

(α -Diimine)nickel(II) complexes containing chloro substituted ligands as catalyst precursors for the oligomerization and polymerization of ethylene

Markus Helldörfer, Judith Backhaus, Wolfgang Milius, Helmut G. Alt*

Laboratorium für Anorganische Chemie, Universität Bayreuth, Universitätsstraße 30, NW 1, D-95440 Bayreuth, Germany

Received 15 July 2002; accepted 7 August 2002

Abstract

(α -Diimine)nickel(II) dibromide complexes and their derivatives can be used for the polymerization and oligomerization of ethylene after activation with methyl-aluminoxane (MAO). The activities of these catalysts and the properties of the obtained polyethylenes depend on the structure of the used catalyst precursors. Therefore a variety of (α -diimine)nickel(II) dibromide complexes with chlorine and methyl substituents on the ligands and various substituents on the ligand backbone were studied as catalysts for the homogeneous polymerization of ethylene. The range of the polymerization products reaches from oligomers to polymers of low molecular weights.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: α -Diimine ligands; Nickel; Catalysis; Polymerization; Oligomers; Ethylene

1. Introduction

Homogeneous nickel catalysts for the oligomerization and polymerization of ethylene are available since the 1970s [1–11]. (α -Diimine)nickel(II) complexes have been known since 1975 [12–15]. Brookhart and others discovered them as catalyst precursors for the polymerization of olefins [16–25] (Fig. 1). These catalysts with a late transition metal are suitable to polymerize ethylene to give short chain oligomers and highly branched or linear polymers [26–31].

These investigations are mainly focused on catalyst precursors with more or less bulky aliphatic or aromatic *ortho*-substituents at the arene moiety of the α -diimine ligand in order to study the influence of

the ligand structure on the polymerization products. Here, we report about (α -diimine)nickel(II) dibromide complexes that possess a methyl and a chloro substituent in the ligand framework. These compounds were activated with MAO and tested as catalysts for the polymerization of ethylene. The influence of the functional groups on the arene moiety and the variations of the ligand backbones on the polymerization behaviors of these catalysts were analyzed.

2. Results and discussion

2.1. Synthesis of the catalyst precursors

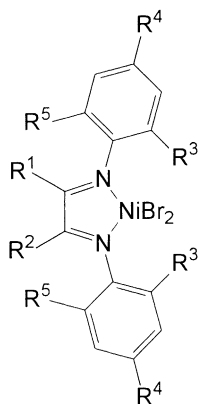
2.1.1. Synthesis of the α -diimine ligands

The α -diimine ligands were synthesized by condensation of two equivalents of a substituted aniline

* Corresponding author. Tel.: +49-921-552555;

fax: +49-921-552157.

E-mail address: helmut.alt@uni-bayreuth.de (H.G. Alt).



R^1, R^2, R^3, R^4, R^5 = different aliphatic or aromatic substituents or H

Fig. 1. (α -Diimine)nickel(II) catalyst precursors.

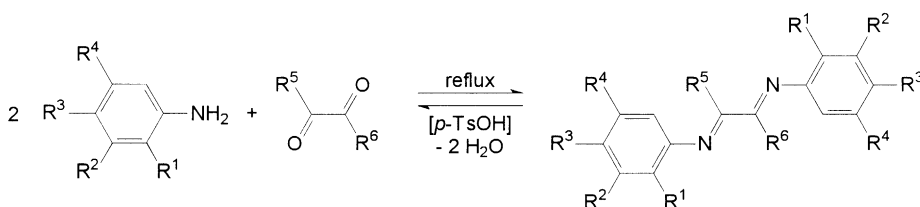
derivative with one equivalent of a 1,2-diketone compound according to Scheme 1.

In case of **1a**, **1b**, **1c** dichloromethane was used as solvent due to the boiling point of the 2,3-butadione (88 °C). For the synthesis of the other ligands toluene was used. The *para*-toluene sulfonic acid was added as catalyst and the aniline derivatives were applied in a small excess. The end of the reaction was recognized by GC. All compounds were characterized by ^1H and

^{13}C NMR spectroscopy. The corresponding data are summarized in third table.

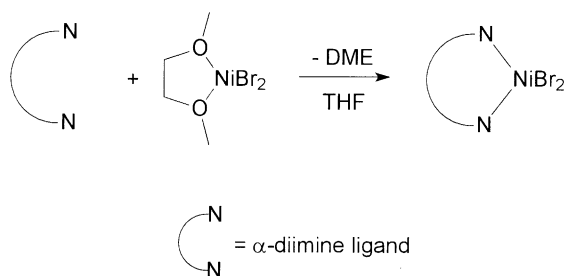
2.1.2. Synthesis of the (α -diimine)nickel(II) dibromide complexes

(α -Diimine)nickel(II) complexes become available by the reaction of dimethoxyethane nickel dibromide [32] with the corresponding α -diimine ligand [12,13]. Therefore the α -diimine compound is dissolved in



	R^1	R^2	R^3	R^4	R^5	R^6		R^1	R^2	R^3	R^4	R^5	R^6
1a	Me	Cl	H	H	Me	Me	2a	Me	Cl	H	H	Me	Et
1b	Me	H	Cl	H	Me	Me	2b	Me	H	Cl	H	Me	Et
1c	Me	H	H	Cl	Me	Me	2c	Me	H	H	Cl	Me	Et
3a	Me	Cl	H	H	Et	Et	4a	Me	Cl	H	H	Ph	Ph
3b	Me	H	H	Cl	Et	Et	4b	Me	H	Cl	H	Ph	Ph
3c	Cl	H	Me	H	Et	Et	4c	Me	H	H	Cl	Ph	Ph
							4d	Cl	H	Me	H	Ph	Ph

Scheme 1. Synthesis of the α -diimine ligands.

Scheme 2. Synthesis of (α -diimine)nickel(II) dibromide complexes.

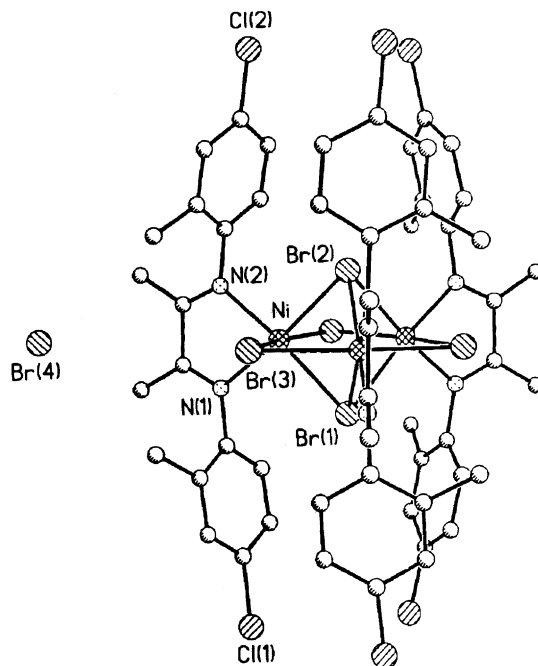
tetrahydrofuran and reacted with an equimolar amount of the nickel complex (Scheme 2).

The reaction starts immediately and can be observed by a color change of the reaction mixture from yellow to dark red. The yields of the complexes are almost quantitative. All synthesized (α -diimine)nickel(II) dibromide complexes are summarized in Scheme 3.

Due to the paramagnetic nature of this type of complexes it is not very informative to characterize them by NMR spectroscopy. The mass spectrometric analyses revealed the molecule ion in the case of complexes **5a** and **6b**. In all the other cases fragments with the loss of bromine and chlorine atoms or a methyl group were observed. The mass spectrometric data with typical fragments and their intensities are given for the complexes **5a–8d** in fourth table.

Complex **5b** gave single crystals that were suitable for an X-ray analysis (Fig. 2). The crystal structure of **5b** shows a trinuclear cationic complex, each nickel atom has the coordination number six. The three nickel atoms together with three bromine atoms form a planar six membered ring. Above and below the ring plane is a bromine atom that bridges all three nickel atoms. The remaining bromine atom is located as counteranion in the lattice. The two nitrogen atoms of the α -diimine ligand complete the distorted octahedral coordination of the nickel atoms. The aryl rings of the α -diimine lie nearly perpendicular to the plane formed by the metal and the coordinated nitrogen atoms like in related structures [17,26,33]. The crystals show the symmetric trigonal space group $P\bar{3}$. The quality of the crystals allowed only a R -value of 10.45%. Some important bond lengths and angles are given in Table 1.

Although **5b** is trinuclear in the solid state, the paramagnetism of the dissolved complex is indicative for a monomeric structure in solution.

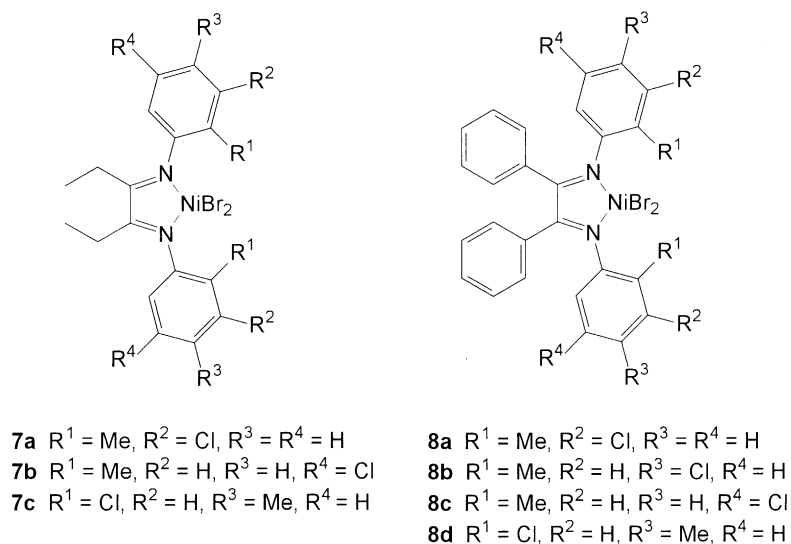
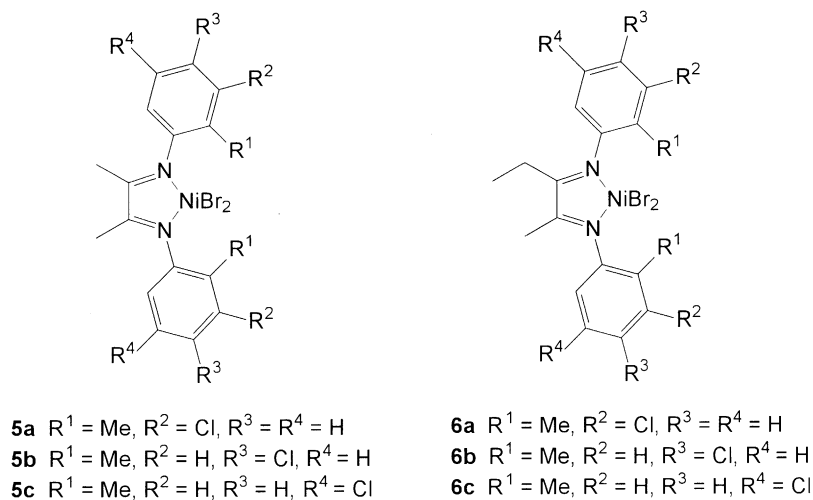
Fig. 2. Molecular structure of **5b**.

2.2. Polymerization of ethylene with the (α -diimine)nickel(II) complexes **5a–8d**

The (α -diimine)nickel dibromide complexes synthesized above were tested for homogeneous ethylene polymerization. After activation with MAO (30 wt.%

Table 1
Selected bond lengths and angles of the molecular structure of **5b**

Bond lengths (Å)			
Ni–N(1)	2.058(15)	Ni–Br(3)	2.595(3)
Ni–N(2)	2.071(14)	N(1)–C(1)	1.27(2)
Ni–Br(1)	2.546(3)	N(2)–C(2)	1.25(2)
Ni–Br(2)	2.551(3)	C(1)–C(2)	1.54(3)
Bond angles (°)			
N(1)–Ni–N(2)	77.9(6)	Br(3)–Ni–Br(3)1	164.36(11)
N(1)–Ni–Br(1)	97.9(5)	Ni1–Br(1)–Ni	77.98(10)
N(2)–Ni–Br(1)	175.4(4)	Ni1–Br(2)–Ni	77.79(10)
N(1)–Ni–Br(2)	174.8(5)	Ni–Br(3)–Ni(2)	75.64(11)
N(2)–Ni–Br(2)	97.2(4)	C(1)–N(1)–C(12)	121.1(15)
Br(1)–Ni–Br(2)	86.94(10)	C(1)–N(1)–Ni	116.8(12)
N(1)–Ni–Br(3)	97.7(4)	C(12)–N(1)–Ni	122.1(11)
N(2)–Ni–Br(3)	97.6(4)	C(2)–N(2)–C(5)	121.0(15)
Br(1)–Ni–Br(3)	84.67(8)	C(2)–N(2)–Ni	115.6(13)
Br(2)–Ni–Br(3)	84.71(8)	C(5)–N(2)–Ni	123.3(11)

Scheme 3. Synthesized (α -diimine)nickel(II) complexes.

in toluene), the solvent was removed in vacuo. The dried catalysts were suspended in pentane and used for slurry polymerization reactions. The results are summarized in Table 2.

In all cases a mixture of oligomers and polymers was obtained. In order to analyze the products, the polymerization mixture was filtered to separate the oligomers and the polymers. The polymer was washed with half concentrated hydrochloric acid in order to remove MAO and then it was dried in vacuo. The

pentane of the oligomeric solution was distilled over a Vigreux column. The remaining oligomers were analyzed by GC. The classification for oligomers and polymers was the solubility of the products in pentane. Mass spectrometric analyses suggested a molecular weight of ca. 1000 g mol^{-1} as the border line.

A comparison of the observed activities reveals that chloro substituents in the *para*-position (**5b**, **6b**) or the *ortho*-position (**7c**, **8d**) at the aryl groups of the α -diimine ligand lead to the highest activities (Fig. 3).

Table 2

Results of the homogeneous ethylene polymerization for the α -(diimine)nickel(II) complexes **5a–8d** activated with MAO

No.	Activity ^a (g(product) mmol ⁻¹ (Ni) h)	TOF ^b (mol(C ₂ H ₄) mol ⁻¹ (Kat.) h)	Polymer share (wt.%)	<i>M_w</i> (polymer share) (g mol ⁻¹)	<i>D</i> ^c
5a	1,350	50,625	75	5,469	4.5
5b	2,230	83,625	24.7	6,900	2.7
5c	1,467	55,013	90	6,170	3.7
6a	1,021	38,288	59	n.d. ^d	n.d.
6b	1,497	56,138	49.5	n.d.	n.d.
6c	951	35,663	54	n.d.	n.d.
7a	1,162	43,575	66.7	12,240	7.9
7b	346	12,975	95	5,600	10.5
7c	2,636	98,850	83.3	1,475	5.6
8a	270	10,125	74.1	6,110	26.8
8b	235	8,813	70	5,920	12.3
8c	270	10,125	95.2	n.d.	n.d.
8d	2,870	107,625	62.1	1,520	8.6

Polymerization conditions: activation with 30 wt.% MAO in toluene (Al/Ni = 1000/1; polymerization in 250 ml pentane, 60 °C, 11 autoclave, 10 bar ethylene pressure, 60 min).

^a The activities were calculated from the total consumption of ethylene (1.01 ethylene = 1.2 g product).

^b Turn over frequency.

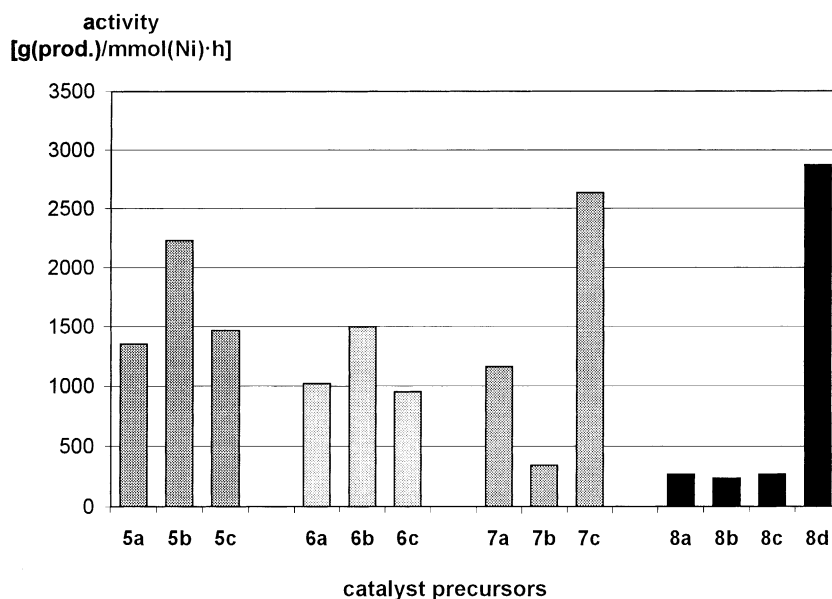
^c Polydispersity M_w/M_n of the polymer share.

^d Not determined.

There is also a trend that bulkier substituents at the ligand backbone lead to a decrease of the activities. Therefore, the activity of **5b** (2230 g(product) mmol⁻¹ (Ni) h) with two methyl groups at the ligand backbone is nearly 10 times higher than the activity of

8b (235 g(product) mmol⁻¹ (Ni) h) bearing two phenyl groups.

The relations for the polymer share determined for the different catalysts show also some clear trends (Fig. 4). A comparison of the catalysts with the same

Fig. 3. Comparison of the observed activities of the catalyst precursors **5a–8d**.

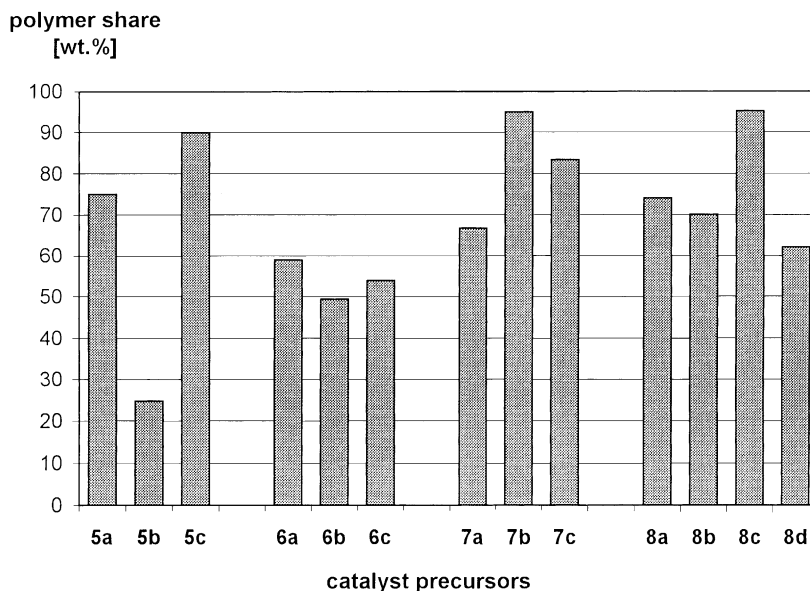


Fig. 4. Comparison of the polymer share obtained with the catalyst precursors **5a–8d**.

substituents at the ligand backbone obtained from **5a**, **5b** and **5c** shows that **5b** with a chloro substituent in the *para*-position produces the lowest polymer share. Similar effects were also observed for the catalysts derived from **6a**, **6b**, **6c**, **8a**, **8b** and **8c**.

It is obvious that there is an increase of the polymer share from the catalysts with two methyl groups at the ligand backbone to those with two ethyl groups and further a little decrease of the polymer share for the catalysts with two phenyl groups at the ligand backbone.

The GC analyses of the oligomer mixtures show the formation of almost all isomers that are possible for olefins with an even carbon number (Fig. 5). All oligomer mixtures were viscous oils or waxes. Therefore, it can be assumed that the produced polymers are not a consequence of a copolymerization of low molecular olefins and ethylene, but direct polymerization products that show a higher molecular weight than 1000 g mol^{-1} and are insoluble in pentane.

Most of these results can be explained with the so called “chain running mechanism” suggested by Brookhart and others [16–26,34] (Scheme 4).

With this mechanism the formation of oligomers and polymers can be explained. An important role

whether polymer or short chain oligomers are formed plays the *ortho*-position at the aryl rings of the α -diimine ligand. Deng et al. [35,36] proved this with calculations for the transition states of the chain propagation and the chain transfer reaction. The *ortho*-substituents have a considerable influence on the monomer addition to the catalytic center and the dissociation of the formed polymer from the metal due to their interaction with the axial coordination sites of the metal center (Fig. 6).

Considering this background, the comparatively high activities of **5b** and **6b** can be related to the low influence of the *para*-chloro substituent on the catalytic center. For these catalysts the coordination of the monomer and the dissociation of the formed oligomers is privileged. Therefore, high activities and a low polymer share are observed. On the other hand, a chloro substituent in the *ortho*-position like in the case of **7c** and **8d** seems to stabilize the catalytic species better than a methyl group in that position. As a consequence for these catalysts, very high activities are observed, whereas the polymer share is already bigger than 60 wt.%. The decrease of activities and the increase of the polymer share with bulkier substituents at the ligand backbone results from to the

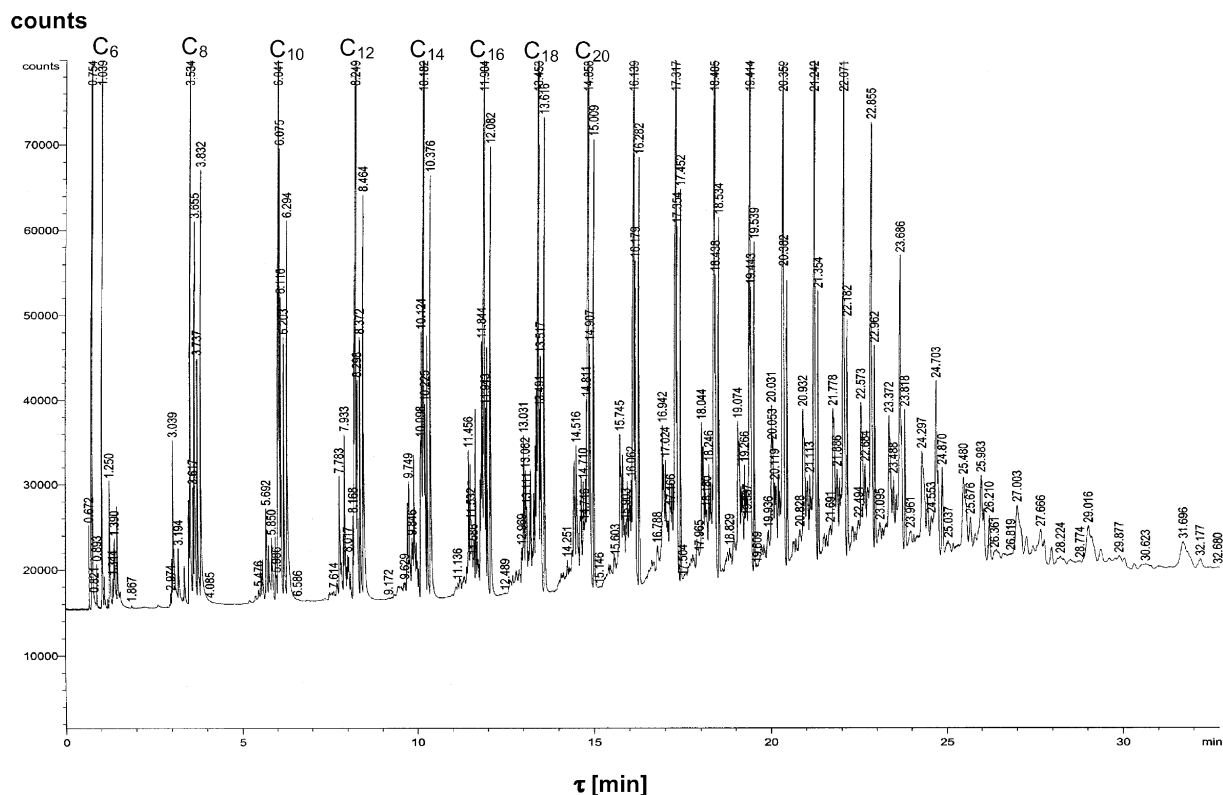


Fig. 5. GC plot of the oligomers obtained with complex **6c**/MAO.

interaction between the backbone and the aryl groups of the ligand. Bulkier groups at the backbone reduce the free rotation of the aryl rings. Therefore, the axial coordination sites of the metal center are sterically more hindered.

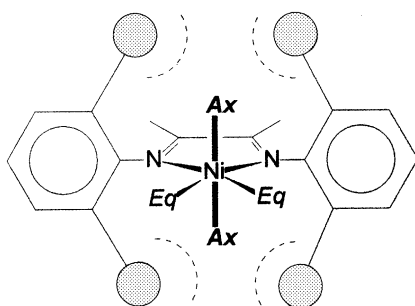


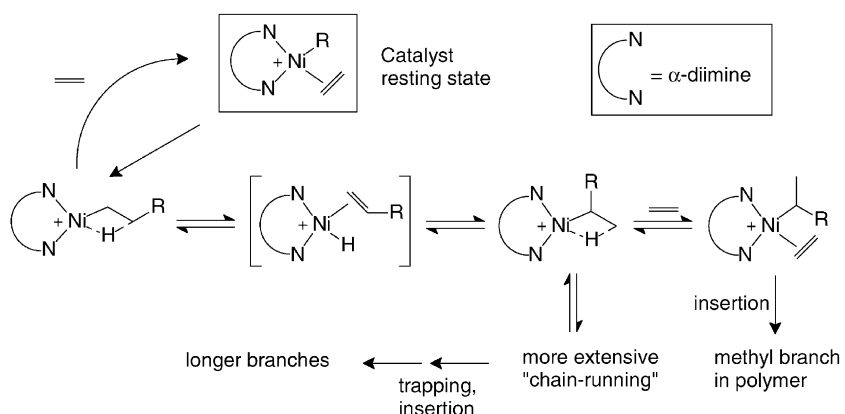
Fig. 6. Axial (Ax) and equatorial (Eq) coordination sites of the metal center and their steric interactions with the *ortho*-substituents.

In contradiction to the results of Killian et al. [21], we found the formation of isomers of the short chain oligomers. Brookhart et al. reported a high selectivity to the formation of α -olefins. This observation can be related to the polymerization conditions. Here an ethylene pressure of 10 bar was used whereas Brookhart carried out his polymerization reactions at comparatively high pressures (56 atm) favoring the ethylene insertion process. The considerable isomerization and the production of both oligomers and polymers made it almost impossible to calculate a Schulz–Flory distribution for the obtained oligomer mixtures.

3. Experimental

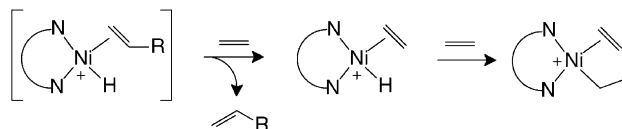
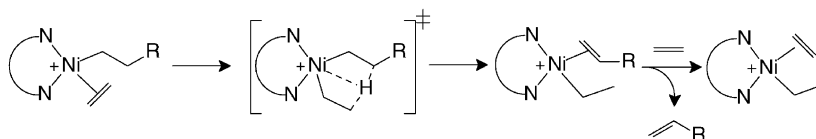
NMR spectroscopic investigations were performed with a Bruker ARX 250 instrument. All organometal-

A. Propagation and Isomerization:



Chain Transfer:

(1) Associative displacement:

(2) Concerted β -H transfer to bound monomer:

Scheme 4. Chain running mechanism [16–25,34].

lic samples were prepared 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 in ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for chloroform- d_1).

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.

Molecular weight determinations of the polyethylene samples were performed using a Millipore Waters 150C HT-GPC with refractometric detection (RI Waters 401). The polymer samples were dissolved in 1,2,4-trichlorobenzene (flow rate 1 ml min^{-1}) and measured at 150 °C.

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

Temperature program include the following:

- starting phase: 3 min at 50 °C;

- heating phase: 5 °C min⁻¹ (15 min); and
- plateau phase: 310 °C (15 min).

Methyl-aluminoxane (MAO) was supplied by Witco GmbH, Bergkamen, as 30% solution in toluene (average molecular weight 1100 g mol⁻¹, aluminum content: 13.1%, 3.5% as trimethylaluminum).

3.1. General synthesis procedure for the α -diimine ligands **1a–1c**

To a solution of 40 mmol of the respective aniline derivative in dichloromethane, 15 mmol of the corresponding diketo compound and a catalytic amount of *p*-toluene sulfonic acid were added. The mixture was heated under reflux. The progress of the reaction was observed by GC. After 12–24 h the reaction mixture was cooled to room temperature and filtered over silica. After removing the solvent in vacuo, the product was precipitated with cold methanol. For purification the products were recrystallized from a methanol/ethanol mixture (3:1). The ligands were obtained as yellow crystals. Yields: **1a**, 75%; **1b**, 80%; **1c**, 80%. All compounds were characterized by NMR spectroscopy (Table 3).

3.2. General synthesis procedure for the α -diimine ligands **2a–4d**

To a solution of 40 mmol of the respective aniline derivative in toluene, 15 mmol of the corresponding diketo compound and a catalytic amount of *p*-toluenesulfonic acid were given. The mixture was heated under reflux. The resulting water was removed as azeotropic mixture using a Dean–Stark apparatus. The progress of the reaction was observed by GC. After 12–24 h the reaction mixture was cooled to room temperature and filtered over silica. After removing the solvent in vacuo, the product was precipitated with cold methanol. For purification, the products were recrystallized from a methanol/ethanol mixture (3:1). The ligands were obtained as yellow crystals. Yields: **2a**, 55%; **2b**, 65%; **2c**, 65%; **3a**, 35%; **3b**, 45%; **3c**, 50%; **4a**, 25%; **4b**, 25%; **4c**, 30%; **4d**, 35%. All compounds were characterized by NMR spectroscopy (Table 3).

3.3. General synthesis procedure for the (α -diimine)nickel dibromide complexes **5a–8d**

A 5 mmol of the respective α -diimine ligand were dissolved in 150 ml THF. Then 5 mmol of dimethoxyethane nickel dibromide were added under argon atmosphere. The mixture was stirred for 8 h at room temperature. For purification, the volume of the solvent was reduced in vacuo and the complexes were precipitated by adding pentane. After washing several times with pentane until the solvent stayed colorless, the products were dried in vacuo. The complexes were obtained as crystalline powders. Yields: **5a**, 95%; **5b**, 95%; **5c**, 90%; **6a**, 95%; **6b**, 90%; **6c**, 90%; **7a**, 90%; **7b**, 90%; **7c**, 85%; **8a**, 85%; **8b**, 85%; **8c**, 85%; **8d**, 90%. The complexes were identified by mass spectrometry (Table 4).

The synthesized complexes did not show a melting point under inert atmosphere but decomposition at higher temperatures. Decomposition temperatures: **5a**, 230 °C; **5b**, 240 °C; **5c**, 235 °C; **6a**, 230 °C; **6b**, 250 °C; **6c**, 240 °C; **7a**, 235 °C; **7b**, 230 °C; **7c**, 240 °C; **8a**, 220 °C; **8b**, 225 °C; **8c**, 240 °C; **8d**, 210 °C.

The purity of complexes **5a**, **6a** and **6b** was tested by microanalyses: **5a**, C = 39.92% (C_{calc.} = 39.18%), H = 4.00% (H_{calc.} = 3.29%); **6a**, C = 38.93 (C_{calc.} = 40.33), H = 3.86 (H_{calc.} = 3.56); **6b**, C = 40.54 (C_{calc.} = 40.33), H = 4.00 (H_{calc.} = 3.56).

3.4. General procedure for the activation of the (α -diimine)nickel(II) complexes

A 5–10 mg of the complex were suspended in toluene and activated with the corresponding amount of MAO (Al/Ni = 1000/1). The solvent was removed in vacuo and the activated catalyst was suspended in 50 ml *n*-pentane. The catalyst suspension was used for ethylene polymerization within 30 min.

3.5. Homogeneous ethylene polymerization

The activated complex was added to a 1 l metal autoclave (Büchi), filled with 250 ml *n*-pentane. The polymerizations were performed under an ethylene pressure of 10 bar (99.98% ethylene, dried over aluminium oxide) and at a temperature of 60 °C. After a period of

Table 3

 ^1H and ^{13}C NMR data of compounds **1a–4d**

No.	^1H NMR ^a	^{13}C NMR ^b
1a	7.18 (m, 4H), 6.59 (m, 2H), 2.20 (s, 6H), 2.15 (s, 6H)	C _q : 168.0, 150.4, 135.1, 124.9; CH: 126.6, 124.4, 115.9; CH ₃ : 15.5, 14.5
1b	7.20 (d, 2H, $^4J_{\text{HH}} = 2.0$ Hz), 7.15 (dd, 2H, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 2.2$ Hz), 6.55 (d, 2H, $^3J_{\text{HH}} = 8.3$ Hz), 2.09 (s, 6H), 2.07 (s, 6H)	C _q : 168.2, 147.8, 129.0, 128.8; CH: 130.2, 126.3, 118.8; CH ₃ : 17.7, 15.6
1c	7.18 (d, 2H, $^3J_{\text{HH}} = 8.1$ Hz), 7.03 (dd, 2H, $^3J_{\text{HH}} = 8.1$ Hz, $^4J_{\text{HH}} = 2.7$ Hz), 6.70 (d, 2H, $^4J_{\text{HH}} = 2.2$ Hz), 2.13 (s, 6H), 2.12 (s, 6H)	C _q : 167.9, 150.1, 131.4, 124.9; CH: 131.3, 123.5, 117.3; CH ₃ : 17.0, 15.4
2a	7.11 (m, 4H), 6.54 (m, 2H), 2.60 (q, 2H, $^3J_{\text{HH}} = 7.6$ Hz), 2.15 (s, 6H), 2.09 (s, 3H), 1.04 (t, 3H, $^3J_{\text{HH}} = 7.6$ Hz)	C _q : 172.6, 167.3, 150.7, 150.4, 135.3, 135.2, 124.9, 124.6; CH: 126.9, 126.8, 124.6, 124.4, 116.1, 116.0; CH ₂ : 21.9; CH ₃ : 16.1, 14.9, 14.8, 12.3
2b	7.20 (d, 2H, $^4J_{\text{HH}} = 1.9$ Hz), 7.13 (d, 2H, $^3J_{\text{HH}} = 8.2$ Hz), 6.55 (dd, 2H, $^3J_{\text{HH}} = 8.2$ Hz, $^4J_{\text{HH}} = 2.0$ Hz), 2.59 (q, 2H, $^3J_{\text{HH}} = 7.6$ Hz), 2.08 (s, 3H), 2.06 (s, 6H), 1.03 (t, 3H, $^3J_{\text{HH}} = 7.6$ Hz)	C _q : 172.6, 167.2, 147.9, 147.7, 128.9, 128.7, 128.6, 128.4; CH: 130.3, 130.2, 126.4, 126.3, 118.8, 118.6; CH ₂ : 21.7; CH ₃ : 17.82, 17.79, 16.0, 12.3
2c	7.13 (d, br, 2H, $^3J_{\text{HH}} = 8.2$ Hz, $^4J_{\text{HH}} = 2.1$ Hz), 6.99 (dd, 1H, $^3J_{\text{HH}} = 8.2$ Hz, $^4J_{\text{HH}} = 1.3$ Hz), 6.98 (dd, 1H, $^3J_{\text{HH}} = 8.2$ Hz, $^4J_{\text{HH}} = 1.3$ Hz), 6.65 (Vt, $^4J_{\text{HH}} = 2.1$ Hz), 2.60 (q, 2H, $^3J_{\text{HH}} = 7.5$ Hz), 2.07 (s, 3H), 2.05 (s, br, 3H), 2.04 (s, br, 3H), 1.05 (t, 3H, $^3J_{\text{HH}} = 7.5$ Hz)	C _q : 172.5, 167.3, 150.4, 150.1, 138.7, 125.0, 124.8; CH: 131.5, 131.4, 123.7, 123.5, 117.5, 117.3; CH ₂ : 21.9; CH ₃ : 17.4, 17.3, 16.1, 12.3
3a	7.11 (t, 2H, $^3J_{\text{HH}} = 2.9$ Hz), 6.77 (d, 2H, $^3J_{\text{HH}} = 2.8$ Hz), 6.56 (d, 2H, $^3J_{\text{HH}} = 2.8$ Hz), 2.58 (q, 4H, $^3J_{\text{HH}} = 7.5$ Hz), 2.15 (s, 6H), 1.04 (t, 6H, $^3J_{\text{HH}} = 7.5$ Hz)	C _q : 171.7, 150.6, 135.3, 124.6; CH: 126.8, 124.4, 116.0; CH ₂ : 22.1; CH ₃ : 14.9, 12.0
3b	7.24 (s, 2H), 7.12 (d, 2H, $^3J_{\text{HH}} = 8.3$ Hz), 6.64 (dd, 2H, $^3J_{\text{HH}} = 5$ Hz, $^4J_{\text{HH}} = 1.8$ Hz), 2.56 (q, 4H, $^3J_{\text{HH}} = 7.5$ Hz), 2.05 (s, 6H), 1.03 (t, 6H, $^3J_{\text{HH}} = 7.5$ Hz)	C _q : 171.6, 150.2, 131.6, 124.8; CH: 131.3, 123.5, 117.3; CH ₂ : 22.1; CH ₃ : 17.5, 12.0
3c	7.24 (d, 2H, $^4J_{\text{HH}} = 1.3$ Hz), 7.04 (dd, 2H, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 1.3$ Hz), 6.65 (d, 2H, $^3J_{\text{HH}} = 8$ Hz), 2.58 (q, 4H, $^3J_{\text{HH}} = 7.5$ Hz), 2.31 (s, 6H), 1.09 (t, 6H, $^3J_{\text{HH}} = 7.5$ Hz)	C _q : 173.2, 145.1, 134.4, 123.1; CH: 130.2, 127.9, 119.3; CH ₂ : 22.7; CH ₃ : 20.6, 11.7
4a	7.92 (m, 2H), 7.68 (m, 2H), 7.47 (m, 10H), 7.20 (m, 2H)	C _q : 164.3, 148.1, 137.4, 134.8, 127.5; CH: 134.5, 131.9, 128.9, 128.2, 126.1, 117.7; CH ₃ : 15.3
4b	7.87 (m, 4H), 7.41 (m, 6H), 6.92 (d, 2H, $^4J_{\text{HH}} = 2.3$ Hz), 6.73 (dd, 2H, $^3J_{\text{HH}} = 7.5$ Hz, $^4J_{\text{HH}} = 2.3$ Hz), 6.35 (d, 2H, $^3J_{\text{HH}} = 8.3$ Hz), 1.31 (s, 6H)	C _q : 163.1, 147.3, 137.9, 134.3, 129.7; CH: 131.4, 130.3, 128.9, 128.4, 125.5, 118.0; CH ₃ : 16.5
4c	7.89 (m, 4H), 7.44 (m, 6H), 6.83 (m, 4H), 6.36 (m, 2H), 1.35 (s, 6H)	C _q : 163.6, 148.4, 137.8, 130.6, 130.4; CH: 131.6, 130.9, 129.0, 128.3, 124.7, 117.0; CH ₃ : 16.3
4d	7.88 (m, 4H), 7.47–7.30 (m, 6H), 6.99 (d, 2H, $^4J_{\text{HH}} = 2.0$ Hz), 6.65 (dd, 2H, $^3J_{\text{HH}} = 8.3$ Hz, $^4J_{\text{HH}} = 2.0$ Hz), 6.47 (d, 2H, $^3J_{\text{HH}} = 7.5$ Hz), 2.16 (s, 6H)	C _q : 164.0, 143.1, 137.4, 136.4, 128.1; CH: 131.4, 130.1, 128.8, 128.5, 127.5, 118.6; CH ₃ : 20.6

^a 250.13 MHz, 25 °C, in chloroform-*d*₁, δ (ppm) rel. chloroform (7.24).^b 62.9 MHz, 25 °C, in chloroform-*d*₁, δ (ppm) rel. chloroform (77.0).

In the autoclave was cooled to room temperature and the pressure was reduced. The polymerization mixture was filtered, the remaining polymer was washed with half concentrated hydrochloric acid, dried in vacuo and weighted. After removing *n*-pentane by distillation over a Vigreux column, the obtained oligomers were analyzed by GC.

3.6. X-ray analysis

A Siemens P4 diffractometer (Mo K α radiation; $\lambda = 0.71073$ Å) with a graphite monochromator was used for the measurement of the reflection intensities. The structure calculation was performed with Siemens SHELXTL PLUS (VMS).

Table 4

Mass spectrometric data of complexes **5a–8d**

No.	Fragment (<i>m/z</i>) (intensity (%))
5a	M^+ (–Me) = 537 (1), 421 (5), 377 (15), 332 (35), 297 (15), 210 (45), 166 (100), 130 (35), 125 (38)
5b	M^+ = 552 (1), 472 (3), 377 (10), 362 (15), 332 (90), 317 (100), 297 (18), 210 (28), 166 (100), 130 (100), 125 (100), 89 (100)
5c	M^+ (–Br, –Cl, –Me) = 422 (1), 332 (5), 317 (25), 166 (100), 131 (15), 125 (20), 89 (15)
6a	M^+ = 565 (1), 485 (1), 345 (30), 311 (10), 180 (100), 165 (75), 124 (50), 89 (20)
6b	M^+ (–Br) = 485 (1), 394 (5), 345 (15), 331 (20), 180 (100), 166 (80), 131 (15), 125 (15), 89 (10)
6c	M^+ (–Br) = 486 (1), 377 (5), 346 (5), 331 (20), 180 (100), 166 (80), 131 (10), 125 (45), 89 (20)
7a	M^+ (–Br, –Cl, –Me) = 450 (5), 406 (10), 360 (15), 325 (8), 226 (40), 180 (100), 146 (20), 125 (15), 89 (20)
7c	M^+ (–Br, –Cl, –Me) = 450 (1), 406 (4), 360 (8), 345 (10), 325 (4), 226 (10), 180 (100), 146 (10), 125 (15), 89 (10)
7b	M^+ (–Cl) = 545 (1), 406 (10), 360 (5), 325 (95), 226 (10), 180 (100), 125 (15), 89 (10)
8a	M^+ (–2Br, –Me) = 501 (2), 456 (75), 421 (5), 379 (2), 272 (5), 228 (100), 193 (90), 125 (65), 89 (60)
8b	M^+ (–Br, –Cl, –Me) = 546 (5), 502 (10), 456 (10), 422 (5), 272 (30), 228 (100), 193 (65), 125 (30), 89 (45)
8c	M^+ (–Br, –Cl, –Me) = 546 (5), 502 (10), 456 (15), 441 (5), 422 (3), 272 (15), 228 (100), 193 (20), 125 (10), 89 (10)
8d	M^+ (–Br, –Cl, –Me) = 546 (8), 502 (10), 487 (8), 456 (15), 441 (8), 422 (3), 272 (45), 228 (100), 193 (50), 125 (25), 89 (35)

$C_{54}H_{54}Br_6Cl_6N_6Ni_3$ (**5b**): red brown hexagonal prism crystallized in diethylether/acetone of the dimension 0.18 mm × 0.12 mm × 0.10 mm trigonal; space group: *P*-3; *a* = 13.1758(13) Å, *c* = 23.958(6) Å, *Z* = 2, $d_{(calc.)}$ = 1.526 mg m^{−3}, absorption coefficient: 4.362 mm^{−1}, minimum/maximum transmission coefficients: 0.9413/0.534, *F*(000) = 1632, measured reflections: 5437, independent reflections: 4179, goodness-of-fit: 1.000, *R* = 10.45%.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-xxxx. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@chemcrs.cam.ac.uk).

Acknowledgements

We thank Chevron Phillips Chemical Co., USA, for the financial support and Dr. C. Erdelen for the HT-GPC measurements.

References

- [1] F. Heydenreich, A. Mollbach, G. Wilke, H. Dreeskamp, E.G. Hoffmann, G. Schroth, K. Seevogel, W. Stempfle, *Israel J. Chem.* 10 (1972) 293.
- [2] G. Wilke, *Angew. Chem.* 100 (1988) 189; G. Wilke, *Angew. Chem. Int. Ed. Engl.* 100 (1988) 185.
- [3] W. Keim, F.H. Kowaldt, R. Goddard, C. Krüger, *Angew. Chem.* 90 (1978) 493; W. Keim, F.H. Kowaldt, R. Goddard, C. Krüger, *Angew. Chem. Int. Ed. Engl.* 90 (1978) 466.
- [4] W. Keim, R.S. Bauer, H.C. Chung, P. Glockner, US Patent 3635937 (1969).
- [5] W. Keim, R.F. Mason, P. Glockner, US Patent 3647914 (1972).
- [6] W. Keim, R. Appel, A. Storeck, C. Krüger, R. Goddard, *Angew. Chem.* 93 (1981) 91; W. Keim, R. Appel, A. Storeck, C. Krüger, R. Goddard, *Angew. Chem. Int. Ed. Engl.* 93 (1981) 116.
- [7] M. Peuckert, W. Keim, *Organometallics* 2 (1983) 594.
- [8] U. Klabunde, S.D. Ittel, *J. Mol. Catal.* 41 (1987) 123.
- [9] K.A. Ostoja Starzewski, J. Witte, *Angew. Chem.* 100 (1988) 861; K.A. Ostoja Starzewski, J. Witte, *Angew. Chem. Int. Ed. Engl.* 100 (1988) 839.
- [10] K.A. Ostoja Starzewski, J. Witte, *Angew. Chem.* 97 (1985) 610; K.A. Ostoja Starzewski, J. Witte, *Angew. Chem. Int. Ed. Engl.* 24 (1985) 599.
- [11] K.A. Ostoja Starzewski, J. Witte, H. Barti, European Patent Appl. EP 101927 A1 19840307 (1984).
- [12] H. torn Dieck, M. Svoboda, *Chem. Berlin* 109 (1976) 1657.
- [13] H. torn Dieck, M. Svoboda, *Z. Naturforsch. B* 33 (1978) 1381.
- [14] M. Svoboda, H. torn Dieck, *J. Organomet. Chem.* 191 (1980) 321.
- [15] H. torn Deck, M. Svoboda, T. Greiser, *Z. Naturforsch. B* 36 (1981) 814.
- [16] R.L. Huff, S.A. Svejda, D.J. Tempel, M.D. Leatherman, L.K. Johnson, M. Brookhart, *Polym. Prep., Am. Chem. Soc., Div. Polym. Chem.* 41 (2000) 401.
- [17] D.P. Gates, S.A. Svejda, E. Onate, C.M. Killian, L.K. Johnson, P.S. White, M. Brookhart, *Macromolecules* 33 (2000) 2320.

- [18] S.A. Svejda, L.K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* 121 (1999) 10634.
- [19] M. Brookhart, L.K. Johnson, C.M. Killian, E.F. McCord, S.J. McLain, K.A. Kreutzer, S.D. Ittel, D.J. Tempel, Du Pont Co., US Patent Appl. US 5880241 (1999).
- [20] S.A. Svejda, M. Brookhart, *Organometallics* 18 (1999) 65.
- [21] C.M. Killian, L.K. Johnson, M. Brookhart, *Organometallics* 16 (1997) 2005.
- [22] S.J. McLain, J. Feldman, E.F. McCord, K.H. Gardner, M.F. Teasley, E.B. Coughlin, K.J. Sweetman, L.K. Johnson, M. Brookhart, *Polym. Mater. Sci. Eng.* 76 (1997) 20.
- [23] C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* 118 (1996) 11664.
- [24] M. Brookhart, L.K. Johnson, C.M. Killian, S. Mecking, D.J. Tempel, *Polym. Prep., Am. Chem. Soc., Div. Polym. Chem.* 37 (1996) 254.
- [25] L.K. Johnson, M. Christopher, M. Brookhart, *J. Am. Chem. Soc.* 117 (1995) 6414.
- [26] T. Schleis, T.P. Spaniol, J. Okuda, J. Heinemann, R. Mülhaupt, *J. Organomet. Chem.* 569 (1998) 159.
- [27] D. Pappalardo, M. Mazzeo, C. Pelleccia, *Macromol. Rapid Commun.* 18 (1997) 1017.
- [28] C. Pelleccia, A. Zambelli, M. Mazzeo, D. Pappalardo, *J. Mol. Catal. A* 128 (1998) 229.
- [29] A. Köppl, H.G. Alt, *J. Mol. Catal. A* 154 (2000) 45.
- [30] G.B. Galland, R.F. de Souza, R.S. Mauler, F.F. Nunes, *Macromolecules* 32 (1999) 1620.
- [31] Z. Zeng, K. Zetterberg, *Macromol. Chem. Phys.* 199 (1998) 2677.
- [32] L.G.L. Ward, *Inorg. Synth.* 13 (1972) 154.
- [33] R. van Asselt, C.J. Elsevier, W.J.J. Smeets, A.L. Spek, R. Benedix, *Recl. Trav. Chim. Pays-Bas* 113 (1994) 88.
- [34] D.J. Tempel, L.K. Johnson, R.L. Huff, P.S. White, M. Brookhart, *J. Am. Chem. Soc.* 122 (2000) 6686.
- [35] L. Deng, I. Woo, L. Cavallo, P.M. Margl, T. Ziegler, *J. Am. Chem. Soc.* 119 (1997) 6177.
- [36] L. Deng, P.M. Margl, T. Ziegler, *J. Am. Chem. Soc.* 119 (1997) 1094.