

The influence of halogen substituents at the ligand framework of (α -diimine)nickel(II) catalyst precursors on their behavior in ethylene oligomerization and polymerization

Markus Helldörfer, Wolfgang Milius, Helmut G. Alt*

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

Received 1 August 2002; received in revised form 20 August 2002; accepted 23 August 2002

Abstract

The ligand structure of (α -diimine)nickel(II) catalyst precursors has a significant influence on the behavior of these catalysts in the polymerization of ethylene. After activation with MAO, homogeneous nickel catalysts of this type are suitable to polymerize olefins to low molecular oligomers and/or more or less branched polymers. The variation of the ligand framework of the catalysts with halogen substituents in different positions shows clear dependencies between these substituents and the properties of the polymerization products. Unsaturated oligomers with an even number of carbon atoms (4–50) and all possible isomers as well as polymers up to a molecular weight of 36,000 g/mol can be obtained.

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

Keywords: Halogen substituent; (α -Diimine)nickel(II) complexes; Ethylene; Oligomer; Polymerization

1. Introduction

Various types of nickel catalysts for the oligomerization and polymerization of olefins are known for 30 years [1–9]. Some of them found an application in the Shell Higher Olefin Process (SHOP) [10–14]. During the last few years, investigations were mainly focused on (α -diimine)nickel(II) complexes [15–18] that were discovered by Brookhart and co-workers [19–28] as suitable catalysts in combination with methylaluminoxane (MAO) (Fig. 1).

Other research groups have reported identical or closely related catalyst systems that can be used for the

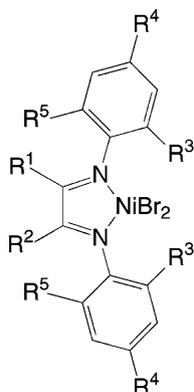
polymerization of olefins [29–34]. The catalytic potential of these (α -diimine)nickel(II) complexes depends on the structure of the catalyst precursors and is explained with the so called “chain running mechanism” [19–28,35] (Scheme 1).

This mechanism gives reasons for the formation of linear and branched polymers and short chain oligomers in the ethylene polymerization with nickel catalysts. The influence of the ligand structure on this mechanism is mainly caused by the interaction of substituents with the axial coordination sites of the metal center [35–37]. Especially the steric demands of the substituents are important (Fig. 2).

Here, we report about the behavior of (α -diimine)nickel(II) catalysts that bear halogen substituents at the ligand framework when used in the polymerization

* Corresponding author. Fax: +49-921-552157.

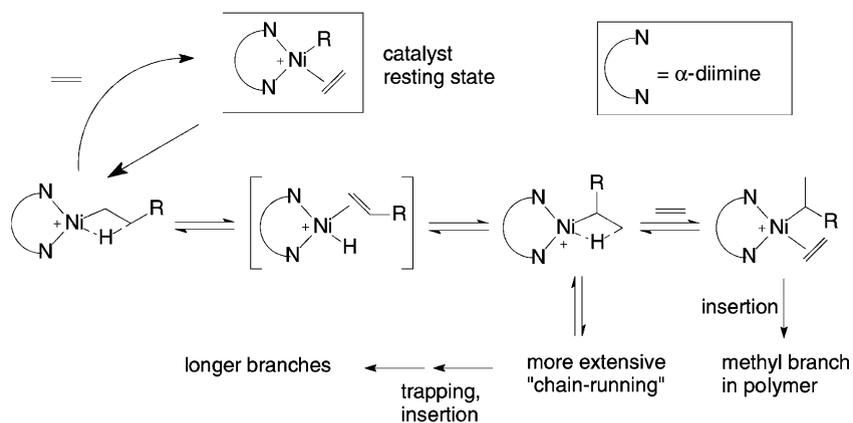
E-mail address: helmut.alt@uni-bayreuth.de (H.G. Alt).



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

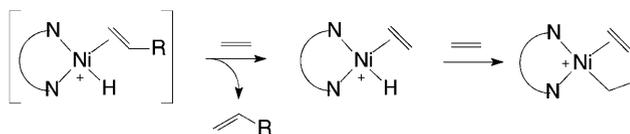
Fig. 1. (α -Diimine)nickel(II) catalyst precursors.

A. Propagation and Isomerization:

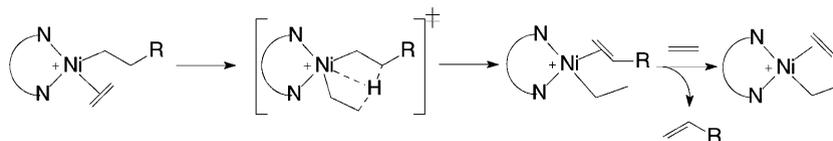


B. Chain Transfer:

(1) Associative displacement:



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



Scheme 1. Chain running mechanism [19–28,35].

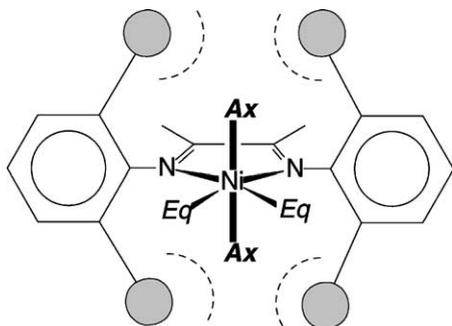


Fig. 2. Axial (Ax) and equatorial (Eq) coordination sites of the metal center and their steric interactions with the *ortho*-substituents.

of ethylene. Relationships between the nature and the position of substituents and the catalytic potential were investigated.

2. Results and discussion

2.1. Synthesis of the catalyst precursors

2.1.1. Synthesis of the α -diimine ligands

The α -diimine ligands become available by a condensation reaction of 2,3-butadione with the corresponding aniline derivative according Scheme 2.

The synthesized ligands differ in the nature and position of the substituents at the aryl moiety. Mainly compounds with halogen substituents were studied. All ligands are listed in Fig. 3.

The compounds were characterized by NMR spectroscopy (Table 3).

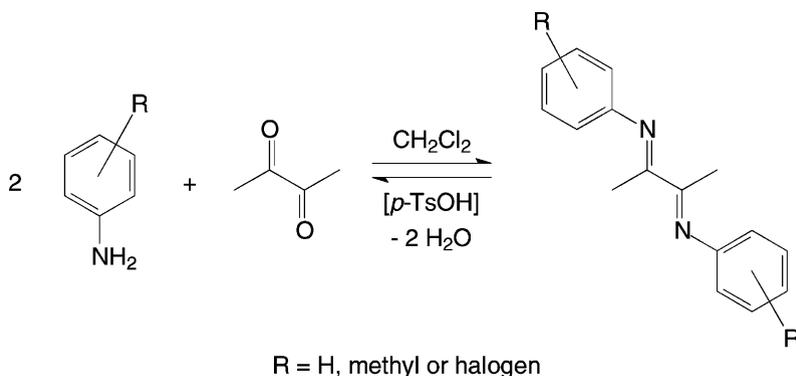
2.1.2. Synthesis of the (α -diimine)nickel(II) complexes

The (α -diimine)nickel dibromide complexes were prepared according to procedures described in the literature [15,16]: the corresponding α -diimine ligand is dissolved in tetrahydrofuran and reacted with an equimolar amount of dimethoxyethane nickel dibromide [38]. The synthesized complexes are summarized in Scheme 3.

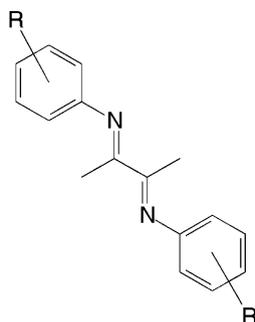
Due to the paramagnetic nature of this type of complexes, it is not very informative to characterize them by NMR spectroscopy. The mass spectrometric analyses did not reveal the molecule ion in the case of complexes **7a**, **7b**, **8a**, **8c**, **10a** and **10b**. Their fragments deriving from the loss of bromine or iodine atoms were observed. All mass spectrometric data with typical fragments and their intensity for the complexes **6a–10b** are given in Table 4.

In case of **10a**, single crystals could be obtained that were suitable for an X-ray analysis (Fig. 4).

The complex crystallized from a solution in acetone/diethylether. Therefore, one acetone molecule is coordinated to the metal center in order to compensate the electron deficit of the complex. The nickel atom has the coordination number five and shows a distorted square-planar pyramidal environment that can be derived from an octahedron where one axial position is not occupied due to the steric hindering of the two iodine 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 [20–39]. Some important bond lengths and angles are given in Table 1.



Scheme 2. Synthesis of the α -diimine ligands.



	R	R	R	R	R
1a	H	2a	<i>ortho</i> -F	3a	<i>ortho</i> -Cl
1b	<i>ortho</i> -Me	2b	<i>meta</i> -F	3b	<i>meta</i> -Cl
1c	<i>para</i> -Me	2c	<i>para</i> -F	3c	<i>para</i> -Cl

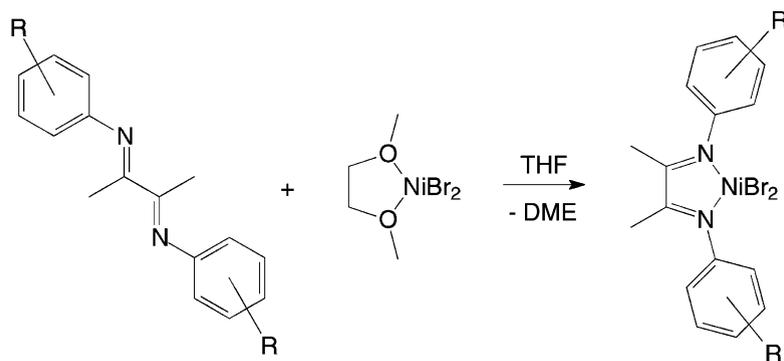
Fig. 3. Synthesized α -diimine ligands.

2.2. Polymerization of ethylene with the (α -diimine)nickel(II) complexes **6a–10b**

After activation with MAO (30 wt.% in toluene), the (α -diimine)nickel dibromide complexes synthesized previously were tested for the homogeneous ethylene

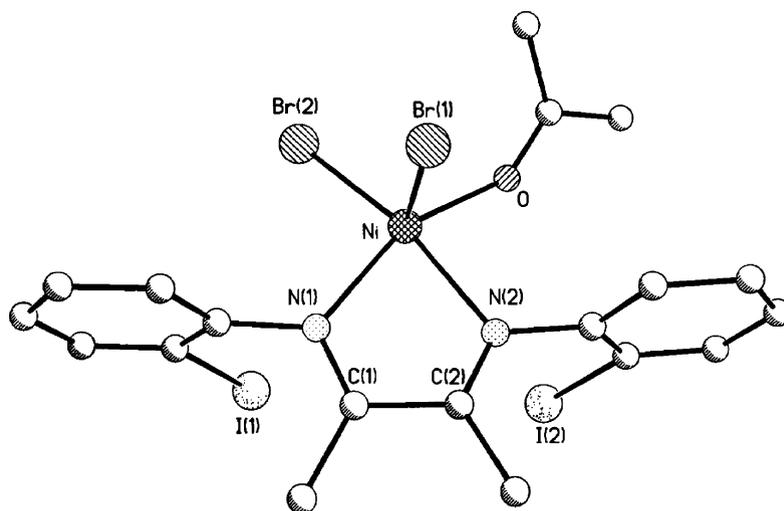
polymerization. The toluene was removed in vacuo and the dried catalysts were suspended in pentane and used for a slurry polymerization reaction. The results are summarized in [Table 2](#).

The range of the obtained products reached from low molecular olefinic oligomers to polymers. For



	R	R	R	R	R
6a	H	7a	<i>ortho</i> -F	8a	<i>ortho</i> -Cl
6b	<i>ortho</i> -Me	7b	<i>meta</i> -F	8b	<i>meta</i> -Cl
6c	<i>para</i> -Me	7c	<i>para</i> -F	8c	<i>para</i> -Cl
				9a	<i>ortho</i> -Br
				9b	<i>para</i> -Br
				10a	<i>ortho</i> -I
				10b	<i>para</i> -I

Scheme 3. Synthesis of the (α -diimine)nickel dibromide complexes **6a–10b**.

Fig. 4. Molecular structure of **10a**.

the separation of the oligomers and the polymers, the polymerization mixture was filtered and the remaining polymer was washed with half concentrated hydrochloric acid in order to remove MAO. After that it 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. 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 as the border line.

A comparison of the observed activities reveals that complexes bearing the same substituent only in different positions of the aryl moiety show the highest activities if the substituent is located in the *ortho*-position (Fig. 5).

Only the fluorine containing complexes **7a**, **7b** and **7c** show a different behavior. There, **7c** with a *para*-fluorine substituent provides the highest activity. It can be assumed that two effects are responsible for the activity. An *ortho*-substituent interacts with the catalytic center via the axial coordination sites of the metal. Therefore, halogens in that position seem to stabilize the active species. Especially **10a** with two iodine atoms suits into that theory and provides the highest activity of the catalysts studied here. The other effect can be related to the electronic conditions of the complex. If the electron density at the

metal center is comparatively low, the coordination of the monomer is favored. In **7c** with the strong electronegative fluorine substituent in *para*-position, this electronic effect superimposes the *ortho*-effect of the corresponding *ortho*-substituted complex **7a**. In case of fluorine substituents, the low steric demands of the fluorine atom additionally do not cause an intensive interaction of these substituents with the metal center. Therefore, it can be concluded that the activity of (α -diimine)nickel(II) catalysts of this type is a correlation between electronic and steric effects caused by the substituents at the aryl moiety of the ligand.

In this context, the formation of oligomers and polymers also can be explained. The obtained oligomer/polymer ratios are shown in Fig. 6.

According to the "chain running mechanism" the formation of oligomers depends on the number of chain transfers. After a coordinated higher olefin has been formed, it has to be replaced by an ethylene molecule. For this replacement, the axial coordination sites of the metal are decisive. If they are sterically hindered by a substituent, chain transfer is suppressed and polymer is produced. Therefore, the unsubstituted complex **6a** is only able to dimerize ethylene to butene. Higher olefins can only be detected in slight traces. The fluorine substituted complexes **7a**, **7b** and **7c** and the complexes with substituents in the *meta*- or *para*-position (**6c**, **8b**, **8c**, **9b**, **10b**) produce

Table 1
Selected bond lengths and angles of the molecular structure of **10a**

Bond lengths (Å)	
Ni–N(1)	2.061 (5)
Ni–O	2.076 (4)
Ni–N(2)	2.081 (5)
Ni–Br(2)	2.4137 (10)
Ni–Br(1)	2.4415 (10)
N(1)–C(1)	1.277 (7)
N(2)–C(2)	1.275 (7)
C(1)–C(2)	1.496 (8)
Bond angles (°)	
N(1)–Ni–O	154.98 (19)
N(1)–Ni–N(2)	77.56 (19)
O–Ni–N(2)	85.25 (19)
N(1)–Ni–Br(2)	97.55 (14)
O–Ni–Br(2)	92.24 (14)
N(2)–Ni–Br(2)	159.57 (14)
N(1)–Ni–Br(1)	95.79 (13)
O–Ni–Br(1)	103.07 (13)
N(2)–Ni–Br(1)	92.55 (14)
Br(2)–Ni–Br(1)	107.75 (4)
C(1)–N(1)–C(5)	118.7 (5)
C(1)–N(1)–Ni	116.0 (4)
C(5)–N(1)–Ni	125.3 (4)
C(2)–N(2)–C(11)	120.7 (5)
C(2)–N(2)–Ni	114.6 (4)
C(11)–N(2)–Ni	124.0 (4)
N(1)–C(1)–C(2)	115.0 (5)
N(1)–C(1)–C(4)	125.8 (5)
C(2)–C(1)–C(4)	119.1 (5)
N(2)–C(2)–C(1)	115.6 (5)
N(2)–C(2)–C(3)	125.7 (6)
C(1)–C(2)–C(3)	118.7 (5)

oligomers with an even carbon number up to ca. 50 carbon atoms. The GC-plot of the oligomer mixture produced with **7c**/MAO is shown in Fig. 7.

The catalysts bearing a substituent in the *ortho*-position of the aryl moiety produce polymers to a certain extent. The amount of polymer is closely related to the bulk of the substituent. Therefore, **10a** with the most bulky iodine substituents only forms a polymer with an average molecular weight of 36,000 g/mol. The oligomer mixtures obtained with **6b**, **8a** and **9a** are viscous oils or waxes. Compared to the oligomers produced with the other catalysts, olefins with higher carbon numbers are dominating. This can easily be seen in the GC-plot of the oligomer mixture produced with **6b**/MAO (Fig. 8).

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 and are insoluble in pentane.

Based on the GC analyses of the oligomer mixtures, it is possible to calculate the Schulz–Flory-constant α [40–43] for the distribution of the oligomer fractions. For this calculation, the area integrals of the oligomer fractions with a carbon number from 10 to 30 were used. Due to the formation of both isomers of the olefins and polymers, the values of α imply a statistical error especially in the cases of **6b** and **9a** were $\alpha \geq 1$. All values of α are included in Table 2.

Beside activity and oligomer/polymer ratio, also the selectivity for the formation of α -olefins depends on the nature and the position of the substituents at the aryl moiety of the ligands. For a quantitative discussion, the selectivity towards 1-octene was examined. The results are summarized in Fig. 9.

Whereas in the case of the fluorine substituted complexes **7a**, **7b** and **7c**, no influence of the position of the fluorine atoms on the oligomer/polymer ratio could be observed. A view on the selectivity to α -olefins reveals certain dependencies: The *para*-substituted complex **7c** shows almost no selectivity. In turn from *meta*- (**7b**) to *ortho*-substitution (**7a**), the selectivity for 1-octene is rising nearly linear. This trend can also be observed for **6b** and **6c**. For the other catalyst precursors, no such relations can be determined because they produce too little octene or only polymers.

An explanation for this behavior is rather difficult. According to the “chain running mechanism”, the formation of α -olefins should be favored. A high selectivity for these products, however, is only observed under comparatively high polymerization pressures [24]. Under these conditions, the monomer concentration is sufficient to replace the formed olefin in a chain transfer reaction before a double bond isomerization takes place. Therefore, complexes with an easily accessible catalytic center should produce mainly α -olefins. But in the case of *para*- and *meta*-substituted catalysts, the selectivity is very low. Only *ortho*-substituted catalysts are able to oligomerize ethylene to α -olefins with good selectivity. It can be assumed that the isomerization of the olefins proceeds via a mechanism that includes the axial coordination sites of the metal center. If these coordination sites are sterically hindered by an *ortho*-substituent of the ligand, the isomerization step is suppressed.

Table 2

Results of the homogeneous ethylene polymerization for the (α -diimine)nickel(II) complexes **6a–10b** activated with MAO^a

No.	Activity ^b	TOF ^c	Polymer share (wt.%)	α ^d	1-Octene ^e	M_w (polymer share) (g/mol)	D ^f
6a	822	30,825	0	–	0	–	–
6b	869	32,588	41	1.00	37.6	69,000	3.0
6c	464	17,400	<1	0.64	30.8	n.d. ^g	n.d.
7a	939	35,213	<1	0.65	47.7	n.d.	n.d.
7b	499	18,713	0.7	0.66	26.4	n.d.	n.d.
7c	1843	69,113	<1	0.68	7.6	n.d.	n.d.
8a	1702	63,825	22	n.d.	n.d.	6,700	1.3
8b	1321	49,538	1.2	0.72	12.8	n.d.	n.d.
8c	505	18,938	3.1	0.65	25.8	n.d.	n.d.
9a	733	27,488	27	1.22	n.d.	18,460	1.6
9b	587	22,013	1.1	0.54	34.5	n.d.	n.d.
10a	3991	149,663	100	n. d.	–	35,870	23.6
10b	1056	39,600	4.2	0.67	49.3	n.d.	n.d.

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

^b The activities [g (product)/mmol (Ni)·h] were calculated from the total consumption of ethylene (1.01 ethylene = 1.2 g product).

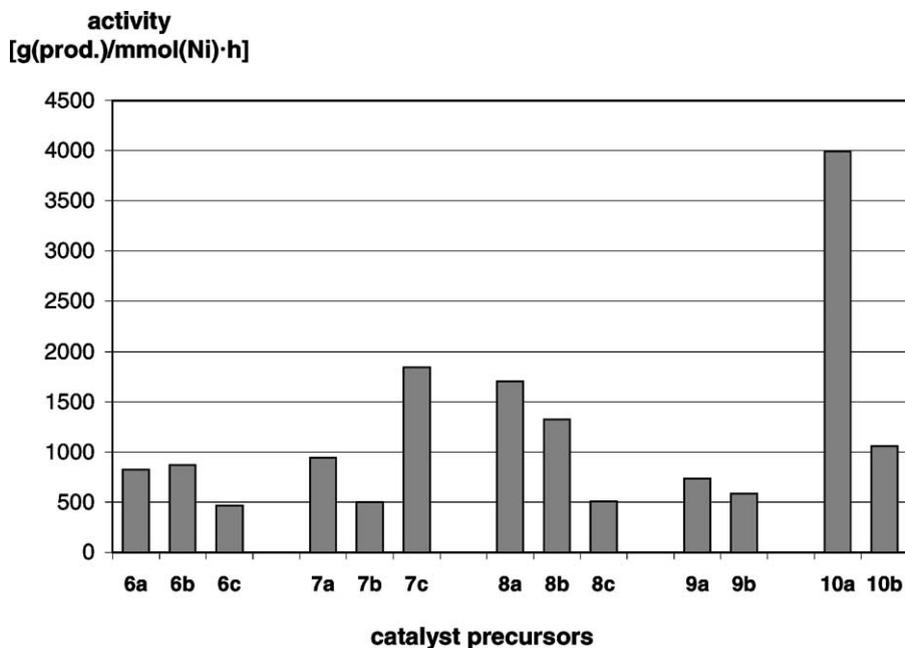
^c TOF [mol(C₂H₄)/mol(cat.)·h]: turn over frequency.

^d $\alpha = \frac{k_p}{(k_p + k_{ct})} = \frac{\text{rate of propagation}}{\text{rate of propagation} + \text{rate of chain transfer}} = \text{Schulz-Flory-constant}$.

^e 1-Octene share (mol%) of all octene isomers.

^f D : polydispersity M_w/M_n of the polymer share.

^g n.d.: not determined.

Fig. 5. Comparison of the observed activities of the catalyst precursors **6a–10b**.

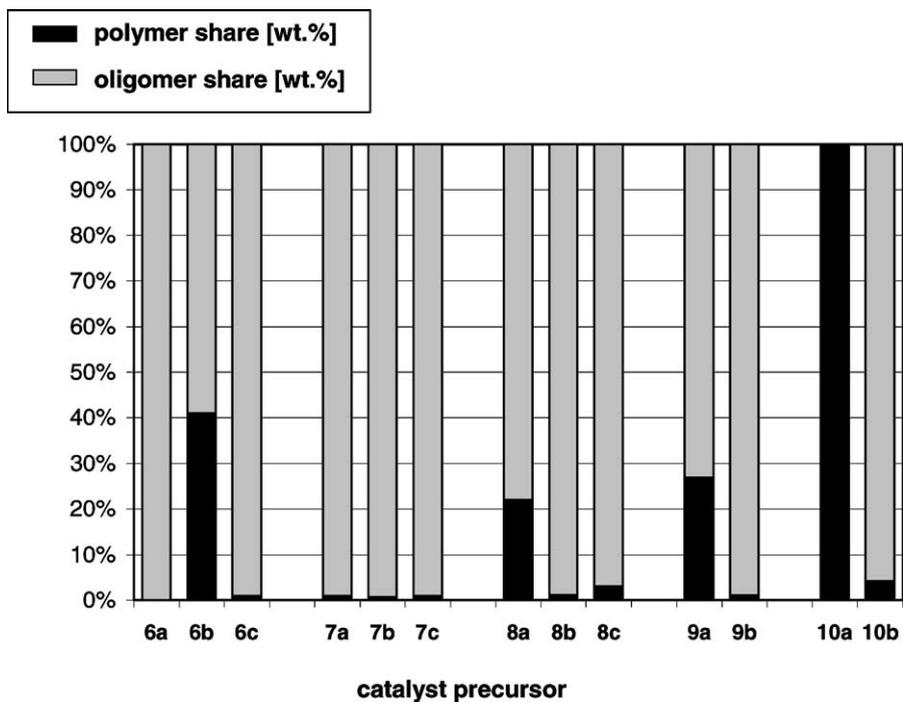


Fig. 6. Oligomer/polymer ratio obtained with the catalyst precursors 6a–10b.

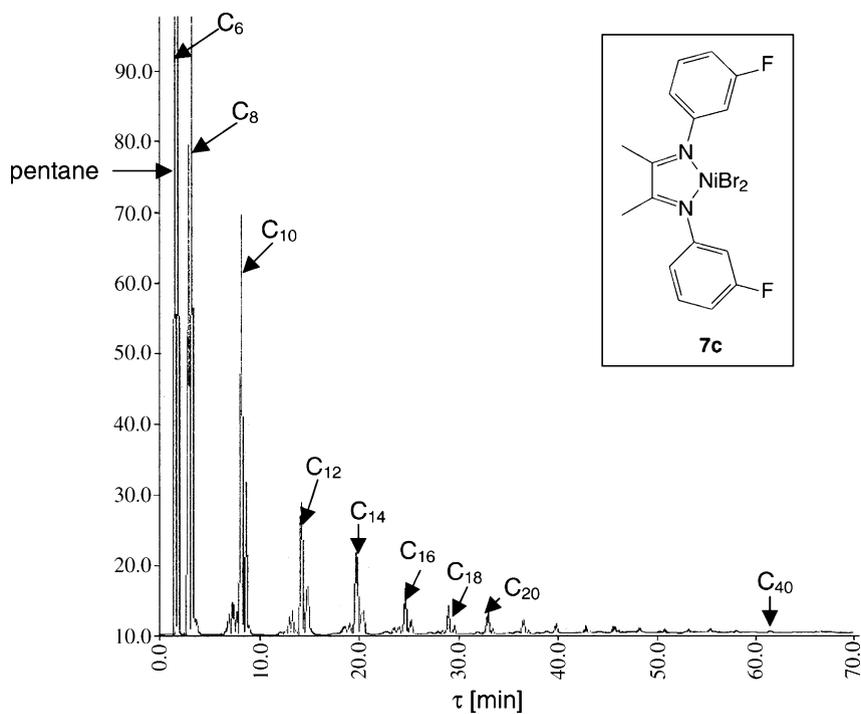
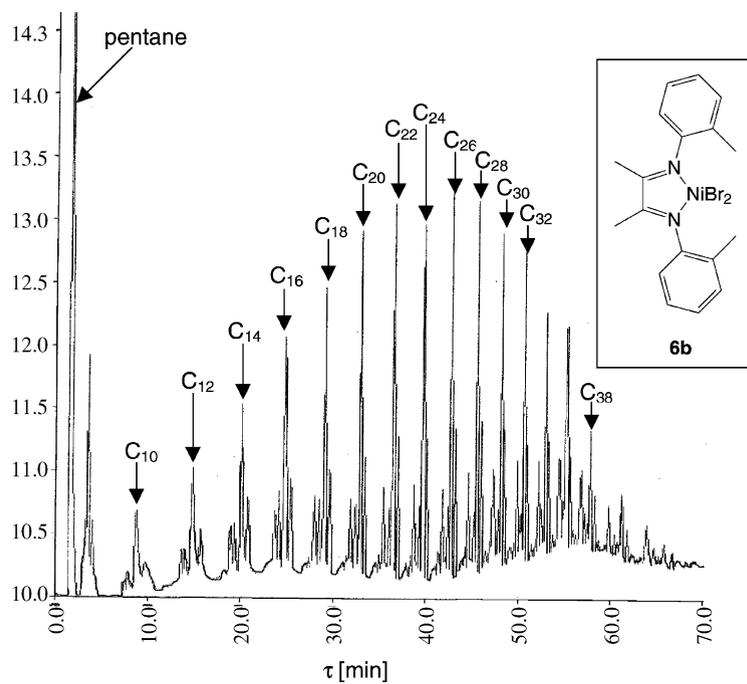
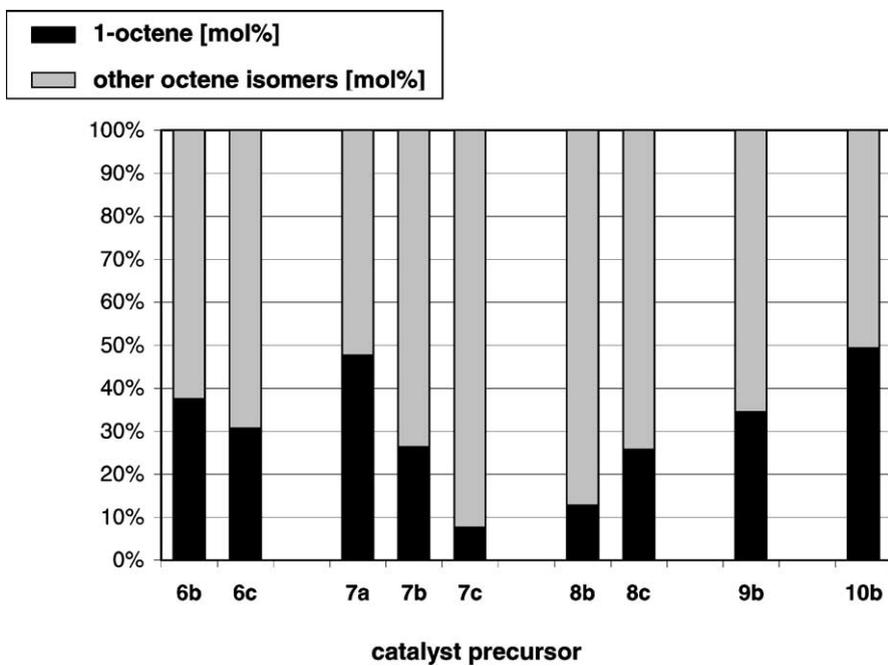


Fig. 7. Oligomer mixture obtained with 7c/MAO.

Fig. 8. Oligomer mixture obtained with **6b**/MAO.Fig. 9. Selectivity for the formation of 1-octene in the case of **6b**, **6c**, **7a**, **7b**, **7c**, **8b**, **8c**, **9b**, **10b**.

Over all, the selectivity of the examined catalysts to α -olefins is in all cases lower than 50%.

3. Experimental

NMR spectroscopic investigations were performed with a Bruker ARX 250 instrument. All organometallic 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 150 C HT-GPC with refractometric detection (RI Waters 401). The polymer samples were dissolved in 1,2,4-trichlorobenzene (flow rate 1 ml/min) 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).

The temperature program is as follows.

Starting phase: 3 min at 50 °C.

Heating phase: 5 °C/min (15 min).

Plateau phase: 310 °C (15 min).

Methylaluminumoxane was supplied by Witco GmbH, 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 α -diimine ligands **1a–5b**

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 reac-

tion 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**, 80%; **1b**, 65%; **1c**, 70%; **2a**, 45%; **2b**, 45%; **2c**, 65%; **3a**, 75%; **3b**, 25%; **3c**, 60%; **4a**, 30%; **4b**, 55%; **5a**, 70%; **5b**, 80%.

All compounds were characterized by NMR spectroscopy (Table 3).

3.2. General synthesis procedure for the (α -diimine)nickel dibromide complexes **6a–10b**

A concentration of 5 mmol of the respective α -diimine ligand were dissolved in 150 ml THF and 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: **6a**, 95%; **6b**, 90%; **6c**, 90%; **7a**, 85%; **7b**, 90%; **7c**, 90%; **8a**, 85%; **8b**, 80%; **8c**, 85%; **9a**, 80%; **9b**, 90%; **10a**, 85%; **10b**, 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: **6a**, 205 °C; **6b**, 200 °C; **6c**, 205 °C; **7a**, 210 °C; **7b**, 200 °C; **7c**, 210 °C; **8a**, 220 °C; **8b**, 210 °C; **8c**, 210 °C; **9a**, 240 °C; **9b**, 230 °C; **10a**, 220 °C; **10b**, 230 °C.

The purity of complexes **7c** and **9b** was tested by microanalyses: **7c**, C = 41.36% ($C_{\text{calc.}} = 39.16\%$), H = 4.62% ($H_{\text{calc.}} = 2.88\%$); **9b**, C = 29.55 ($C_{\text{calc.}} = 31.37$), H = 2.75 ($H_{\text{calc.}} = 2.30$).

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

An amount of 5–10 mg of the complex were suspended in toluene and activated with the correspond-

Table 3
NMR data for compounds **1a–5b**

No.	¹ H NMR ^a	¹³ C NMR ^b
1a	7.29 (m, 4H), 7.06 (m, 2H), 6.85 (m, 4H), 2.19 (s, 6H)	C _q : 168.3, 150.9; CH: 129.0, 123.8, 118.7; CH ₃ : 15.4
1b	7.12 (m, 8H), 6.93 (dt, 2H, ³ J _{HH} = 7.5 Hz, ⁴ J _{HH} = 1.2 Hz), 6.55 (dd, 2H, ³ J _{HH} = 7.8 Hz, ³ J _{HH} = 0.9 Hz), 2.03 (s, 6H)	C _q : 167.7, 149.5, 126.7; CH: 130.4, 126.4, 123.9, 117.6; CH ₃ : 17.8, 15.6
1c	7.16 (m, 4H), 6.68 (m, 4H), 2.34 (s, 6H), 2.15 (s, 6H)	C _q : 168.3, 148.3, 133.2; CH: 129.5, 118.8; CH ₃ : 20.8, 15.3
2a	6.85 (m, 8H), 2.24 (s, 6H)	C _q : 170.2, 151.3 (d, ¹ J _{CF} = 239 Hz), 128.5; CH: 124.8 (d, ³ J _{CF} = 7 Hz), 124.0, 121.2, 115.7 (d, ² J _{CF} = 20 Hz); CH ₃ : 15.4
2b	7.20 (m, 2H), 6.70 (m, 2H), 6.42 (m, 4H), 2.02 (s, 6H)	C _q : 168.7, 163.3 (d, ¹ J _{CF} = 247 Hz), 152.5 (d, ³ J _{CF} = 9 Hz); CH: 130.3 (d, ³ J _{CF} = 9 Hz), 114.3, 110.5 (d, ² J _{CF} = 21 Hz), 106.1 (d, ² J _{CF} = 23 Hz); CH ₃ : 15.4
2c	7.05 (m, 4H), 6.73 (m, 4H), 2.13 (s, 6H)	C _q : 168.7, 159.7 (d, ¹ J _{CF} = 242 Hz), 146.7; CH: 120.3 (d, ³ J _{CF} = 8 Hz), 115.7 (d, ² J _{CF} = 23 Hz); CH ₃ : 15.4
3a	7.46 (dd, 2H, ³ J _{HH} = 8.0 Hz, ⁴ J _{HH} = 1.2 Hz), 7.29 (dt, 2H, ³ J _{HH} = 7.5 Hz, ⁴ J _{HH} = 1.2 Hz), 7.09 (dt, 2H, ³ J _{HH} = 9.3 Hz, ⁴ J _{HH} = 1.5 Hz), 6.84 (dd, 2H, ³ J _{HH} = 9.2 Hz, ⁴ J _{HH} = 1.4 Hz), 2.19 (s, 6H)	C _q : 168.5, 144.1, 122.3; CH: 129.7, 127.1, 124.6, 119.5; CH ₃ : 15.9
3b	7.25 (m, 2H), 6.74 (m, 2H), 6.35 (m, 4H), 2.09 (s, 6H)	C _q : 168.5, 146.1, 121.3; CH: 126.7, 125.1, 124.6, 115.5; CH ₃ : 15.5
3c	7.31 (m, 4H), 6.70 (m, 4H), 2.11 (s, 6H)	C _q : 168.7, 149.2, 129.3; CH: 129.1, 120.2; CH ₃ : 15.4
4a	7.63 (dd, 2H, ³ J _{HH} = 8.0 Hz, ⁴ J _{HH} = 1.3 Hz), 7.33 (dt, 2H, ³ J _{HH} = 7.6 Hz, ⁴ J _{HH} = 1.3 Hz), 6.97 (dt, 2H, ³ J _{HH} = 7.9 Hz, ⁴ J _{HH} = 1.6 Hz), 6.80 (dd, 2H, ³ J _{HH} = 7.9 Hz, ⁴ J _{HH} = 1.6 Hz), 2.16 (s, 6H)	C _q : 169.5, 149.1, 113.1; CH: 132.9, 128.0, 125.1, 119.4; CH ₃ : 16.2
4b	7.42 (m, 4H), 6.61 (m, 4H), 2.11 (s, 6H)	C _q : 169.4, 149.8, 114.3; CH: 130.2, 122.5; CH ₃ : 15.3
5a	7.86 (dd, 2H, ³ J _{HH} = 7.9 Hz, ⁴ J _{HH} = 1.3 Hz), 7.34 (dt, 2H, ³ J _{HH} = 7.6 Hz, ⁴ J _{HH} = 1.3 Hz), 6.83 (dt, 2H, ³ J _{HH} = 7.8 Hz, ⁴ J _{HH} = 1.6 Hz), 6.74 (dd, 2H, ³ J _{HH} = 7.8 Hz, ⁴ J _{HH} = 1.4 Hz), 2.16 (s, 6H)	C _q : 169.2, 151.9, 88.9; CH: 139.0, 128.9, 125.4, 118.3; CH ₃ : 16.2
5b	7.65 (m, 4H), 6.53 (m, 4H), 2.10 (s, 6H)	C _q : 168.5, 150.4, 87.5; CH: 138.0, 120.9; CH ₃ : 15.4

^a 250.13 MHz, 25 °C, in chloroform-d₁, δ [ppm] rel. chloroform (7.24).

^b 62.9 MHz, 25 °C, in chloroform-d₁, δ [ppm] rel. chloroform-d₁ (77.0).

Table 4
Mass spectrometric data of complexes **6a–10b**

No.	Fragment (m/z) (intensity (%))
6a	M ⁺ = 455 (2), 375 (10), 236 (100), 118 (100), 77 (85)
6b	M ⁺ = 481 (4), 402 (8), 264 (42), 249 (100), 132 (100), 91 (100)
6c	M ⁺ = 481 (1), 402 (7), 264 (38), 249 (23), 131 (100), 91 (55)
7a	M ⁺ (-Br) = 411 (3), 321 (10), 272 (90), 253 (30), 135 (100), 95 (90)
7b	M ⁺ (-Br) = 411 (1), 321 (5), 272 (80), 253 (4), 135 (100), 95 (95), 75 (48)
7c	M ⁺ = 491 (2), 410 (5), 272 (45), 161 (60), 156 (35), 135 (100), 111 (95), 95 (70)
8a	M ⁺ (-Br) = 445 (1), 409 (2), 374 (3), 315 (8), 304 (2), 269 (85), 152 (100), 111 (40)
8b	M ⁺ = 525 (4), 443 (5), 394 (6), 350 (30), 304 (100), 269 (25), 198 (23), 152 (100), 111 (95), 75 (20)
8c	M ⁺ (-Br) = 445 (2), 350 (5), 304 (25), 269 (8), 152 (100), 111 (20)
9a	M ⁺ = 612 (4), 533 (4), 394 (5), 312 (90), 233 (15), 196 (100), 154 (28)
9b	M ⁺ = 612 (3), 532 (10), 451 (4), 394 (90), 312 (80), 195 (100), 154 (95), 117 (75), 84 (80), 76 (85)
10a	M ⁺ (-Br, -I) = 503 (4), 429 (8), 361 (100), 244 (95), 203 (45), 76 (55)
10b	M ⁺ (-Br) = 626 (2), 488 (20), 442 (15), 361 (10), 244 (100), 203 (15), 117 (15)

ing 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.

3.4. Homogeneous ethylene polymerization

The activated complex was added to a 1l steel autoclave (Büchi), filled with 250 ml of *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 1 h, 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 weighed. After removing *n*-pentane by distillation over a Vigreux column, the obtained oligomers were analyzed by GC.

3.5. X-ray analysis

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

C₁₉H₂₀Br₂I₂N₂NiO (**10a**): orange-red prism of the dimension 0.20 mm \times 0.17 mm \times 0.08 mm crystallized in diethylether/acetone; monoclinic; space group: *P*2(1)/*c*; *a* = 10.7504(6) \AA , *b* = 14.1471(7) \AA , *c* = 16.2055(9) \AA , $\beta = 101.181(5)^\circ$, *Z* = 4, $d_{\text{calc.}} = 2.101 \text{ Mg/m}^3$, absorption coefficient: 6.672 mm^{-1} , min/max transmission coefficients: 0.7070/0.2253, *F*(000) = 1440, measured reflections: 5122, independent reflections: 4059, goodness-of-fit: 1.013, *R* = 3.80%.

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-194008. 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, *Isr. 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. 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.
- [5] M. Peuckert, W. Keim, *Organometallics* 2 (1983) 594.
- [6] U. Klabunde, S.D. Ittel, *J. Mol. Catal.* 41 (1987) 123.
- [7] 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.
- [8] 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.
- [9] K.A. Ostoja Starzewski, J. Witte, H. Bartl, *Eur. Pat. Appl. EP 101,927 A1 19,840,307* (1984).
- [10] W. Keim, R.S. Bauer, H. C.Chung, P. Glockner, *US Patent 3,635,937* (1969).
- [11] W. Keim, R.F. Mason, P. Glockner, *US Patent 3,647,914* (1972); W. Keim, R.F. Mason, P. Glockner, *Eur. Chem. News* 16 (1977) 60.
- [12] A. Behr, W. Keim, *Arabian J. Sci. Eng.* 10 (1985) 377.
- [13] B. Reuben, H. Wittcoff, *J. Chem. Ed.* 65 (1988) 605.
- [14] E.F. Lutz, *J. Chem. Ed.* 63 (1986) 202.
- [15] H. tom Dieck, M. Svoboda, *Chem. Ber.* 109 (1976) 1657.
- [16] H. tom Dieck, M. Svoboda, *Z. Naturforsch. B* 33 (1978) 1381.
- [17] M. Svoboda, H. tom Dieck, *J. Organomet. Chem.* 191 (1980) 321.
- [18] H. tom Dieck, M. Svoboda, T. Greiser, *Z. Naturforsch. B* 36 (1981) 814.
- [19] 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.
- [20] D.P. Gates, S.A. Svejda, E. Onate, C.M. Killian, L.K. Johnson, P.S. White, M. Brookhart, *Macromolecules* 33 (2000) 2320.
- [21] S.A. Svejda, L.K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* 121 (1999) 10634.

- [22] 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 Pat. Appl. US 5,880,241 (1999).
- [23] S.A. Svejda, M. Brookhart, *Organometallics* 18 (1999) 65.
- [24] C.M. Killian, L.K. Johnson, M. Brookhart, *Organometallics* 16 (1997) 2005.
- [25] 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.
- [26] C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* 118 (1996) 11664.
- [27] M. Brookhart, L.K. Johnson, C.M. Killian, S. Mecking, D.J. Tempel, *Polym. Prep. Am. Chem. Soc., Div. Polym. Chem.* 37 (1996) 254.
- [28] L.K. Johnson, M. Christopher, M. Brookhart, *J. Am. Chem. Soc.* 117 (1995) 6414.
- [29] T. Schleis, T.P. Spaniol, J. Okuda, J. Heinemann, R. Mülhaupt, *J. Organomet. Chem.* 569 (1998) 159.
- [30] D. Pappalardo, M. Mazzeo, C. Pelleccia, *Macromol. Rapid Commun.* 18 (1997) 1017.
- [31] C. Pelleccia, A. Zambelli, M. Mazzeo, D. Pappalardo, *J. Mol. Catal. A* 128 (1998) 229.
- [32] A. Köppl, H.G. Alt, *J. Mol. Catal. A* 154 (2000) 45.
- [33] G.B. Galland, R.F. de Souza, R.S. Mauler, F.F. Nunes, *Macromolecules* 32 (1999) 1620.
- [34] Z. Zeng, K. Zetterberg, *Macromol. Chem. Phys.* 199 (1998) 2677.
- [35] D.J. Tempel, L.K. Johnson, R.L. Huff, P.S. White, M. Brookhart, *J. Am. Chem. Soc.* 122 (2000) 6686.
- [36] L. Deng, T. Woo, L. Cavallo, P.M. Margl, T. Ziegler, *J. Am. Chem. Soc.* 119 (1997) 6177.
- [37] L. Deng, P.M. Margl, T. Ziegler, *J. Am. Chem. Soc.* 119 (1997) 1094.
- [38] L.G.L. Ward, *Inorg. Synth.* 13 (1972) 154.
- [39] R. van Asselt, C.J. Elsevier, W.J.J. Smeets, A.L. Spek, R. Benedix, *Recl. Trav. Chim. Pays-Bas* 113 (1994) 88.
- [40] G.V. Schulz, *Z. Phys. Chem. B* 30 (1935) 379.
- [41] G.V. Schulz, *Z. Phys. Chem. B* 43 (1939) 25.
- [42] P.J. Flory, *J. Am. Chem. Soc.* 62 (1940) 1561.
- [43] H. Kehlen, H.T. Rättsch, *Z. Phys. Chem.* 265 (1984) 1049.