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#### FULL PAPER



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# NNNO-Heteroscorpionate nickel (II) and cobalt (II) complexes for ethylene oligomerization: the unprecedented formation of odd carbon number olefins

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The unprecedented observation of odd carbon number olefins is reported dur-

ing nickel- catalyzed ethylene oligomerization. Two complexes based on Co

(II) and Ni (II) with novel tetradentate heteroscorpionate ligand have been

synthesized and fully characterized. These complexes showed the ability to oli-

gomerize ethylene upon activation with various organoaluminum compounds

(Et<sub>2</sub>AlCl, Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, EtAlCl<sub>2</sub>, MMAO). Ni (II) based catalytic systems were suf-

ficiently more active (up to 1900 kg·mol (Ni)<sup>-1</sup>·h<sup>-1</sup>·atm<sup>-1</sup>) than Co (II) analogs

and have been found to be strongly dependent on the activator composition.

The use of PPh<sub>3</sub> as an additive to catalytic systems resulted in the increase of

activity up to 4,150 kg·mol  $(Ni)^{-1} \cdot h^{-1} \cdot atm^{-1}$  and in the alteration of selectivity. All Ni (II) based systems activated with EtAlCl<sub>2</sub> produce up to 5 mol. % of odd

carbon number olefins; two probable mechanisms for their formation are

cobalt, ethylene oligomerization, heteroscorpionate, nickel, odd carbon number olefins

suggested – metathesis and  $\beta$ -alkyl elimination.

**KEYWORDS** 

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### **1** | INTRODUCTION

The transition metal complexes with heteroscorpionate ligands have been intensively studied recently because of their ability to mediate various catalytic reactions.<sup>[1]</sup> The catalytic properties of corresponding chromium-based complexes, which selectively trimerize ethylene to 1-hexene, have been studied in sufficient detail.<sup>[2-4]</sup> The

use of heteroscorpionate complexes of transition,<sup>[5,6]</sup> sblock<sup>[7,8]</sup> and p-block<sup>[9,10]</sup> metals as catalysts for lactide and *\varepsilon*-caprolactone ring-opening polymerization has also attracted scientific attention in the last decade. At the same time, the heteroscorpionate complexes of the iron triad metals, unlike other N-donor ligands,<sup>[11,12]</sup> have been studied very superficially in the olefin coupling catalysis. Casagrande et al.<sup>[13]</sup> investigated nickel complexes with boron-containing scorpionate ligands (Figure 1, **a**) in ethylene oligomerization. Several MOF based on nickel with scorpionate-like coordination are active in ethylene dimerization.<sup>[14–16]</sup>

Earlier, we have obtained a number of nickel (II) complexes with heteroscorpionate ligands (Figure 1, **b**-g), which showed moderate activities towards ethylene oligomerization with predominant formation of butenes.<sup>[17]</sup> However, nickel halide complexes with tridentate heteroscorpionates easily undergo isomerization<sup>[18]</sup> yielding ionic complexes  $[NiL_2]^{+2}[NiHal_4]^{-2}$ , which are inactive in oligo- /polymerization of ethylene. So thermodynamically stable molecular complexes nickel halides with heteroscorpionates<sup>[19]</sup> of or scorpionates<sup>[20]</sup> are obtained only when bulky substituents are introduced. In this study, we have designed novel tetradentate NNNO-heteroscorpionate ligand with 8-methoxyquinoline pendant arm, and synthesized monomeric molecular complexes based on Ni (II) and Co (II) halides with it. The obtained complexes have been studied for their ability to catalyze ethylene oligomerization upon activation with Et<sub>2</sub>AlCl, Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, EtAlCl<sub>2</sub> or MMAO. Quite unexpectedly, Ni (II) based systems, activated with EtAlCl<sub>2</sub>, produced up to 5 mol. % of odd carbon number olefins. Previously several catalytic systems based on Fe (II) and Cr (III), that exhibit such properties, were described in literature.<sup>[21-24]</sup> Two mechanisms have been introduced to describe the formation of odd-carbon number olefins: metathesis<sup>[21,23]</sup> and transfer to aluminum.<sup>[25]</sup>

### 2 | EXPERIMENTAL

### 2.1 | Materials and methods

All manipulations with air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in oven-dried Schlenk glassware using a dual manifold Schlenk line. Argon (grade 4.8) and ethylene of specialpurity grade (Linde gas) were dried by purging through a Super Clean<sup>™</sup> Gas Filters. Unless otherwise noted, all reagents were purchased from Sigma-Aldrich and used without further purification. Et<sub>2</sub>AlCl, EtAlCl<sub>2</sub> were supplied as 1 M solutions in hexane. Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> was supplied as 1 M solution in toluene, MMAO (MMAO-12) was supplied as 7% wt. solution in toluene. Toluene, THF and diethyl ether were distilled over Na/benzophenone. Dichloromethane was refluxed over CaH<sub>2</sub> and distilled prior to use. CDCl<sub>3</sub>, CD<sub>3</sub>CN and CD<sub>3</sub>OD were stored under inert atmosphere. 8-methoxyquinoline-2-carbaldehyde was prepared close to the method described in literature.<sup>[26]</sup> Bis(3,5-dimethylpyrazolyl)methanone was prepared according to literature procedure<sup>[27]</sup> and recrystallized from THF. 2-[bis(3,5-dimethylpyrazol-1-yl) methyl]-8-methoxy-quinoline L was prepared similar to Higgs and Carrano.<sup>[28]</sup> It has been characterized by <sup>1</sup>H and <sup>13</sup>C NMR and X-ray diffraction analyses. Synthetic details and spectra are given in supplementary information. Complexes were prepared by the direct interaction of CoCl<sub>2</sub> or Ni (DME)Br<sub>2</sub> with the ligand in THF.

# 2.2 | Physical and analytical measurements

NMR spectra were recorded on Bruker Avance-400 and 600 FT-spectrometers (400.13 and 600.22 MHz). Chemical shifts are reported in ppm and were determined by reference to the residual solvent peaks. All coupling constants are given in Hertz. IR spectra were recorded on a Magna-IR 750 spectrophotometer. Elemental analysis was performed by the microanalytical laboratory at A. N. Nesmeyanov Institute of Organoelement Compounds. Mass spectra under atmospheric pressure electrospray (ESI) were recorded in the full scan mass of positive and negative ions on the dynamic tandem mass spectrometer Finnigan LCQ Advantage (USA), equipped with a mass analyzer oktapol ion trap pump MS Surveyor, Surveyor autosampler, nitrogen generator Schmidlin-Lab



FIGURE 1 Examples of and Ni(II) scorpionate<sup>[13]</sup> and heteroscorpionate<sup>[17]</sup> complexes used as precatalysts in ethylene oligomerization

(Germany) and a system for collecting and processing the data using the X Calibur program (version 1.3, Finnigan). Transfer capillary temperature of 150 °C, voltage field between the needle and counter electrode 4.5 kV. Samples were introduced into the ion source with the input syringe acetonitrile at a 50 ml/min flow rate through the 5 mL Reodyne injector loop. High-resolution MALDI mass spectra were registered on a Bruker ULTRAFLEX II TOF/TOF instrument with 2,5- dihydroxybenzoic acid (DHB) as the matrix.

#### 2.3 | Synthesis and characterization

### 2.3.1 | Synthesis of LCoCl<sub>2</sub> (L = 2-[bis (3,5-dimethylpyrazol-1-yl)methyl]-8-methoxyquinoline) (1)

2-[bis(3,5-dimethylpyrazol-1-yl)methyl]-

8-methoxyquinoline L (250 mg, 0.69 mmol) was dissolved in 20 ml of anhydrous THF and added to suspension of CoCl<sub>2</sub> (90 mg, 0.69 mmol) in anhydrous THF (20 ml). The mixture was refluxed until complete dissolution and then 30 min more. The resulting solution was concentrated and anhydrous diethyl ether was added. The precipitate was filtered off washed with anhydrous Et<sub>2</sub>O (2 × 10 ml) and dried in vacuo. Yield: 246 mg (72.4%). <sup>1</sup>H NMR (600 MHz, Methanol- $d_4$ )  $\delta$  122.55 (s, 1H), 110.97 (s, 1H), 41.90 (s, 6H), 41.43 (s, 2H), 30.03 (s, 1H), 28.34 (s, 1H), 23.96 (s, 3H), -6.85 (s, 1H), -19.91 (s, 1H), -73.42 (s, 6H). Anal. Calcd. for C<sub>21</sub>H<sub>23</sub>Cl<sub>2</sub>CoN<sub>5</sub>O (491.28) C, 51.3; H, 4.7; N, 14.3; O 3.3; Cl, 14.4; Co, 12. Found: C, 51.5; H, 4.52; N, 13.74; Co 11.8. ESI-MS: m/z (%) 440 [M - CH<sub>3</sub>, - Cl, 16%], 405 [M<sup>+</sup> - CH<sub>3</sub>, - 2Cl, 7%].

## 2.3.2 | Synthesis of LNiBr<sub>2</sub> (L = 2-[bis (3,5-dimethylpyrazol-1-yl)methyl]-8-methoxyquinoline) (2)

2-[bis(3,5-dimethylpyrazol-1-yl)methyl]-

8-methoxyquinoline **L** (188 mg, 0.52 mmol) was dissolved in 20 ml of anhydrous THF. The resulting solution was added dropwise to solution of Ni (DME)Br<sub>2</sub> (160 mg, 0.52 mmol) in 20 ml of anhydrous THF. The solution was stirred for 2 hr and concentrated to 3 ml. The complex crystallized from this solution as orange powder in 10 min. It was filtered off and washed with anhydrous Et<sub>2</sub>O (2 × 10 ml) and dried in vacuo. Yield: 205 mg (74.8%). <sup>1</sup>H NMR (600 MHz, Methanol- $d_4$ )  $\delta$  56.85 (s, 2H), 43.94 (s, 1H), 38.03 (s, 1H), 21.59 (s, 1H), 15.82 (s, 3H), 14.39 (s, 1H), 10.17 (s, 1H), -3.16 (s, 6H), -9.53 (s, 6H), -11.05 (s, 1H). Anal. Calcd. for C<sub>21</sub>H<sub>23</sub>Br<sub>2</sub>N<sub>5</sub>NiO (579.94) C, 43.5; H, 4; N, 10.1; O 2.8; Br, 27.6; Ni, 12.1. Found: C, 43.2; H, 4.16; N, 10.37; Ni 11.97. MALDI-TOF: m/z (%) 500 [M –Br, 100%].

### 2.4 | DFT calculations

All quantum chemical DFT calculations were carried out in ORCA package v. 3.0.3. X-ray structures of the complexes were used as an initial structure for geometry optimization. It was performed with non-hybrid PBE functional<sup>[29,30]</sup> and using def2-TZVP basis sets.<sup>[31]</sup> After geometry optimization tensors of hyperfine interactions for hydrogen and carbon nuclei were calculated using hybrid PBE0 functional<sup>[32]</sup> and the same basis sets def2-TZVP, but with addition primitives with higher order of exponent to better description of electron density around a nucleus.

Observed chemical shifts of the nuclei of the paramagnetic complexes were divided into diamagnetic ( $\delta_{DIA}$ ), contact ( $\delta_{CS}$ ) and pseudocontact ( $\delta_{PCS}$ ) contributions:

$$\delta_{OBS} = \delta_{DIA} + \delta_{CS} + \delta_{PCS} \tag{1}$$

As the diamagnetic contribution, the chemical shifts in the <sup>1</sup>H NMR spectrum of an initial ligand was used. The contact contribution to the chemical shifts was calculated by Equation 2:

$$\delta_{CS} = \frac{S(S+1)\mu_B}{3kTg_N\mu_N} \cdot \bar{g} \cdot A_{iso}$$
(2)

 $(A_{iso}$  is the DFT-calculated isotropic hyperfine coupling constant,  $\bar{g}$  is the DFT-calculated rotationally averaged electronic g-value,  $g_N$  is the nuclear g-value,  $\mu_B$  and  $\mu_N$  are the Bohr and nuclear magnetons, respectively, and kT is the thermal energy), and the pseudocontact contribution, by Equation 3:

$$\delta_{PCS} = \frac{1}{12\pi r^3} \left[ \Delta Xax \left( 3COS^2 \theta - 1 \right) \right] \tag{3}$$

 $(\Delta \chi_{ax}$  is the axial anisotropy of the magnetic susceptibility tensor). The polar coordinates r and  $\theta$  of the nuclei were taken from the DFT-optimized geometry of the complexes.

The value of  $\Delta \chi_{ax}$  was estimated by fitting the chemical shifts in the <sup>1</sup>H NMR spectrum measured experimentally to those calculated with Equation 4:

$$\delta_{OBS} = \delta_{DIA} + \delta_{CS} + \frac{1}{12\pi r^3} \left[ \Delta Xax \left( 3COS^2 \theta - 1 \right) \right] \quad (4)$$

# 2.5 | X-ray crystal structure determination

The single-crystal X-ray diffraction data for L and 1 was collected on the 'Belok' beamline of the Kurchatov Synchrotron Radiation Source (National Research Center 'Kurchatov Institute', Moscow, Russian Federation) using a Ravonix SX165 CCD detector. In total, 720 frames were collected with an oscillation range of  $1.0^{\circ}$  in the  $\varphi$  scanning mode using two different orientations for each crystal. The semi-empirical correction for absorption was applied using the Scala program.<sup>[33]</sup> The data were indexed and integrated using the utility iMOSFLM from the CCP4 software suite.<sup>[34]</sup> For details, see SI, Table S2. The structure was determined by direct methods and refined by full-matrix least square technique on  $F^2$  in anisotropic approximation for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters  $[U_{iso}(H) = 1.5U_{eq}(C)$  for the methyl groups and  $1.2U_{eq}(C)$  for the other groups]. All calculations were carried out using the SHELXTL program suite.<sup>[35]</sup>

Crystallographic data for **1** and ligand **L** has been deposited with the Cambridge Crystallographic Data Center, CCDC 1915444 and CCDC 1915445. The supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Oligomerization of Ethylene was performed in a 450 ml reactor (Parr Instrument Co.) equipped with a magnetic stirrer and inlets for loading components of catalytic systems and ethylene at a total ethylene and toluene vapors pressure of 4 atm. Before the experiment the reactor was heated up to 100 °C and then vacuumed for 10 min to remove residual moisture. Further, it was cooled to 30 °C filled with argon and solid catalyst was injected as suspension in toluene/chlorobenzene (40 ml). Then necessary amount of co-catalyst solution dissolved in additional toluene/chlorobenzene (10 ml) was loaded in the reactor. The reactor was flushed with ethylene to remove argon atmosphere. Oligomerization was initiated by pressurization of 3 additional atm. of ethylene in the reactor. The pressure of ethylene was maintained constant during oligomerization. After the end of the process, the reaction solution was quickly cooled down and then quenched with 15 ml of isopropanol and 10 ml of 5% dilute hydrochloric acid. The organic phase was further dried over Na<sub>2</sub>SO<sub>4</sub> and the organic compounds were characterized with GC and GC-MS to determine the composition and molecular mass distribution. Samples with desiccant were stored in sealed flasks in a refrigerator. The consumption of ethylene was measured using Alicat Scientific massflow detector M-500SCCM-D and

Alicat's Flow Vision<sup>TM</sup> software. GC analysis was performed on Chromatec-Crystall 5000.2, equipped with flame ionization detector and capillary column Restek Rt<sup>®</sup>-Alumina BOND/MAPD (length 50 m, inner diameter 0.53 mm). Initial temperature - 70 °C, 5 min, heating rate - 10 °C/min, up to 200 °C. GC–MS analysis was performed on GC–MS scectrometer Trace GC Ultra – DSQII, capillary column TR-5MS (length 30 m, inner diameter 0.25 mm, phase thickness 0.25 µm). Initial temperature -70 °C, 2 min, heating rate - 15 °C/min, up to 280 °C.

Oligomerization of 1-Hexene was performed in a 450-ml reactor (Parr Instrument Co.) equipped with a magnetic stirrer and inlets for loading components of catalytic systems. Before the experiment the reactor was heated up to 100 °C and then vacuumed for 10 minutes to remove residual moisture. Further, it was cooled to 30 °C filled with argon and solid catalyst was injected as suspension in toluene (40 ml). Then necessary amount of co-catalyst solution dissolved in additional toluene (10 ml) was loaded in the reactor. Then 10 ml of 1-hexene were injected in the reactor via syringe and the system was pressurized with additional 3 atm. of argon. The reaction was conducted for 30 min. After the end of the process, the reaction solution was quickly cooled down and then quenched with 15 ml of isopropanol and 10 ml of 5% dilute hydrochloric acid. The organic phase was further dried over Na2SO4 and the organic compounds were characterized with GC-MS to determine the composition and molecular mass distribution.

### **3** | **RESULTS AND DISCUSSION**

### 3.2 | Synthesis and characterization

То obtain the desired NNNO-tetradentate heteroscorpionate ligand, at first, 8-methoxyquinoline-2-carbaldehyde has been prepared from 8-methoxy-2-methylquinoline close to literature procedure.<sup>[26]</sup> Then, 2-[bis(3,5-dimethylpyrazol-1-yl)methyl]-8-methoxyguino line L has been prepared from 8-methoxyquinoline-2-carbaldehyde and bis(3,5-dimethylpyrazol-1-yl)methanone following the synthetic procedure adopted from Higgs and Carrano.<sup>[28]</sup> (Scheme 1) It was characterized using <sup>1</sup>H and <sup>13</sup>C NMR (SI, Figures S2,S3) (annotations were proposed based on<sup>[17,36]</sup>), IR (SI, Figures S4, S5) and elemental analysis.

Co (II) **1** and Ni (II) **2** monomeric complexes of general composition  $LMHal_2$  have been synthesized by interaction of the ligand **L** with  $CoCl_2$  or Ni (DME)Br<sub>2</sub>, correspondingly (Scheme 1). They have been characterized by IR-, mass-, <sup>1</sup>H NMR-spectroscopies and elemental analysis.



SCHEME 1 Synthesis of 2-[bis(3,5-dimethylpyrazol-1-yl)methyl]-8-methoxyquinoline L and complexes 1 and 2

According to ESI-MS mass spectra, complexes **1–2** do not yield the corresponding molecular ions. For Co (II) complex **1** the meaningful fragments were obtained, attributed to the loss of chlorine atom and  $-CH_3$  group (m/z = 440) and to the loss of two chlorine atoms and –  $CH_3$  group (m/z = 405) (SI, Figure S8). Complex **2** under the same conditions undergoes complete destruction and can be analyzed only using MALDI-TOF mass spectrometry yielding a fragment with m/z = 500, attributed to the loss of the bromine atom (SI, Figure S13).

The structures of ligand L and cobalt (II) complex 1 were unambiguously established by X-ray diffraction study and are shown in Figure 2 along with the atomic numbering scheme. The selected bond lengths and angles are given in Supporting Information, Table S3. Complex 1 is mononuclear and contains six-coordinated cobalt atom: three coordination sites are occupied by the three nitrogen donors of the heteroscorpionate ligand, one is occupied by the oxygen donor of the methoxy-quinoline fragment, and the other two are occupied by two halogenido ligands, which complete a distorted octahedral coordination environment. Hence, the organic ligand is tetra-dentate and form the three six-membered and one five-membered chelate rings. The six-membered chelate rings are non-planar and adopt a boat conformation, with the Co1 cobalt and C1 carbon atoms deviating from the mean plane passed through the other atoms of the ring. The five-membered chelate ring is in usual envelope conformation, with the Co1 cobalt atom out of the mean plane passed through the other atoms of the ring. The distortion of the ideal octahedron is directed toward the

square bipyramid, in which the pyrazolyl N1 and quinolinyl N5 nitrogen atoms, methoxy-O1 oxygen atom, and chlorido-Cl1 ligand constitute the basal plane, whereas the pyrazolyl N3 and chlorido-Cl2 ligand occupy the apical positions. Because of that, the apical Co1-Cl2 (2.3897 (7) Å) and Co1–N3 (2.2363(19) Å) bonds are longer than the corresponding basal Co1-Cl1 (2.3159(8) Å) and Co1-N1 (2.1292(18) Å) bonds (SI, Table S3). The long Co1-O1 (2.4196(17)) distance together with the narrow O1-Co1-N5 (69.58(7)°) intrachelate bite angle is determined by the rigid geometry of the scorpionate fragment. Nevertheless, the basal N1-Co1-N5 (91.11(7)°) bond angle is significant larger than the apical N1-Co1-N3 (81.09(7)°) and N3-Co1-N5 (76.48(7)°) bond angles indicating the more flexibility of an apical position compared to a basal one. This fact is also confirmed by the more deviation of the apical Cl2-Co1-O1 (82.25(4)°) bond angle from the ideal octahedral value of 90° than the basal Cl1-Co1-O1 (93.65(5)°) bond angle. The  $Cl2_{ap}$ —Co1—N3<sub>ap</sub> bond angle is equal to 169.07(5)°.

Crystal packing of **1** is stacking along the crystallographic **b** axis (SI, Figure S14). The stacks are linked to each other by weak C—H…Cl (SI, Table S4) hydrogen bonding interactions into three-dimensional framework.

It is interesting to point out that the geometry of ligand L almost does not change upon the complexation (Figure 2; SI, Table S3). So, the bond lengths at the central C1 carbon atom are equal to 1.470(2) Å (C1–N2), 1.444(2) Å (C1–N4) and 1.530(3) Å (C1–C2) for L and 1.452(3) Å (C1–N2), 1.458(3) Å (C1–N4) and 1.522(3) Å (C1–C12) for 1. Moreover, a sum of the bond angles at



**FIGURE 2** Molecular structure representations of ligand L and complex 1 in 50% thermal ellipsoids 6 of 14 WILEY Organometallic Chemistry

the C1 carbon atom is 333.4(5) and  $332.9(5)^{\circ}$  for ligand L and complex 1, respectively.

The use of tetradentate NNNO-ligand makes it possible to obtain the cobalt complex 1 with four coordination bonds to a metal center in the crystalline state. However, analysis of <sup>1</sup>H NMR spectra of complexes 1 and 2 dissolved in methanol- $d_4$  revealed that they possess similar structures in solution, that are different from the ones in solid. Ni (II) and Co (II) compounds are of paramagnetic nature, so the signals of protons in the <sup>1</sup>H NMR spectra are significantly broadened and have large chemical shifts. (SI, Figures S9, S12) The DFT calculations have been used to assign the signals in the spectra (see experimental part for more details). The list of calculated and corresponding experimental chemical shift values of protons in complexes 1 and 2 is given in supporting information (SI, Table S1). The correlations between experimental and calculated chemical shifts (Figure 3) of ligand protons are fitted by linear function with a good  $R^2$ -factor ( $R^2 > 0.95$ ) for both complexes except for signals of -OCH<sub>3</sub> group (marked with red dot). Such difference between theoretical and experimental values suppose that these complexes have only tridentate coordination of the ligand in solution. Indeed, according to Xray data the Co1–O1 bond is rather long (2.4196(17) Å) and weak, so it easily breaks upon dissolution in polar solvent. Nevertheless, the steric hindrance of the ligand does not allow these complexes to isomerize into the ionic form  $([ML_2]^{+2}[MHal_4]^{-2})$ , typical for nickel halides,<sup>[18,37]</sup> that does not exhibit catalytic activity in ethylene oligomerization.<sup>[17]</sup>

#### 3.3 | Oligomerization of ethylene

# 3.3.1 | Oligomerization of ethylene in toluene medium

Cobalt (II) **1** and nickel (II) **2** complexes exhibited moderate catalytic activity in ethylene oligomerization in toluene medium. All experimental results for catalytic systems based on **1** and **2** are listed in Table 1.

Complex 1 was moderately active from 60 to 130 kg<sub>oligomer</sub>·mol $[Co]^{-1}$ ·h<sup>-1</sup>·atm<sup>-1</sup>, but only in combination with  $Et_2AlCl$  or  $Et_3Al_2Cl_3$ . When other organoaluminum compounds (OAC) such as MMAO, Al(i-Bu)<sub>3</sub>, AlEt<sub>3</sub> or AlMe<sub>3</sub> have been employed, it showed no activity. The mixture of butenes and hexenes is formed during ethylene oligomerization with the  $\alpha$ -olefin share (average of 1-butene and 1-hexene) > 70%. The increase of ethylene pressure in the reactor (up to 5.77 atm.) and temperature in the range from 30 to 40  $^{\circ}$ C has a little effect on the catalytic properties of the system (Table 1, entries 2 vs 6; 9-11). The decrease of the temperature below 30 °C significantly reduces catalytic activity (Table 1, entry 8). The use of 1 equiv. of PPh<sub>3</sub>, that usually significantly alters the catalytic properties of nickel based systems,<sup>[17,38-52]</sup> results only in the slight activity increase (Table 1, entries 1 vs 3 and 2 vs 4). Moreover, no change in the distribution of oligomers when the PPh<sub>3</sub> was used in the combination with Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, suggests that triphenylphosphine is not involved in the catalytic process.

The composition of the activator has a notable effect both on activity and selectivity of the studied systems. Thus, the use of Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, that has higher Lewis acidity,<sup>[53]</sup> instead of Et<sub>2</sub>AlCl, with the same Co/Al molar ratio results in growth of hexenes share from 4 to 18% (Table 1, entries 1 vs 2). This trend becomes even more noticeable at the elevated pressure of ethylene (Table 1, entries 2 vs 5). At the same time, an increase in the amount of  $Et_3Al_2Cl_3$  in the system to 600 equiv., despite increasing its activity, significantly reduces the share of hexenes to 9% (Table 1, entries 5 vs 6 and 7). The optimal composition of the system that allows to achieve the highest activity and comparable selectivity for  $\alpha$ -olefins (Table 1, entries 2 vs 9, 5 vs 6) is [Co]/[Al] = 1/300. However, catalytic system  $1/Et_3Al_2Cl_3$ showed low thermic stability, becoming inactive at 50 °C (Table 1, entry 12).



**FIGURE 3** Comparison of experimental and calculated <sup>1</sup>H chemical shifts for complexes **1** and **2** 

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**TABLE 1** Ethylene oligomerization with 1–2/OAC in toluene<sup>[a]</sup>

					Oligom	er distribu	ition <sup>c</sup> , %		
Entry	Precatalyst	Cocatalyst, [Al]/[M]	<b>Τ,</b> ° <b>C</b>	Activity <sup>b</sup>	C <sub>4</sub>	C <sub>6</sub>	C <sub>8</sub>	α-C <sub>4</sub>	α-C <sub>6</sub>
1	1	Et <sub>2</sub> AlCl, 150	30	63	95.9	4.1	-	84.9	67.3
2	1	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> , 150	30	106	81.7	18.3	-	79.2	74
3 <sup>d</sup>	1	Et <sub>2</sub> AlCl, 150	30	79	93.6	6.4	-	6.4	4.6
4 <sup>d</sup>	1	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> , 150	30	116	86	14	-	80.7	74.3
5 <sup>e</sup>	1	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> , 150	30	62	59.5	40.5	-	70.4	66.8
6 <sup>e</sup>	1	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> , 300	30	89	83.3	16.7	-	84.2	80.2
7 <sup>e</sup>	1	$Et_3Al_2Cl_3$ , 600	30	90	90.4	9.6	-	85.7	79.6
8	1	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> , 300	25	70	72.7	23.7	-	67	63.2
9	1	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> , 300	30	120	75.8	24.2	-	73	69
10	1	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> , 300	35	107	64.8	35.2	-	70.5	67.3
11	1	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> , 300	40	129	83.8	16.2	-	71.6	66.5
12	1	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> , 300	50	0	n.d.	n.d.	n.d.	n.d.	n.d.
13	2	Et <sub>2</sub> AlCl, 150	30	60	96	4	-	72.4	37.7
14	2	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub> , 150	30	324	89.8	9.5	0.6	47.7	25.9

<sup>a</sup>Oligomerization has been carried out in 50 mL of toluene at constant excessive ethylene pressure – 42 psi (2.9 atm), time: 30 min,  $1 \cdot 10^{-5}$  mol of corresponding complex.

 ${}^{b}kg_{oligomer} \cdot mol[M]^{-1} \cdot h^{-1} \cdot atm^{-1}$  (M = Ni, Co. The activities were calculated from the total consumption of ethylene (1.0 L ethylene = 1.18 g product)).

<sup>c</sup>Determined by GC ( $C_n$  – share of each oligomer fraction;  $\alpha$ - $C_n$  – share of  $\alpha$ -isomers in their fraction).

<sup>d</sup>Additive: Ph<sub>3</sub>P 1 equiv.

<sup>e</sup>Excessive pressure of ethylene – 86 psi (5.77 atm).

The activity of systems based on complex **2** (Table 1, entry 13) was equal to **1** (Table 1, entry 1), when  $Et_2AlCl$  was employed, but increased more than five times to 324 kg<sub>oligomer</sub>·mol[Ni]<sup>-1</sup>·h<sup>-1</sup>·atm<sup>-1</sup>, when activator was substituted for  $Et_3Al_2Cl_3$  (Table 1, entry 14). The same pattern was observed by us earlier,<sup>[17]</sup> when similar complex with tridentate ligand without –OMe group was used. The major products of the ethylene oligomerization with the **2**/OAC are butene isomers.

It should be noted, that Ni (II) and Co (II) complexes show the ability not only to oligomerize ethylene, but also to perform Friedel-Crafts alkylation of toluene with the resulting oligomers.<sup>[54]</sup> Usually this process is unfinished, since the oligomerization reaction predominates over the alkylation reaction, although there are reverse examples when the toluene alkylation is quantitative.<sup>[55]</sup> To prevent this side reaction in our study, the catalytic properties of systems based on complexes **1** and **2** were studied in the chlorobenzene medium.

# 3.3.2 | Oligomerization of ethylene in chlorobenzene

In addition to the previously used  $Et_2AlCl$  and  $Et_3Al_2Cl_3$  two new activators:  $EtAlCl_2$  (with higher Lewis acidity)

and MMAO, have been introduced in this set of experiments. The results of the catalytic experiments are shown in Table 2.

The activity of catalytic systems based on Co (II) complex **1** in chlorobenzene medium has increased to 140–200 kg<sub>oligomer</sub>·mol[Co]<sup>-1</sup>·h<sup>-1</sup>·atm<sup>-1</sup> (Table 2, entries 1, 2) due to greater solubility of the complex **1** in more polar solvent. However, the shares of 1-butene and 1-hexene in the reaction products decreased significantly compared to experiments in toluene ( $\alpha$ -C<sub>4</sub> < 45%,  $\alpha$ -C<sub>6</sub> < 35%). The use of EtAlCl<sub>2</sub> as co-catalyst does not increase the catalytic activity, compared to Et<sub>2</sub>AlCl (Table 2, entries 3 vs 1).

The activity of catalytic systems based on complex **2** is significantly higher than of systems with complex **1** (Table 2, entries 2 vs 7, 3 vs 11). It increases from 163 to 1912 kg<sub>oligomer</sub>·mol[Ni]<sup>-1</sup>·h<sup>-1</sup>·atm<sup>-1</sup> (Table 2, entries 5,7,11) in a row of activators: Et<sub>2</sub>AlCl < Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> < EtAlCl<sub>2</sub> according to the increase of their Lewis acidity.<sup>[56]</sup> The use of MMAO also affords the active system, but with the minimal activity – 89 kg<sub>oligomer</sub>·mol[Ni]<sup>-1</sup>·h<sup>-1</sup>·atm<sup>-1</sup> (Table 2, entry 9). Such effect of the activator composition on activity was previously observed in.<sup>[17,51,57-60]</sup> The use of 1 mol. Equiv. of PPh<sub>3</sub> increases the activity from 2 (EtAlCl<sub>2</sub>, Table 2, entries 11,12) to 12 times (MMAO, Table 2, entries 9,10) with the maximum value for system

				Oligor	ner distribution <sup>c</sup> ,	%					
Entry	Precatalyst	Cocatalyst, [Al]/[M]	Activity <sup>b</sup>	C 4	C,	c,	C <sub>10</sub>	C <sub>12</sub>	C <sub>14</sub> +	$\alpha$ -C <sub>4</sub> <sup>d</sup>	$\alpha$ -C <sub>6</sub> <sup>d</sup>
1	1	$Et_2AlCl$ , 300	211	52.6	47.3	0.1	ı	ı		9.3	5.9
7	1	$Et_3Al_2Cl_3$ , 300	144	86.9	10.9	0.7	0.1	0.4	Traces $\pm 1.0$ Alk <sup>g</sup>	45.3	35.0
ю	1	$EtAlCl_2$ , 300	199	45.2	47.1	2.4	0.8	4	0.5	41.3	16.2
4	1	MMAO, 500	traces	n.d.	n.d.	n.d.	p.u	n.d.	n.d.	n.d.	n.d.
5	2	$Et_2AlCl$ , 300	163	37.0	68.2	0.2	ı	ı	ı	47.0	14.3
6 <sup>e</sup>	7	$Et_2AlCl$ , 300	1,013	86.9	12.9	0.2	,	ı		3.1	2.2
7	7	$Et_3Al_2Cl_3$ , 300	1,021	49.7	40.5	4.8	4.3	0.1	0.5 Alk <sup>g</sup>	10.1	3.3
8 <sup>e</sup>	7	$Et_3Al_2Cl_3$ , 300	2,124	15.0	71.3	11.6	1.9	0.1	0.1 Alk <sup>g</sup>	6.3	3.7
6	7	MMAO, 500	89	31.8	10.8	24.8	1.9	1.0	$29.7  \mathrm{Alk}^{\mathrm{g}}$	63.6	17.4
$10^{\rm e}$	7	MMAO, 500	1,107	44.9	37.5	10.8	2.5	0.4	1.6 Alk <sup>g</sup>	3.9	0.8
$11^{\rm h}$	7	$EtAlCl_2$ , 300	1912	14.7	32.9 + 2.25 C <sub>7</sub>	$18.6 \pm 0.7 C_9$	12.1 + 1.4 C <sub>11</sub>	$11.9 \pm 0.5 C_{13}$	2.4 + 0.15 C <sub>15+</sub>	4.1	2.3
$12^{\rm e,h}$	7	$EtAlCl_2$ , 300	4,173	20.8	$34.3 + 2.2 C_7$	$19.0 \pm 0.45 C_9$	$10.8 + 2.2 C_{11}$	8.3 + 0.3 C <sub>13</sub>	$1.6 + 0.05 \text{ C}_{15+}$	5.1	2.4
$13^{\rm f,h}$	2	$EtAlCl_2$ , 300	3,457	13.9	30.0	$19.2 \pm 0.4 C_9$	$9.1 + 1.8 C_{11}$	$8.1 + 1.5 C_{13}$	24.2 + 1.5 C <sub>15+</sub>	5.4	2.6
<sup>a</sup> Oligomer <sup>b</sup> kgoligomer	ization has been mol[M] <sup>-1</sup> .h <sup>-1</sup> .ati	carried out in 50 mL of chlor $m^{-1}$ (M = Ni. Co. The activ	orobenzene at ities were calc	constant ulated fr	: excessive ethylene om the total consu	e pressure – 42 psi motion of ethylen	(2.9 atm), time: 30 e (1.0 L ethvlene =	min, 1·10 <sup>-5</sup> mol o: 1.18 g product)).	of corresponding comp	olex, $T=3$	0°C.

Ethylene oligomerization with 1--2/OAC in chlorobenzene $^{[a]}$ TABLE 2

<sup>a</sup> Soligoner models  $T_{14}$  -  $T_{14}$  - <sup>b</sup>kg, aOli

<sup>d</sup>Determined using GC.

<sup>e</sup>Additive: Ph<sub>3</sub>P 1 equiv. <sup>f</sup>Additive: Ph<sub>3</sub>P 2 equiv.

<sup>B</sup> $\Sigma$  amount of alkyltoluenes, Alk =  $R_{1-3}MePh$ . <sup>h</sup>Odd carbon number olefins are present in the resulting mixture.

The graph displaying oligomer distributions for systems based on complexes 1 and 2 is shown on Figure 4. The obtained oligomers are highly-branched, because numerous isomers have been observed on GC-MS curves (Figure 5; SI, Figures S15-S26). When Et<sub>2</sub>AlCl was used as the activator, the resulting systems produced only C<sub>4</sub> and C<sub>6</sub> fractions with traces of octenes both for complexes 1 and 2 (Figure 4; Table 2, entries 1,5,6). On the other hand, when activators with higher Lewis acidity were employed, oligomer mixtures with broader distributions up to C<sub>20</sub> were obtained. The share of obtained hexenes was higher than share of butenes in some experiments (Table 2, entries 3, 5, 8, 11-13). That fact cannot be ascribed just to the higher volatility of the last. The maximum hexene/butene ratio is observed for the system 2/300Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>/PPh<sub>3</sub> (Table 2, entry 8) and reaches 71.3/15. This difference, apparently, arises from the high reaction rate of 1-butene and ethylene co-dimerization, since the probable reaction mechanism, described below, does not imply the formation of metallocyclic intermediates (see paragraph 3.3.4).

It was also found that for catalytic systems based on complex **1** the share of  $C_{12}$  was higher than the share of  $C_{10}$  (Table 2, entry 2) and even than the one of  $C_8$  (Table 2, entry 3), which in this case indicates a significantly high reaction rate of 1-hexene dimerization. More equal distributions of oligomers are observed for systems based on complex **2**. Moreover, we were not able to use any of the previously proposed mathematical models<sup>[61]</sup>



**FIGURE 4** Distribution of ethylene oligomers obtained with catalytic systems based on complexes **1** and **2** 



**FIGURE 5** Part of GC–MS total ion current chromatogram of entry 8, Table 2, system 2/300 Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>/Ph<sub>3</sub>P

for the description of such distribution. This fact is attributed to a large number of ongoing co-oligomerization reactions between various olefins obtained during the catalytic process.

Upon a more detailed consideration of the analysis results of oligomer mixtures compositions, the formation of alkyltoluenes in the experiments 2, 7, 8, 10 should be noted. Their formation is explained by the use of MMAO and  $Et_3Al_2Cl_3$  toluene solutions as activators. In this regard, the 2/MMAO system deserves special attention, because, despite its low activity, it efficiently alkylates toluene with the obtained oligomers (29.7% of alkyltoluenes).

# 3.3.3 | Formation of odd carbon number olefins

The most intriguing results have been observed using 2/ EtAlCl<sub>2</sub> and 2/EtAlCl<sub>2</sub>/PPh<sub>3</sub> catalytic systems. In addition to expected ethylene oligomers with an even number of carbon atoms (C<sub>4</sub>-C<sub>20</sub>), olefins with an odd number of carbon atoms (C<sub>7</sub>-C<sub>15</sub>) have been obtained (See Figure 6A; Table 2, entries 11–13). The C<sub>7</sub> and C<sub>11</sub> fractions prevail among odd carbon number olefins, with the total amount of such products about 5%. Mass spectra of odd carbon number olefins are given in supporting information (SI, Figures S27-S41).

A more detailed analysis was carried out for the fraction with a boiling point >140 °C (Figure 6B) isolated from the oligomer mixture produced in entry 13 (Table 2). The results showed that the heaviest odd carbon number olefin ( $C_{19}$ ) is shorter by only one carbon atom than the heaviest even carbon number olefin ( $C_{20}$ ). The use of 1-hexene instead of ethylene significantly alters the distribution pattern of the reaction products. Thus, the oligomerization of 1-hexene with the system **2**/EtAlCl<sub>2</sub>



**FIGURE 6 (A)** compositions of oligomer mixtures obtained with systems based on 2/EtAlCl<sub>2</sub> (Table 2, entries 11–13); **(B)** composition of oligomer fraction with b.p. > 140 °C for 2/300 EtAlCl<sub>2</sub>/2 PPh<sub>3</sub> (Table 2, entry 13)

(Figure 7) results in 6.75% of hexene dimers, 0.86% of trimers and a minor amount of tetramers (not possible to identify single peaks due to overlap). The bulk of the reaction mixture (up to 90%) consists of the monomer, which has undergone significant isomerization (SI, Figure S42).

Besides the above-mentioned components, insignificant amounts of  $C_7$  and  $C_{10}$  isomers are present in the reaction mixture as well as  $C_8$  isomers and their cooligomerization products with 1-hexene –  $C_{14}$ ,  $C_{20}$  and  $C_{26}$  (the mass spectra of these compounds are presented in SI (Figures S43–S50)).

Previously, the formation off odd carbon number oligomers during ethylene oligomerization was observed for chromium-containing systems activated with MAO.<sup>[21,22]</sup> Initially, the formation of such products was explained by a mechanism presupposing the formation of a chromium carbene complex and further olefin metathesis.<sup>[21]</sup> Later a mechanism, involving chain-transfer to aluminum was introduced,<sup>[25]</sup> but in our case it is not likely due to the absence of methyl groups in the activator. Other reports<sup>[23,24]</sup> showed that formation of odd carbon



**FIGURE 7** Composition of the oligomer mixture obtained during 1-hexene oligomerization with 2/300 EtAlCl<sub>2</sub>

number olefins can proceed with Fe (II) bisiminopyridine complexes. A mechanism explaining these experimental facts suggests three simultaneous processes: oligomerization, isomerization and metathesis catalyzed by iron bisiminopyridine complex. Later several theoretical and computational studies<sup>[62,63]</sup> established that iron catalysts have a high potential in the reaction of olefin metathesis.

We cannot suggest a reliable mechanism of formation of odd carbon number olefins during ethylene oligomerization and unexpected products ( $C_7$ ,  $C_8$ ,  $C_{10}$ ,  $C_{14}$ ,  $C_{20}$ ,  $C_{26}$ ) during 1-hexene oligomerization using the available data. Based on the distribution of reaction products, it could be assumed that there is a probability of the following processes:

1). Cross-metathesis and ethylenolysis reactions (Figure 8) catalyzed by Ni complex **2** in the presence of EtAlCl<sub>2</sub>. According to<sup>[64]</sup> the equilibrium shift to the ethylenolysis reaction occurs at elevated ethylene pressure (in our experiments  $p_{ethylene} \ge 2.9$  atm.). If the ethylenolysis reaction really occurs, the formation of two terminal odd carbon number oligomers is quite natural during the reaction of an even carbon number olefin molecule with inner double bond and ethylene, although unexpected. For example, for  $C_{15}^{=}$ :  $C_2^{=} + 2 \cdot C_{16}^{=} = C_3^{=} + 1 \cdot C_{15}^{=}$ , followed by subsequent isomerization.

2).  $\beta$ -alkyl elimination,<sup>[65]</sup> as an alternative mechanism of chain termination. Cleavage of  $\beta$ -CH<sub>3</sub> gives products that differ by only one carbon atom, considering the case of ethylene oligomerization. However, this mechanism much worse describes the distribution of products formed during the oligomerization of 1-hexene, because it requires the preferable  $\beta$ -C<sub>2</sub>H<sub>5</sub> elimination.



**FIGURE 8** Schematic representation of equilibrium between cross-metathesis and ethylenolysis

**FIGURE 9** Part of <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>) spectrum of oligomer mixture obtained with **2**/300 EtAlCl<sub>2</sub>/2 PPh3 (Table 2, run 13)



The possible formation of odd carbon number olefins, as a result of side-reactions in the presence of the  $EtAlCl_2$ , is not supported neither by literature<sup>[57,66–82]</sup> nor by experimental data (SI, Figure S51).

# 3.3.4 | The mechanistic aspects of ethylene oligomerization

In accordance with the most common point of view,<sup>[83,84]</sup> ethylene oligomerization with catalytic system based on nickel and cobalt complexes proceeds via the Cossee–Arlman coordination–migration mechanism.<sup>[85,86]</sup> Taking into account the tetradentate nature of the ligand, the active species are probably generated through complete substitution of halide ligands on the metal center. However, the <sup>1</sup>H NMR spectra of methanol solutions of these complexes revealed only tridentate coordination. It is

possible that -OMe group can play a role of oscillating donor during the catalytic process in less polar medium (toluene, chlorobenzene), but the additional experiments are required to determine the coordination mode of the ligand during the catalytic process and the active species.

Earlier, we have considered the probable mechanism of formation of hexene isomers using catalytic systems based on NNN-nickel (II) complexes<sup>[43]</sup> and showed that it doesn't differ from the generally accepted model. However, the <sup>13</sup>C NMR spectrum of oligomer mixture obtained with 2/300 EtAlCl<sub>2</sub>/2 PPh<sub>3</sub> (Figure 9) shows the presence of intensive signals that belong to cis-3-methyl-2-pentene (137.91 ppm and 118.09 ppm), trans-3-methyl-2-pentene (137.69 ppm and 116.97 ppm) and 3-methyl-1-pentene (144.77 ppm and 112.54 ppm). In addition, the signals of 1-butene (140.67 ppm and 113.24 ppm), cis-2-butene (124.72 ppm), trans-2-butene (125.96 ppm), cis-2-hexene (131.02 ppm) and trans-2-hexene (131.56 ppm)



**SCHEME 2** Proposed mechanism for the formation of butene and hexene isomers, during ethylene oligomerization

are clearly visible in the spectrum. The assignments of these signals have been proposed based on.<sup>[43,87]</sup>

The formation of 3-methyl-2-pentene may indicate that the oligomerization process proceeds according to the metallocyclic mechanism.<sup>[88-90]</sup> In this case, branched hexene isomers, such as 3-methyl-2-pentene, 3-methyl-1-pentene, 2-ethyl-1-butene, are formed by the co-dimerization of ethylene and butene through the formation of metallocycle. Thus, the co-dimerization product obtained from ethylene and 1-butene will be 2-ethyl-1-butene, which signals (153.36 ppm and 106.76 ppm) are absent in the <sup>13</sup>C spectrum. Therefore, we proposed a mechanism for the formation of cis–/trans-3-methyl-2-pentene and 3-methyl-1-pentene according to the Cossee mechanism (Scheme 2).

According to this mechanism, at the first stage of the process, two ethylene molecules sequentially insert into the nickel hydride complex to form LNi<sup>+</sup>n-Bu. Further proceeds the formation either of 1-butene via  $\beta$ -H elimination, or of LNi<sup>+</sup>sec-Bu via chain-walking. Also the consecutive chain growth can occur, resulting in the formation of linear hexenes upon their elimination from  $LNi^+n$ -Hex. At the same time, the formation of 1-butene and 1-hexene can be considered reversible, since they can easily reinsert to metal center and undergo further transformations. Starting from LNi<sup>+</sup>sec-Bu either cis-/trans-2-butenes or isomers of 3-methylpentene are formed, the latter via consecutive chain-walking and insertion steps. The high speed of chain-walking rearrangements is worth mentioning - the signals corresponding to internal olefins are dominating the <sup>13</sup>C NMR spectrum of the oligomer mixture.

### 4 | CONCLUSIONS

In this work, we have obtained and characterized neutral monoligated Ni (II) and Co (II) complexes with the new NNNO-heteroscorpionate ligand. The first two, activated by Et<sub>2</sub>AlCl, Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> or EtAlCl<sub>2</sub>, catalyze ethylene oligomerization. The activity of the nickel-based catalytic sysis tem significantly higher and reaches 1900  $kg_{oligomer} \cdot mol[Ni]^{-1} \cdot h^{-1} \cdot atm^{-1}$  when  $EtAlCl_2$  is used. The addition of triphenylphosphine to this system increases catalytic activity by 2-12 times. The maximum value of activity was obtained for system 2/EtAlCl<sub>2</sub>/PPh<sub>3</sub>-4,173  $kg_{oligomer} \cdot mol[Ni]^{-1} \cdot h^{-1} \cdot atm^{-1}$ . The products of ethylene oligomerization reaction consisted of branched olefins with chain lengths ranging from  $C_4$  to  $C_{20}$ . Catalytic oligomerization of ethylene with the  $2/EtAlCl_2$  and 2/EtAlCl<sub>2</sub>/PPh<sub>3</sub> systems revealed the formation of oligomers with an odd number of carbon atoms, the amount of which is  $\sim$ 5% of entire oligomer mixture. Two possible mechanisms for the formation of these products have been proposed: ethylenolysis of  $\beta$ -olefins and  $\beta$ -alkyl elimination during oligomerization. The presence of branched oligomers (in particular hexenes) in the oligomer mixture is most likely the result of chain migration and subsequent ethylene insertion processes, which is in accordance with the Cossee mechanism.

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