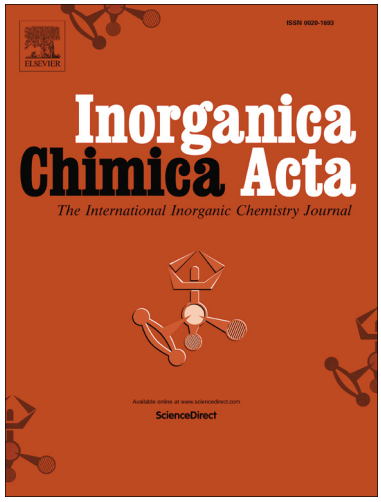

Research paper

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Synthesis and Reactivity in Ethylene Oligomerization by Heteroscorpionate Dibromonickel (II) Complexes

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Abstract

Novel heteroscorpionate ligands were synthesized by a Peterson rearrangement during the reaction of 2-pyridinecarboxaldehyde (or 2-quinolinecarboxaldehyde) and 1,1-carbonyl-bis(pyrazoles). Nickel (II) dibromide reacts with these ligands in THF to give the heteroscorpionate dibromo complexes of general formula $LNiBr_2$. Crystal structures of two full-sandwich heteroscorpionate Ni(II) complexes were determined. Preliminary studies of catalytic activity in ethylene oligomerization using different organoaluminum cocatalysts were performed. The addition of one equivalent of triphenylphosphine resulted in increased catalytic activity for most examples. The catalyst system of (2-[bis(3,5-dimethylpyrazol-1-yl)methyl]pyridine nickel (II) dibromide / Et_2AlCl / PPh_3 dimerized ethylene with an activity of 650 g oligomer mol^{-1} Ni h^{-1} while the share of 1-butene in the mixture has reached 75%. Tris(3,5-dimethylpyrazol-1-yl)methyl nickel (II) dibromide, activated by Et_2AlCl / PPh_3 produced isobutylene (75% of the butene fraction).

Keywords: ethylene; oligomerization; heteroscorpionate nickel (II) complexes, selectivity

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1. Introduction

Scorpionate ligands have been demonstrated as attractive ancillary ligands for the synthesis of transition metal complexes [1-2]. These classes of tridentante ligands whose steric environment and electronic structure can be easily modified can coordinate to a wide variety of elements, e.g. from early to late transition metals.

A broad range of transition metal complexes bearing these ligands revealed they behave as catalysts for ethylene oligo- or polymerization [3-4]. The vast majority of such catalysts are formed on the basis of chromium complexes. Despite the fact that the nickel compounds are also active in the oligomerization [5], only a few examples of tris(pyrazolyl)borate Ni complexes have been employed as catalysts in the olefin oligomerization [6] and copolymerization of ethylene and carbon monoxide [7].

The electronic and steric properties of an ancillary ligand can dramatically influence the reactivity of a metal ion to which it is bound. As such, extensive efforts have been focused on the development of ligand systems whose steric environment and electronic structure can be easily modified, with the ultimate goal being the ability to ‘‘fine-tune’’ a metal complex to produce a desired type of chemical reactivity.

Herein we report the synthesis and the structural research of the novel nickel (II) dibromide complexes and their reactivity toward ethylene. Additionally, the influence of the additive of triphenylphosphine on the catalytic activity and selectivity was investigated.

2. 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 and ethylene of special-purity grade (Linde gas) were dried by purging through a Super Clean™ Gas Filters. Toluene, diethyl ether, and tetrahydrofuran were distilled over Na/benzophenone ketyl. Dichloromethane was distilled over calcium hydride. The water contents in these solvents were periodically controlled by Karl-Fischer coulometry by using a Methrom 756 KF. $CDCl_3$ and CD_2Cl_2 were degassed and stored over 4 Å sieves. Diethylaluminumcloride and aluminium sesquichloride (Aldrich) were used as 1.0 M solution in heptane. Unless otherwise noted, all reagents were purchased from Sigma-Aldrich. 4-Bromo-2,5-dimethylpyrazole [8], 3-*tert*-butyl-pentan-2,4-dione [9], 3,5-dimethyl-4-tert-butilpirazol [10], bis(pyrazol-1-yl)methanone [11], bis(3,5-dimethylpyrazol-1-yl) methanone [11] and tris(3,5-dimethylpyrazol-1-yl)methane **19** [12] were prepared by following literature procedures; their ^{1}H and ^{13}C NMR spectra were found to match the published data.

Physical and Analytical Measurements.

NMR spectra were recorded on Bruker AMX-400. Chemical shifts are reported in ppm *vs.* $SiMe_4$ and were determined by reference to the residual solvent peaks. All coupling constants are given in Hertz.

IR spectra were recorded on a Magna-IR 750 spectrophotometer. Elemental analysis was performed by the microanalytical laboratory at A. N. Nesmeyanov Institute of Organoelement Compounds. Mass spectra under atmospheric pressure electrospray (ESI) were recorded in the full scan mass of positive and negative ions on the dynamic tandem mass spectrometer Finnigan LCQ Advantage (USA), equipped with a mass analyzer oktapol ion trap pump MS Surveyor, Surveyor autosampler, nitrogen generator Schmidlin-Lab (Germany) and a system for collecting and processing the data using the X Calibur program (version 1.3, Finnigan). Transfer capillary temperature of 150 °C, voltage field between the needle and counter electrode 4.5 kV. Samples were introduced into the ion source with the input syringe acetonitrile at a 50 ml/min flow rate through the 5 mL Reodyne injector loop.

Bis(4-*tert*-butyl-3,5-dimethylpyrazol-1-yl)methanone (7). 4-*tert*-butyl-3,5-dimethylpyrazole **3** (2.37 g, 15.6 mmol) was dissolved in THF (20 mL) and NEt_3 (2.13 mL) was added afterwards. Triphosgene, $Cl_3COCOOCCl_3$ (0.772 g, 2.60 mmol), was dissolved in THF (20 mL) and the resulting solution was added as quickly as possible to the initial one. After 16 h of stirring at room temperature, the white solid formed was filtered off and washed twice with THF. The THF fractions were combined and the solvent evaporated. The product was obtained as an orange-brown oil in a yield of 1.055 g (69.3%).^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 6H), 2.36 (s, 6H), 1.36 (s, 18H). Anal. Calcd for $C_{19}H_{30}N_4O$ (330.48): C, 69.06; H, 9.15; N, 16.95; O, 4.84. Found: C, 68.95; H, 9.01; N, 16.88.

Bis(4-bromo-3,5-dimethylpyrazol-1-yl)methanone (8). The method was similar to that used for **7.** The obtained solid was recrystallised from toluene/hexane obtaining white crystals. Yield: 1.88 g (64.2 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 6H), 2.29 (s, 6H). Anal. Calcd for $C_{11}H_{12}Br_2N_4O$ (376,05): C, 35.13; H, 3.22; Br, 42.50; N, 14.90; O, 4.25. Found: C, 35.07; H, 3.16; Br, 42.38; N, 14.81.

2-[Di(pyrazol-1-yl)methyl]pyridine (9). A mixture of bis(pyrazol-1-yl)methanone **5** (0.74 g, 4.59 mmol), 2-formylpyridine (0.492 g, 4.59 mmol) and $CoCl_2 \cdot 6H_2O$ (0.011 g, 0.046 mmol) was heated with vigorous stirring at 100 °C during 4 h. Resulting solid was dissolved in CH_2Cl_2, washed with water three times and dried over Na_2SO_4. Then, solvent was removed by rotary evaporation and the resulting black product was dissolved in CH_2Cl_2 and filtered through a short pad of silica gel, and then the solvent was removed by rotary evaporation and the resulting viscous burgundy oil was crystallized from toluene / petroleum ether 1: 3, to give oranges brown crystals. Yield - 0.444 g (31.8%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, J = 4.5 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.67 – 7.61 (m, 4H), 7.30 (dd, J = 7.5, 4.9 Hz, 1H), 7.04 (d, J = 7.9

Hz, 1H), 6.35 (s, 2H). Anal. Calcd for $C_{12}H_{11}N_5$ (225.25): C, 63.99; H, 4.92; N, 31.09. Found: C, 63.78; H, 4.88; N, 30.98.

2-[Bis(3,5-dimethylpyrazol-1-yl)methyl]pyridine (10). The method was similar to that used for **9**. Amounts were as follows: bis(3,5-dimethylpyrazol-1-yl)methanone (1.0 g, 4.59 mmol), 2-formylpyridine (0.492 g, 4.59 mmol) and $CoCl_2 \cdot 6H_2O$ (0.011 g, 0.046 mmol). Resulting brown solid was washed with minimal Et_2O and was recrystallized by cooling a hot hexane solution to room temperature to give 0.886 g (68.7%) of **10** .^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.5 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.56 (s, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 5.85 (s, 2H), 2.20 (s, 6H), 2.18 (s, 6H). Anal. Calcd for $C_{16}H_{19}N_5$ (281.36): C, 68.30; H, 6.81; N, 24.89. Found: C, 68.26; H, 6.80; N, 24.80.

2-[Bis(4-*tert*-buthyl-3,5-dimethylpyrazol-1-yl)methyl]pyridine (11). The method was similar to that used for **10**. Amounts were as follows: bis(4-*tert*-buthyl-3,5-dimethylpyrazol-1-yl)methanone (1.0 g, 4.59 mmol), 2-formylpyridine (0.492 g, 4.59 mmol) and $CoCl_2 \cdot 6H_2O$ (0.011 g, 0.046 mmol). Brown oil was triturated with petroleum ether and the precipitate formed is filtered off. Evaporation of the filtrate gave a brownish yellow oil which was dried under vacuum and identified as **11.** Yield - 0.812 g (85.9%). M.p.=145-147 ^{o}C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 4.2 Hz, 1H), 7.65 (td, *J* = 7.8, 1.6 Hz, 1H), 7.55 (s, 1H), 7.21 (dd, *J* = 7.3, 5.0 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 2.28 (s, 6H), 2.22 (s, 6H), 1.32 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.35 (Py, C_2), 149.38 (Py, C_6), 146.05 (Pz, C_5), 137.06 (Pz, C_3), 136.50 (Py, C_4), 124.64 (Pz, C_4), 123.05 (Py, C_3), 122.33 (Py, C_5), 74.96 (C^{α}), 31.80 (t-Bu, Me), 31.54 (t-Bu, C), 16.96 (Me_5), 12.58 (Me_3). Масс-спектр 393 (M-1, 4.05); 241 (66,75). Anal. Calcd for $C_{24}H_{35}N_5$ (393.58): C, 73.24; H, 8.96; N, 17.79. Found: C, 73.19; H, 8.91; N, 17.70.

2-[Bis(4-bromo-3,5-dimethylpyrazol-1-yl)methyl]pyridine (12). The method was similar to that used for **10**. Amounts were as follows: bis(4-bromo-3,5-dimethylpyrazol-1-yl)methanone (1.0 g, 4.59 mmol), 2-formylpyridine (0.492 g, 4.59 mmol) and $CoCl_2 \cdot 6H_2O$ (0.011 g, 0.046 mmol). Obtained solid was dissolved in toluene and filtered through a short pad of silica gel, and then the solvent was removed by rotary evaporation to give beige crystals. Yield – 0.178 g (32.4%). M.p. =171-172 ^{o}C.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.0 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.58 (s, 1H), 7.33 – 7.28 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 2.20 (d, *J* = 1.1 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.30 (Py, C_2), 149.83 (Py, C_6), 147.74 (Pz, C_5), 139.06 (Pz, C_3), 137.22 (Py, C_4), 123.75 (Py, C_3), 122.48 (Py, C_5), 96.71 (Pz, C_4), 76.11 (C^{α}), 12.77 (Me_5), 11.01 (Me_3). Mass-spectrum (E.I., 70 eV, m/z, %): 439 (4.99); 264 (100).

Anal. Calcd for $C_{16}H_{17}Br_2N_5$ (439.16): C, 43.76; H, 3.90; Br; 36.39; N, 15.95. Found: C, 43.88; H, 3.92; Br, 36.32; N, 15.70.

2-[Bis(3,5-dimethylpyrazol-1-yl)methyl]quinoline (13). The method was similar to that used for **10**. Amounts were as follows: bis(3,5-dimethylpyrazol-1-yl)methanone (0.62 g, 2,85 mmol), 2-formylquinoline (0.447 r, 2,85 mmol) and $CoCl_2 \cdot 6H_2O$ (0.010 g, 0,028 mmol). Orange-brown crystals, yield 0.672 g (71.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.26 (t, J = 4.2 Hz, 2H), 5.89 (s, 2H), 2.19 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.57 (Quin., C_2), 148.61 (Pz, C_5), 147.51 (Quin., C_8[a]), 140.95 (Pz, C_3), 136.81 (Quin., C_4), 129.83 (Quin., C_7), 129.60 (Quin., C_8), 127.78 (Quin., C_5), 127.59 (Quin., C_4[a]), 127.04 (Quin., C_6), 120.46 (Quin., C_3), 106.97 (Pz, C_4), 75.54 (C^{α}), 13.94 (Me_5), 11.52 (Me_3). Mass-spectrum (E.I., 70 eV, m/z, %): 331 (7.5); 236 (100). Anal. Calcd for $C_{20}H_{21}N_5$ (331.42): C, 72.48; H, 6.39; N, 21.13. Found: C, 72.42; H, 6.31; N, 21.01.

Synthesis of Nickel(II) complexes

[**N,N,N-(2-[bis(pyrazol-1-yl)methyl]pyridine nickel (II) dibromide (14).** A solution of 2-[bis(pyrazol-1-yl)methyl]pyridine **9** (0.342 g, 1.52 mmol) in THF (10 mL) was slowly added to a stirred solution of [$NiBr_2$ DME] (0.470 g, 1.52 mmol) in THF (15 mL). After brief stirring at r.t., the beige precipitate was separated out by filtration, washed with THF and dried in vacuum. Yield: 0.384 g (57%). Anal. Calcd for $C_{12}H_{14}Br_2N_5Ni \cdot 2C_4H_8O$ (590.98): C 40.65; H 5.12; N 11.85; O 5.41; Br 27.04; Ni 9.93. Found: C 40.23; H 4.69; N 11.32; Ni 9.58. IR, cm^{-1}: ν(Ni-N) 489, 420. Mass spectrum (E.I., 70 eV, m/z, %): 366 [M^+-Br]. ESI-MS: m/z (%) 366 [$(M - Br)^+$, 100%].

[**N,N,N-(2-[bis(3,5-dimethylpyrazol-1-yl)methyl]pyridine nickel (II) dibromide (15).** The method was similar to that used for **14**. Amounts were as follows: [$NiBr_2$ DME] (0.179 g, 0.58 mmol), 2-[bis(3,5-dimethylpyrazol-1-yl)methyl]pyridine **10** (0.163 g, 0,58 mmol). Bluish-green solid. Yield: 0.241 g (83%). Anal. Calcd for $C_{16}H_{22}Br_2N_5Ni \cdot C_4H_8O$ (572,02): C 41.78; H 5.2l; N 12.18; O 2.78; Br 27.79; Ni 10.21. Found: C, 41.45; H 5.08; N 12.04; Ni 9.97. IR, cm^{-1}: ν(Ni-N) 447. Mass spectrum (E.I., 70 eV, m/z, %): 423 (M-Br, 100%). ESI-MS: m/z (%) 423 [$(M - Br)^+$, 100%].

[**N,N,N-(2-[bis(4-*tert*-buthyl-3,5-dimethylpyrazol-1-yl)methyl]pyridine nickel (II) dibromide (16).** The method was similar to that used for **14**. Amounts were as follows: [$NiBr_2$

DME] (0.636 g, 2.06 mmol), 2-[bis(4-*tert*-buthyl-3,5-dimethylpyrazol-1-yl)methyl]pyridine (0.812 g, 2,06 mmol). Yield: 0.847 g (67,1%). Anal. Calcd for $C_{24}H_{20}Br_2N_5Ni\ C_4H_8O$ (687.20): C 48.94; H 6.75; N 10.19; O 2.33; Br 23.25; Ni 8.54. Found: C 47.99; H 6.43; N 10.20; Ni 8.20. IR, cm^{-1}: ν(Ni-N) 531, 412. Mass spectrum (E.I., 70 eV, m/z, %): 535 [$(M-Br)^+$, 100%].

[N,N,N-(2-[bis(4-bromo-3,5-dimethylpyrazol-1-yl)methyl]pyridine nickel (II) dibromide (17). The method was similar to that used for **14**. Amounts were as follows: [$NiBr_2$ DME] (0.155 g, 0.50 mmol), 2-[bis(4-bromo-3,5-dimethylpyrazol-1-yl)methyl]pyridine (0.220 g, 0.50 mmol). Yield: 0.290 g (72%). Anal. Calcd for $C_{16}H_{20}Br_4N_5Ni.2C_4H_8O$ (804.88): C 35.8; H 4.51; N 8.70; O 3.98; Br 39.71; Ni 7.29. Found: C 35.20; H 4.12; N 8.20; Ni 7.00. IR, cm^{-1}: ν(Ni-N) 497, 435. ESI-MS: m/z (%) 501 [$(M-Br)^+$, 100%].

[N,N,N-(2-[bis(3,5-dimethylpyrazol-1-yl)methyl]quinoline nickel (II) dibromide (18). The method was similar to that used for **14**. Amounts were as follows: [$NiBr_2$ DME] (0.327 g, 1.06 mmol), 2-[bis(3,5-dimethylpyrazol-1-yl)methyl]quinoline (0.351 g, 1,06 mmol). Yield: 0.489 g (83,9%). Anal. Calcd for $C_{20}H_{24}Br_2N_5Ni\cdot C_4H_8O$ (625.04): C 46.12; H 5.16; N 11.20; O 2.56; Br 25.57; Ni 9.39. Found: C 45.20; H 4.96; N 10.32; Ni 8.75. IR, cm^{-1}: ν(Ni-N) 597, 418. Mass spectrum (E.I., 70 eV, m/z, %): 545 [$(M-Br)^+$, 100%].

N,N,N-tris(3,5-dimethylpyrazol-1-yl)methyl nickel (II) dibromide (20). The method was similar to that used for **14**. Amounts were as follows: [$NiBr_2$ DME] (0.519 g, 1,68 mmol), tris(3,5-dimethylpyrazol-1-yl)methane (0.500 g, 1.68 mmol). Yield: 0.847 g (67,1%). Anal. Calcd for $C_{20}H_{35}Br_2N_6Ni\cdot C_4H_8O$ (594.03): C 40.44; H 5.94; N 14.15; O 2.69; Br 26.90; Ni 9.88. Found: C 40.23; H 4.92; N 14.05; Ni 8.77. IR, cm^{-1}: ν(Ni-N) 520, 440. MALDI-TOF-MS (m/z): calcd for $C_{20}H_{35}BrN_6Ni\cdot C_4H_8O$: 515.0315; found: 515.0279 $[M-Br]^+$.

Bis- [tris(3,5-dimethylpyrazol-1-yl)methane] nickel (II) tetrabromine nickelate (21).

Anhydrous $NiBr_2$ (0.219 g, 1.00 mmol) was added to a CH_3CN solution (20 mL) of tris(3,5-dimethylpyrazol-1-yl)methane **19** (0.298 g, 1.00 mmol). The resulting solution was refluxed for 48 h. The brown-green precipitate was separated out by filtration, washed with CH_3CN and dried in vacuo. Yield: 0.425 g (79%). Anal. Calcd for $C_{32}H_{50}Br_4N_{12}Ni_2\ 2CH_3CN$: C 38.54; H 5.03; N 17.48; Br 28.49; Ni 10.46. Found: C, 38.42; H 4.86; N 17.37; Br 28.37; Ni 10.27. IR, cm^{-1}: ν(Ni-N) 423, 499. ESI-MS, m/z (%):1039.82 [(M)+, 97%].

Bis-2-[bis(3,5-dimethylpyrazol-1-yl)methyl]pyridine nickel (II) tetrabromine nickelate (22).

Anhydrous $NiBr_2$ (0.127 g, 0.58 mmol) was added to a CH_3OH solution (20 mL) of 2-[bis(3,5-dimethylpyrazol-1-yl)methyl]pyridine **10** (0.163 g, 0.58 mmol). The resulting suspension was refluxed for 48 h. The green precipitate was separated out by filtration, washed with CH_3OH and dried in vacuo. Yield: 0.269 g (85%). Anal. Calcd for $C_{32}H_{44}N_{10}Ni_2Br_4$ CH_3OH: C 38.19; H 4.66; N 13.50; Br 30.80; Ni 13.50. Found: C, 38.03; H 4.27; N 13.17; Br 30.15; Ni 11.15. IR, cm^{-1}: ν(Ni-N) 418, 497. ESI-MS, m/z (%): 1005.76 [(M)+, 95%].

X-ray diffraction studies.

The single-crystal X-ray diffraction data for **21** and **22** 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 at λ = 0.96990 Å. A total of 720 images for two different orientations in the case of each crystal were collected using an oscillation range of 1.0° and φ scan mode. The data were indexed and integrated using the utility iMOSFLM from the CCP4 program suite [13] and then scaled and corrected for absorption using the Scala program [14]. For details, see Table 2. The structures were determined by direct methods and refined by full-matrix least square technique on F^2 in anisotropic approximation for non-hydrogen atoms. The independent parts of the unit cells of **21** and **22** contained two acetonitrile and one methanol solvate molecules, respectively. The hydrogen atoms of the solvate molecules were objectively localized in the difference-Fourier map and included in the refinement within the riding model with isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(O, N or C)]. The other hydrogen atoms in **21** and **22** were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the methyl groups and 1.2U_{eq}(C) for the other groups]. All calculations were carried out using the SHELXTL program suite [15]. Crystallographic data for **21**•2CH_3CN and **22**•CH_3OH have been deposited with the Cambridge Crystallographic Data Center, CCDC 1511204 (**21**) and CCDC 1511203 (**22**).

Table 1. Crystal data and structure refinements.

Compound	**21** •2CH_3CN	**22** • CH_3OH
Empirical formula	$C_{36}H_{50}Br_4N_{14}Ni_2$	$C_{33}H_{42}Br_4N_{10}Ni_2O$
Formula weight	1115.88	1031.82
Temperature, K	100.0(2)	100.0(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$

a, Å	10.300(2)	9.6801(19)
b, Å	23.867(5)	19.060(4)
c, Å	18.967(4)	21.750(4)
α, deg.	90	90
β, deg.	92.95(3)	93.68(3)
γ, deg.	90	90
V, Å^3	4656.5(17)	4004.8(14)
Z	4	4
D_{calc}, g·cm^{-3}	1.592	1.711
Absorption coefficient, μ	3.065	3.547
F(000)	2240	2056
Crystal size, mm	0.02×0.10×0.15	0.08×0.10×0.12
Theta range for data collection	3.35 – 38.41	3.39 – 39.79
Index ranges	-13 < h < 13 -29 < k < 29 -22 < l < 18	-11 < h < 11 -23 < k < 23 -27 < l < 27
Reflections collected	61005	36804
Independent reflections, R_{int}	9485, 0.076	8261, 0.071
Reflections observed with $I > 2\sigma(I)$	7057	6595
Absorption correction	semi-empirical	semi-empirical
Data / restraints/ parameters	9485 / 0 / 523	8261 / 0/ 464
Goodness-of-fit on F^2	1.051	1.050
R_1 [$I > 2\sigma(I)$]	0.061	0.065
wR_2 [all data]	0.177	0.190
Extinction coefficient	0.00183(19)	0.00184(19)
T_{min} / T_{max}	0.660 / 0.930	0.666 / 0.737

Oligomerization of Ethylene was performed in a 100-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 3 atm. Toluene (50 ml) and the necessary amount of a co-catalyst (Et_2AlCl, $Et_3Al_2Cl_3$) were loaded in the reactor. The reactor was heated to a specified temperature, and reaction mixture was saturated with ethylene. Oligomerization was initiated by addition of pre-catalyst to the reaction mixture and pressurization of 3 atm of ethylene in the reactor. The pressure of ethylene was maintained constant during

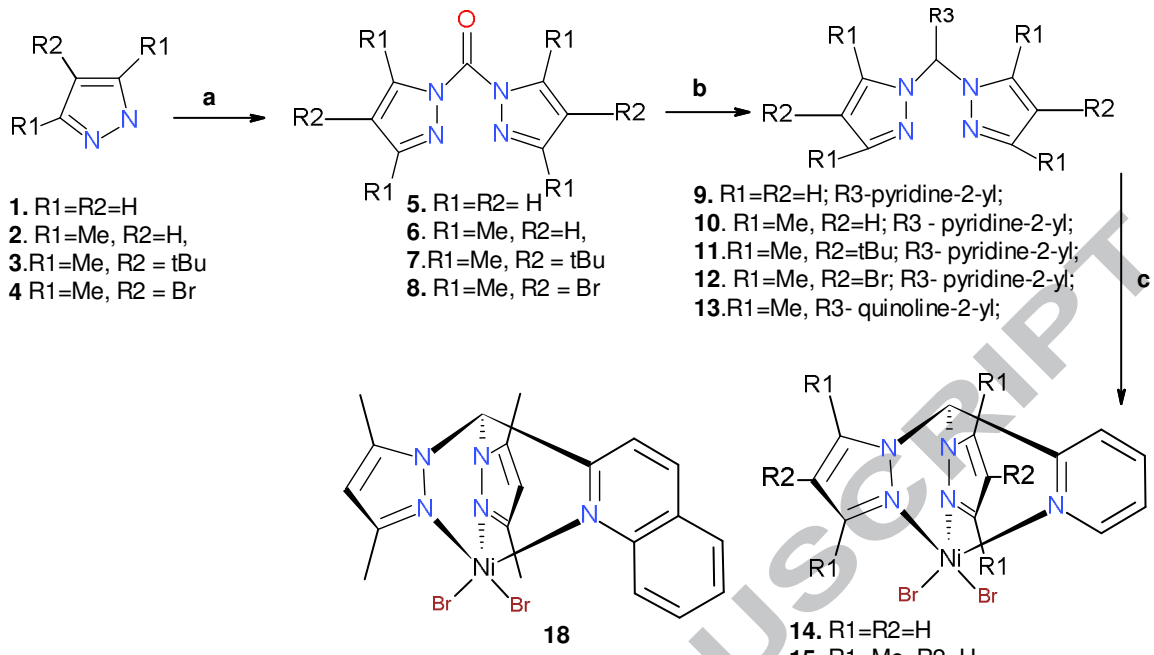
oligomerization. After a desired time, the reaction solution was quickly cooled down and then quenched with 5 ml isopropanol and 5 ml 5% dilute hydrochloric acid. After washed by water and dried by Na_2SO_4, the organic compounds were characterized by gas chromatography and GC–MS to determine the composition and molar mass distribution. Samples with desiccant were stored in sealed flasks in the refrigerator**.** Samples (1.0 μl) were injected into the chromatograph Trace GC ultra, connected to the mass spectrometer Finnigan Polaris Q (Ion Trap, EI, 70 eV, mass range 33 -1000 aem). The separation was performed on a capillary column RTX-5ms (5% Phenyl Polysilphenylene-siloxane; an inner diameter - 0.53 mm, length 50 m). Injector temperature - 270 °C; reset 1: 200; initial column temperature -90 °C; isotherm – 4 min; further heating at a rate of 10 degrees per minute up to 320 °C, and holding at 320°C – 3 min.

3. Results and Discussion

3.1. Synthesis and characterization.

The synthetic procedure for the heteroscorpionate ligands consisting of azine and substituted pyrazole rings is shown in Scheme 1. The substituted pyrazoles **1-4** were treated with bis(trichloromethyl)carbonate in THF solution in the presence of trimethylamine. The resulting bis(pyrazolyl)methanones **5-8** was converted by Peterson rearrangement into the heteroscorpionate ligands **9-13.**

Structure of the ligands **9-13, 19** was confirmed by NMR and mass spectroscopy. Reactions of the ligands with [$NiBr_2$ DME] in THF at room temperature resulted in the corresponding complexes **14-18, 20**. These Ni(II) complexes were isolated in 57–84% yields and characterized by elemental analysis, IR spectra and mass spectrometry. Their IR spectra in nujol mull showed all the bands required by coordination of the scorpionate ligand; bands at 420-497 cm^{-1} were assigned to the stretching vibrations ν (N→Ni). Meaningful signals in the MS spectra of the complexes **14-18, 20** were attributed to the loss of a bromine atom what is fairly well-known in the chemistry of nickel halide complexes, e.g. [16].



1. R1=R2=H
2. R1=Me, R2=H,
3.R1=Me, R2 = tBu
4 R1=Me, R2 = Br

5. R1=R2= H
6. R1=Me, R2=H,
7.R1=Me, R2 = tBu
8. R1=Me, R2 = Br

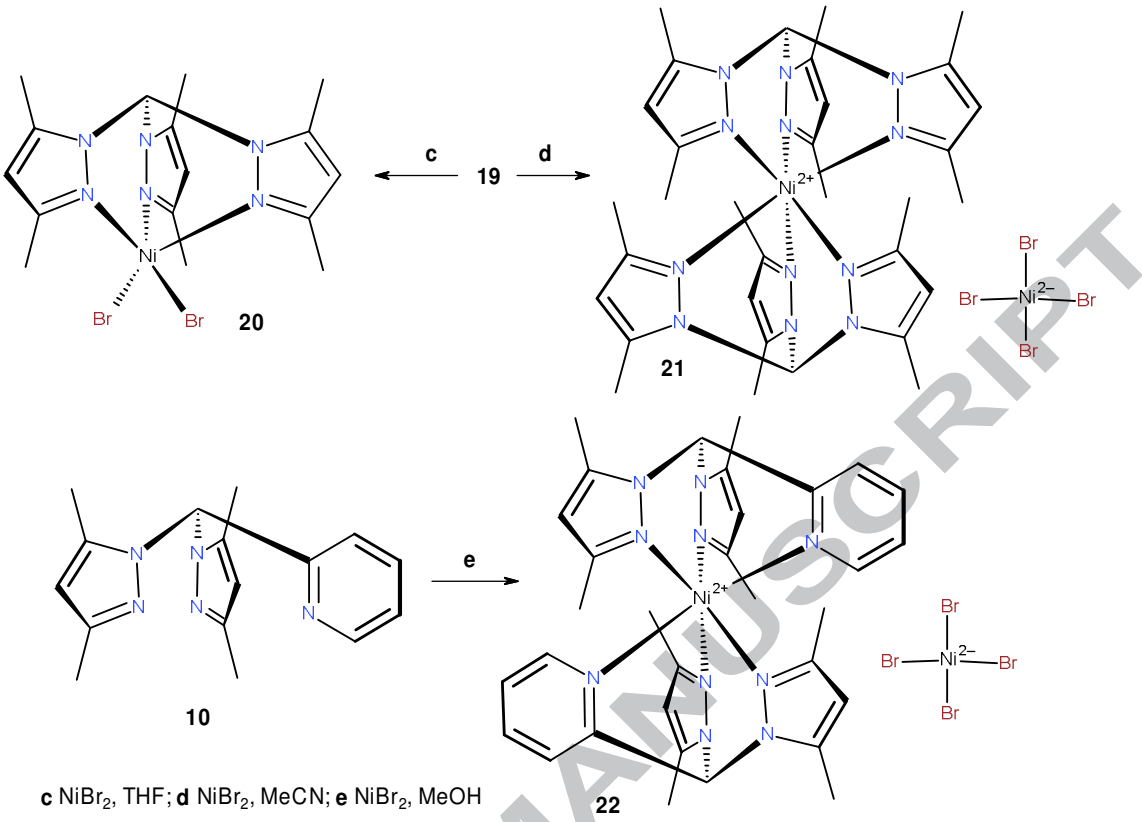
9. R1=R2=H; R3-pyridine-2-yl;
10. R1=Me, R2=H; R3 - pyridine-2-yl;
11.R1=Me, R2=tBu; R3- pyridine-2-yl;
12. R1=Me, R2=Br; R3- pyridine-2-yl;
13.R1=Me, R3- quinoline-2-yl;

14. R1=R2=H
15. R1=Me, R2=H,
16.R1=Me, R2 = tBu
17. R1=Me, R2 = Br

a NEt_3, THF, $Cl_3OC(O)OCl_3$;
b 2-formylpyridine/2-formylquinoline, $CoCl_2$ $6H_2O$;
c $NiBr_2$DME, THF.

Scheme 1. Synthesis of heteroscorpionate ligands and their dibromonickel(+2) complexes**.**

To identify the impact of azine ring on the catalytic activity we used known ligand **19** containing only pyrazole rings – tris(3,5-dimethylpyrazole-1-yl)methane [12]. Reactions of scorpionate ligands with Ni(II) salts can, in principle, give half-sandwich or full-sandwich complexes through the tripodal coordination of one or two scorpionates via the pyrazolyl ring's nitrogen atom. Numerous examples of such cationic spiro-complexes are given in [17-21]. Indeed, the interaction of the ligand **19** with anhydrous $NiBr_2$ in CH_3CN medium results in the formation of ionic complex $[L_2Ni]^+[NiBr_4]^-\cdot CH_3CN$ (**21**). Complex **22** having a similar structure was obtained under the same conditions starting from the ligand **10** in methanol medium (scheme 2). Structures containing nickel both in the cation and in the anion fragments have been previously known (for example, $[(tpm)_2Ni^{II}][(tpm)Ni^{II}(NCS)_3]_2\cdot 2CH_3OH$ [21]). Structurally related to **20** - complex $LNiCl_2\cdot H_2O$ was obtained in methanol-dichloromethane medium [22].



Scheme 2. Synthesis of full- and half-sandwich heteroscorpionate Ni(II) complexes.

The structures of the products **21** and **22** were unambiguously established by X-ray diffraction study and are shown in Figures 1 and 2 along with the atomic numbering scheme. The selected bond lengths and angles are given in Table 2.

The both nickel complexes crystallize in the monoclinic space group $P2_1/c$ with two crystallographically independent dications occupying special positions on the inversion centers. It is important to note that complex **21** is structurally similar to $\{Ni[HC(3,5\text{-}Me_2pz)_3]_2\}(BF_4)_2$ (**23**) and $\{Ni[HC(3,5\text{-}Me_2pz)_3]_2\}Br_2$ (**24**) reported previously [23, 24]. However, there are three main differences between them: (i) the counter-anion $NiBr_4$ (in **21**) instead of BF_4 (in **23**) and Br (in **24**), (ii) no any solvate molecules are found in the crystals of **23** and **24**, and (iii) the cations of **23** and **24** possess the intrinsic C_i ($\bar{1}$, at 220 K) and C_{2h} (2/m) symmetry, respectively, those are absent within the cation of **21**. Moreover, the crystal of **23** undergoes the low temperature phase transition (from monoclinic to triclinic syngony) at 163 K, but no phase transition is observed for **21** at lowering of temperature to 100 K. In the case of complexes **21** and **22** the bite of the tripodal ligand and the geometry of the ligand result in an unsymmetrical orientation of the

azaheterocycles relative to each other. The tridentate ligands subtend the N─M─N angles to 85.80(16)-86.53(16) and 85.89(16)-87.24(16)° (for two independent dications of **22**) and 85.41(16)-86.33(15) and 84.88(16)-87.28(16)° (for two independent dications of **21**) resulting in a trigonal distortion from octahedral co-ordination geometry. The interplane angles between the azaheterocycles are 52.8(2), 60.2(2), 67.1(2) and 57.8(2), 60.2(2), 62.1(2)° (for two independent dications of **22**) and 57.3(2), 57.9(2), 64.8(2) and 52.4(2), 62.5(2), 65.3(2)° (for two independent dications of **21**). The nickel-pyrazole bond lengths in **21** and **22** are significantly longer than those in complexes involving monodentate pyrazole ligands (Table 2) [25, 26]. For the pyrazole rings, the M─N─N angles are substantially smaller than the M─N─C angles (Table 2). The pyridine rings are more symmetrically disposed, exhibiting the *endo*-cyclic M─N─C angles about 4° smaller than the *exo*-cyclic M─N─C angles (Table 2). The tetrabromo-nickel(II) dianions in **21** and **22** have a typical distorted tetrahedral geometry (Table 2).

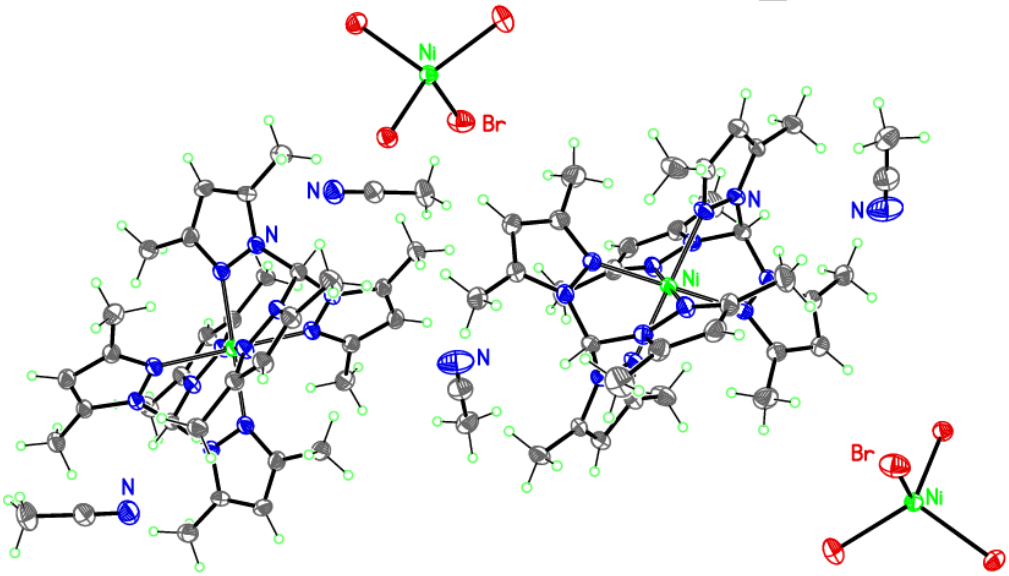


Fig. 1. Molecular structure of **21**•2CH_3CN.

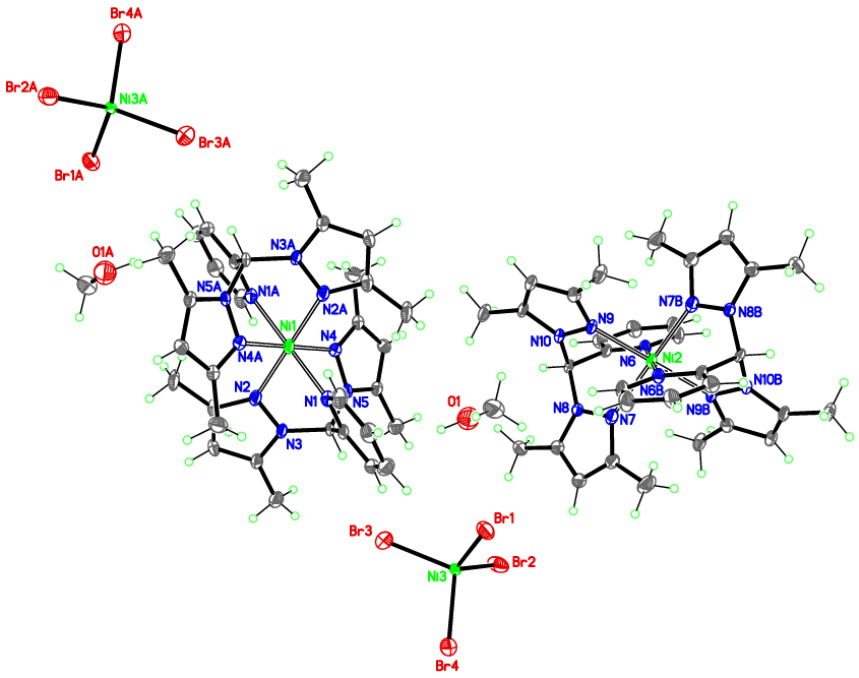


Fig. 2. Molecular structure of **22•CH_3OH**.

In the crystal of **22**, the solvate methanol molecule forms the strong O1─H1O···π(C2─C3─C4) (H1O···C3 2.49 Å, O1···C3 3.377(7) Å, ∠O1─H1O···C3 170°) hydrogen bond to dication. Crystal packing of **21** and **22** is stacking along the crystallographic ***a*** axis (Figures 3 and 4). The dianions, dications and solvate molecules are linked by weak C─H···Br and C─H···N hydrogen bonding interactions into three-dimensional framework.

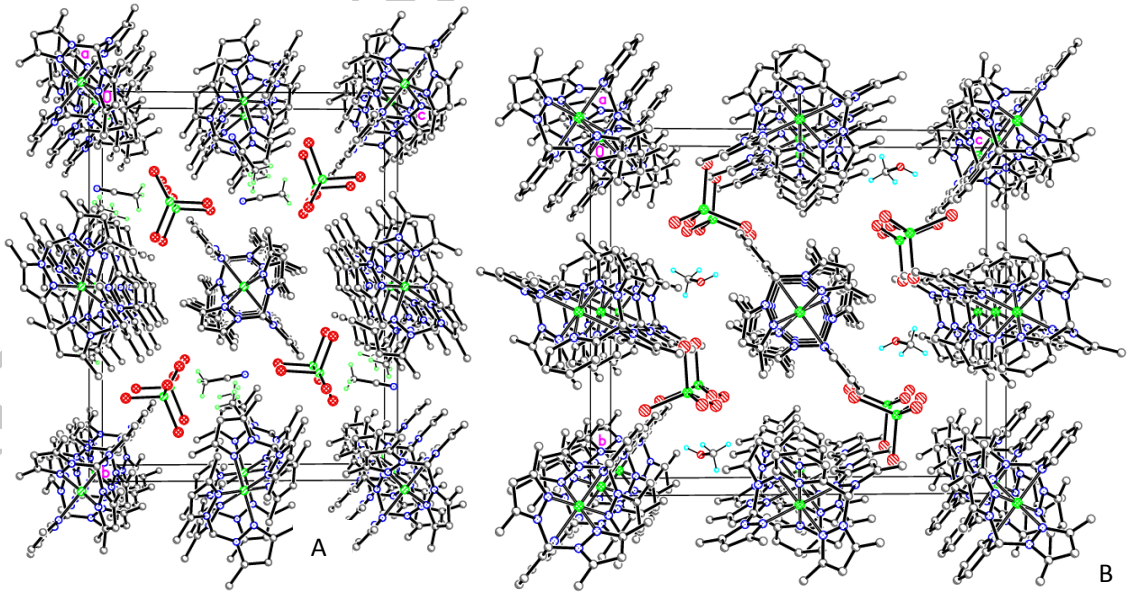


Fig. 3. Crystal structures of **21**•2CH_3CN (A) and **22•CH_3OH** along the crystallographic ***a*** axis.

Table 2. Bond distances (Å) and angles (°) for Ni(II) and the bridgehead carbon in **21** and **22**.

Compound	**21**	**22**
Ni1─N	2.093(4)	2.098(4)
	2.134(4)	2.116(4)
	2.157(4)	2.126(4)
Ni2─N	2.110(4)	2.085(4)
	2.117(4)	2.090(4)
	2.132(4)	2.105(4)
N─Ni1─N	85.41(16)	85.80(16)
	85.82(15)	86.28(17)
	86.33(15)	86.53(16)
N─Ni2─N	84.88(16)	85.89(16)
	87.22(16)	86.76(16)
	87.28(16)	87.24(16)
Ni1─N─X (endo)	115.5(3)	116.1(3)
	116.3(3)	116.5(3)
	117.5(3)	118.5(3)
Ni2─N─X (endo)	116.0(3)	116.0(3)
	117.0(3)	116.5(3)
	119.7(4)	119.0(3)
Ni1─N─C (exo)	137.6(3)	137.9(4)
	138.1(3)	137.8(3)
	139.2(3)	122.2(4)
Ni2─N─C (exo)	138.1(3)	138.6(4)
	138.5(3)	138.2(3)
	138.9(3)	122.9(3)
N─C1─X	110.0(4)	110.4(4)
	111.6(4)	111.6(4)
	111.7(4)	111.9(4)
N─C17─X	110.3(4)	110.8(4)
	111.7(4)	110.9(4)
	111.7(4)	111.6(4)
Ni3─Br	2.3675(12)	2.3905(10)
	2.4340(9)	2.3959(10)
	2.4389(9)	2.4117(11)

	2.4680(9)	2.4190(11)
Br─Ni3─Br	103.85(3)	105.80(3)
	104.64(3)	106.05(4)
	107.25(4)	108.19(3)
	108.39(4)	109.82(4)
	112.28(4)	112.52(4)
	119.88(3)	114.35(4)

3.2. Oligomerization experiments

The performance of the nickel complexes **14-18, 20-22** in ethylene oligomerization was investigated using diethylaluminum chloride and ethylaluminum sesquichloride as activators and under standard experimental conditions: temperature: 30°C, constant ethylene pressure 3 atm., molar ratio Ni/Al = 1/75. The main results are summarized in Table 3.

Table 3. Ethylene oligomerization with **1**/OAC [a]

Entry	Pre-catalyst	[Ni], mol	Co-catalyst, [Al]/[Ni]	Additive, [PPh_3], equiv.	A[b]	Oligomer distribution,%	
						C_4	C_6
1	**14**	$4\cdot10^{-5}$	Et_2AlCl, 75/1	-	55	n.d.[c]	n.d. [c]
2	**14**	$4\cdot10^{-5}$	$Et_3Al_2Cl_3$, 75/1	-	63.5	n.d.[c]	n.d.[c]
3	**14**	$1\cdot10^{-5}$	Et_2AlCl, 75/1	1	120	n.d.[c]	n.d.[c]
4	**14**	$1\cdot10^{-5}$	$Et_3Al_2Cl_3$, 75/1	1	100	n.d.[c]	n.d.[c]
5	**15**	$4\cdot10^{-5}$	Et_2AlCl, 75/1	-	323	**95** ((Z)-2-butene – 52; (E)-2-butene – 32; 1-butene – 16)	**5**
6	**15**	$4\cdot10^{-5}$	$Et_3Al_2Cl_3$, 75/1	-	320.5	**100** ((Z)-2-butene – 35**;** (E)-2-butene – 24; 1-butene – 41)	-
7	**15**	$1\cdot10^{-5}$	Et_2AlCl, 75/1	1	650	**100** ((Z)-2-butene – 15**;** (E)-2-butene – 10; 1-butene – 75)	
8	**15**	$1\cdot10^{-5}$	$Et_3Al_2Cl_3$, 75/1	1	408	**97** ((Z)-2-butene – 68**;** (E)-2-butene – 22; 1-butene – 10)	**3**

9	**16**	$4 \cdot 10^{-5}$	Et_2AlCl, 75/1	-	270	**94.7** ((Z)-2-butene – 40**;** (E)-2-butene – 27; isobutene – 1; 1-butene – 32)	**5.3** (1-hexene – 55, 2-hexene – 45)
10	**16**	$4 \cdot 10^{-5}$	$Et_3Al_2Cl_3$, 75/1	-	192.5	**95** ((Z)-2-butene – 29**;** (E)-2-butene – 23; 1-butene – 48)	**5** (1-hexene – 53.7, 2-hexene – 46.3)
11	**16**	$1 \cdot 10^{-5}$	Et_2AlCl, 75/1	1	400	**96** ((Z)-2-butene – 19.3**;** (E)-2-butene – 16.3; 1-butene – 64.4)	**4**
12	**16**	$1 \cdot 10^{-5}$	$Et_3Al_2Cl_3$, 75/1	1	348	**91** ((Z)-2-butene – 25**;** (E)-2-butene – 21.7; 1-butene – 53.3)	**9**
13	**17**	$4 \cdot 10^{-5}$	Et_2AlCl, 75/1	-	87	**91** ((Z)-2-butene – 20**;** (E)-2-butene – 15.1; isobutene – 4.9; 1-butene – 60)	**9** (1-hexene – 35, 2-hexene – 65)
14	**17**	$4 \cdot 10^{-5}$	$Et_3Al_2Cl_3$, 75/1	-	65	**92** ((Z)-2-butene – 16**;** (E)-2-butene – 13; isobutene – 1; 1-butene– 70)	**8** (1-hexene – 67, 2-hexene – 33)
15	**17**	$1 \cdot 10^{-5}$	Et_2AlCl, 75/1	1	370	**85** ((Z)-2-butene – 23**;** (E)-2-butene – 15.6; 1-butene – 61.4)	**15**
16	**17**	$1 \cdot 10^{-5}$	$Et_3Al_2Cl_3$, 75/1	1	312	**90** ((Z)-2-butene – 40**;** (E)-2-butene – 20; 1-butene – 40)	**10**
17	**18**	$4 \cdot 10^{-5}$	Et_2AlCl, 75/1	-	133,5	**90** ((Z)-2-butene – 17.5**;**; (E)-2-butene – 12.8; 1-butene – 69.1)	**10**
18	**18**	$4 \cdot 10^{-5}$	$Et_3Al_2Cl_3$, 75/1	-	408	**92.6** ((Z)-2-butene – 42.9**;** (E)-2-butene – 28.5; 1-butene – 28.6)	**7.4**
19	**18**	$1 \cdot 10^{-5}$	Et_2AlCl, 75/1	1	340	**97** ((Z)-2-butene – 37.8**;** (E)-2-butene – 31.4; isobutene – 4; 1-butene – 26.8)	**3**

20	**18**	$1 \cdot 10^{-5}$	$Et_3Al_2Cl_3$, 75/1	1	348	**100** ((Z)-2-butene – 30**;** (E)-2-butene – 27; isobutene – 6; 1-butene – 37)	-
21	**20**	$4 \cdot 10^{-5}$	Et_2AlCl, 75/1	-	97	**86** ((Z)-2-butene – 9.7**;** (E)-2-butene – 90.3)	**14**
22	**20**	$4 \cdot 10^{-5}$	$Et_3Al_2Cl_3$, 75/1	-	120	**94** ((Z)-2-butene – 10**;** (E)-2-butene – 23; 1-butene – 81)	**6**
23	**20**	$1 \cdot 10^{-5}$	Et_2AlCl, 75/1	1	398	**98** ((Z)-2-butene – 8**;** (E)-2-butene – 2; isobutene – 75; 1-butene – 13)	**2**
24	**20**	$1 \cdot 10^{-5}$	$Et_3Al_2Cl_3$, 75/1	1	298	**97** ((Z)-2-butene – 3**;** (E)-2-butene – 2; 1-butene – 95)	**3**
25	**21**	$4 \cdot 10^{-5}$	Et_2AlCl, 75/1	-	48	**95** ((Z)-2-butene – 47; (E)-2-butene – 13; 1-butene – 40)	**5**
26	**22**	$4 \cdot 10^{-5}$	Et_2AlCl, 75/1	-	51	**99** ((Z)-2-butene – 36; (E)-2-butene – 28; 1-butene – 36)	**1**

[a)] Oligomerization carried out in 50 mL of toluene at a constant ethylene pressure for 30 min, temperature 30°C, ethylene pressure 3 atm; [b)] $kg_{oligomer}$ mol^{-1} Ni h^{-1} (The activities were calculated from the total consumption of ethylene (1.0 L ethylene = 1.2 g product); [c)] not determined.

The pre-catalyst **14** containing unsubstituted pyrazole rings showed lowest activity among all the tested complexes (Table 3, entries 1-2), which is probably explained by its very low solubility in toluene. Due to these results, further studies of its catalytic properties were not conducted.

Complex **15** containing methyl groups in positions 3 and 5 of the pyrazole ring is significantly more active (Table 3, entries 5-6, Fig.4). Such increase of activity can be assigned to growth of precatalyst solubility in toluene. The reaction products are mixtures of butene and hexene isomers with predominance of internal olefins.

Introduction a *tert*-butyl group in position 4 of the pyrazole ring further increases the solubility of the complex **16** in toluene, but in spite of this fact its catalytic activity with both co-catalysts is

reduced in comparison to **15** (entries 9-10). Since the bulky *tert*-butyl groups are at a considerable distance from the metal center, one would assume that the observed effect is not due to steric, but electronic factors leading to an increase in electron density at the metal center.

However, the introduction of electron-withdrawing substituents - bromine in the 4-position of the pyrazole ring (complex **17**, entries 13-14) also was accompanied by a reduction in catalytic activity, although an increase in the acidity of the metal center might be accompanied by the growth of activity. Nonetheless, the ratio of α-olefins in the reaction products greatly increased. Thus, for system **17** / $Et_3Al_2Cl_3$, the share of 1-butene in the C4 fraction amounted to 70%, and in the C6 fraction was detected up to 67% of 1-hexene. In the case of **17** /Et_2AlCl, reaction product comprises about 5% of isobutene, which was not observed earlier in such systems.

Replacement of the pyridine ring by the quinoline (complex **18**) leads not only to increased lipophilicity, but also to an increase in steric hindrance of metal center. Activity of catalyst systems involving compound **18** depends on the nature of the co-catalysts to the much more extent, and reaches the maximum - 408 g / mmol Ni per hour while using $Et_3Al_2Cl_3$ (entry 18). However, the increased activity is accompanied by a decline in selectivity: the share of 1-butene in the C4 fraction does not exceed 29%.

Complex **20**, stabilized by tris(pyrazolyl)methane ligand, exhibits a rather low reactivity.

The nature of organoaluminum cocatalyst has a considerable but ambiguous effect on the activity and selectivity of the catalytic systems. Thus, it has practically no influence on the activity of complexes **14, 15**, but in the case of complexes **18, 20** there is a some increase in activity while using $Et_3Al_2Cl_3$. With the exception of complex **18**, the use of $Et_3Al_2Cl_3$ increases the content of 1-butene and decreases the content of hexene isomers. For complexes **16, 17** activated by $Et_3Al_2Cl_3$, growth of activity is not observed but the selectivity of the process is similar to the previously discussed.

The effect of the PPh_3 additive (1 equiv.) on the activity and selectivity of the catalyst systems was studied. According to the literature the addition of Ph_3P can significantly increase the activity of catalytic systems based on nickel [27-34] and other metals complexes [35]. The addition of the PPh_3 to catalyst systems involving complex **15** led to a significant increase in activity, which made it impossible to use the flow meters correctly. Such high values of activity determined the necessity to reduce the amount of catalyst: in all experiments involving phosphine, pre-catalyst concentration was 4 times reduced. For pre-catalysts **14, 15** activated by Et_2AlCl, addition of 1 equiv. of triphenylphosphine was accompanied by increased activity by ≈

2 times. The ability of triphenylphosphine to increase the activity by almost 5 times was discovered for compound **17** (entries 15-16, Fig.4).

Oligomers obtained on pre-catalyst **15** consisted of 95-100% of butene isomers. The content of α-isomer in the butene fraction was low (16% for system **15** / Et_2AlCl; 41% for **15** / $Et_3Al_2Cl_3$). Addition of triphenylphosphine to the catalyst system **15** / Et_2AlCl improved selectivity to 1-butene up to 75%.

The addition of PPh_3 to the system **15** / $Et_3Al_2Cl_3$ had the opposite effect: the content of 1-butene in the C_4-fraction droped to 10%, while at the same time a small increase (to 3%) of hexenes was observed.

For pre-catalyst **17**, the addition of triphenylphosphine led to a substantial increase both in activity and in the content of hexenes fraction. However, when $Et_3Al_2Cl_3$ was used as co-catalyst simultaneous decrease in the ratio of 1-butene to 40% was observed.

The most exciting results were obtained while studying the effect of PPh_3 on the selectivity of the pre-catalyst **20**. Thus, while using Et_2AlCl, hexenes (14%) and 2-butene isomers (86%) were obtained. In the presence of triphenylphosphine the share of butene isomers increased to 98%, and 75% of this fraction falls on isobutylene. Addition of phosphine to **20** / $Et_3Al_2Cl_3$ not only increased the activity, but also gives a significant increase in selectivity to 1-butene – up to 95% of the whole C4 fraction.

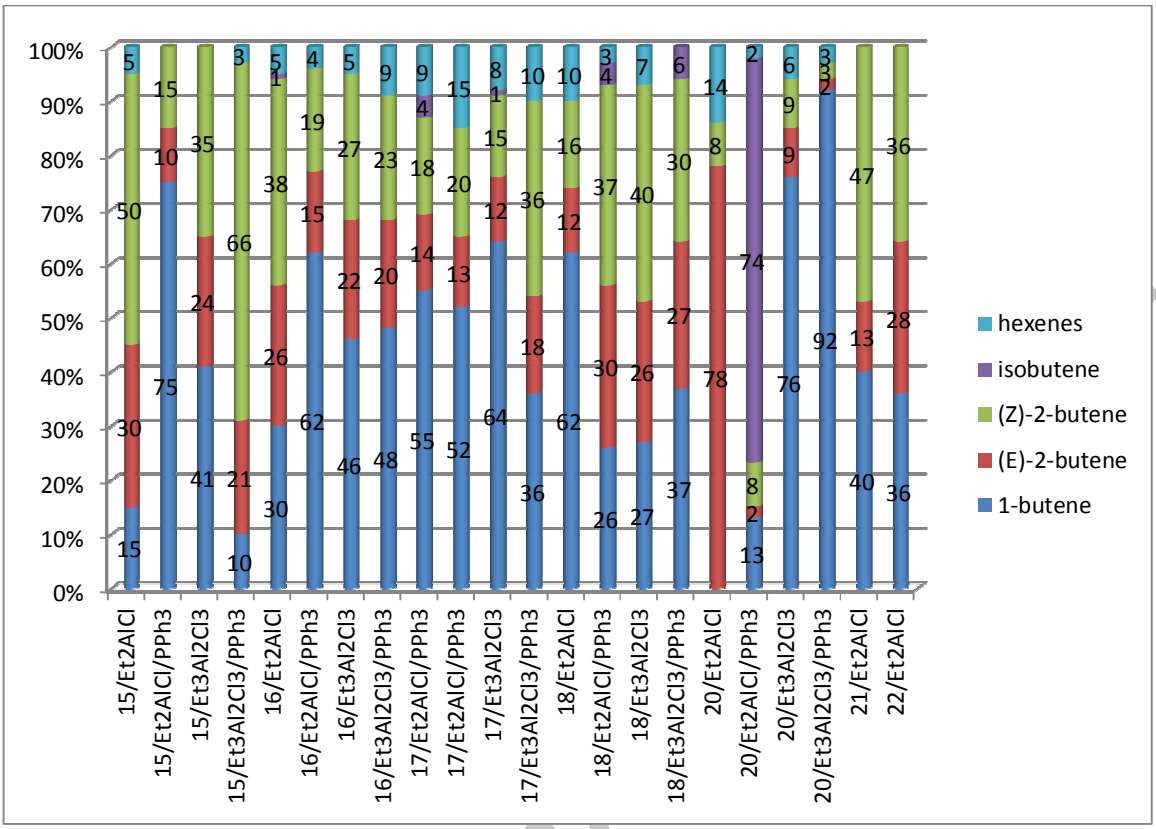


Fig. 4. Composition of oligomer mixtures obtained with pre-catalysts **15-18, 20-22.**

Thus, the system **20** / Et_2AlCl / PPh_3 is simultaneously "working" not only as ethylene dimerization catalyst, but also is able to catalyze the isomerization of butane oligomers yielding isobutene.

The coordinatively saturated complexes **21-22**, as expected, showed a very moderate activity.

The general positive impact of PPh_3 additive on catalytic activity was previously investigated and can be attributed to several factors. First, it coordinates to the nickel core and further dissociation and association of PPh_3 molecule leads to activation and protection of metal center. [30] Second, this additive can act as electron donor agent, while coordinated to metal core, and thus enhances the oligomerization reaction. [35] But none of these factors can explain a sharp increase of selectivity in some cases. So there may be another acting factor that is responsible for these dramatic changes in catalytic behavior. In our view reversible coordination of PPh_3 can prevent formation of catalytically inactive structures with the formula L_2Ni^{2+}.

4. Conclusion

A series of new neutral tridentate *N,N,N*-heteroscorpionate ligands **9-13** and their Ni(II) complexes **14-18, 20-22** have been prepared and characterized. Ligands were modified in an attempt to change steric effects and the electronic density of the metal center and eventually to improve the activity in oligomerization of ethylene and to control the oligomer structure. The

behavior of **14-18, 20-22** as ethylene oligomerization catalysts was preliminary explored after activation with several co-catalysts.

The product distribution from oligomerization reactions, however, is frequently difficult to control and optimize. In present paper it is shown that the addition of PPh_3, in some cases, has a significant influence on the selectivity. Thus, the phosphine role can be explained not only by the reversible coordination with nickel atom that can facilitate the formation of vacant coordination sites required for the realization of catalytic activity. Probably, the coordination of triphenylphosphine molecule can prevent rearrangement of complexes to more thermodynamically advantageous, but catalytically inactive structures with the formula L_2Ni^{2+}. Further work will be focused on the design and optimization of the heteroscorpionate ligand and the process condition to produce oligomers with high selectivity.

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Appendix A. Supplementary material

CCDC 1511204 and CCDC 1511203 contain the supplementary crystallographic data for **21** and **22**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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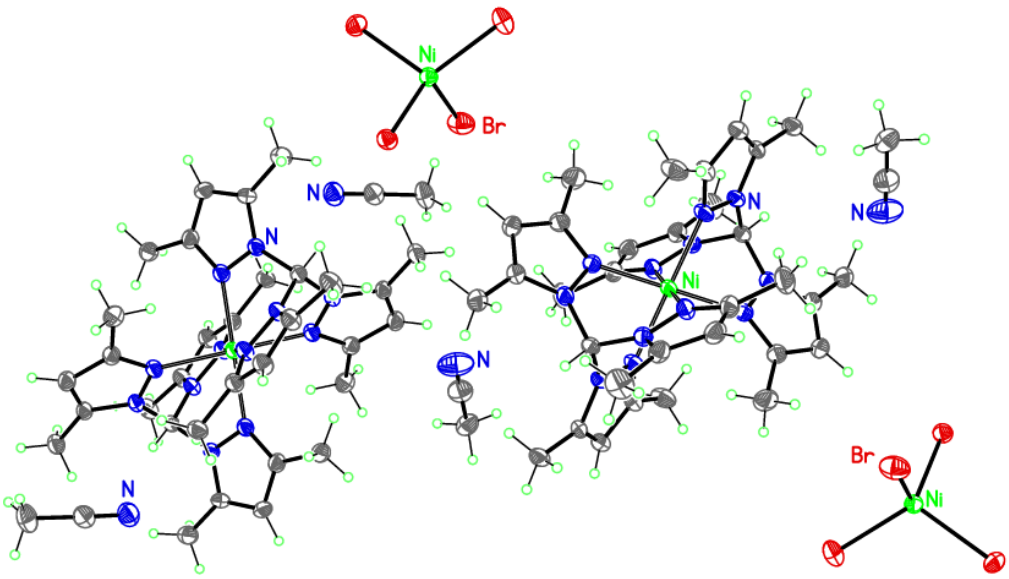
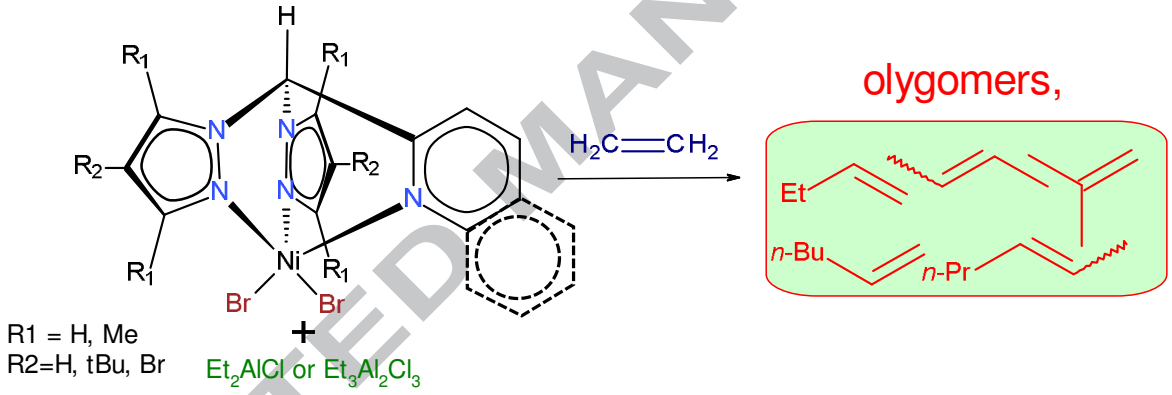


Fig. 1. Molecular structure of **21**•2CH_3CN.



Highlights

- A series of heteroscorpionate dibromonickel (II) complexes have been synthesized and characterized.
- Their behavior as ethylene oligomerization catalysts was preliminary explored.
- The addition of PPh_3 has a significant influence on the selectivity.