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# 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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# **Keywords**

Ethylene | Oligomerization | Friedel-Crafts alkylation | Nickel(II) complexes | N-ligands | Odd carbon number olefins

# **Comprehensive Summary**



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(azolyl)methanes. They have been characterized using <sup>1</sup>H NMR, IR, high resolution mass spectrometry 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 a 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>).

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### **Background and Originality Content**

The use of nickel(II) complexes with nitrogen-based ligands for ethylene polymerization was first reported in 1995 by Brookhart *et al.*<sup>[1]</sup> The subsequent studies revealed that similar  $\alpha$ -diimine complexes were capable of catalyzing the oligomerization of ethylene and propylene.<sup>[2-3]</sup> Recently, nickel complexes have been widely used in processes of chain-walking ethylene polymerization<sup>[4-11]</sup> and copolymerization of ethylene with polar monomers.<sup>[4,12-18]</sup> However, the interest in the development of new nickel-based catalytic systems for ethylene oligomerization is still high,<sup>[6,19-20]</sup> due to their high activity and selectivity toward butenes<sup>[21-24]</sup> and, in some cases, toward hexenes and higher olefins.<sup>[25]</sup> Moreover, such systems are also able to catalyze Friedel-Crafts alkylation of toluene with low molecular weight<sup>[26-29]</sup> or high molecular weight<sup>[30-32]</sup> ethylene oligomers. The resulting polyalkyltoluenes can be further used in the production of surfactants and detergents.<sup>[33]</sup>

Nickel(II) complexes with N-donor bidentate pyrazole-based ligands can effectively catalyze ethylene oligomerization (Figure 1). The derivatives of original Brookhart-type catalysts – (pyrazol-1-yl)imine nickel(II) complexes **A**,<sup>[34]</sup> upon activation with MAO, produced 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**<sup>[35]</sup> 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.<sup>[36-37]</sup> Nickel(II) complexes with (pyrazol-1-ylethyl)amines **C**,<sup>[38-39]</sup> 1,2-bis(pyrazol-1-ylmethyl)benzene **D**<sup>[40]</sup> and 2-(pyrazol-1-ylmethyl)pyridines **E**<sup>[37-38,41-42]</sup> were highly active both in ethylene oligomerization and Friedel-Crafts alkylation of toluene.

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.<sup>[43-45]</sup> Recently, we have reported catalytic studies of bis(3,5-dimethylpyrazol-1-yl)methane nickel(II) bromide in ethylene oligomerization.<sup>[46-47]</sup> 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.<sup>[48]</sup>

Bis(pyrazol-1-yl)methane bidentate ligands are highly versatile due to the well-established pyrazole chemistry. Such fine-tuning of the ligand potentially allows to control the catalytic properties of resulting complexes with high precision. 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)-based catalytic systems was for the first time reported by us for complex **F** (Figure 1A).<sup>[49]</sup>

### **Results and Discussion**

### Synthesis and characterization

The library of bis(azolyl)methane ligands, bearing various substituents, have been prepared using three different synthetic approaches. Ligands  $L_1-L_3$ ,  $L_6-L_8$  were prepared according to a modified procedure,<sup>[50]</sup> where Aliquat 336<sup>®</sup> was used instead of  $(nBu_4N)Br$  (Figure 1B). Ligand  $L_9$  was prepared by iodation of  $L_3$  according to Ref. [51] (Figure 1B). However, alternative methods were employed to prepare ligand  $L_{12}$  (with highly electron withdrawing CF<sub>3</sub>- groups) or ligands  $L_4$ ,  $L_5$ ,  $L_{13}$  (with bulky substituents) in high yields<sup>[52-53]</sup> (Figure 1C). 1,1'-Bis(indazolyl)methane  $L_{10}$  and 1,1'-bis(benzotriazolyl)methane  $L_{11}$  were also prepared according to Ref. [53] (Figure 1C) 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 (SI, Figures S1–29).

Synthesis of complex **3** was previously reported by us in Ref. [46]. All other nickel(II) dibromide complexes have been prepared by reacting Ni(DME)Br<sub>2</sub> with corresponding ligands in THF (**1**, **4**–**11**) or CH<sub>3</sub>CN (**2**) (Figure 2). However, stable complexes have not been obtained for ligands L<sub>2</sub>, L<sub>12</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 -NO<sub>2</sub> (L<sub>2</sub>) or -CF<sub>3</sub> (L<sub>12</sub>)). All complexes have been characterized with IR spectroscopy (SI, Figures S30–39), high-resolution mass spectrometry (HRMS; SI, Figures S51–60) and elemental analysis.

According to the HRMS data, all complexes except **1** were monoligated compounds that were observed as  $[NiLBr]^+$  cations in corresponding mass-spectra. A bisligated structure was proposed for complex **1** based on observation of positively charged ion (m/z= 435.112) with the composition  $[NiL_2Br]^+$  (SI, Figure S51) and elemental analysis data. Some signals with m/z higher than that of



Figure 1 (A) Structures of nickel(II) halide complexes with pyrazole containing ligands active in ethylene oligomerization; (B) synthesis of bis(pyrazolyl)methane ligands  $L_1 - L_3$ ,  $L_6 - L_9$ ; (C) synthesis of bis(azolyl)methane ligands  $L_4 - L_5$ ,  $L_{10} - L_{13}$ .





Figure 2 (A) Synthesis of nickel(II) complexes 1—9; (B) synthesis of nickel(II) complexes 10—11.

 $[NiLBr]^+$  were observed for complexes **1**, **7** and **9**. They were not attributed to any particular composition and are probably the result of the recombination of ions formed upon ionization of parent complexes. For complex **8** such signal (m/z = 673.678) was attributed to the addition of the pyrazole unit to  $[NiLBr]^+$  (SI, Figure S57).

The structures of complexes **5a**, **5b**, **6** and **8** were unambiguously established by X-ray diffraction study and are shown in Figure 3 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							
	5a	5b	6	8				
Ni—Br <sub>ax</sub>	2.3576(14)	2.3784(12)	2.3741(14)	2.372(3)				
$Ni-Br_{eq}$	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.

All studied complexes are mononuclear compounds bearing one bidentate bis(pyrazolyl)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. 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 Brax-Ni-N bond angles are significantly smaller than the Br<sub>eq</sub>-Ni-N bond angles (Table 1).



Figure 3 Molecular structures of complexes 5a, 5b, 6 and 8. Thermal ellipsoids are shown at the 50% probability level.

The bis(pyrazolyl)methane ligands in **5a**, **5b**, **6** and **8** adopt a *butterfly* conformation with the interplane angle between the pyrazole rings of  $60.8(2)^{\circ}/57.3(2)^{\circ}$ ,  $61.86(17)^{\circ}$ ,  $55.64(16)^{\circ}/45.69(17)^{\circ}$  and  $56.6(2)^{\circ}$  for **5a**, **5b**, **6** and **8**, respectively. As 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, Figures S43—49). 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 density functional theory (DFT) calculations have been performed.<sup>[46]</sup> Complexes without substituents near to the donor nitrogen atom (1, 2, 10, 11) are insoluble in common organic solvents except alcohols. The <sup>1</sup>H NMR spectra of complexes **1** and **2** are similar and uninformative (SI, Figures S40-42) probably because the use of polar coordinating solvent (CD<sub>3</sub>OD) leads to the formation of new adducts. Complexes 6-8 are co-crystallized with 0.5 or 1 eq. THF according to <sup>1</sup>H NMR spectra (SI, Figures 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, Figure S38) and elemental analysis.

The UV-Vis adsorption spectra (SI, Figure S50) of dichloromethane solutions of complexes **3**–**9** are similar, differing mostly in intensity. The maximum intensity was observed 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 form ligand to nickel atom), that are typical for Ni<sup>2+</sup>(d<sup>8</sup>) complexes/<sup>[54-55]</sup>

# Ethylene oligomerization and Friedel-Crafts alkylation of toluene

Complexes 1, 2, 4–11 were activated either with  $Et_2AlCl$  or  $Et_3Al_2Cl_3$  and evaluated for their ability to catalyze ethylene oligomerization (Table 2). Precatalyst 3, previously described by us in

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

Run Comple	Constant	ex Co-catalyst	Activity <sup>b</sup> -	Butene/Hexene distribution <sup>c</sup> /%			
	Complex			$C_4^{=}$	C <sub>6</sub> <sup>=</sup>	$\alpha - C_4^{=}$	$\alpha - C_6^{=}$
1	1	Et <sub>2</sub> AICI	3160	92.9	7.1	11.1	12.7
2	1	$Et_3Al_2Cl_3$	3720	89.8	10.2	15.0	21.3
3 <sup>e</sup>	2	Et <sub>2</sub> AICI	660	94.2	5.6	50.3	27.5
<b>4</b> <sup><i>d</i></sup>	3	Et <sub>2</sub> AICI	700	94.1	5.9	47.6	27.0
5 <sup><i>d</i></sup>	3	$Et_3Al_2Cl_3$	280	95.7	4.3	93.2	60.1
6	4	Et <sub>2</sub> AICI	1780	90.3	9.7	26.0	17.6
7	4	$Et_3Al_2Cl_3$	1420	88.8	11.2	33.6	19.6
8 <sup>e</sup>	5	Et <sub>2</sub> AICI	1630	90.0	9.4	28.5	18.1
9 <sup>e</sup>	5	$Et_3Al_2Cl_3$	1410	89.0	10.1	33.1	19.4
10	6	Et <sub>2</sub> AICI	1560	90.1	9.9	34.5	19.4
$11^e$	6	$Et_3Al_2Cl_3$	610	89.0	10.2	38.3	20.6
$12^e$	7	Et <sub>2</sub> AICI	1240	91.5	8.0	38.6	21.4
13	7	$Et_3Al_2Cl_3$	1100	90.8	9.2	43.1	22.5
14	8	Et <sub>2</sub> AICI	1220	91.4	8.6	40.5	21.8
$15^e$	8	$Et_3Al_2Cl_3$	1210	89.7	9.5	39.8	21.8
16 <sup>e</sup>	9	Et <sub>2</sub> AICI	1420	92.4	7.2	29.3	18.8
17 <sup>e</sup>	9	$Et_3Al_2Cl_3$	910	90.9	8.4	48.9	23.8
18	10	Et <sub>2</sub> AICI	1710	91.2	8.8	25.4	17.0
19 <sup>e</sup>	10	$Et_3Al_2Cl_3$	1180	90.3	8.9	42.7	23.2
20	11	Et <sub>2</sub> AICI	1990	93.3	6.7	16.1	13.7
21	11	$Et_3Al_2Cl_3$	1370	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 (the molar equivalent of Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> was two times lower due to its dimeric structure). <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 Refs. [46-47], used for comparison of the results <sup>*e*</sup> trace amounts of octenes (< 1%) are present in the mixture.



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

Refs. [46-47], was introduced for proper comparison of the results.

Pristine nickel(II) complexes were poorly soluble in toluene media, however, were readily dissolved upon addition of organoaluminium activator. All complexes except **2** after activation with Et<sub>2</sub>AlCl 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

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reported parent complex **3**. The lowest activity of **2** (Table 2, run 3) can be attributed to low solubility of already activated compound in reaction media (toluene) and to poor stabilization of active site 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 (Figure 4A). However, the use of Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>

resulted in a higher share of 1-butene in the oligomer mixture (Figure 4B). This fact can be attributed to different alkylating ability and Lewis acidity of these activators.<sup>[56-57]</sup> The 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<sup>[58-60]</sup> (Figure 5B).

According to literature,<sup>[61-62]</sup> the activation of  $\alpha$ -diimine nickel(II) complexes proceeds in a similar manner for both Et<sub>2</sub>AlCl and Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> activators with the formation of ionic species where cationic alkylated nickel complex is stabilized with organoaluminium anion. In this study, we have assumed similar activation mechanism for bis(pyrazolyl)methane nickel complexes (Figure 5A). The major difference between the two activators is that Et<sub>2</sub>AlCl can only form one type of anion – Et<sub>3</sub>AlCl<sup>-</sup> and dimeric Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> forms two anions during the activation process (Et<sub>3</sub>AlCl<sup>-</sup> and Et<sub>2</sub>AlCl<sub>2</sub>). To investigate the differences in stabilization of precursors of active species with these anions, the interaction energies between nickel cation and corresponding anion were calculated.



Figure 5 (A) Plausible activation pathway for nickel complex with Et<sub>2</sub>AlCl and formation of anions for Et<sub>2</sub>AlCl and Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>; (B) simplified catalytic cycle for chain propagation and  $\beta$ -H elimination on cationic nickel sites stabilized with organoaluminium anions; (C) calculated interaction energies for two possible ionic pairs forming upon activation with Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>.

Complex **3** was used as model compound for these calculations. The ionic pairs LNiEt<sup>+</sup> (**3**)…Et<sub>3</sub>AlCl<sup>-</sup> and LNiEt<sup>+</sup> (**3**)…Et<sub>2</sub>AlCl<sub>2</sub><sup>-</sup> were optimized and the interaction energies between anion (Et<sub>3</sub>AlCl<sup>-</sup> or Et<sub>2</sub>AlCl<sub>2</sub><sup>-</sup>), and cation (LNiEt<sup>+</sup>) were calculated by DFT computation. It was found that the interaction energies between Et<sub>3</sub>AlCl<sup>-</sup> and LNiEt<sup>+</sup> is –92.5 kcal/mol, slightly stronger than that (–91.4 kcal/mol) between Et<sub>2</sub>AlCl<sub>2</sub><sup>-</sup> and LNiEt<sup>+</sup> (Figure 5C). This probably means that when two Al activators were added with the same [Al]/[Ni] ratio, Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> only gave half amount of better stabilizing Et<sub>3</sub>AlCl<sup>-</sup> anion compared with Et<sub>2</sub>AlCl, so the catalytic activity was lower in that case.

The maximum catalytic activity was achieved for catalytic systems based on complex 1 (Table 2, runs 1–2) – 3160  $\mu$  3720 kg·mol[Ni]<sup>-1</sup>·h<sup>-1</sup> after treatment with Et\_2AlCl or Et\_3Al\_2Cl\_3 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 HRMS (SI, Figure S51) and elemental analysis is a bisligated compound with the chemical formula – NiL\_2Br\_2. 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<sup>[63]</sup> and bisligated compounds exhibited more stability during catalytic tests under various reaction conditions.

However, such small differences in activity and selectivity between the catalytic systems needed an additional and more profound explanation. To get some insights in such catalytic behavior we have drawn the topographic steric maps for complexes 2, 3, 4 and 6 (Figure 6) which show the progressive increase in steric bulk around the metal centre with an increase in the volume of the substituents in the 3<sup>rd</sup> position of pyrazole rings. It can be noted that less sterically hindered complexes 2 and 3 activated with Et<sub>2</sub>AlCl, exhibited lower catalytic activity - 660 and 700 kg mol $[Ni]^{-1}$  h<sup>-1</sup> (Table 2, runs 3, 4) compared to those of more hindered complexes 4 and 6 – 1780 and 1560 kg·mol[Ni]<sup>-1</sup>·h<sup>-1</sup> (Table 2, runs 6, 10). Such difference might be a consequence of better protection of active site by substituents in the ligand that results in slower deactivation and higher stability of active species. However, the distribution of ethylene oligomers was almost the same for all catalytic systems and the share of hexenes and higher olefins has not increased with the increase in the bulk of the substituents. This uniformity of selectivity among all studied catalytic systems can be caused by non-planar structure of the precursor complexes. Indeed, if we look at the steric maps along the optimized structures of complexes 2, 3, 4 and 6, we can see that substituents are creating steric bulk only below the plane formed by N-Ni-N bonds. Such orientation of the ligand in these structures leaves the top part of the complex almost unprotected, thus allowing an easy access to the active site both for activator and monomer, and significantly reducing the influence of the ligand's substituents on the selectivity of the catalytic system.

An interesting dependence was observed when we plotted the share of 1-butene against the activity of the catalytic system



Figure 6 Topographic steric maps of nickel complexes 2, 3, 4 and 6 and corresponding DFT-optimized structures of these complexes oriented the same way as topographic steric maps.

(Figure 4C): the higher the catalytic activity is, the lower the share of 1-butene is. 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 composition of oligomerization products 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, Figure 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 reported data.<sup>[64-65]</sup> 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 that in the butene fraction. This feature originates from the co-dimerization of ethylene and butene isomers predominantly yielding branched internal hexenes.<sup>[66]</sup> 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 number 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).

First, studied catalytic systems catalyzed Friedel-Crafts alkylation of toluene with produced ethylene oligomers or ethylene itself (Figure 7A). The latter feature of nickel(II)-based systems has been previously reported by other researchers.<sup>[40]</sup> The share of alkyltoluenes in the reaction mixture was up to 60% (for  $6/Et_3Al_2Cl_3$  – Table 2, run 11). When a stronger Lewis acidic activator –  $Et_3Al_2Cl_3$  was used, a higher amount of alkyltoluenes was formed than for  $Et_2AlCl$  activator. It seems that the introduction of any substituent in the pyrazole ring leads to an increase in 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 range of alkylated products starting from ethyltoluene (Tol+C<sub>2</sub>) is formed during the catalytic process including trace amounts of heavy alkyltoluenes (Tol+C<sub>16</sub> and Tol+C<sub>18</sub>) (Figure 7A). 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 beyond Tol+C<sub>8</sub> share in some cases (for example  $6/Et_3Al_2Cl_3 - Table 2$ , run 11).

Second, the formation of small amounts of odd carbon number olefins was detected for complexes **1**, **4**, **5**, **8**, **10** activated with  $Et_3Al_2Cl_3$  (Figure 7C). It is interesting that complex **6** with phenyl substituents in the 3<sup>rd</sup> position of pyrazole ring does not produce any odd carbon number olefins, compared to other compounds including complex **4** with bulky *iso*-propyl substituents. 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>.<sup>[49]</sup>

The detailed 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 (Figure 7C). Both plausible reaction mechanisms –  $\beta$ -methyl elimination and olefin cross-metathesis (Figures 8A—B) suggest that C<sub>3</sub> and C<sub>5</sub> odd carbon number olefins should be also formed during these processes. Nevertheless, the odd carbon number olefins with chain lengths less than C<sub>7</sub> were not observed among reaction products neither in this study nor in the our first publication<sup>[49]</sup>.

However, the occurrence of simultaneous Friedel-Crafts alkylation process allowed us to capture these light fractions as alkyltoluenes with odd carbon number substituents (Figure 8C). 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> was formed. The molar shares of these alkyltoluenes were comparable to the shares of heavier odd carbon number olefins (Figures 7B–C) and had not exceeded 0.4 mol% for any individual component. Such distribution of odd carbon number olefins does not contradict any of the considered plausible mechanisms (Figures



Figure 7 Shares of toluene alkylated with even carbon number olefins (A), toluene alkylated with odd carbon number olefins (B) and  $C_2 - C_{11}$  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).

(A) Competition between  $\beta$ -Me and  $\beta$ -H elimination



(B) Equibrium between ethenolysis and cross-metathesis



**Figure 8** Simplified  $\beta$ -methyl elimination (A) and ethenolysis (B) reaction pathways for formation of odd carbon number olefins; (C) simplified catalytic cycle of ethylene oligomerization, formation of odd carbon number olefins and subsequent alkylation of toluene with these products.

According to the literature,<sup>[25,49]</sup> two main pathways can be considered for the formation of odd carbon number olefins in the studied catalytic systems –  $\beta$ -methyl elimination (Figure 8A) and cross-metathesis between  $\beta$ -olefin and ethylene (ethenolysis) (Figure 8B). The presumable ethenolysis reaction involving  $\beta$ -olefin (C<sub>n</sub>) results in the formation of propylene (C<sub>3</sub>) and corresponding odd carbon number olefin ( $C_{n-1}$ ). It is favored over reverse cross-metathesis due to huge excess of ethylene dissolved in reaction media. Alternative process that can cause the formation of odd carbon number olefins is  $\beta$ -methyl elimination, which is in constant competition with conventional chain termination pathway  $\beta$ -H elimination (Figure 8A).  $\beta$ -methyl elimination leads to direct formation of odd carbon number olefins  $(C_{n-1})$  differing by one carbon atom from the 'parent' compounds  $(C_n)$ . The lower shares off 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> resulted 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 resulted in a higher activity of the resulting catalytic systems and the use of Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> resulted in a 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 served 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 P2O5. The water contents in these solvents were periodically controlled by Karl-Fischer coulometry by using a Metrohm 756 KF.  $CDCl_3$  and acetone- $d_6$  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 ethylaluminium 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 by us.<sup>[46]</sup> Bis(pyrazol-1-yl)methane L<sub>1</sub>, bis(3,5-dimethyl-4-nitropyrazol-1-yl)methane L<sub>2</sub>, bis(3-phenylpyrazol-1-yl)methane L<sub>6</sub>, bis(3,5-dimethyl-4-chloropyrazol-1-yl) methane L7, bis(3,5-dimethyl-4-bromopyrazol-1-yl)methane  $L_8$ , were prepared by modified literature procedure<sup>[50]</sup> where tetrabutylamoniumbromide was substituted by Aliquat 336<sup>®</sup>. Bis(3,5-di-isopropylpyrazol-1-yl)methane L<sub>4</sub>, bis(3,5-dimethyl-4-tert-butylpyrazol-1-yl)methane L<sub>5</sub>, 1,1'-bis(indazol-1-yl)methane  $L_{10}$ , 1,1'-bis(benzotriazol-1-yl)methane  $L_{11}$ , and bis(3,5-di-tert-butylpyrazol-1-yl)methane L13 were prepared according to Ref. [53]. Bis(3,5-ditrifluoromethylpyrazol-1-yl)methane L12 was prepared according to Ref. [52]. Bis(3,5-dimethyl-4-iodopyrazol-1-yl)methane L<sub>9</sub> was prepared by iodation of bis(3,5-dimethylpyrazol-1-yl)methane  $L_3$ .<sup>[51]</sup> 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.

### 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  $400-4000 \text{ cm}^{-1}$  range were obtained for KBr pellets on Bruker Tensor 37 FTIR spectrometer, and absorption IR spectra in the  $400-50 \text{ cm}^{-1}$  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 microanalyticcal 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).<sup>[68]</sup> The measurements were done in a positive ion mode (interface capillary voltage - 4500 V); mass range was from m/z 50 to m/z 3000 Da; external or internal calibration was done with Electrospray Calibrant Solution (Fluka). A syringe injection

### General procedure for the synthesis of Ni complexes

 $Ni(DME)Br_2$  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 h 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)

**1** was prepared according to general procedure: bis(pyrazol-1-yl)methane  $L_1$  (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  $C_{14}H_{16}Br_2N_8Ni$  (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): 3102 (s,  $v_s$  (Pz, C—H)), 3001 (s,  $v_s$  (Pz, C—H)), 2960 (m,  $v_s$  (-CH<sub>2</sub>-, C—H)), 1612 (m,  $v_s$  (Pz, C=N)), 1527 (m,  $v_s$  (Pz, C=C)), 1512 (m,  $v_s$  (Pz, C=C)) cm<sup>-1</sup>. IR (nujol): 376 (w), 254 (w), 226 (m), 163 (w), 104 (w), 70 (w) cm<sup>-1</sup>.

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

**2** was 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 **L**<sub>1</sub> (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): 3100 (s, *v*<sub>s</sub> (Pz, C—H)), 3000 (m, *v*<sub>s</sub> (Pz, C—H)), 2960 (m, *v*<sub>s</sub> (-CH<sub>2</sub>-, C—H)), 1611 (m, *v*<sub>s</sub> (Pz, C=C)), 1511 (m, *v*<sub>s</sub> (Pz, C=C)) cm<sup>-1</sup>. IR (nujol): 374 (w), 252 (w), 223 (w), 158 (w), 101 (w), 66 (w) cm<sup>-1</sup>.

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

**4** was prepared according to general procedure: bis(3,5-diisopropylpyrazol-1-yl)methane  $L_4$  (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- $d_2$ )  $\delta$ : 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,  $v_s$  (Pz, C-H)), 2967 (vs,  $v_s$  (i-Pr, C-H)), 2930 (s,  $v_s$  (-CH<sub>2</sub>-, C-H)), 2870 (m,  $v_s$  (i-Pr, C-H)), 1549 (s,  $v_s$  (Pz, C=C)) cm<sup>-1</sup>.

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

**5** was prepared according to general procedure: bis(3,5-dimethyl-4-*tert*-butylpyrazol-1-yl)methane  $L_5$  (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- $d_2$ )  $\delta$ : 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): 3034 (w,  $v_s$  (-CH<sub>2</sub>-, C—H)), 2965 (vs,  $v_s$  (t-Bu, C—H)), 2870 (m,  $v_s$  (Me, C—H)), 1537 (m,  $v_s$  (Pz, C=C)) cm<sup>-1</sup>.

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

**6** was prepared according to general procedure: bis(3-phenyl-pyrazol-1-yl)methane  $L_6$  (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- $d_2$ )  $\delta$ : 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- $d_6$ )  $\delta$ : 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): 3107 (m,  $v_s$  (Pz, C–H)), 3000 (m,  $v_s$  (Ph, C–H)), 1529 (m,  $v_s$  (Pz, C=C)) cm<sup>-1</sup>.

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

**7** was prepared according to general procedure: bis(3,5-dimethyl-4-chloropyrazol-1-yl)methane  $L_7$  (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- $d_2$ )  $\delta$ : 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): 3033 (m,  $v_s$  (-CH<sub>2</sub>-, C-H)), 2978 (m,  $v_s$  (-CH<sub>2</sub>-, C-H)), 2956 (m,  $v_s$  (Me, C-H)), 2923 (m,  $v_s$  (Me, C-H)), 2878 (m,  $v_s$  (Me, C-H)), 1559 (m,  $v_s$  (Pz, C=C)) cm<sup>-1</sup>.

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

**8** was prepared according to general procedure: bis(3,5-dimethyl-4-bromopyrazol-1-yl)methane  $L_{48}$  (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. <sup>1</sup>H NMR (600 MHz, methylene chloride- $d_2$ )  $\delta$ : 2.47 (5-CH<sub>3</sub>; s, 6H), -2.00 (3-CH<sub>3</sub>, s, 6H), -6.35 (-CH<sub>2</sub>-; s, 2H). MALDI-TOF (m/z, %): [NiLBr]<sup>+</sup> (501.314, 100%), Calc. m/z 501.815. Anal. calcd. for C<sub>11</sub>H<sub>14</sub>Br<sub>4</sub>N<sub>4</sub>Ni\*C<sub>4</sub>H<sub>8</sub>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): 3038 (m,  $v_s$  (-CH<sub>2</sub>-, C-H)), 2981 (m,  $v_s$  (-CH<sub>2</sub>-, C-H)), 2981 (m,  $v_s$  (Me, C-H)), 1529 (m,  $v_s$  (Pz, C=C)) cm<sup>-1</sup>.

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

**9** was prepared according to general procedure: bis(3,5-dimethyl-4-iodopyrazol-1-yl)methane **L**<sub>9</sub> (300 mg, 0.66 mmol), Ni(DME)Br<sub>2</sub> (204 mg, 0.66 mmol). Purple powder, yield: 414 mg (93.0%). <sup>1</sup>H NMR (600 MHz, methylene chloride- $d_2$ )  $\delta$ : 3.30 (5-CH<sub>3</sub>; s, 6H), -1.89 (3-CH<sub>3</sub>; s, 6H), -6.01 (-CH<sub>2</sub>-; s, 2H). MALDI-TOF (m/z, %): [NiL<sup>-1</sup>Br]<sup>+</sup> (468.948, 25%), Calc. m/z 468.885; [NiLBr]<sup>+</sup> (594.781, 100%), Calc. m/z 595.022. Anal. calcd. for C<sub>11</sub>H<sub>14</sub>Br<sub>2</sub>I<sub>2</sub>N<sub>4</sub>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): 3027 (w,  $v_s$  (-CH<sub>2</sub>-, C-H)), 2921 (w,  $v_s$  (Me, C-H)), 2874 (w,  $v_s$  (Me, C-H)), 2854 (w,  $v_s$  (Me, C-H)), 1535 (m,  $v_s$  (Pz, C=C)) cm<sup>-1</sup>.

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

**10** was prepared according to general procedure: bis(indazol-1-yl) methane  $L_{10}$  (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*, %): [L-H]<sup>+</sup> (247.200, 28%), Calc. *m/z* 247.099; [NiLBr]<sup>+</sup> (387.141, 86%), Calc. *m/z* 386.957. Anal. calcd. for  $C_{15}H_{12}Br_2N_4Ni^*0.5C_4H_8O$  (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): 3111 (w,  $v_s$  (Ind, C—H)), 3056 (w,  $v_s$  (Ind, C—H)), 2994 (w,  $v_s$  (Ind, C—H)), 1622 (s,  $v_s$  (Ind, C=N)), 1507 (m,  $v_s$  (Ind, C=C)) cm<sup>-1</sup>.

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

**11** was prepared according to general procedure: bis(benzo-triazol-1-yl) methane  $L_{11}$  (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*, %): [NiL(H<sub>2</sub>O)]<sup>+</sup> (326.285, 95%), Calc. *m/z* 326.042; [NiBtz<sub>2</sub>Br<sub>2</sub>]<sup>+</sup> (455.582, 24%, Btz = benzotriazole), Calc. *m/z* 455.866. Anal. calcd. for  $C_{14}H_{16}Br_2N_8Ni$  (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): 2998 (w,  $v_s$  (Btz, C—H)), 2954 (w,  $v_s$  (-CH<sub>2</sub>-, C—H)), 2925 (w,  $v_s$  (-CH<sub>2</sub>-, C—H)), 1494 (w,  $v_s$  (Btz, C=C)) cm<sup>-1</sup>.

### X-ray diffraction studies

The single-crystal X-ray diffraction data for 5a, 5b, 6 and 8 were collected on the synchrotron Radiation Source using a Rayonix SX165 CCD detector (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<sup>[69]</sup> and then scaled and corrected for absorption using the Scala program.<sup>[70]</sup> For details, see Supporting Information Table S1. The structures were solved by direct methods and refined by a fullmatrix 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.[71] Based on these calculations, the content of THF solvate molecules was equal to 1/5 per 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  $[U_{iso}(H) = 1.5U_{eq}(C)$  for the methyl groups and  $1.2U_{en}(C)$  for the other groups]. All calculations were carried out using the SHELXTL program suite.<sup>[72]</sup> Crystallographic data for **5a**, **5b**, 6.1/5THF 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.

### Calculations

DFT optimization of structures of complexes **2**, **3**, **4** and **6** was performed in ORCA 4.2.1 using PBE0 hybrid functionality,<sup>[73]</sup> def2-TZVP basis<sup>[74]</sup> and D4 dispersion corrections.<sup>[75]</sup> Topographic steric maps of the nickel complexes **2**, **3**, **4** and **6** were calculated and visualized with SambVca 2.1 web tool<sup>[76-77]</sup> using DFT optimized structures of complexes. Only bis(pyrazolyl)methane ligands have been considered for calculations of  $\% V_{bur}$ . Ni atom was placed as the center of the sphere and *xz*-plane was defined by Ni and 2 coordinated nitrogen atoms; the *z*-axis bisects N–Ni–N angle.

### **Oligomerization of ethylene**

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 min 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 (150 mol. equiv. for  $Et_2AICI$ , 75 mol. equiv. for  $Et_3AI_2CI_3$ ) dissolved in additional toluene (10 mL) was loaded in the reactor. The reactor was heated to a specified temperature and then argon at-

mosphere 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<sup>™</sup> software. After the end of the process, the reaction solution was guickly cooled down, excessive ethylene pressure was released and the solution was guenched with 15 mL isopropanol and 10 mL 5% hydrochloric acid. The organic phase was further dried by Na<sub>2</sub>SO<sub>4</sub> 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  $\times$  0.25 mm (id)  $\times$  0.25  $\mu$ m (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.

### **Supporting Information**

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.202300175.

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