.2	103
26	MAO	2.0	0.32 ^b	–	–	237
36	SiO ₂ –PHT	8.7	66	127.6	5.3	33
36	MAO	29.1	112	–	–	98

^aThe branches were determined using ¹H and ¹³C NMR spectroscopy [17–19].

^bThe average molecular weight of the oligomers was determined using GC–MS.

due to the absence of bulky shielding groups. Fig. 1 shows a ^{13}C NMR spectrum of the polyethylene made with complex **25**/MAO. It has been identified as a highly branched polyethylene [19–21] containing 116 branches per 1000 carbons (Fig. 1).

Active polymerization centers involved in the “chain-running” mechanism do not participate in chain growth reactions. Therefore, the total activity of the system decreases. The molecular weight of the polymers produced with **25** and **26** in heterogeneous polymerization is also lower by about a factor of three compared to the polyethylene synthesized with **36**.

In homogeneous polymerization reactions using complexes **25** and **26** and MAO, solids do not precipitate during polymerization, instead highly viscous oligomers with molecular weights between 100 and 600 g/mol are formed. However, in heterogeneous ethylene polymerizations using silica gel–PHT [18] for immobilization, higher molecular weighted polymers are obtained. A reduction of β -hydrogen elimination processes resulting from the influence of the support is very likely.

Despite the low melting points of the polymers obtained with complexes **25** and **26** and SiO_2 –PHT, the data from the thermal analysis of the polymers exhibit twice the fusion enthalpy of **36**. The reason for this contradictory phenomenon is still unclear. It could arise from a more regular branching in the polyethylene obtained from **25**/ SiO_2 –PHT.

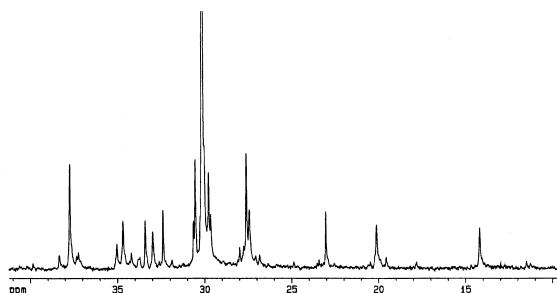


Fig. 1. ^{13}C NMR spectrum (62.90 MHz) of the polyethylene produced with **25**/MAO in 1,2,4-trichlorobenzene/benzene- d_6 , 80°C.

3. Experimental

NMR spectroscopic investigations were performed with a Bruker ARX 250 instrument. All organometallic samples were filled under argon and measured at 25°C. CDCl_3 served as solvent. The chemical shifts (δ) in the ^1H NMR spectra are referenced to the residual proton signal of the solvent ($\delta = 7.24$ ppm for chloroform and $\delta = 7.15$ ppm for benzene) and in ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for chloroform- d_1 and $\delta = 128.0$ ppm for benzene- d_6). The polyethylenes were dissolved at 80°C in 1,2,4-trichlorobenzene/ C_6D_6 (4:1; v/v) and measured at 80°C using ^1H and ^{13}C NMR spectroscopy [17–19] to determine the degree of branching.

MS spectra were recorded with a VARIAN MAT CH7 mass spectrometer (direct inlet system, electron impact ionization 70 eV). In addition, a Hewlett Packard 5917A mass spectrometer was routinely used to record MS spectra and in combination with a Hewlett Packard Series II 5890 gas chromatograph to record GC/MS spectra.

The molecular weight determination of the polymer samples was performed using an Ubbelohde precision capillary viscometer in *cis/trans* decalin at $135 \pm 0.1^\circ\text{C}$. The polymer samples were completely dissolved in decalin at 130°C over a period of 3–4 h. M_η was determined using calibration curves.

The thermal properties of the polymer samples were investigated for phase transitions using a NETZSCH DSC 200 instrument. For the measurements, 3–6 mg dried polymer were fused into standard aluminum pans (\varnothing 5 mm) and measured under nitrogen cooling using the following temperature program: (1) heating phase: from 60°C to 200°C, heating rate 20 K/min, isothermal phase (3 min), cooling phase from 200°C to 60°C, cooling rate 20 K/min. (2) Heating phase from 60°C to 200°C, heating rate 20 K/min, isothermal phase (3 min), cooling phase from 200°C to 20°C, cooling rate 20 K/min. Melting points and fusion enthalpies

were derived from the two heating steps. The temperature was linearly corrected relative to indium (m.p. 429.78 K). The fusion enthalpy of indium ($\Delta H_m = 28.45 \text{ J/g}$) was used for calibration.

Methylaluminoxane was supplied by Witco, Bergkamen, as 30% solution in toluene (average molecular weight 1100 g/mol, aluminum content: 13.1%, 3.5% as trimethylaluminum).

3.1. General synthesis procedure for the quinoline derivatives **1** and **2**

At 25°C, 0.40 mol of the aniline derivative were slowly added to 200 ml aqueous, 6 M HCl solution. Subsequently, the mixture was heated under reflux, whereby the precipitated aniline salt dissolved. During a period of 1 h, 0.42 mol freshly distilled crotonaldehyde were added dropwise and heated for another hour under reflux. After the mixture was cooled down to room temperature (RT), it was extracted twice with diethylether. The clear, aqueous solution was stirred and mixed with 54.4 g (0.40 mol) zinc(II)-chloride. After the mixture was stirred for 30 min at RT, it was cooled to 0°C and stirred for another 15 min. The reaction mixture was filtered, washed twice with 100 ml aqueous, 2 M HCl solution and dried. The brown solids were suspended in 350 ml 2-propanol, filtered, extracted three times with 100 ml 2-propanol and two times with 100 ml diethylether and dried. The ochre colored zinc complex was dissolved in 250 ml cold water and under vigorous stirring slowly mixed with 100 ml 15% ammonia solution. Subsequently, the mixture was extracted three times with 100 ml diethylether, the solution was dried over sodium sulfate, and the solvent was evaporated in vacuo. Yields: 40–50%.

3.2. General synthesis procedure for the quinoline-2-carbaldehyde derivatives **3–5**

A total of 13.5 g of selenium dioxide was dissolved in 120 ml dioxane and 5 ml H₂O at 45°C. Within 15 min, 0.105 mol of the quino-

line derivative dissolved in 25 ml dioxane were added to the solution, and the solution was heated for 1 h under reflux. The precipitated, metallic selenium was separated from the hot solution by filtration. After the solvent was evaporated, the red-brown aldehyde was washed three times with 50 ml *n*-pentane and used without purification. Yields: 90–98%.

3.3. General synthesis procedure for the ligands **6, 8, 10, 12, 14–20**

A total of 0.105 mol of the above synthesized aldehyde and an equimolar amount of the corresponding aniline derivative were dissolved in 50 ml ethanol and heated for one hour under reflux. The solvent was evaporated in vacuo. The remaining crude product was dissolved in *n*-pentane and the solution was dried with Na₂SO₄. The compounds **6** and **10** were crystallized from *n*-pentane at –25°C. The ligands **8, 12** and **14–20** were dissolved in *n*-pentane and the solution was filtered over silica gel. The compounds were obtained as colorless oils after the solvent was evaporated. Yields: 85–95%.

3.4. General synthesis procedure for the ligands **7, 9, 11, 13**

A total of 12.72 g (0.105 mol) 2-acetylpyridine and an equimolar amount of the corresponding aniline derivative were dissolved in 50 ml toluene and mixed with 0.01 mol *p*-toluene sulphonic acid. Subsequently, the mixture was heated for 1 h under reflux. The solvent was evaporated in vacuo. The remaining crude product was dissolved in *n*-pentane, dried with Na₂SO₄ and filtered over silica gel. The compounds were obtained as colorless oils after the solvent was evaporated. Yields: 80–95%.

3.5. General synthesis procedure for the diazadiene nickel dibromide complexes **21–35**

A total of 1.0 g (0.00324 mol) dimethoxyethane nickel dibromide [14] was dissolved in 150 ml tetrahydrofurane, mixed with an

equimolar amount of the diazadiene ligand and stirred for 4 h at RT. The mixture was processed according to the solubility of the complexes. For compounds **25**, **26** and **35**, the solution was reduced to half of its volume and crystallized at -25°C . All other complexes precipitated almost quantitatively from the reaction solution. The complexes were successively washed with 50 ml diethylether and 50 ml *n*-pentane, dissolved in dichloromethane and crystallized at -25°C . Yields: 50–90%.

3.6. General synthesis procedure for the silica gel–PHT catalyst system

At RT, 30 ml of a 2.0 M trimethylaluminum solution in toluene were added to a suspension of 2.0 g of calcined silica gel (Davison type 948) in 100 ml toluene. Subsequently, the temperature was brought to 40°C and within 15 min, 0.75 ml water was transferred into the suspension using a wet argon flow. Thereupon, the reaction mixture heated itself to 60°C . After 10 min, the suspension became suddenly highly viscous. After cooling to RT, the mixture was stirred vigorously for 2 h. Finally, 0.23 mmol of the catalyst precursor were added as a solid. After 10 min, the mixture was filtered and dried in high vacuum. The preparation of the catalyst yielded 5.40 g ($> 95\%$ calculated on the aluminum content) of a colored powder.

3.7. Homogeneous activation of the catalyst precursors

Two to ten milligrams of the corresponding catalyst precursor were weighed into a Schlenk tube and activated with methylaluminoxane (30 wt.% in toluene, Al:Ni = 2500:1). The catalyst solution was used for polymerization within 30 min.

3.8. Homogeneous polymerization with the co-catalyst methylaluminoxane

A pressure Schlenk tube was charged with 50 ml *n*-pentane and 1.0 ml methylaluminoxane

solution (30 wt.% in toluene). After 10 min, the corresponding amount of catalyst solution was added. Then, the mixture was heated to 70°C and an ethylene pressure of 5.0 bar was applied (99.98% ethylene, previously dried over aluminum oxide). The polymerization reaction was terminated after 5 min by releasing the pressure and treatment with methanol/HCl (5:1 (v/v)). The polymer was washed twice with 50 ml methanol and dried to constant weight under high vacuum.

3.9. Polymerization with the heterogeneously effective silica gel–PHT catalyst system

500 ml *n*-pentane, containing 1.0 ml triisobutylaluminum (1.6 M solution in *n*-hexane) were added to a 1-l round flask and stirred for 10 min. An amount of 0.20 g of the catalyst prepared as above was added as a powder to this solution. The suspension was then transferred into a 1l Büchi laboratory autoclave under argon, heated to 70°C and an ethylene pressure of 10 bar was applied (99.98% ethylene, previously dried over aluminum oxide). The mixture was stirred for 1 h and the reaction terminated by releasing the pressure from the reactor. The polymer obtained was dried under vacuum until a constant weight was achieved.

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