

# Trapping the Short-Chain Odd Carbon Number Olefins Using Nickel(II)-catalyzed Tandem Ethylene Oligomerization and Friedel-Crafts Alkylation of Toluene

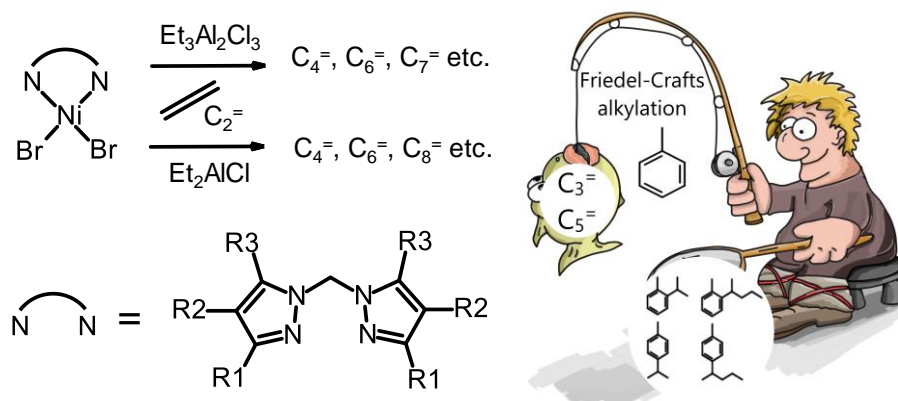
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## Abstract

Nickel(II) complexes with pyrazole-based ligands are widely employed in catalysis of ethylene oligomerization and subsequent Friedel-Crafts alkylation of toluene. We have prepared ten new nickel(II) dibromide complexes with various substituted bis(azoly)methanes. They have been characterized using <sup>1</sup>H NMR, IR, MALDI-TOF and elemental analysis. The structures of three complexes have been unambiguously established using X-ray diffraction. It was found that these complexes in the presence of Et<sub>2</sub>AlCl or Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> are active both in ethylene oligomerization and Friedel-Crafts alkylation processes (activity up to 3720 kg<sub>oligomer</sub>·mol[Ni]<sup>-1</sup>·h<sup>-1</sup>). The use of Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> results in the higher share of alkylated products (up to 60%). Moreover, catalytic systems activated with Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> produced small amounts of odd carbon number olefins (up to 0.8%). The Friedel-Crafts alkylation was used as a trap for previously undetected short-chain odd carbon number olefins (C<sub>3</sub> and C<sub>5</sub>).

**Keywords:** ethylene; oligomerization; Friedel-Crafts alkylation; nickel(II) complexes; bis(azoly)methane; odd carbon number olefins.

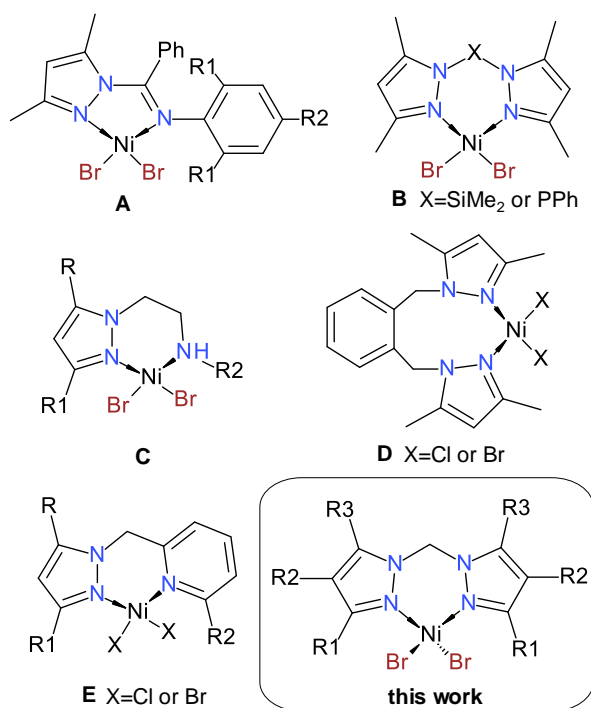
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## 1. Introduction

The use of nickel(II) complexes with nitrogen-based ligands for ethylene polymerization was first reported in 1995 by Brookhart *et al.* [1]. The subsequent studies revealed that similar  $\alpha$ -diimine complexes were capable of catalyzing the oligomerization of ethylene and propylene [2,3]. Recently the area of nickel-catalyzed oligomerization and polymerization of olefins received a new boost. Nickel complexes are being widely employed for processes of chain-walking ethylene polymerization [4,5,14–23,6,24–27,7–13] and copolymerization of ethylene with polar monomers [22,24,35–44,27–34]. However, the interest in the development of new nickel-based catalytic systems for ethylene oligomerization is still high [4,6,53–62,45–52], especially, regarding recent discoveries of tandem Friedel-Crafts alkylation of toluene with ethylene oligomers [63]. The resulting polyalkyltoluenes can be further used in the production of surfactants and detergents [64].

Nickel(II) complexes with N-donor bidentate pyrazole-based ligands can effectively catalyze ethylene oligomerization (Fig. 1). The derivatives of original Brookhart-type catalysts – (pyrazol-1-yl)imine nickel(II) complexes **A** [65], upon activation with MAO, produce C<sub>4</sub>–C<sub>14</sub> olefins with moderate activities. Bis(pyrazol-1-yl)silane and bis(pyrazol-1-yl)phosphine complexes **B** [66] also exhibited moderate activities, but produced only butenes (70-90%) and hexenes (10-30%). Moreover, nickel(II) pyrazole complexes were among the first precatalysts that showed the ability to catalyze ethylene oligomerization and Friedel-Crafts alkylation of toluene simultaneously [63]. Nickel(II) complexes with (pyrazol-1-ylethyl)amines **C** [67,68], 1,2-bis(pyrazol-1-ylmethyl)benzene **D** [69] and 2-(pyrazol-1-ylmethyl)pyridines **E** [67,70–72] were highly active both in ethylene oligomerization and Friedel-Crafts alkylation of toluene.



**Figure 1.** Structures of nickel(II) halide complexes with pyrazole containing ligands active in ethylene oligomerization.

However, to our surprise, simple bis(pyrazol-1-yl)methane nickel complexes were poorly studied. Nickel(II) halide complexes with bis(3,5-dimethylpyrazol-1-yl)methane have been earlier described by Reedjik and coworkers [73–75]. Recently we have reported catalytic studies of bis(3,5-dimethylpyrazol-

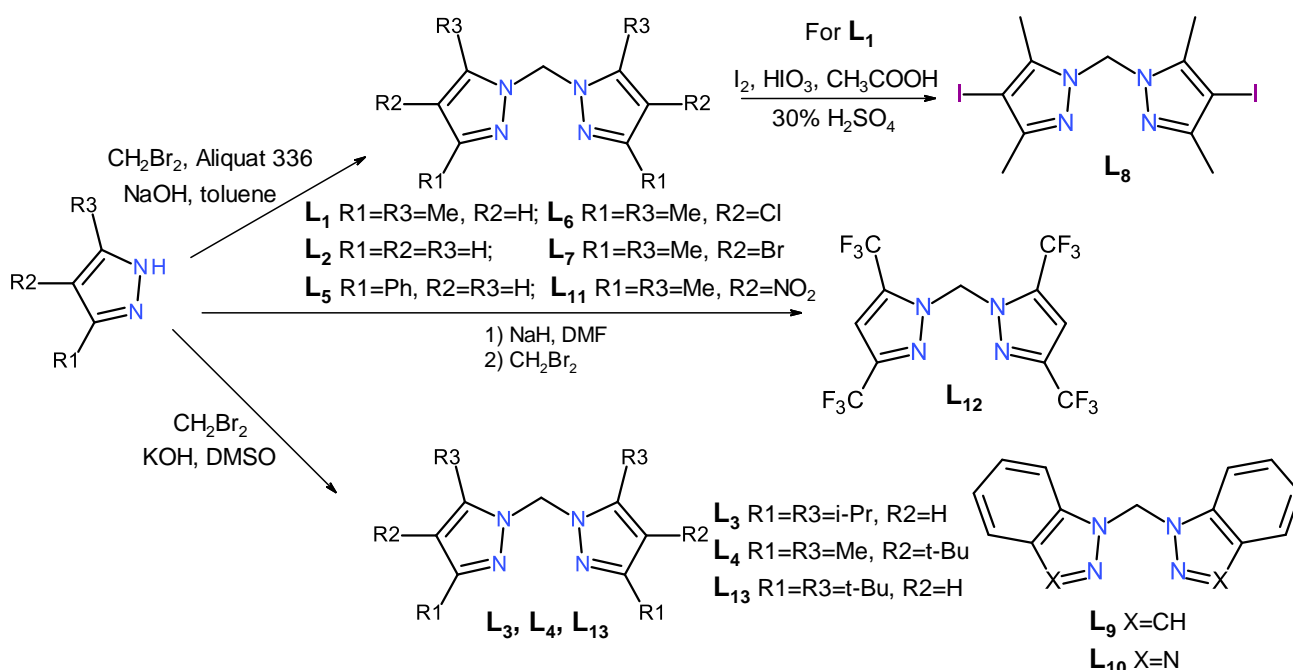
1-yl)methane nickel(II) bromide in ethylene oligomerization [56,57]. Oligomerization of ethylene yielding C<sub>4</sub>-C<sub>20</sub> branched olefins catalyzed by substituted bis(pyrazolyl)methane nickel complexes was also reported by Fumiyuki [76].

In this study we report synthesis and characterization of nickel(II) dibromide complexes with 1,1'-bis(indazolyl)methane, 1,1'-bis(benzotriazolyl)methane and bis(pyrazolyl)methane ligands, bearing various substituents in the pyrazole rings. These compounds, after treatment with Et<sub>2</sub>AlCl or Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, were active both in ethylene oligomerization and subsequent Friedel-Crafts alkylation of toluene. Moreover, the unexpected formation of small amounts of odd carbon number olefins was observed. This feature of nickel(II) complexes with heteroscorpionate ligands was previously reported by us in [60].

## Results and Discussion

### 1.1. Synthesis and characterization.

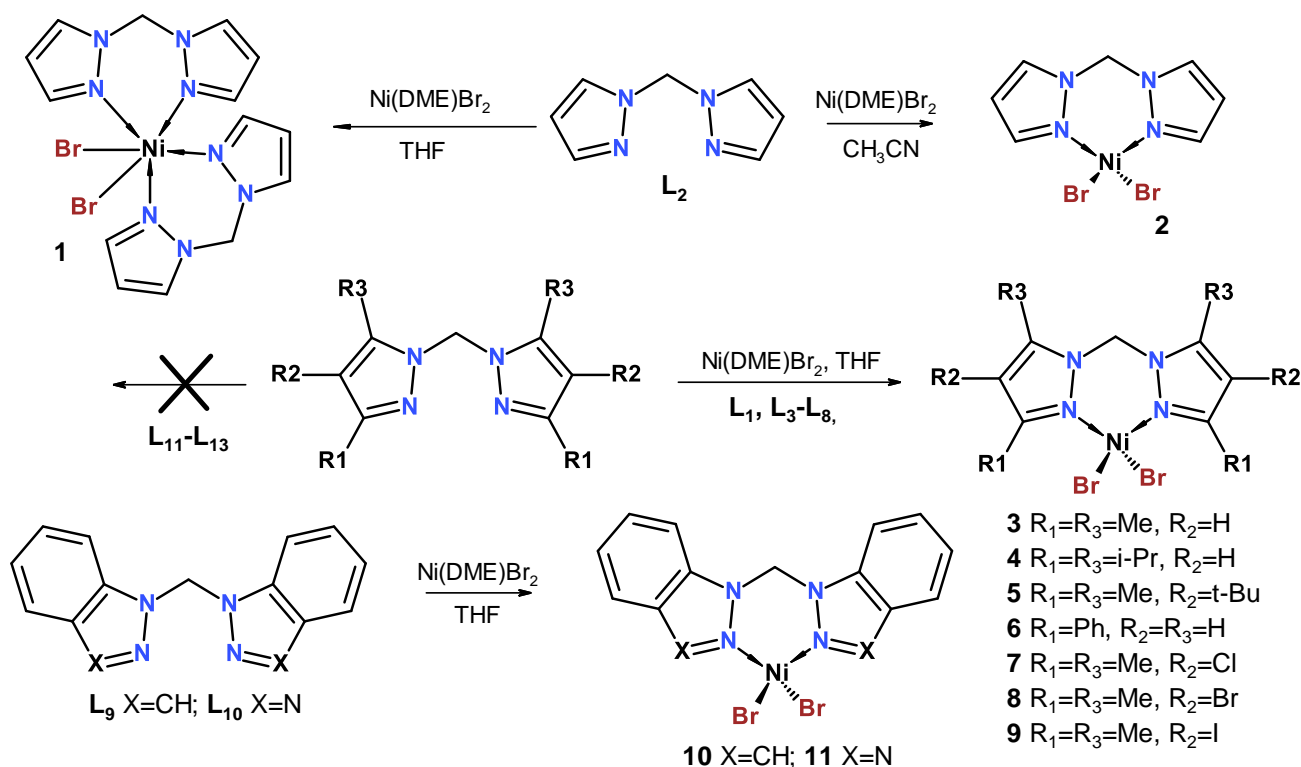
The library of bis(azolyl)methane ligands, bearing various substituents, has been prepared using three different synthetic pathways (Scheme 1). Ligands **L**<sub>1</sub>, **L**<sub>2</sub>, **L**<sub>5</sub>-**L**<sub>7</sub> and **L**<sub>11</sub> were prepared according to modified procedure [77], where Aliquat 336<sup>®</sup> was used instead of (*n*Bu<sub>4</sub>N)Br. Ligand **L**<sub>8</sub> was prepared by iodation of **L**<sub>1</sub> according to [78]. However, to prepare ligand **L**<sub>12</sub> (with highly electron withdrawing CF<sub>3</sub>- groups) or ligands **L**<sub>3</sub>, **L**<sub>4</sub>, **L**<sub>13</sub> (with bulky substituents) in high yields alternative methods were employed [79,80]. 1,1'-bis(indazolyl)methane **L**<sub>9</sub> and 1,1'-bis(benzotriazolyl)methane **L**<sub>10</sub> were also prepared according to [80] and then purified using column chromatography. The detailed synthetic procedures and <sup>1</sup>H, <sup>13</sup>C NMR and IR spectra of organic ligands are given in supporting information (Figs. S1-29).



**Scheme 1.** Synthesis of bis(azolyl)methane ligands **L**<sub>1</sub>-**L**<sub>13</sub>.

Synthesis of complex **3** was previously reported by us in [56]. All other nickel(II) dibromide complexes have been prepared by interaction of Ni(DME)Br<sub>2</sub> with corresponding ligand in THF (**1**, **4**-**11**) or CH<sub>3</sub>CN (**2**) (Scheme 2). However, stable complexes have not been obtained for ligands **L**<sub>11</sub>-**L**<sub>13</sub>, which may be due either to an increase in steric load (*t*-Bu group in the 3<sup>rd</sup> position of the pyrazole ring, **L**<sub>13</sub>) or to

electronic effects (introduction of electron withdrawing groups  $-\text{NO}_2$  (**L**<sub>11</sub>) or  $-\text{CF}_3$  (**L**<sub>12</sub>)). All complexes have been characterized with IR spectroscopy (SI, Figs. S30-39), high-resolution MALDI-TOF spectrometry (SI, Figs. S51-60) and elemental analysis. According to the MALDI-TOF data all complexes except for **1** are monoligated compounds that are observed as  $[\text{NiLBr}]^+$  cations in the mass-spectra. For complex **1** a bisligated structure was proposed based on observation of positively charged ion ( $m/z = 435.112$ ) with the composition  $[\text{NiL}_2\text{Br}]^+$  (SI, Fig. S51) and elemental analysis data. For complexes **1** and **9** some minor signals with  $m/z$  higher than of  $[\text{NiLBr}]^+$  were observed. They were not attributed to any particular composition and are probably the result of the recombination of ions formed upon ionization of the parent complexes. For complex **8** such signal ( $m/z = 673.678$ ) was attributed to the addition of the pyrazole unit to  $[\text{NiLBr}]^+$  (SI, Fig. S57).



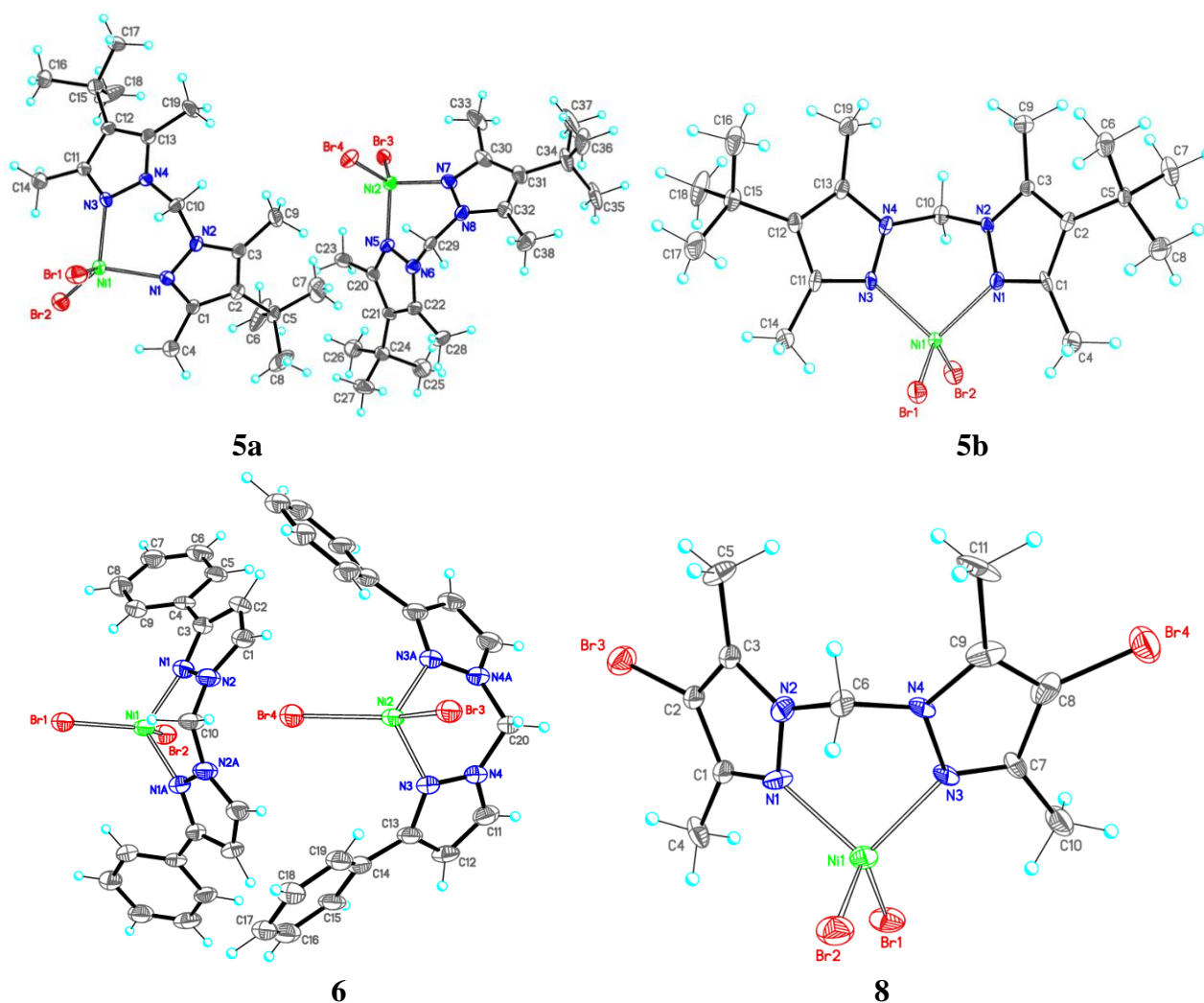
**Scheme 2.** Synthesis of nickel(II) complexes **1-11**.

The structures of complexes **5a**, **5b**, **6** and **8** were unambiguously established by X-ray diffraction study and are shown in Figure 2 along with the atomic numbering schemes. The selected bond lengths and angles are given in Table 1.

**Table 1.** Bond distances (Å) and angles (°) (*average values*) for Ni(II) in **5a**, **5b**, **6** and **8**.

Compound	<b>5a</b>	<b>5b</b>	<b>6</b>	<b>8</b>
Ni—Br <sub>ax</sub>	2.3576(14)	2.3784(12)	2.3741(14)	2.372(3)
Ni—Br <sub>eq</sub>	2.3625(13)	2.3508(11)	2.3683(16)	2.358(3)
Ni—N	2.015(6)	2.013(5)	2.035(4)	2.021(14)
Br <sub>ax</sub> —Ni—Br <sub>eq</sub>	123.93(5)	132.13(4)	129.22(5)	122.20(13)
Br <sub>ax</sub> —Ni—N	104.19(19)	103.95(16)	102.28(12)	102.7(4)
Br <sub>eq</sub> —Ni—N	113.33(18)	108.06(16)	111.07(12)	115.8(4)
N—Ni—N	93.2(2)	94.2(2)	95.6(2)	92.9(6)

The crystals of **5a** and **5b** are the two different polymorphic modifications of compound **5**, which crystallize in the orthorhombic *Pbca* (with the two crystallographically independent molecules) and monoclinic *Cc* space groups, respectively. Moreover, compound **6** crystallizes in monoclinic *C2/m* space group with the two crystallographically independent molecules occupying special positions on the mirror planes.



**Figure 2.** Molecular structures of complexes **5a**, **5b**, **6** and **8**. Thermal ellipsoids are shown at the 50% probability level.

All studied complexes are mononuclear with a bidentate (bispyrazolyl)methane ligand and two terminal bromide ligands. Thus, the nickel atom has the distorted tetrahedral environment. The organic ligand forms a chelate six-membered ring in a *boat* conformation, with the four nitrogen atoms composing the basal plane (rms deviations are 0.001/0.040, 0.016, 0.0/0.0 (due to the intrinsic symmetry), and 0.044 Å for **5a**, **5b**, **6** and **8**, respectively) and the metal and bridged carbon atoms deviating from this plane by 0.604(9)/0.586(10) and 0.696(10)/0.677(9), 0.399(9) and 0.688(8), 0.435(9)/0.685(10) and 0.479(9)/0.695(9), and 0.58(2) and 0.66(2) Å for **5a**, **5b**, **6** and **8**, respectively. Consequently, one of the two bromide ligands is in the axial position, and the other one – in the equatorial position. It is important to note that the Ni–Br<sub>ax</sub> and Ni–Br<sub>eq</sub> distances are close to each other. Nevertheless, due to the steric reasons, the Br<sub>ax</sub>–Ni–N bond angles are significantly smaller than the Br<sub>eq</sub>–Ni–N bond angles (Table 1).

The bis(pyrazolyl)methane ligands in **5a**, **5b**, **6** and **8** adopt a *butterfly* conformation with the interplane angle between the pyrazole rings of 60.8(2)/57.3(2), 61.86(17), 55.64(16)/45.69(17) and 56.6(2)° for **5a**, **5b**, **6** and **8**, respectively. As it can be expected, the *endo*-cyclic Ni—N—N angles are substantially smaller than the *exo*-cyclic Ni—N—C angles.

In the crystals, molecules of **5a**, **5b**, **6** and **8** are packed in stacks along the crystallographic *a*, *c*, *b* and *a* axes, respectively. The stacks are linked to each other by weak C—H···Br hydrogen bonding interactions.

Complexes **4-9**, that are soluble in CH<sub>2</sub>Cl<sub>2</sub>, were also characterized using <sup>1</sup>H NMR (SI, Figs. S43-S49). All studied compounds are paramagnetic and exhibit sharp or broad signals, depending on the position of hydrogen atoms, in the area from -10 to 75 ppm. The annotations of these signals (see experimental section and SI for details) were proposed using normalized integrals and widths of the signals. It is known, that the closer is the nucleus to the paramagnetic metal the faster is the relaxation and, thus, the width of the signal increases. The proposed annotations are consistent with those of similar complexes for which the DFT calculations have been performed [56]. Complexes without substituents near to the donor nitrogen atom (**1**, **2**, **10**, **11**) are insoluble in common organic solvents except alcohols. The use of polar coordinating solvent (CD<sub>3</sub>OD) probably leads to the formation of new adducts and so the <sup>1</sup>H NMR spectra of complexes **1** and **2** are similar and uninformative (SI, Figs. S40-42). Complexes **6-8** are co-crystallized with 0.5 or 1 eq. THF according to <sup>1</sup>H NMR spectra (SI, Figs. S45-48) and elemental analysis. Complex **10** also contains 0.5 eq. THF according to the IR spectrum (presence of the band at 1046 cm<sup>-1</sup>) (SI, Fig. S38) and elemental analysis.

The UV-Vis spectra (SI, Fig. S50) of dichloromethane solutions of complexes **3-9** are similar, differing mostly in intensity. The maximum intensities were achieved for halogen substituted complexes **7-9** and the lowest was exhibited by complex **6** with *ortho*-phenyl substituents. All studied complexes have 4 main absorption bands: 310-320 nm ( $\pi \rightarrow \pi^*$  transitions in aromatic rings), 330-360 nm (charge transfer from bromine atoms to nickel), 500-600 nm and 870-900 nm (charge transfer from ligand to nickel atom), that are typical for Ni<sup>2+</sup>(d<sup>8</sup>) complexes [81,82].

## 1.2. Ethylene oligomerization and Friedel-Crafts alkylation of toluene

Complexes **1,2,4-11** were activated either with Et<sub>2</sub>AlCl or Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> and evaluated for their ability to catalyze ethylene oligomerization (Table 2). Precatalyst **3**, previously described by us in [56,57], was introduced for proper comparison of the results.

**Table 2.** Ethylene oligomerization with catalytic systems based on complexes **1-11**<sup>a</sup>.

Run	Complex	Co-catalyst	Activity <sup>b</sup>	Butene/Hexene distribution <sup>c</sup> , %			
				C <sub>4</sub> <sup>=</sup>	C <sub>6</sub> <sup>=</sup>	$\alpha$ -C <sub>4</sub> <sup>=</sup>	$\alpha$ -C <sub>6</sub> <sup>=</sup>
1	<b>1</b>	Et <sub>2</sub> AlCl	3165	92.9	7.1	11.1	12.7
2	<b>1</b>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	3720	89.8	10.2	15	21.3
3 <sup>e</sup>	<b>2</b>	Et <sub>2</sub> AlCl	657	94.2	5.6	50.3	27.5
4 <sup>d</sup>	<b>3</b>	Et <sub>2</sub> AlCl	705	94.1	5.9	47.6	27
5 <sup>d</sup>	<b>3</b>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	282	95.7	4.3	93.2	60.1
6	<b>4</b>	Et <sub>2</sub> AlCl	1797	90.3	9.7	26	17.6
7	<b>4</b>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	1425	88.8	11.2	33.6	19.6
8 <sup>e</sup>	<b>5</b>	Et <sub>2</sub> AlCl	1629	90	9.4	28.5	18.1
9 <sup>e</sup>	<b>5</b>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	1407	89	10.1	33.1	19.4
10	<b>6</b>	Et <sub>2</sub> AlCl	1560	90.1	9.9	34.5	19.4
11 <sup>e</sup>	<b>6</b>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	606	89	10.2	38.3	20.6
12 <sup>e</sup>	<b>7</b>	Et <sub>2</sub> AlCl	1242	91.5	8	38.6	21.4
13	<b>7</b>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	1107	90.8	9.2	43.1	22.5
14	<b>8</b>	Et <sub>2</sub> AlCl	1224	91.4	8.6	40.5	21.8
15 <sup>e</sup>	<b>8</b>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	1209	89.7	9.5	39.8	21.8
16 <sup>e</sup>	<b>9</b>	Et <sub>2</sub> AlCl	1419	92.4	7.2	29.3	18.8
17 <sup>e</sup>	<b>9</b>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	909	90.9	8.4	48.9	23.8
20	<b>10</b>	Et <sub>2</sub> AlCl	1710	91.2	8.8	25.4	17
21 <sup>e</sup>	<b>10</b>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	1185	90.3	8.9	42.7	23.2
22	<b>11</b>	Et <sub>2</sub> AlCl	1992	93.3	6.7	16.1	13.7
23	<b>11</b>	Et <sub>3</sub> Al <sub>2</sub> Cl <sub>3</sub>	1371	90.7	9.3	35.6	21.3

<sup>a</sup> Oligomerization has been carried out in 50 mL of toluene at constant pressure of ethylene and toluene vapors – 56 psi (3.8 atm), time: 30 min, temperature – 30 °C, [Ni]=1·10<sup>-5</sup> mol, [Al]/[Ni]=150/1.

<sup>b</sup> kg<sub>oligomer</sub>·mol[Ni]<sup>-1</sup>·h<sup>-1</sup>

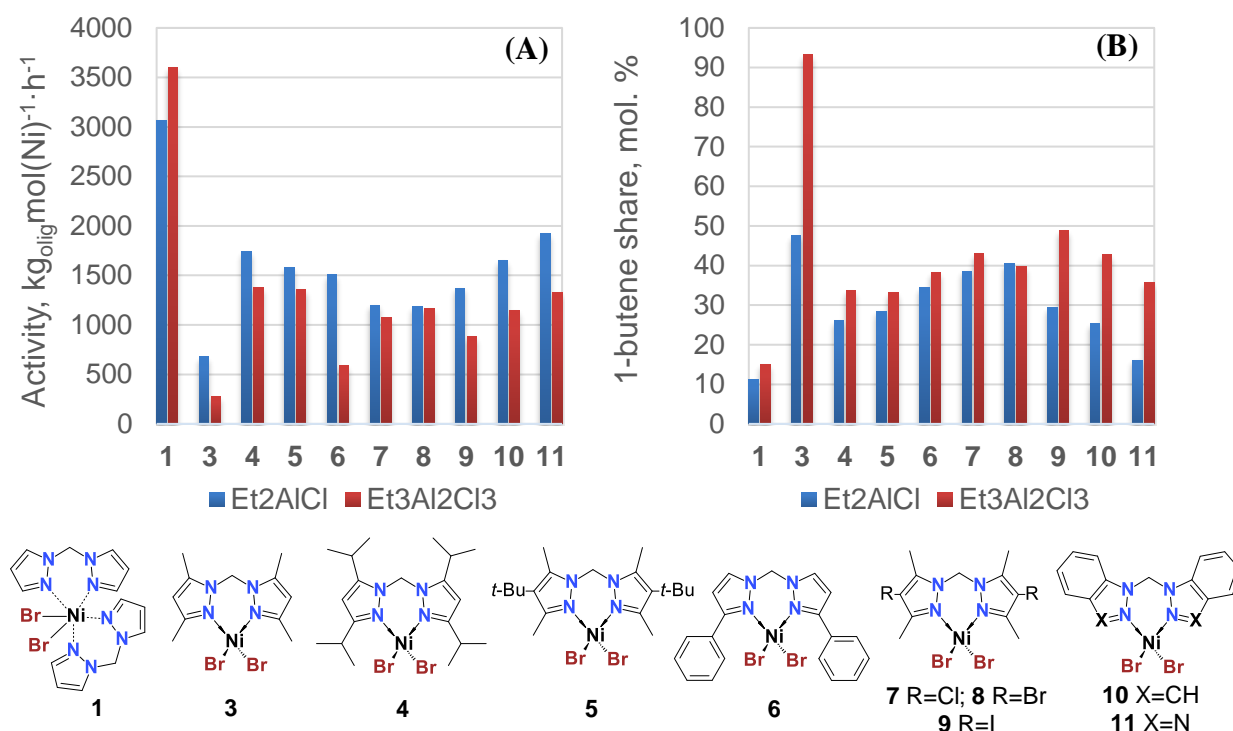
<sup>c</sup> determined using GC; C<sub>4</sub><sup>=</sup>, C<sub>6</sub><sup>=</sup> – total shares of each oligomer fraction;  $\alpha$ -C<sub>4</sub><sup>=</sup>,  $\alpha$ -C<sub>6</sub><sup>=</sup> – shares of  $\alpha$ -isomer in each fraction.

<sup>d</sup> reported in [56,57], used for comparison of the results

<sup>e</sup> trace amounts of octenes (< 1%) are present in the mixture

All complexes except **2** exhibited catalytic activities higher than 1000 kg<sub>oligomer</sub>·mol[Ni]<sup>-1</sup>·h<sup>-1</sup> that exceed the activity of previously reported parent complex **3**. The lowest activity of **2** is attributed to the low solubility of compound in reaction media (toluene) in the absence of substituents in pyrazole rings. Generally, the values of catalytic activity were higher when Et<sub>2</sub>AlCl had been used as an activator (Fig. 3A). However, the use of Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> resulted in the higher share of 1-butene in the oligomer mixture (Fig. 3B). This fact can be attributed to different alkylating ability and Lewis acidity of these activators [83,84]. The diethylaluminium chloride (Et<sub>2</sub>AlCl) easily alkylates nickel that results in the fast formation of active centers. At the same time it possesses lower Lewis acidity, compared to Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, that results in the better stabilization of nickel hydride complexes, which are considered to be the catalytically active species [85–87]. The maximum catalytic activity was achieved for catalytic systems based on complex **1** (Table 2, runs 1-2) – 3160 и 3720 kg·mol[Ni]<sup>-1</sup>·h<sup>-1</sup> after treatment with Et<sub>2</sub>AlCl or Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>

correspondingly. Such a large difference in activity compared to other systems can be ascribed to the different structure of the pre-catalyst. Complex **1** according to MALDI-TOF (SI, Fig. S51) and elemental analysis is a bisligated compound with the chemical formula – NiL<sub>2</sub>Br<sub>2</sub>. It can be speculated that two bidentate donor ligands increase the donation of electrons to the nickel atom thus increasing the stability of the catalytically active center. Previously monoligated and bisligated Ni(II) complexes supported with bulky iminopyridine ligands have been compared for their ability to catalyze ethylene polymerization [88] and bisligated compounds exhibited more stability during catalytic tests under various reaction conditions.



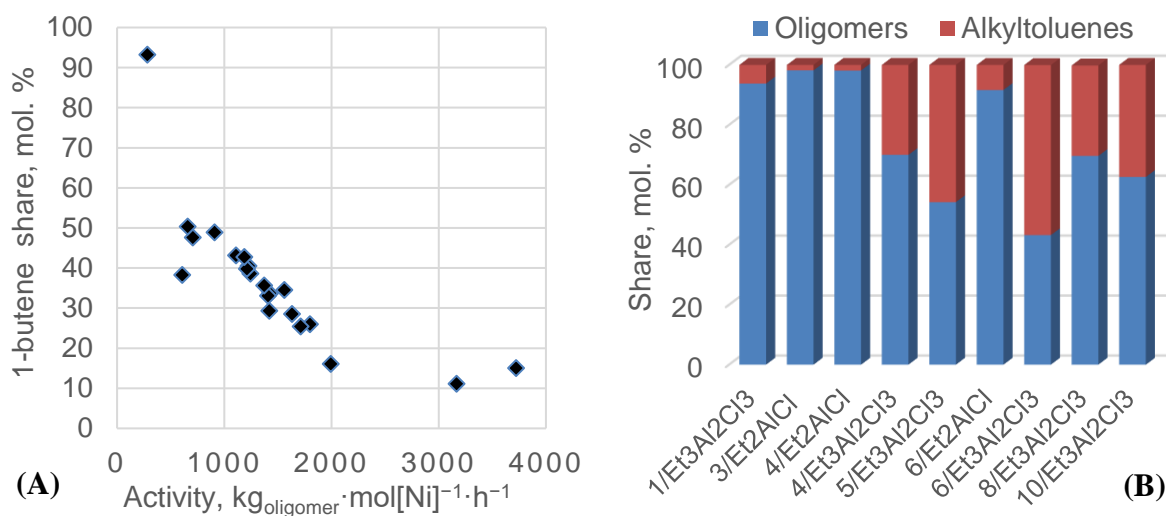
**Figure 3.** Dependencies of catalytic activity (A) and 1-butene share (B) on the composition of catalytic system.

An interesting dependence can be observed, if we plot the share of 1-butene against the activity of the catalytic system (Fig. 4A): the higher is the catalytic activity the lower is the share of 1-butene. Possibly such dependence originates from the equilibrium between the rates of chain propagation and  $\beta$ -hydrogen elimination that increase simultaneously. Thus, more active catalytic systems produce a higher share of internal olefins. Moreover, it can be observed that in the middle of the chart this dependence is almost linear ( $R^2 = 0.928$ ).

The initial analysis of the oligomerization products composition using GC showed that only C<sub>4</sub> (88.8 – 95.7 %) and C<sub>6</sub> (4.3 – 11.2 %) fractions with a small amount of octenes (0 – 0.8%) were produced. Both butene and hexene fractions consist of different isomers according to <sup>13</sup>C NMR analysis (SI, Fig. S61). Signals corresponding to 1-butene (140.38 and 113.11 ppm), cis-2-butene (124.5 ppm), trans-2-butene (125.75 ppm), cis-2-hexene (130.84 ppm), trans-2-hexene (131.37 ppm), cis-3-methyl-2-pentene (117.98 ppm), trans-3-methyl-2-pentene (116.84 ppm) and 2-ethyl-1-butene (106.31 ppm) are observed in the reaction mixture obtained with **6**/Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> (Table 2, run 11). The annotations have been proposed using previously described data [55,89]. As can be seen both from <sup>13</sup>C NMR and GC analyses the content of internal olefins in the hexene fraction is much higher than in butene fraction. This feature originates from the co-dimerization of ethylene and butene isomers predominantly yielding branched internal



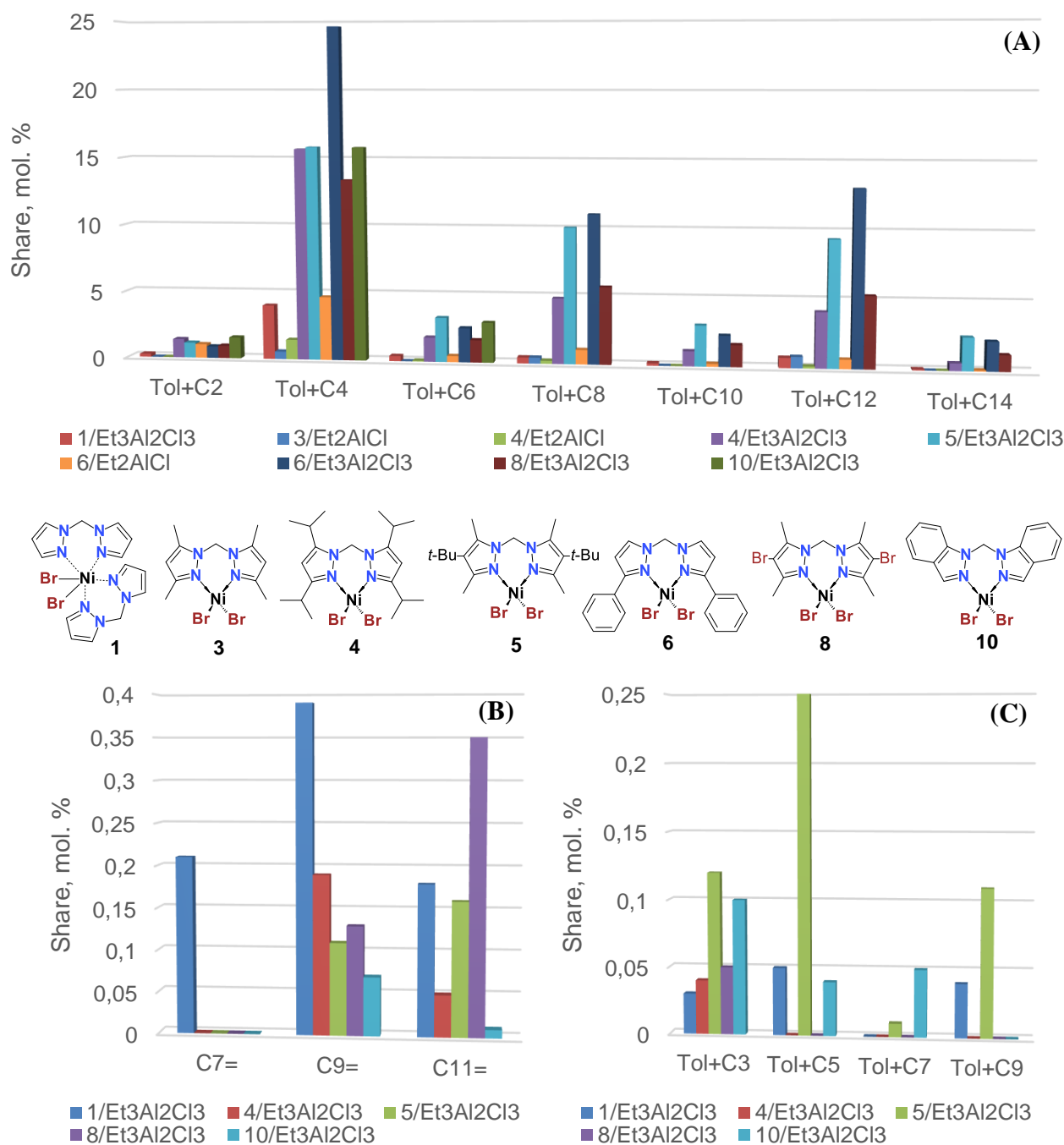
hexenes [90]. It can be suggested that the facility of  $\beta$ -H elimination and subsequent extensive isomerization of the obtained olefins results in highly branched oligomer mixtures containing vast amount of different isomers. However, the use of a more sensitive GC-MS technique for selected samples revealed that the composition of reaction products is even more complex (SI, Table S22).



**Figure 4.** (A) Dependence of 1-butene share on catalytic activity; (B) shares of oligomers and alkyltoluenes for catalytic systems based on complexes **1**, **3-6**, **8**, **10** (determined using GC-MS).

First, the studied catalytic systems are able to catalyze Friedel-Crafts alkylation of toluene with produced ethylene oligomers or ethylene itself (Fig. 4B). That feature of nickel(II) based systems is frequently reported by other researchers [69]. The share of alkyltoluenes in the reaction mixture is up to 60% (for **6**/Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> – Table 2, run 11). The use of a more Lewis acidic activator – Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, results in the formation of a higher amount of alkyltoluenes than the use of Et<sub>2</sub>AlCl. It seems that the introduction of any substituent in the pyrazole ring leads to the increase of the alkylation rate. The shares of alkyltoluenes increase in the following order **1**<**4**<**8**<**10**<**5**<**6** for the catalytic systems activated with Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>. The whole set of alkylated products is formed during the catalytic process including trace amounts of heavy alkyltoluenes (Tol+C<sub>16</sub> and Tol+C<sub>18</sub>) (Fig. 5A). The main products of Friedel-Crafts alkylation are mono-, di- and tributyltoluenes along with mono- and dihexyltoluenes that results in the prevalence of Tol+C<sub>12</sub> share over Tol+C<sub>8</sub> share in some cases (for example **6**/Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> – Table 2, run 11).

Second, the formation of small amounts of odd carbon number olefins was detected for complexes **1**, **4**, **5**, **8**, **10** activated with Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> (Fig. 5B). Previously we have reported the formation of up to 5 mol. % of odd carbon number olefins during ethylene oligomerization using Ni (II) NNNO-heteroscorpionate complex activated with EtAlCl<sub>2</sub> [60]. Two mechanisms were considered to describe the formation of these products – metathesis and  $\beta$ -alkyl elimination.



**Figure 5.** Shares of alkyltoluenes (A), odd carbon number olefins (B) and toluene alkylated with different odd carbon number olefins (C) in the reaction mixtures produced with catalytic systems based on complexes **1**, **3-6**, **8**, **10** (determined using GC-MS).

The thorough study of GC-MS chromatograms, using previous data as the reference, allowed us to identify the presence of C<sub>7</sub>, C<sub>9</sub> and C<sub>11</sub> olefin isomers with total content less than 0.8 mol. % for each run (Fig. 5B). It is interesting that complex **6** with phenyl substituents in the 3<sup>rd</sup> position of the pyrazole ring, compared to other compounds including complex **4** with bulky *iso*-propyl substituents, does not produce any odd carbon number olefins. The 1/Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> catalytic system was the most active (3720 kg<sub>oligomer</sub>·mol[Ni]<sup>-1</sup>·h<sup>-1</sup>) and thus produced the highest amount of odd carbon number olefins. Nevertheless, the odd carbon number olefins with chain lengths less than C<sub>7</sub> cannot be traced even for such an active system. However, the Friedel-Crafts alkylation process comes to our aid and allows to capture these light fractions as alkyltoluenes with odd carbon number substituents (Fig. 5C). The formation of

isopropyltoluene isomers (Tol+C<sub>3</sub>) and pentyltoluene isomers (Tol+C<sub>5</sub>) indicates that the whole set of olefins differing by one carbon atom in the range of chain lengths from C<sub>3</sub> to C<sub>12</sub> is formed. That distribution of odd carbon number olefins does not contradict neither with metathesis nor with  $\beta$ -alkyl elimination mechanisms. During presumable cross-metathesis the reaction between  $\beta$ -olefin (C<sub>n</sub>) and ethylene results in the formation of propylene (C<sub>3</sub>) and corresponding odd carbon number olefin (C<sub>n-1</sub>). Alternatively,  $\beta$ -methyl elimination would lead to direct formation of odd carbon number olefins (C<sub>n-1</sub>) differing by one carbon atom from the 'parent' fraction (C<sub>n</sub>). The lower shares of light odd carbon number olefins compared to the heavier ones are probably explained by their higher reactivity towards ethylene. The resulting co-oligomerization leads to the accumulation of heavier odd carbon number olefins in the reaction mixture, while light odd carbon number olefins are almost fully converted, making it impossible to detect them without the concurrent Friedel-Crafts alkylation process.

## Conclusions

In summary, we have described synthesis and characterization of ten new nickel(II) dibromide complexes with bis(azolyl)methane ligands. The treatment of these complexes with Et<sub>2</sub>AlCl or Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> results in the formation of catalytic systems active both in ethylene oligomerization and Friedel-Crafts alkylation of toluene. The maximum catalytic activity – 3720 kg<sub>oligomer</sub>·mol[Ni]<sup>-1</sup>·h<sup>-1</sup> was achieved for bisligated (NiL<sub>2</sub>Br<sub>2</sub>) complex **1** in the presence of Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>. The use of Et<sub>2</sub>AlCl as the co-catalyst results in the higher activity of the resulting catalytic systems and the use of Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> results in the higher selectivity towards 1-butene. It was also observed that 1-butene share linearly decreases with the increase of the catalytic activity. Catalytic systems with Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> produced higher shares of alkyltoluenes (up to 60% – 6/Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>) and were found to catalyze the formation of odd carbon number olefins. Moreover, the Friedel-Crafts alkylation reaction serves as a trap for light carbon number olefins, allowing to trace previously undetected propene and pentene isomers in the form of corresponding alkylated toluenes.

## Experimental

**Materials and Methods.** All manipulations with air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in oven-dried Schlenk glassware on a dual manifold Schlenk line, interfaced to a high-vacuum line. Argon (grade 4.8) and ethylene of special-purity grade (Linde gas) were dried by purging through a Super Clean™ Gas Filters. Toluene, THF and diethyl ether, were distilled over Na/benzophenone ketyl. Acetonitrile was purified by double distillation over P<sub>2</sub>O<sub>5</sub>. The water contents in these solvents were periodically controlled by Karl-Fischer coulometry by using a Metrohm 756 KF. CDCl<sub>3</sub> and acetone-*d*<sub>6</sub> were degassed and stored over 3 Å sieves. CD<sub>2</sub>Cl<sub>2</sub> was distilled over P<sub>2</sub>O<sub>5</sub>, degassed and stored over 3 Å molecular sieves. Diethylaluminum chloride and aluminium sesquichloride (Aldrich) were used as 1.0 M solution in heptane. Unless otherwise noted, all reagents were purchased from Sigma-Aldrich. The synthesis of bis(3,5-dimethylpyrazolyl)methane nickel bromide **1** was previously reported in [56] by us. Bis(pyrazol-1-yl)methane **L**<sub>2</sub>, bis(3-phenylpyrazol-1-yl)methane **L**<sub>5</sub>, bis(3,5-dimethyl-4-chloropyrazol-1-yl)methane **L**<sub>6</sub>, bis(3,5-dimethyl-4-bromopyrazol-1-yl)methane **L**<sub>7</sub>, bis(3,5-dimethyl-4-nitropyrazol-1-yl)methane **L**<sub>11</sub> were prepared by modified literature procedure [77] where tetrabutylammoniumbromide was substituted by Aliquat 336®. Bis(3,5-diisopropylpyrazol-1-yl)methane **L**<sub>3</sub>, bis(3,5-dimethyl-4-*tert*-butylpyrazol-1-yl)methane **L**<sub>4</sub>, 1,1'-bis(indazol-1-yl)methane **L**<sub>9</sub> and 1,1'-bis(benzotriazol-1-yl)methane **L**<sub>10</sub>, bis(3,5-di-*tert*-butylpyrazol-1-yl)methane **L**<sub>13</sub> were prepared according to [80]. Bis(3,5-ditrifluoromethylpyrazol-1-yl)methane **L**<sub>12</sub> was prepared according to [79]. Bis(3,5-dimethyl-4-iodopyrazol-1-yl)methane **L**<sub>8</sub> was prepared by iodation

of bis(3,5-dimethylpyrazol-1-yl)methane **L**<sub>1</sub> [78]. Synthetic details and spectra for all organic ligands can be found in supporting information. Ni(DME)Br<sub>2</sub> was obtained, using literature procedure [91].

### 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. Absorption IR spectra in the 400-4000 cm<sup>-1</sup> range were obtained for KBr pellets on Bruker Tensor 37 FTIR spectrometer, absorption IR spectra in the 400-50 cm<sup>-1</sup> region were recorded for nujol mulls on a Magna-IR 750 FTIR spectrophotometer. ATR spectra were registered using diamond cell on Bruker Vertex 70v FTIR spectrometer. Elemental analysis was performed by the microanalytical laboratory of A. N. Nesmeyanov Institute of Organoelement Compounds. High-resolution MALDI-TOF mass spectra were registered on a Bruker ULTRAFLEX II TOF/TOF instrument without the use of the matrix. High resolution mass spectra (HR MS) were measured on a Bruker microTOF II instrument using electrospray ionization (ESI) [92]. The measurements were done in a positive ion mode (interface capillary voltage – 4500 V); mass range from *m/z* 50 to *m/z* 3000 Da; external or internal calibration was done with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in acetonitrile, methanol, or water (flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. UV-vis spectra were recorded using JASCO V-770 spectrophotometer.

### General procedure for the synthesis of Ni complexes

Ni(DME)Br<sub>2</sub> was dissolved in freshly distilled THF (30 ml). The corresponding ligand dissolved in THF (20 ml) was added dropwise. The resulting solution was stirred for 1 hour at room temperature. The solvent was concentrated under reduced pressure to volume of 3-4 ml and diethyl ether (2-3 ml) was added to give the precipitate. The solid product was isolated by filtration, washed twice with diethyl ether and dried in vacuum.

### Synthesis of (bis(pyrazol-1-yl)methane)<sub>2</sub>NiBr<sub>2</sub> (1)

Prepared according to general procedure: bis(pyrazol-1-yl)methane (200 mg, 1.35 mmol), Ni(DME)Br<sub>2</sub> (416 mg, 1.35 mmol). Pale green powder, yield: 304 mg (43.7%). MALDI-TOF (*m/z*, %): [NiLBr]<sup>+</sup> (287.012, 100%), Calc. *m/z* 286.925; [NiL<sub>2</sub>Br]<sup>+</sup> (435.112, 22%), Calc. *m/z* 435.000. Anal. calcd. For C<sub>14</sub>H<sub>16</sub>Br<sub>2</sub>N<sub>8</sub>Ni (514.83) C, 32.7; H, 3.1; Br, 31; N, 21.8; Ni, 11.4 Found: C, 32.05; H, 3.05; Br, 31.35; N, 21.2; Ni, 11.6. IR (ATR diamond), cm<sup>-1</sup>: 3102 (s, ν<sub>s</sub> (Pz, C–H)), 3001 (s, ν<sub>s</sub> (Pz, C–H)), 2960 (m, ν<sub>s</sub> (–CH<sub>2</sub>–, C–H)), 1612 (m, ν<sub>s</sub> (Pz, C=N)), 1527 (m, ν<sub>s</sub> (Pz, C=C)), 1512 (m, ν<sub>s</sub> (Pz, C=C)). IR (nujol), cm<sup>-1</sup>: 376 (w), 254 (w), 226 (m), 163 (w), 104 (w), 70 (w).

### Synthesis of (bis(pyrazol-1-yl)methane)NiBr<sub>2</sub> (2)

Prepared according to general procedure using CH<sub>3</sub>CN instead of THF, crystallization was performed without diethyl ether: bis(pyrazol-1-yl)methane (200 mg, 1.35 mmol), Ni(DME)Br<sub>2</sub> (416 mg, 1.35 mmol). Pale yellow-green powder, yield: 415 mg (75.4%). MALDI-TOF (*m/z*, %): [NiLBr]<sup>+</sup> (287.026, 100%), Calc. *m/z* 286.925. Anal. calcd. For C<sub>7</sub>H<sub>8</sub>Br<sub>2</sub>N<sub>4</sub>Ni\*CH<sub>3</sub>CN (407.73) C, 26.5; H, 2.7; Br, 39.2; N, 17.2; Ni, 14.4 Found: C, 25.89; H, 2.95; N, 16.5. IR (ATR diamond), cm<sup>-1</sup>: 3100 (s, ν<sub>s</sub> (Pz, C–H)), 3000 (m, ν<sub>s</sub> (Pz, C–H)), 2960 (m, ν<sub>s</sub> (–CH<sub>2</sub>–, C–H)), 1611 (m, ν<sub>s</sub> (Pz, C=N)), 1527 (m, ν<sub>s</sub> (Pz, C=C)), 1511 (m, ν<sub>s</sub> (Pz, C=C)). IR (nujol), cm<sup>-1</sup>: 374 (w), 252 (w), 223 (w), 158 (w), 101 (w), 66 (w).

### Synthesis of (bis(3,5-diisopropylpyrazol-1-yl)methane)NiBr<sub>2</sub> (4)

Prepared according to general procedure: bis(3,5-diisopropylpyrazol-1-yl)methane (298 mg, 0.945 mmol), Ni(DME)Br<sub>2</sub> (291 mg, 0.945 mmol). Dark purple crystals, yield: 267 mg (52.8%). <sup>1</sup>H NMR (600 MHz, Methylene Chloride-*d*<sub>2</sub>) δ 75.44 (Pz, 4-CH=; s, 2H), 15.67 (3-*i*Pr, -CH=; s, 2H), 6.91 (3-*i*Pr, -CH<sub>3</sub>; s, 12H), 3.69 (5-*i*Pr, -CH<sub>3</sub>; s, 12H), 2.67 (5-*i*Pr, -CH=; s, 2H), -7.09 (-CH<sub>2</sub>-; s, 2H). MALDI-TOF (m/z, %): [NiLBr]<sup>+</sup> (455.095, 16%), Calc. m/z 455.113. Anal. calcd. For C<sub>19</sub>H<sub>32</sub>Br<sub>2</sub>N<sub>4</sub>Ni (534.98) C, 42.7; H, 6; Br, 29.9; N, 10.5; Ni, 11 Found: C, 42.5; H, 6.2; N, 9.91; Ni, 10.6. IR (KBr), cm<sup>-1</sup>: 3125 (w, ν<sub>s</sub> (Pz, C-H)), 2967 (vs, ν<sub>s</sub> (i-Pr, C-H)), 2930 (s, ν<sub>s</sub> (-CH<sub>2</sub>-, C-H)), 2870 (m, ν<sub>s</sub> (i-Pr, C-H)), 1549 (s, ν<sub>s</sub> (Pz, C=C)).

### Synthesis of (bis(3,5-dimethyl-4-tert-butylpyrazol-1-yl)methane)NiBr<sub>2</sub> (5)

Prepared according to general procedure: bis(3,5-dimethyl-4-tert-butylpyrazol-1-yl)methane (200 mg, 0.633 mmol), Ni(DME)Br<sub>2</sub> (195 mg, 0.633 mmol). Dark purple crystals, yield: 246 mg (72.6%). Crystals suitable for X-ray analysis were obtained by addition of a few drops of diethyl ether to the concentrated THF solution. <sup>1</sup>H NMR (600 MHz, Methylene Chloride-*d*<sub>2</sub>) δ 4.52 (3-CH<sub>3</sub>; s, 6H), 4.13 (5-CH<sub>3</sub>; s, 6H), 3.65 (4-*t*Bu; s, 18H), -7.31 (-CH<sub>2</sub>-; s, 2H). MALDI-TOF (m/z, %): [NiLBr]<sup>+</sup> (455.171, 100%), Calc. m/z 455.113. Anal. calcd. For C<sub>19</sub>H<sub>32</sub>Br<sub>2</sub>N<sub>4</sub>Ni (534.98) C, 42.7; H, 6.0; Br, 29.9; N, 10.5; Ni, 11 Found: C, 41.95; H, 6.05; N, 10.2. IR (KBr), cm<sup>-1</sup>: 3034 (w, ν<sub>s</sub> (-CH<sub>2</sub>-, C-H)), 2965 (vs, ν<sub>s</sub> (t-Bu, C-H)), 2870 (m, ν<sub>s</sub> (Me, C-H)), 1537 (m, ν<sub>s</sub> (Pz, C=C)).

### Synthesis of (bis(3-phenylpyrazol-1-yl)methane)NiBr<sub>2</sub> (6)

Prepared according to general procedure: bis(3-phenylpyrazol-1-yl)methane (300 mg, 1 mmol), Ni(DME)Br<sub>2</sub> (308 mg, 1 mmol). Dark purple crystals, yield: 278 mg (53.7%). Crystals suitable for X-ray analysis were obtained by addition of a few drops of diethyl ether to the concentrated THF solution. <sup>1</sup>H NMR (600 MHz, Methylene Chloride-*d*<sub>2</sub>) δ 66.20 (Pz, 4-CH=; s, 2H), 48.59 (Pz, 5-CH=; s, 2H), 25.47 (Ph, *o*-H; s, 4H), 10.17 (-CH<sub>2</sub>-; s, 2H), 8.07 (Ph, *m*-H; s, 4H), 7.96 (Ph, *p*-H; s, 2H). <sup>1</sup>H NMR (600 MHz, Acetone-*d*<sub>6</sub>) δ 66.49 (Pz, 4-CH=; s, 2H), 47.91 (Pz, 5-CH=; s, 2H), 25.20 (Ph, *o*-H; s, 4H), 10.16 (-CH<sub>2</sub>-; s, 2H), 8.02 (Ph, *m,p*-H; s, 8H). MALDI-TOF (m/z, %): [NiLBr]<sup>+</sup> (438.974, 25.06%), Calc. m/z 438.989. Anal. calcd. For C<sub>19</sub>H<sub>16</sub>Br<sub>2</sub>N<sub>4</sub>Ni (518.85) C, 44; H, 3.1; Br, 30.8; N, 10.8; Ni, 11.3 Found: C, 43.7; H, 3.3; N, 10.8; Br 30.3; Ni 11.2. IR (KBr), cm<sup>-1</sup>: 3107 (m, ν<sub>s</sub> (Pz, C-H)), 3000 (m, ν<sub>s</sub> (Ph, C-H)), 1529 (m, ν<sub>s</sub> (Pz, C=C)).

### Synthesis of (bis(3,5-dimethyl-4-chloropyrazol-1-yl)methane)NiBr<sub>2</sub> (7)

Prepared according to general procedure: bis(3,5-dimethyl-4-chloropyrazol-1-yl)methane (200 mg, 0.733 mmol), Ni(DME)Br<sub>2</sub> (226 mg, 0.733 mmol). Grey-blue powder, yield: 288 mg (74.4%). <sup>1</sup>H NMR (600 MHz, Methylene Chloride-*d*<sub>2</sub>) δ 1.99 (5-CH<sub>3</sub>; s, 6H), -1.78 (3-CH<sub>3</sub>; s, 6H), -7.08 (-CH<sub>2</sub>-; s, 2H). ESI-TOF (m/z, %): [NiLBr]<sup>+</sup> (410.910, 23%), Calc. m/z 410.910. Anal. calcd. For C<sub>11</sub>H<sub>14</sub>Br<sub>2</sub>Cl<sub>2</sub>N<sub>4</sub>Ni\*0.5C<sub>4</sub>H<sub>8</sub>O (527.71) C, 29.6; H, 3.4; Br, 30.3; N, 10.6; Cl, 13.4; O, 1.5; Ni, 11.1. Found: C, 29.1; H, 3.5; N, 10.7. IR (KBr), cm<sup>-1</sup>: 3033 (m, ν<sub>s</sub> (-CH<sub>2</sub>-, C-H)), 2978 (m, ν<sub>s</sub> (-CH<sub>2</sub>-, C-H)), 2956 (m, ν<sub>s</sub> (Me, C-H)), 2923 (m, ν<sub>s</sub> (Me, C-H)), 2878 (m, ν<sub>s</sub> (Me, C-H)), 1559 (m, ν<sub>s</sub> (Pz, C=C)).

### Synthesis of (bis(3,5-dimethyl-4-bromopyrazol-1-yl)methane)NiBr<sub>2</sub> (8)

Prepared according to general procedure: bis(3,5-dimethyl-4-bromopyrazol-1-yl)methane (300 mg, 0.825 mmol), Ni(DME)Br<sub>2</sub> (254 mg, 0.825 mmol). Yellow powder, yield: 330 mg (61.3%). Crystals

suitable for X-ray analysis were obtained by addition of a few drops of diethyl ether to the concentrated THF solution.  $^1\text{H}$  NMR (600 MHz, Methylene Chloride- $d_2$ )  $\delta$  2.47 (5- $\text{CH}_3$ ; s, 6H), -2.00 (3- $\text{CH}_3$ , s, 6H), -6.35 ( $-\text{CH}_2-$ ; s, 2H). MALDI-TOF (m/z, %):  $[\text{NiLBr}]^+$  (501.314, 100%), Calc. m/z 501.815. Anal. calcd. For  $\text{C}_{11}\text{H}_{14}\text{Br}_4\text{N}_4\text{Ni}\cdot\text{C}_4\text{H}_8\text{O}$  (652.67) C, 27.6; H, 3.4; Br, 49; N, 8.6; O, 2.5; Ni, 9. Found: C, 27.1; H, 3.6; N, 8.3. IR (ATR diamond),  $\text{cm}^{-1}$ : 3038 (m,  $\nu_s(-\text{CH}_2-, \text{C}-\text{H})$ ), 2981 (m,  $\nu_s(-\text{CH}_2-, \text{C}-\text{H})$ ), 2964, (m,  $\nu_s(\text{Me}, \text{C}-\text{H})$ ), 2931 (m,  $\nu_s(\text{Me}, \text{C}-\text{H})$ ), 2863 (m,  $\nu_s(\text{Me}, \text{C}-\text{H})$ ), 1529 (m,  $\nu_s(\text{Pz}, \text{C}=\text{C})$ ).

### Synthesis of (bis(3,5-dimethyl-4-iodopyrazol-1-yl)methane)NiBr<sub>2</sub> (9)

Prepared according to general procedure: bis(3,5-dimethyl-4-iodopyrazol-1-yl)methane (300 mg, 0.66 mmol), Ni(DME)Br<sub>2</sub> (204 mg, 0.66 mmol). Purple powder, yield: 414 mg (93.0%).  $^1\text{H}$  NMR (600 MHz, Methylene Chloride- $d_2$ )  $\delta$  3.30 (5- $\text{CH}_3$ ; s, 6H), -1.89 (3- $\text{CH}_3$ ; s, 6H), -6.01 ( $-\text{CH}_2-$ ; s, 2H). MALDI-TOF (m/z, %):  $[\text{NiL}^-\text{Br}]^+$  (468.948, 25%), Calc. m/z 468.885;  $[\text{NiLBr}]^+$  (594.781, 100%), Calc. m/z 595.022. Anal. calcd. For  $\text{C}_{11}\text{H}_{14}\text{Br}_2\text{I}_2\text{N}_4\text{Ni}$  (674.56) C, 19.6; H, 2.1; Br, 23.7; I, 37.6; N, 8.6; Ni, 9. Found: C, 19.85; H, 2.5; N, 8.3. IR (KBr),  $\text{cm}^{-1}$ : 3027 (w,  $\nu_s(-\text{CH}_2-, \text{C}-\text{H})$ ), 2921 (w,  $\nu_s(\text{Me}, \text{C}-\text{H})$ ), 2874 (w,  $\nu_s(\text{Me}, \text{C}-\text{H})$ ), 2854 (w,  $\nu_s(\text{Me}, \text{C}-\text{H})$ ), 1535 (m,  $\nu_s(\text{Pz}, \text{C}=\text{C})$ ).

### Synthesis of (1,1'-bis(indazol-1-yl)methane)NiBr<sub>2</sub> (10)

Prepared according to general procedure: bis(indazol-1-yl)methane (200 mg, 0.808 mmol), Ni(DME)Br<sub>2</sub> (249 mg, 0.808 mmol). Yellow-green powder, yield: 245 mg (60.3%). MALDI-TOF (m/z, %):  $[\text{L}^-\text{H}]^+$  (247.200, 28%), Calc. m/z 247.099;  $[\text{NiLBr}]^+$  (387.141, 86%), Calc. m/z 386.957. Anal. calcd. For  $\text{C}_{15}\text{H}_{12}\text{Br}_2\text{N}_4\text{Ni}\cdot 0.5\text{C}_4\text{H}_8\text{O}$  (502.83) C, 40.6; H, 3.2; Br, 31.8; N, 11.1; O, 1.6; Ni, 11.7 Found: C, 39.9; H, 3.4; N, 10.7. IR (KBr),  $\text{cm}^{-1}$ : 3111 (w,  $\nu_s(\text{Ind}, \text{C}-\text{H})$ ), 3056 (w,  $\nu_s(\text{Ind}, \text{C}-\text{H})$ ), 2994 (w,  $\nu_s(\text{Ind}, \text{C}-\text{H})$ ), 1622 (s,  $\nu_s(\text{Ind}, \text{C}=\text{N})$ ), 1507 (m,  $\nu_s(\text{Ind}, \text{C}=\text{C})$ ).

### Synthesis of (1,1'-bis(benzotriazol-1-yl)methane)NiBr<sub>2</sub> (11)

Prepared according to general procedure: bis(benzotriazol-1-yl)methane (200 mg, 0.799 mmol), Ni(DME)Br<sub>2</sub> (246 mg, 0.799 mmol). Yellow-green powder, yield: 242 mg (64.7%). MALDI-TOF (m/z, %):  $[\text{NiL}(\text{H}_2\text{O})]^+$  (326.285, 95%), Calc. m/z 326.042;  $[\text{NiBtz}_2\text{Br}_2]^+$  (455.582, 24%, Btz = benzotriazole), Calc. m/z 455.866. Anal. calcd. For  $\text{C}_{14}\text{H}_{16}\text{Br}_2\text{N}_8\text{Ni}$  (468.76) C, 33.3; H, 2.2; Br, 34.1; N, 17.9; Ni, 12.5. Found: C, 33.2; H, 2.3; N, 17.8; Ni, 12.1. IR (KBr),  $\text{cm}^{-1}$ : 2998 (w,  $\nu_s(\text{Btz}, \text{C}-\text{H})$ ), 2954 (w,  $\nu_s(-\text{CH}_2-, \text{C}-\text{H})$ ), 2925 (w,  $\nu_s(-\text{CH}_2-, \text{C}-\text{H})$ ), 1494 (w,  $\nu_s(\text{Btz}, \text{C}=\text{C})$ ).

**X-ray diffraction studies.** The single-crystal X-ray diffraction data for **5a**, **5b**, **6** and **8** were collected on the 'Belok' beamline of the Kurchatov Synchrotron Radiation Source (National Research Center 'Kurchatov Institute', Moscow, Russian Federation) using a Rayonix SX165 CCD detector. A total of 720 images for two different orientations of each crystal were collected using an oscillation range of  $1.0^\circ$  and  $\varphi$  scan mode. The data were indexed and integrated using the utility *iMOSFLM* from the CCP4 program suite [93] and then scaled and corrected for absorption using the *Scala* program [94]. For details, see supplementary information Table S1. The structures were solved by direct methods and refined by a full-matrix least square technique on  $F^2$  in anisotropic approximation for non-hydrogen atoms. The crystal of **6** contained strongly disordered tetrahydrofuran (THF) solvate molecules. All attempts to model and refine positions of the solvate molecules were unsuccessful. Therefore, their contribution to the total scattering pattern was removed by use of the utility *SQUEEZE* in PLATON06 [95]. Based on these calculations, the content of THF solvate molecules was equal to  $\frac{1}{2}$  per the independent part of the

unit cell. The hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for the methyl groups and  $1.2U_{\text{eq}}(\text{C})$  for the other groups]. All calculations were carried out using the SHELXTL program suite [96]. Crystallographic data for **5a**, **5b**, **6** •  $\frac{1}{2}$ THF and **8** have been deposited with the Cambridge Crystallographic Data Center, CCDC **1996488-1996491**. 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](http://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 56 psi (3.8 atm). Before the experiment the reactor was heated up to 100 °C and then vacuumed for 10 minutes to eliminate residual moisture. Further, it was filled with argon and solid catalyst was injected as suspension in toluene (40 ml). Then necessary amount of co-catalyst ( $\text{Et}_2\text{AlCl}$ ,  $\text{Et}_3\text{Al}_2\text{Cl}_3$ ) dissolved in additional toluene (10 ml) was loaded in the reactor. The reactor was heated to a specified temperature and then argon atmosphere was rapidly removed using vacuum pump. Oligomerization was initiated by pressurization of 56 psi (3.8 atm.) of ethylene in the reactor. The pressure of ethylene was maintained constant during oligomerization. The consumption of ethylene was measured using Alicat Scientific massflow detector M-500SCCM-D and Alicat's Flow Vision™ software. After the end of the process, the reaction solution was quickly cooled down, excessive ethylene pressure was released and the solution was quenched with 15 ml isopropanol and 10 ml 5% hydrochloric acid. The organic phase was further dried by  $\text{Na}_2\text{SO}_4$  and the organic compounds were characterized by GC (gas chromatography) and GC-MS (gas chromatography-mass-spectrometry) to determine the composition and molecular mass distribution. Samples with desiccant were stored in sealed flasks in a refrigerator. Chromatographic analyses were performed on Chromatec-Crystall 5000.2, equipped with flame ionization detector and capillary column Restek Rt®-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 analyses were performed on Pegasus MS time-of-flight mass spectrometer (LECO Corporation, Saint Joseph, MI, USA) paired with an Agilent 6890N gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a Rtx-5MS 30 m × 0.25 mm (id) × 0.25 μm (df) capillary column (Restek, Bellefonte, PA). The GC oven program was as follows: a 2 min isothermal hold at 50 °C, then ramping at 20 °C min<sup>-1</sup> to 280 °C followed by a 10 min isothermal hold at 280 °C. The system was controlled by ChromaTOF® software (Version 4.24, LECO Corporation), which was also used for spectra collection and data processing. Mass spectra were acquired at the rate of 20 spectra per second in the mass range of m/z 33–800.

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