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New  $\alpha$ -diimine nickel complexes - synthesis and catalysis of alkene oligomerization reactions

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#### **Graphical abstract**



Synthesis of new Ni<sup>II</sup>  $\alpha$ -diimine complexes **I-III** from substituted anilines, 2,3-butanedione (reaction  $R_a$ ), and NiBr<sub>2</sub> (reaction  $R_b$ ). **I** - R<sub>1</sub>=R<sub>2</sub>=R<sub>4</sub>=R<sub>5</sub>=F; R<sub>3</sub>=H; **II** - R<sub>1</sub>=CF<sub>3</sub>; R<sub>2</sub>-R<sub>5</sub>=H; **III** - R<sub>1</sub>=R<sub>3</sub>=CH<sub>3</sub>; R<sub>2</sub>=R<sub>4</sub>=R<sub>5</sub>=H.

Catalysts for oligomerization of ethylene and propylene were produced by activating the complexes with AlEt<sub>2</sub>Cl, Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub>, and with combinations of these compounds and PPh<sub>3</sub>.

## Highlights

"New  $\alpha$ -diimine nickel complexes - synthesis and catalysis of alkene oligomerization reactions" by

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- Three new  $\alpha$ -diimine complexes of Ni are synthesized.
- The complexes are used as catalyst precursors for oligomerization of ethylene and propylene.
- The complexes are activated with AlEt<sub>2</sub>Cl, Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub> and their combinations with PPh<sub>3</sub>.
- The catalysts convert ethylene into liquids and waxes and propylene into light oligomers.

## Abstract

Three  $\alpha$ -diimine complexes of Ni<sup>II</sup> of the general formula {2,3-bis[N,N-(aryl)imino]butane}NiBr<sub>2</sub> with aryl groups 2,3,5,6-F<sub>4</sub>-C<sub>6</sub>H, 2-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub> and 2,4-(CH<sub>3</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub> were synthesized and used as catalyst precursors in oligomerization reactions of ethylene and propylene. Oligomerization catalysts were produced by activating the complexes with AlEt<sub>2</sub>Cl, Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub>, and with combinations of these compounds and PPh<sub>3</sub>. The catalysts convert ethylene into low molecular-weight materials (liquids and waxes) with oligomer chains containing 15-20 mol.% of methyl branches and 4-6 mol.% of ethyl branches, which are apparently produced in "chain-walking" reactions of active centers along oligomer chains. Oligomerization of propylene yields a variety of light products, mostly dimers, which are formed in primary and secondary insertion reactions of propylene into Ni–H and Ni–C bonds in active centers. Reaction schemes of oligomer formation are discussed.

KEYWORDS: Nickel complexes;  $\alpha$ -diimine ligand; oligomerization, alkenes; ethylene, oligomerization; propylene, oligomerization

## 1. Introduction

At the present time, the leading research area in the field of catalytic alkene polymerization is postmetallocene catalysis, studies of homogeneous polymerization catalysts based on multidentate complexes of early- and late-period transition metals. Some of the most interesting among them are complexes of Pd<sup>II</sup> and Ni<sup>II</sup> containing bulky  $\alpha$ -diimine ligands with a particular substitution pattern in their aryl rings which restricts access to the transition metal atom (Scheme 1, these complexes are abbreviated below as **DiiM**):

When *DiiM* complexes of Ni<sup>II</sup> containing two *o*,*o*-disubstituted aryl groups are combined with organoaluminum compounds, such as methylalumoxane or AlR'<sub>x</sub>Cl<sub>3-x</sub> (R'=Me, Et, etc., *x*=1 or 2), they form extremely active catalysts for ethylene polymerization; their productivity at moderate temperatures approaches 200 kg/g Ni·h. A unique feature of the catalysts is their ability to form branched polyethylene chains [1-5].

Polymerization reactions of propylene with *DiiM* complexes under ambient conditions produce polymers of radically different nature depending on the temperature and the type of the substituents R. At low temperatures, the catalysts polymerize propylene to a syndiotactic polymer [6] but the products formed at higher temperatures vary from mostly regioregular polymers to highly branched materials with a chain structure bearing no resemblance to "normal" polypropylene.

This article discusses two subjects:

1. Synthesis of Ni<sup>II</sup> complexes LNiBr<sub>2</sub> (**I** - **III** in Scheme 2) containing three new types of  $\alpha$ -diimine ligands L with the substitution pattern in the aryl rings different from that in *DiiM* complexes:

LI - 2,3-bis[N,N-(2,3,5,6-tetrafuorophenyl)imino]butane

LII - 2,3-bis[N,N-(2-trifluoromethylphenyl)imino]butane

LIII - 2,3-bis[N,N-(2,4-dimethylphenyl)imino]butane

2. Oligomerization reactions of ethylene and propylene with catalysts based on complexes I - III.

The aryl-ring substitution in the *L* ligands provides an easier access of alkene molecules to the Ni atom in active centers derived from the complexes and a larger volume for reorganization of Ni-alkyl species. Complexes **I** - **III** were converted into catalysts with two types of activators (cocatalysts in the terminology of alkene polymerization catalysis); organoaluminum compounds  $AlEt_2Cl$  and  $Al_2Et_3Cl_3$ , and combinations of these compounds and PPh<sub>3</sub>.

## 2. Experimental

#### 2.1. Chemicals

Ethylene and propylene (polymerization grade, 99.9%) were purchased from Moscow Oil Refinery. AlEt<sub>2</sub>Cl (0.8 M heptane or toluene solution), Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub> (1M toluene solution) and PPh<sub>3</sub> were purchased from Acros. Chemicals used for the synthesis of complexes **I** - **III** (NiBr<sub>2</sub>, 2,3,5,6-tetrafluoroanilin, 2trifluoromethylanilin, 2,4-dimethylanilin, *p*-toluenesulfonic acid and 2,3-butanedione) were purchased from Aldrich. Purification of chemicals for the synthesis of complexes **I** - **III** is described in ref. [7]. All manipulations with air-sensitive materials were performed in Schlenk glassware on a dual manifold Schlenk line. Toluene used in oligomerization reactions (analytic grade) was boiled over sodium wire and distilled in an argon flow.

## 2.2. Oligomerization reactions

Ethylene oligomerization reactions were carried out in a 100-mL stainless-steel autoclave equipped with a mechanical stirrer and a temperature controller. Conditions of the reactions are given in Table 1. Toluene, a specified amount of an organoaluminum activator, and toluene solution of a Ni complex were added to the reactor to a total volume of 50 mL under ethylene atmosphere. Once a reaction temperature (30 °C) was reached, ethylene pressure was increased to 3 atm and was maintained at this level during 30-min reactions. The reactions were stopped by cooling the reactor in an ice bath followed by release of excess pressure. The reaction volume was quenched with HCl/ethanol (5%) and then the mixture was separated into a liquid and wax.

Propylene oligomerization reactions were carried out in a 200-mL stainless steel reactor in liquid propylene. Details of the oligomerization procedure are described in ref. [8]. The reaction conditions are given in Table 3. An organoaluminum activator and PPh<sub>3</sub> were added to the propylene-filled reactor, after which a glass ampoule with a Ni complex was broken inside the reactor with a mechanical device. Oligomers and the unreacted monomer were collected in a glass trap cooled with liquid nitrogen and then propylene was slowly released by warming the trap. The reaction products were washed with a 10% HCl/ethanol mixture and water.

To compare catalyst activity in oligomerization reactions of ethylene and propylene, catalyst productivities per mole of Ni were normalized to monomer concentrations,  $C_{\rm E}$  and  $C_{\rm Pr}$  (M).

## 2.3. Oligomer Analysis

GC analysis of oligomers was carried out on a gas chromatograph "Trace GC ultra" equipped with a RTX-5ms capillary column (0.25 mm, length 30 m) and connected to a mass spectrometer Finnegan Polaris Q (ion trap, EI, 70 eV, mass range 33 -1000 atm). The injector temperature was 270 °C, the column temperature was held at 90 °C for 4 min and then increased at a rate of 10 °C/min to 320 °C.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AMX-400 spectrometer at 20 °C in *ortho*dichlorobenzene or in chloroform as solvents using TMS as an internal standard. The signal assignment in NMR spectra was carried out according to refs. [5-7,9,10]. IR spectra of complexes **I** - **III** were recorded on a Magna-IR 750 spectrophotometer and those of oligomers on a Bruker Tensor 27 FTIR spectrometer.

## 3. Results

## 3.1. Synthesis of Ni complexes I - III

Synthesis of complexes **I** - **III** was carried out in two steps according to Scheme 3: synthesis of  $\alpha$ -diimine ligands *L***I** - *L***III** via condensation of two equivalents of a substituted aniline with one equivalent of 2,3-butanedione (Reaction  $R_a$ ) and reactions of the ligands with NiBr<sub>2</sub> (Reaction  $R_b$ ).

#### 3.1.1. Synthesis of ligands LI - LIII

The synthesis of ligand *LI* is described in ref. [7].

*Ligand* **LII**, 2,3-bis[N,N-(2-trifluoromethylphenyl)imino]butane. In a 250 mL Schlenk flask, 2.2 equiv. of 2-trifluoromethylaniline were dissolved in 150 mL of toluene and a catalytic amount of *p*-toluenesulfonic acid monohydrate (0.06 equiv.) was added. One equiv. of 2,3-butanedione was added to the flask dropwise. After refluxing the mixture for 40 h, the solvent was removed under vacuum. The crude product was dissolved in methylene chloride and precipitated with methanol. A yellow product was filtered and dried under vacuum. Analysis: calc. for  $C_{18}H_{14}F_6N_2$  (372.31): C 58.07, H 3.79, N 7.52, F 30.62%; found C 58.01, H 3.64, N 7.22, F 39.81%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.74 (d, J=7.8 Hz, 2H), 7.59 (t, J=7.6 Hz, 2H), 7.26 (t, J=7.7 Hz, 2H), 6.83 (d, J=7.9 Hz, 2H), and 2.18 ppm (s, 6H). <sup>19</sup>F NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = -62.44 ppm (s, 6F); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  170.01, 150.07, 133.18, 126.94, 125.91, 124.84, 124.39, 123.02, 119.93, 118.51, 77.16, 16.93 ppm. M.p. 152-153 °C. *Ligand* **LIII**, 2,3-bis[N,N-(2,4-dimethylphenyl)imino]butane. It was obtained in a similar procedure from 2,4-dimethylaniline. Analysis: calc. for  $C_{20}H_{24}N_2$  (292.42): C 82.15, H 8.27, N 9.58%; found C 82.00, H 8.01, N 9.39%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.26, 7.21, 7.19, 6.75, 6.73, 2.52, 2.29 ppm. <sup>13</sup>C NMR (101 MHz, THF):  $\delta$  165.69, 145.28, 130.98, 128.96, 124.67, 115.48, 22.17, 21.73, 18.07, 15.26, 12.54 ppm. M.p. 131-132 °C (cryst. from ethanol).

3.1.2. Synthesis of complexes I - III

Complexes **I** - **III** were prepared from ligands LI - LIII and NiBr<sub>2</sub> (Reaction  $R_b$  in Scheme 3). All the syntheses were carried out in methanol and the complexes were crystallized from a THF/methanol mixture.

*Complex* I, {2,3-bis[N,N-(2,3,5,6-tetrafluorophenyl)imino]butane}NiBr<sub>2</sub>. Anhydrous NiBr<sub>2</sub> (0.22 g, 1.00 mmol) and *L*I (0.38 g, 1.00 mmol) were combined in a Schlenk flask under argon. Methanol (20 mL) was added and the reaction mixture was refluxed for 24 h. The resulting suspension was filtered and complex I was recrystallized from a 1:1 methanol/THF mixture; yield 0.54 g, 79%.

According to the x-ray data [7], complex I crystallizes from a THF/methanol mixture as an ionic dimer  $\{[L_2Ni_2Br_3(H_2O)_2]^+Br^-\}\cdot 3THF$ . It is shown in Scheme 4. The presence of H<sub>2</sub>O molecules in the crystalline complex (most probably, captured from insufficiently dry methanol) indicates significant coordination options for the Ni<sup>II</sup> atom, which are not restricted by the square-plane configuration typical for Ni<sup>II</sup> complexes in general.

Analysis of I: calc. for C<sub>44</sub>H<sub>44</sub>Br<sub>4</sub>F<sub>16</sub>N<sub>4</sub>Ni<sub>2</sub>O<sub>5</sub> (1450): C 36.45, H 3.06, N 3.86, Ni 8.10%; found C 36.40, H 2.94, N 3.81, Ni 8.07%. <sup>1</sup>H NMR (400 MHz, THF):  $\delta$ =7.31-7.27 ppm (t, 2H, ArH), 3.58 (8H, THF), 2.26 ppm (12H, CH<sub>3</sub>), 1.73 ppm (4H, H<sub>2</sub>O). <sup>19</sup>F NMR (400 MHz, THF):  $\delta$ =-82.48, -82.54, -82.57, -94.61, -94.67, -94.70 ppm. <sup>13</sup>C NMR (400 MHz, THF):  $\delta$ =174.13, 147.54, 145.27, 137.92, 135.65, 129.85, 101.40, 101.26, 100.79, 16.38 ppm. IR (KBr): 3150 cm<sup>-1</sup> v(H<sub>2</sub>O), 1660 cm<sup>-1</sup>  $\delta$ (H<sub>2</sub>O), 1627cm<sup>-1</sup> v(C=N).

Syntheses of complexes **II** and **III** were carried out in similar procedures.

*Complex* **II**, {2,3-bis[N,N-(2-trifluoromethylphenyl)imino]butane}NiBr<sub>2</sub>. Analysis: calc. for C<sub>38</sub>H<sub>40</sub>Br<sub>4</sub>F<sub>12</sub>N<sub>4</sub>Ni<sub>2</sub>O<sub>2</sub> (1250): C 36.52, H 3.23, N 4.48, Ni 9.39%; found C 36.40, H 2.94, N 3.81, Ni 8.07%. <sup>1</sup>H NMR (400 MHz, THF):  $\delta$  7.74 ppm (d, J=7.8 Hz, 4H), 7.59 ppm (t, J=7.6 Hz, 4H), 7.26 ppm (t, J=7.7 Hz, 4H), 6.83 ppm (d, J=7.9 Hz, 4H), 2.18 ppm (s, 12H), 1.56 ppm (s, 4H, H<sub>2</sub>O), <sup>19</sup>F NMR (400 MHz, THF):  $\delta$ =-62.44 ppm. <sup>13</sup>C NMR (400 MHz, THF):  $\delta$  170.01, 150.07, 133.18, 126.94, 125.91, 124.84, 124.39, 123.02, 119.93, 118.51, 77.16, 16.93 ppm. IR (KBr): 1640 cm<sup>-1</sup> v(C=N). *Complex* **III**, {2,3-bis[N,N-(2,4-dimethylphenyl)imino]butane}NiBr<sub>2</sub>. Analysis: calc. for C<sub>42</sub>H<sub>60</sub>Br<sub>4</sub>N<sub>4</sub>Ni<sub>2</sub>O<sub>2</sub> (1090): C 46.28, H 5.55, N 5.14, Ni 10.77%; found C 46.12, H 5.31, N 5.05, Ni 10.65%. <sup>1</sup>H NMR (400 MHz, THF):  $\delta$  7.74 ppm (d, J=7.8 Hz, 2H), 7.59 ppm (t, J=7.6 Hz, 2H), 7.26 ppm (t, J=7.7 Hz, 4H), 6.83 ppm (d, J=7.9 Hz, 4H), 2.52 ppm (s, 6H), 2.18 (s, 12H). <sup>13</sup>C NMR (400 MHz, THF):  $\delta$  167.49, 145.28, 130.98, 128.96, 124.67, 115.48, 22.17, 21.73, 18.07, 15.26, 12.54 ppm.

NMR, IR and analytical data showed that crystalline complexes **II** and **III** also have an ionic structure similar to that of complex **I**.

## 3.2. Ethylene oligomerization reactions

### 3.2.1. General results

The principal data on ethylene oligomerization reactions are given in Table 1. Several trends in productivity of the Ni complexes can be traced. When the oligomerization reactions are carried out in the absence of PPh<sub>3</sub>, AlEt<sub>2</sub>Cl and Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub> are nearly equally effective in activating the Ni complexes. Addition of PPh<sub>3</sub> leads to a significant increase of catalyst productivity. The effect is the largest, nearly 4 times, for the **I** - AlEt<sub>2</sub>Cl system, it is two-fold for the **II** - AlEt<sub>2</sub>Cl system but merely ~7% for the **III** - AlEt<sub>2</sub>Cl system. The activating effect of PPh<sub>3</sub> can be possibly explained as due to its ability to form complexes both with the Ni atom in the active centers of oligomerization reactions and with the organoaluminum compounds; this subject is discussed in Section 4.1.

Oligomerization reactions of ethylene yielded mixtures of liquid and waxy products. This fact reflects a broad molecular weight (MW) distribution of the oligomers: the products of sufficiently high MW crystallize in the course of the reactions whereas the low-MW components remain dissolved in the reaction solvent (toluene). Complex I produces active species which yield only low-MW oligomers irrespectively of the activator type. Complex II yields only high-MW oligomers with both organoaluminum compounds in the absence of PPh<sub>3</sub> but mostly low-MW oligomers in the presence of

PPh<sub>3</sub>. In the case of complex **III**, the yields of low-MW and high-MW oligomers are approximately equal both with AlEt<sub>2</sub>Cl and with Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub>; addition PPh<sub>3</sub> noticeably shifts the MW distribution towards low-MW oligomers.

#### 3.2.2. Oligomer structure

The <sup>13</sup>C NMR spectrum of one of the oligomers produced with the **III** - AlEt<sub>2</sub>Cl/PPh<sub>3</sub> system is shown in Fig. 1 (the range of aliphatic carbon atoms).

The main signals in the spectrum belong to linear  $-(CH_2)_n$ - sequences formed in ethylene homooligomerization reaction (signal at 29.8 ppm) and to linear chain-ends  $CH_3$ - $CH_2$ - $CH_2$ - $CH_2$ - $CH_2$ -: the  $CH_3$ signal at 14.1,  $\alpha$ - $CH_2$  22.8,  $\beta$ - $CH_2$  32.1,  $\gamma$ - $CH_2$  29.5 ppm.

The spectrum also contains signals of the following groups:

1. Isolated methyl branches in linear chains, ~CH2-CH2-CH(CH3)-CH2-CH2~

(<sup>13</sup>C NMR: CH<sub>3</sub> 20.1, CH ~ 34.0, α-CH<sub>2</sub> 37.5, β-CH<sub>2</sub> 27.4 ppm; <sup>1</sup>H NMR: CH<sub>3</sub> ~0.85, CH ~1.70, α-CH<sub>2</sub> 1.15 ppm).

2. Isolated ethyl branches in linear chains, ~CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-C

(CH<sub>3</sub> 11.0, branch-CH<sub>2</sub> 26.0, CH 38.5, α-CH<sub>2</sub> 34.3, β-CH<sub>2</sub> 26.9, γ-CH<sub>2</sub> 26.9 ppm).

3. Isolated longer alkyl branches in linear chains (CH<sub>3</sub>  $\sim$ 14,  $\gamma$ -CH<sub>2</sub>  $\sim$ 30.5 ppm).

<sup>13</sup>C NMR spectra also show the presence of the following unsaturated chain-ends:

*Cis*- and *trans*-CH<sub>3</sub>-CH=CH-R in a 1.7:1 ratio (*cis* - 130.0 and 124.4 ppm, *trans* - 131.8 and 123.9 ppm). *Cis*- and *trans*-R'-CH=CH-R" in a ~1.3:1 ratio (*cis* - 131.1 ppm, *trans* - 130.4 ppm).

CH<sub>2</sub>=CH–R (139.1 and 114.2 ppm).

IR analysis of the oligomers confirmed the NMR data. The IR spectra contain strong out-of-plane deformation bands of the *trans*-CH=CH-bond at 966 cm<sup>-1</sup>, the *cis*-CH=CH-bond at ~700 cm<sup>-1</sup>, and weak bands of the CH<sub>2</sub>=CH-bond at 909 and 992 cm<sup>-1</sup> and the CH<sub>2</sub>=CR-bond at 890 cm<sup>-1</sup>.

Table 2 shows several examples of the branching level in ethylene oligomers produced with complex **III**. The branching degree is given as a mole percent of two types of branches, methyl and ethyl, with respect to all ethylene units in oligomer molecules. To decrease uncertainty related to end-groups, the branching was measured in waxes, oligomer fractions with the highest MW. The mechanism of branch formation is described in Section 4.2. The table also contains the data on the average oligomerization degree of the products, which were calculated from the relative intensity of end-group signals in <sup>13</sup>C NMR spectra.

#### 3.3. Propylene oligomerization reactions

#### 3.3.1. General results

Table 3 presents basic data on propylene oligomerization reactions. In the absence of PPh<sub>3</sub>, AlEt<sub>2</sub>Cl and Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub> do not produce efficient propylene oligomerization catalysts but addition of PPh<sub>3</sub> leads to the

formation of very active catalyst systems. The oligomer yield with the **I** - AlEt<sub>2</sub>Cl/PPh<sub>3</sub> system at 40 °C reaches ~200 kg/mol Ni and with the **II** - AlEt<sub>2</sub>Cl/PPh<sub>3</sub> system ~850 kg/mol Ni.

In the case of complex **I**, replacement of AlEt<sub>2</sub>Cl with Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub> triples the catalyst productivity whereas the other two complexes produce 2-3 times more efficient catalysts when activated with AlEt<sub>2</sub>Cl. The increase of the [P]:[Ni] ratio in the **I** - AlEt<sub>2</sub>Cl/PPh<sub>3</sub> system from ~2 to >25 does not affect the catalyst productivity. Kinetic data in Fig. 2 show that the **I** - AlEt<sub>2</sub>Cl/PPh<sub>3</sub> system is not particularly stable: the reaction rate at 40 °C decreases nearly 1.5 times over the first 10 minutes and then remains approximately constant. An interplay of temperature effects on the initial activity and the deactivation rate of this catalyst leads to an apparent maximum of its oligomerization productivity at 40 °C.

#### 3.3.2. Oligomer structure

Oligomerization reactions of propylene yielded only light liquid products. GC analysis showed that they mostly consist of propylene dimers and relatively small amounts of trimers (from 10 to 12 different isomers). T  $_2$  <sup>'3</sup>C NMR spectrum of the oligomer mixture produced with the **II** - AlEt<sub>2</sub>Cl/PPh<sub>3</sub> system at 40 °C is shown in Fig. 3 in the ranges of aromatic and aliphatic carbon atoms.

The spectrum is quite complex. The following propylene dimers were identified (they are listed in the order of abundance; only non-overlapping NMR signals are given for minor components, the identification is supported by IR):

*Trans-* and *cis-*4-methyl-2-pentenes CH<sub>3</sub>–CH=CH–CH(CH<sub>3</sub>)<sub>2</sub> in a ~3.5:1 ratio [<sup>13</sup>C NMR 138.8 (*tr*), 138.4 (*cis*), 121.5 (*tr*), 121.3 (*cis*), 31.0 (*tr*), 26.3 (*cis*), 22.4-22.8, 17.8 (*tr*), 12.3 (*cis*) ppm; <sup>1</sup>H NMR 5.42 (*tr*), ~5.3 (*cis*), 5.38 (*tr*), ~5.2 (*cis*), 2.63, 1.61, 0.98-0.94 ppm; IR 968 cm<sup>-1</sup> (*tr*), 724 cm<sup>-1</sup> (*cis*)]. *Trans-* and *cis-*2-hexenes CH<sub>3</sub>–CH=CH–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub> in a ~2.5:1 ratio [<sup>13</sup>C NMR 131.4 (*tr*), 130.6 (*cis*), 124.7 (*tr*), 123.8 (*cis*), 39.8 (*tr*), 29.1 (*cis*) ppm, <sup>1</sup>H NMR 1.47 (*tr*), 1.37 (*cis*) ppm]. 2-methyl-2-pentene (CH<sub>3</sub>)<sub>2</sub>C=CH–CH<sub>2</sub>–CH<sub>3</sub> [<sup>13</sup>C NMR 130.6, 126.8, 25.6, 22.0, 14.0 ppm, <sup>1</sup>H NMR 5.1, 2.0, 1.7, ~0.93 ppm, IR 734 cm<sup>-1</sup>].

2-methyl-1-pentene CH<sub>2</sub>=C(CH<sub>3</sub>)–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub> [<sup>13</sup>C NMR 145.8, 109.9, 40.2, 22.3, 20.9, 13.8 ppm, <sup>1</sup>H NMR ~4.7 ppm, IR 889 cm<sup>-1</sup>].

Small signals of four other propylene dimers, 2,3-dimethyl-1-butene  $CH_2=C(CH_3)-CH(CH_3)_2$  (151.8 and 107.8 ppm), 1-hexene (139.2 and 114.2 ppm), 2,3-dimethyl-2-butene  $(CH_3)_2C=C(CH_3)_2$  (123.8 ppm), and 4-methyl-1-pentene  $CH_2=CH-CH_2-CH(CH_2)_3$  (115.4 and 43.5 ppm), were also detected in in the spectra of some oligomer mixtures.

Relative yields of different dimers depend on the catalyst, as Table 4 shows.

The NMR results show that the oligomer mixtures do not contain regular "head-to-tail" structures with the polypropylene motif,  $\sim$ CH<sub>2</sub>–CH(CH<sub>3</sub>)–CH<sub>2</sub>–CH(CH<sub>3</sub>)~, which is characterized by signals of CH<sub>2</sub> groups at ~44-46.5 ppm and CH groups at ~28 ppm [12]. Chain ends typical for such oligomer

molecules, both unsaturated,  $CH_2=C(CH_3)-CH_2\sim$ , and saturated (*n*-propyl, and isobutyl [11]), are also absent.

#### 4. Discussion

### 4.1. Mechanistic features of oligomerization reactions

In general, the mechanism of alkene polymerization reactions (including oligomerization reactions) with soluble catalysts based on *DiiM* complexes of Ni<sup>II</sup> and the mechanism of branch formation in ethylene polymers produced with the catalysts was thoroughly investigated [1,13,14,21]. According to the literature [1,13], *DiiM* complexes (*L*)NiX<sub>2</sub> rapidly react with organoaluminum compounds (AlMe<sub>3</sub> in methylalumoxane or AlR'<sub>x</sub>Cl<sub>3-x</sub>) and form (*L*)NiR'<sub>2</sub> products (R' = Me, Et, etc.). The cocatalysts abstract the R'<sup>-</sup> anion from alkylated *DiiM* complexes and convert them into (L)Ni<sup>+</sup>–R' cations, diamagnetic square-plane Ni<sup>II</sup> species [19,21], which are the active centers in alkene polymerization and oligomerization reactions. The resting state in the polymerization cycle is a  $\pi$ -complex between the (*L*)M<sup>+</sup>–Polymer species and an alkene molecule, (*L*)(Polymer)M<sup>+</sup>…CH<sub>2</sub>=CHR [1,13]. The metal atom in the resting state does not have a proximate counter-ion derived from a cocatalyst and, therefore, the nature of a counter-ion does not significantly affect either the activity of *DiiM*-based catalysts or the nature of the produced polymers [17].

Phosphines are often used to increase the productivity of various nickel-based catalysts in ethylene oligomerization reactions [20]. Their activating effect was attributed to protection of active species during the catalytic cycle by acting as auxiliary ligands [21]. In our case, the role of PPh<sub>3</sub> as such a ligand, which does not directly affect the performance of the active centers, follows from the results in Sections 3.2 and 3.3:

PPh<sub>3</sub> significantly activates the Ni - AlR'<sub>x</sub>Cl<sub>3-x</sub> systems in ethylene oligomerization reactions, especially the catalysts derived from complexes I and II (Table 1). In the case of propylene oligomerization reactions, none of the complexes forms active catalysts without PPh<sub>3</sub> (Table 3).
 Introduction of PPh<sub>3</sub> leads only to a very modest increase of the branching level in the ethylene oligomers (Table 2) and it does not significantly affect their average oligomerization degree.
 An increase of the [P]:[Ni] ratio above 1 does not affect the nature of the oligomer products.

One can expect that, in general, the nature of polymerization products generated by  $\alpha$ -diimine complexes should be strongly affected by the substitution pattern in the diimine ligands. The presence of two *ortho*-substituents R in *DiiM* complexes (Scheme 1) restricts the movement of the growing polymer chain in the resting state (*L*)(Polymer)M<sup>+</sup>...CH<sub>2</sub>=CH*R* and makes the polymerization reaction more regular, both in the kinetic sense (a lower frequency of chain transfer reactions resulting in the formation of high-MW polymers) and with respect to regioregularity (higher probability of head-to-tail chain growth).

The substitution pattern in  $\alpha$ -diimine complexes **I** - **III** (Scheme 2) significantly increases the movement range of the polymer chain-end attached to the Ni atom. It leads to two effects:

1. The probability of  $\beta$ -H elimination in a (*L*)Ni<sup>+</sup>–Polymer species increases:

$$(L)Ni^+-CH_2-CHR-Polymer \rightarrow (L)Ni^+-H^-CH_2=CR-Polymer$$

$$\rightarrow (L)Ni^{+}-H + CH_{2}=CR-Polymer (R=H \text{ or an alkyl group})$$
(1)

This effect signifies that the MW of the reaction products decreases: oligomers with an average length of 6 to 8 ethylene units are formed (Table 2) instead of polymers [1,13,14].

2. The probability of chain isomerization via reversible dissociation of the  $(L)Ni^+$ -Polymer bond increases:

$$(L)Ni^+-CH_2-CHR-Polymer \rightarrow (L)(H)Ni^+\cdots CH_2=CR-Polymer$$

$$\rightarrow (L)(H)Ni^{+} CR(Polymer) = CH_2 \rightarrow (L)Ni^{+} - CR(CH_3) - Polymer$$
(2)

Oligomerization reactions are a particular example of polymerization reactions characterized by high probability of chain transfer reactions; in our case,  $\beta$ -H elimination (Reaction 1).

The chain growth in reactions of 1-alkenes  $CH_2=CHR$  with any multidentate Ni complex starts the (*L*)Ni<sup>+</sup>-H species [18,21]:

$$(L)Ni^{+}-H + CH_{2}=CHR \rightarrow (L)Ni^{+}-CH_{2}-CH_{2}R$$
(3)

Standard chain propagation reactions in the polymerization/oligomerization reactions are consecutive insertions of 1-alkene molecules into the  $(L)Ni^+$ –C bond:

 $(L)Ni^{+}-CH_{2}-CHR-(CH_{2}-CHR)_{n}-R + CH_{2}=CHR \rightarrow (L)Ni^{+}-CH_{2}-CHR-(CH_{2}-CHR)_{n+1}-R$ (4)

The data in Tables 1 and 3 provide information on the relative reactivity of ethylene and propylene in Reaction 4 normalized to monomer concentration. Ethylene is always more reactive than propylene in insertion reactions into a transition metal-carbon bond [14] and the comparison of catalyst productivity in Tables 1 and 3 confirms this rule for the (L)Ni<sup>+</sup>–C bond as well. The difference in reactivity depends also on the type of the Ni complex. For example, the relative yield of ethylene oligomers in a 30-min reaction with complex I activated with AlEtCl<sub>2</sub>/PPh<sub>3</sub> at 30 °C is about ten times higher than the relative yield of propylene oligomers in a 60-min reaction at 40 °C with the same catalyst system, whereas the difference is much higher, over 100 times, for complex III.

### 4.2. Reaction scheme of ethylene oligomerization

The data in Section 3.2.2 show that ethylene oligomerization with complexes **I** - **III** produces branched chains. Similarly to the literature on ethylene polymerization with *DiiM* complexes [1-5], the formation of branches can be explained by "chain-walking" reactions [1,3,5,13,15-17], a series of  $\beta$ -H elimination/alkene reinsertion steps (Reaction 2). Methyl branches in the oligomer chains are formed in Reactions 5-6:

 $(L)Ni^+-CH_2-CH_2-CH_2-CH_2-R \rightarrow (L)(H)Ni^+-CH_2=CH-CH_2-CH_2-R$ 

$$\rightarrow (L)Ni^{+}-CH(CH_{3})-CH_{2}-R \qquad (5)$$

$$(L)Ni^{+}-CH(CH_{3})-CH_{2}-CH_{2}-R + CH_{2}=CH_{2} \rightarrow (L)Ni^{+}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-CH_{2}-R \qquad (6)$$

Formation of ethyl and longer branches can be rationalized in a similar way starting with the product of Reaction 5:

$$(L)Ni^{+}-CH(CH_{3})-CH_{2}-CH_{2}-R \rightarrow (L)(H)Ni^{+}-CH(CH_{3})=CH-CH_{2}-R$$

$$\rightarrow (L)Ni^{+}-CH(C_{2}H_{5})-CH_{2}-CH_{2}-R \qquad (7)$$

$$(L)Ni^{+}-CH(C_{2}H_{5})-CH_{2}-CH_{2}-R + CH_{2}=CH_{2} \rightarrow (L)Ni^{+}-CH_{2}-CH_{2}-CH(C_{2}H_{5})-CH_{2}-R$$
(8)

The data in Table 2 show that methyl branches dominate in ethylene oligomers produced with complexes **I** - **III**. Their content in waxes prepared with complex **III** is about two times higher than in ethylene polymers produced with Ni-based *DiiM* complexes under similar reaction conditions [19], most probably due to lower space restrictions in the transition state of Reaction 5.

The growth of linear and branched oligomer chains is terminated in a  $\beta$ -H elimination reaction (Reaction 1), which leads to the formation of alkenes. Their double bonds are readily identified by <sup>13</sup>C NMR. Dissociation of the complex formed in Reaction 7 produces *cis*- and *trans*-CH<sub>3</sub>-CH=CH–R alkenes, dissociation of complexes produced after a further migration of the Ni atom along the alkyl chain produces *cis*- and *trans*-R'-CH=CH–R" alkenes, and dissociation of the complex formed in Reaction 5 produces CH<sub>2</sub>=CH–R alkenes. All the alkenes are formed at a [CH<sub>3</sub>-CH=CH–R]: [R'-CH=CH–R"]:[CH<sub>2</sub>=CH–R] ratio of ~1:0.7:0.08.

These results are matched by GC data for the lightest ethylene oligomers. The C<sub>4</sub> products include 2butenes and 1-butene in a 1:0.06 ratio and the C<sub>6</sub> products contain 2-hexenes, 3-hexenes and 1-hexene in

a ~1:0.3:0.2 ratio.

Alkenes constitute about 70% of the oligomer molecules; the remaining products are isoalkanes formed in chain transfer reactions with organoaluminum compounds.

#### 4.3. Reaction scheme of propylene oligomerization

Polymerization of propylene with Ni-based *DiiM* complexes at low temperatures, -78°C to -45°C, produces regioregular, predominantly syndiotactic polymers. However, both the regiochemical and the stereochemical control in these reactions deteriorate with temperature and at 50°C stereo-irregular and regio-irregular polymers are formed [6].

In the case of Ni complexes I - III, the only products formed from propylene are light oligomers, mostly dimers. The formation of the four most abundant dimers is explained by the following reaction scheme. A propylene molecule can insert into the (*L*)Ni<sup>+</sup>–H bond both in the primary and the secondary orientation:

$$(L)Ni^{+}-H+CH_{2}=CH-CH_{3} \rightarrow (L)Ni^{+}-CH_{2}-CH_{2}-CH_{3}$$
(9)

$$(L)Ni^{+}-H + CH_{3}-CH=CH_{2} \rightarrow (L)Ni^{+}-CH(CH_{3})_{2}$$
(10)

As the data for ethylene oligomers show, the  $(L)Ni^+$ –CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub> species can isomerize into the  $(L)Ni^+$ -CH(CH<sub>3</sub>)<sub>2</sub> species in a chain-walking reaction similar to Reaction 5.

Primary insertion of a propylene molecule into the (*L*)Ni<sup>+</sup>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub> species followed by  $\beta$ -H elimination produces 2-methyl-1-pentene:

$$(L)Ni^{+}-CH_{2}-CH_{2}-CH_{3} + CH_{2}=CH-CH_{3} \rightarrow (L)Ni^{+}-CH_{2}-CH(CH_{3})-CH_{2}-CH_{2}-CH_{3}$$

$$\rightarrow (L)Ni^{+}-H + CH_{2}=C(CH_{3})-CH_{2}-CH_{2}-CH_{3} \qquad (11)$$

A chain-walking reaction in the  $(L)Ni^+$ –CH<sub>2</sub>–CH(CH<sub>3</sub>)–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub> species leads to the formation of 2-methyl-2-pentene:

$$(L)Ni^{+}-CH_{2}-CH(CH_{3})-CH_{2}-CH_{2}-CH_{3} \rightarrow (L)Ni^{+}-C(CH_{3})_{2}-CH_{2}-CH_{2}-CH_{3}$$

$$\rightarrow (L)Ni^{+}-H + (CH_{3})_{2}C=CH-CH_{2}-CH_{3} \qquad (12)$$

Secondary propylene insertion into the (L)Ni<sup>+</sup>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub> bond produces mostly 2-hexenes and a small quantity of 1-hexene (GC data confirm these NMR results):

$$(L)Ni^{+}-CH_{2}-CH_{2}-CH_{3} + CH_{3}-CH=CH_{2} \rightarrow (L)Ni^{+}-CH(CH_{3})-CH_{2}-CH_{2}-CH_{2}-CH_{3}$$

$$\rightarrow (L)Ni^{+}-H + CH_{3}-CH=CH-CH_{2}-CH_{2}-CH_{3}$$
(13)

In a similar set of reactions, secondary insertion of a propylene molecule into the  $(L)Ni^+$ -CH(CH<sub>3</sub>)<sub>2</sub> species produces 4-methyl-2-pentenes and a small quantity of 4-methyl-1-pentene:

$$(L)Ni^{+}-CH(CH_{3})_{2} + CH_{3}-CH=CH_{2} \rightarrow (L)Ni^{+}-CH(CH_{3})-CH_{2}-CH(CH_{3})_{2}$$

$$\rightarrow (L)Ni^{+}-H + CH_{3}-CH=CH-CH(CH_{3})_{2}$$
(14)

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Several kinetic features of propylene oligomerization reactions can be evaluated from relative yields of different dimers reported in Table 4:

1. The  $([2-Me-2-C_5^{-}]+[2-Me-1-C_5^{-}])/\sum [2-C_6^{-}]$  ratio gives an approximate measure of two probabilities for propylene insertion into the  $(L)Ni^+$ -CH<sub>2</sub>R bond, the primary (Reaction 11) vs. the secondary (Reaction 13):

Catalyst: I - AlEt<sub>2</sub>Cl/PPh<sub>3</sub> I - Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub>/PPh<sub>3</sub> II - AlEt<sub>2</sub>Cl/PPh<sub>3</sub> II - Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub>/PPh<sub>3</sub> *k*primary Ni-C/  $k_{\text{secondary Ni-C}}$ : 3.1 1.6 1.2 1.0

Complex II produces active species which exhibit no regioselectivity whereas complex I produces active species with some preference for primary insertion.

2. Regioselecivity of propylene insertion into the  $(L)Ni^+$ –H bond can be approximately evaluated in a similar manner from the relative yields of  $\Sigma[2-C_6^=]$  vs.  $\Sigma[2-Me-2-C_5^=]$ . This estimation assumes that the frequency of the chain-walking reaction in the  $(L)Ni^+$ –CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>3</sub> species (similar to Reaction 5) is relatively low, as Table 2 shows.

Catalyst: **I** - AlEt<sub>2</sub>Cl/PPh<sub>3</sub> **I** - Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub>/PPh<sub>3</sub> **II** - AlEt<sub>2</sub>Cl/PPh<sub>3</sub> **II** - Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub>/PPh<sub>3</sub>  $k_{\text{primary Ni-H}}/k_{\text{secondary Ni-H}}: 0.7 0.6 1.5 0.5$ 

Thus, in most cases the probability of secondary propylene insertion into the  $(L)Ni^+$ –H bond [which gives a thermodynamically more stable  $(L)Ni^+$ –CH(CH<sub>3</sub>)<sub>2</sub> species] is about 1.5-2 times higher than the probability of primary insertion.

3. Primary propylene insertion into the (L)Ni<sup>+</sup>–CH(CH<sub>3</sub>)<sub>2</sub> species is difficult due to steric reasons and the respective dimers, CH<sub>2</sub>=C(CH<sub>3</sub>)–CH(CH<sub>3</sub>)<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>C=C(CH<sub>3</sub>)<sub>2</sub>, are present in the oligomer mixtures in very small quantities.

#### 5. Conclusions

 $\alpha$ -Diimine Ni complexes **I** - **III** (Scheme 2) containing three new types of diimine ligands were synthesized and characterized. The ligands provide easy access of alkene molecules to the Ni atom in the catalytically active species derived from the complexes. The complexes were converted into efficient ethylene and propylene oligomerization catalysts with organoaluminum compounds, AlEt<sub>2</sub>Cl and Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub>, and with combinations of these compounds and PPh<sub>3</sub>.

Ethylene oligomerization reactions with the catalysts at 30 °C yielded mixtures of waxy and liquid oligomers (the oligomerization degree 6 to 9) containing 14-20 mol. % of methyl branches, 4-6 mol. % of ethyl branches and a small number of longer branches. The branched oligomer chains are apparently formed in chain-isomerization ("chain-walking") steps which occur in the course of ethylene oligomerization reactions.

Propylene oligomerization reactions with the catalysts at 30-70 °C produced mixtures of very light oligomers (mostly dimers), which are formed in competing primary and secondary insertion reaction into Ni–H and Ni–C bonds. The probability of the secondary propylene insertion into the Ni–H bond is ~1.5-2 times higher than the probability of the primary insertion. The regioselectivity of propylene insertion into the Ni–C bond depends on the type of ligand: complex **II** produces active species which exhibit no regioselectivity whereas complex **I** produces active species with some preference for primary insertion.

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**Fig. 1.** <sup>13</sup>C NMR spectrum of ethylene oligomer produced with **III** - AlEt<sub>2</sub>Cl/PPh<sub>3</sub> catalyst system (range of aliphatic carbon atoms).



**Fig. 2.** Kinetics of propylene polymerization with **I** - AlEt<sub>2</sub>Cl/PPh<sub>3</sub> catalyst system at 30 °C (*1*), 40 °C (*2*) and 50 °C (*3*). Ordinate - relative rate per mole of **I**.



**Fig. 3.** <sup>13</sup>C NMR spectrum of propylene oligomer produced with the **II** -  $AlEt_2Cl/PPh_3$  catalyst system at 40 °C. A - range of aromatic carbon atoms (signals at 124.4, 128.3, 129.1 and 137.8 ppm - toluene); B - range of aliphatic carbon atoms (signal at 21.4 ppm - toluene).



## Scheme 1

 $\alpha$ -Diimine complexes *DiiM*. M = Pd<sup>II</sup> and Ni<sup>II</sup>, X = Cl, Br, Me; R'+ R' = cyclohexyl, cyclohexenyl, dinaphthyl; R = Me, *i*-Pr, Ph.



## Scheme 2

 $\alpha$ -Diimine complexes of Ni<sup>II</sup> used in oligomerization reactions of ethylene and propylene.



## Scheme 3

Synthesis of ligands LI - LIII and complexes I - III. LI and  $I - R_1 = R_2 = R_4 = R_5 = F$ ;  $R_3 = H$ ; LII and  $II - R_1 = CF_3$ ;  $R_2 - R_5 = H$ ; LIII and  $III - R_1 = R_3 = CH_3$ ;  $R_2 = R_4 = R_5 = H$ .



Scheme 4. Crystal structure of complex I.

## Table 1

Ethylene oligomerization reactions with complexes I - III.<sup>a</sup>

Organoaluminum	Catalyst	Fraction of						
activator	kg/mol Ni kg/(mol Ni $\cdot C_{\rm E}$ )		liquid products,%					
Complex I								
AlEt <sub>2</sub> Cl <sup>b</sup>	161.8	449	~100					
Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub> <sup>b</sup>	144.1	400	~100					
AlEt <sub>2</sub> Cl <sup>c</sup>	617.3	1714	~100					
Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub> <sup>d</sup>	420.5	1168	~100					
	Complex II							
AlEt <sub>2</sub> Cl <sup>b</sup>	272.5	757	~0					
Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub> <sup>b</sup>	235.0	653	~0					
AlEt <sub>2</sub> Cl <sup>c</sup>	532.5	1479	94					
Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub> <sup>c</sup>	332.5	32.5 9234						
Complex III								
AlEt <sub>2</sub> Cl <sup>b</sup>	412.5	1146	58					
Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub> <sup>b</sup>	422.5	1174	48					
AlEt <sub>2</sub> Cl <sup>c</sup>	462.5	1285	98					
Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub> <sup>c</sup>	480.0	1333	70					

a All experiments at 30 °C,  $P_E = 0.3$  MPa,  $C_E = 0.36$  M,  $[Ni] = 4 \cdot 10^{-2}$  mmol, [Al]:[Ni] = 150, reaction time 30 min.

b Experiments without PPh<sub>3</sub>.

c Experiments at  $[PPh_3]:[Ni] = 1$ .

d Experiments at [PPh<sub>3</sub>]:[Ni] = 25.

## Table 2

Branching<sup>a</sup> and oligomerization degree of ethylene oligomers produced with complex **III**.

Activator	[CH <sub>3</sub> ], mol. %	[C <sub>2</sub> H <sub>5</sub> ], mol. %	Av. oligomer.
			degree n
Al <sub>2</sub> Et <sub>2</sub> Cl	13.6	4.4	8.6
Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub>	15.7	5.2	6.1
AlEt <sub>2</sub> Cl/PPh <sub>3</sub>	18.0	5.0	8.4
Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub> /PPh <sub>3</sub>	19.0	5.6	7.0

a Branches per one ethylene monomer unit.

## Table 3

Temperature, °C	[Ni]×10 <sup>2</sup> , mmol	Organo- aluminum	[Al]:[Ni], molar	[P]:[Ni], molar	Catalyst productivity			
		activator			kg/mol Ni	kg/(mol Ni $\cdot C_{Pr}$ )		
Complex I								
30	5.3	AlEt <sub>2</sub> Cl	154	0	0	0		
30	4.8	"_"	184	1.8	124	10.4		
40	3.0	"_"	224	1.8	195	17.1		
40	3.5	"_"	162	26.0	198	17.4		
50	3.9	"_"	163	2.2	178	15.9		
70	3.5	"_"	173	1.9	120	12.0		
40	4.3	Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub>	153	2.4	580	50.9		
	Complex II							
40	5.3	AlEt <sub>2</sub> Cl	150	0	0	0		
20	9.8	"_"	161	2.1	256	21.3		
40	4.2	"_"	154	2.2	847 74.3			
40	6.3	Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub>	156	2.2	282	24.7		
Complex III								
40	3.74	AlEt <sub>2</sub> Cl	181	2.6	114	10.0		
40	3.7	Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub>	154	2.7	59	5.2		

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a Oligomerization in liquid propylene, run time 60 min;  $C_{Pr}$  (M) at 20°C - 12.4, 30°C - 11.9, 40°C - 11.4, 50°C - 11.2, 70°C - 10.0.

## Table 4

Relative yields of different propylene dimers.<sup>a</sup>

Catalyst system	$[4-Me-2-C_5^{=}]$	$[2-Me-2-C_5^{=}]$	$[2-C_6^{=}]$	$[2-Me-1-C_5^{=}]$
I - AlEt <sub>2</sub> Cl/PPh <sub>3</sub>	1	0.63	0.46	0.81
I - Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub> /PPh <sub>3</sub>	1	0.21	0.63	0.78
II - AlEt <sub>2</sub> Cl/PPh <sub>3</sub>	1	0.66	1.51	1.23
II - Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub> /PPh <sub>3</sub>	1	0.10	0.28	0.19

a All oligomers were prepared at 40 °C.