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Nickel complexes bearing [N,N] 2-pyridylbenzamidine ligands: Syntheses, characterizations, and catalytic properties for ethylene oligomerization

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ABSTRACT

A series of nickel(II) complexes with different steric and electronic substituted 2-pyridylbenzamidine ligands, [2,6-*i*Pr$_2$C$_6$H$_3$–N=C(R$_1$)–NH–(5-R$_3$, 6-R$_2$)Py]NiBr$_2$ (R$_1$ = Ph, R$_2$ = H, R$_3$ = H, **1**; R$_1$ = Ph, R$_2$ = H, R$_3$ = NO$_2$, **2**; R$_1$ = 4-CH$_3$OC$_6$H$_4$, R$_2$ = H, R$_3$ = H, **3**; R$_1$ = 4-CH$_3$C$_6$H$_4$, R$_2$ = Me, R$_3$ = H, **4**), have been synthesized in high yield and the solid state structures of **1**, **2** and **4** have been crystallographically characterized. Activated with methyaluminoxane (MAO), **1**–**4** showed moderate turnover frequency (TOF) for ethylene oligomerization in dichloromethane. The influences of the ligand structure on catalytic properties were studied. Complex **2** with an electron-withdrawing group revealed the highest TOF of up to 11.7×10^3 mol ethylene/(mol Ni h). Moreover, the reaction temperature and Al/Ni molar ratio were also examined in detail.

1. Introduction

The development of late transition metal catalysts for ethylene oligomerization and polymerization has received much attention in both academic and industrial areas in the past decades [1,2]. The representative is famous SHOP-type [P,O] nickel catalyst which can produce linear α-olefins without a cocatalyst [3–6]. Since Brookhart and co-workers reported that α-diimine nickel complexes [7–10], and pyridinediimine iron complexes [11,12] were highly efficient for ethylene polymerization and/or oligomerization in the presence of MAO, various nickel complexes with [N,N] [13–19], [N,O] [20–26], [N,P] [27–31], [P,P] [32–35] ligands were explored as olefin polymerization and/or oligomerization catalyst precursors.

Recently, nickel complexes bearing a [N,N] six-membered chelating ring have been prepared and applied in olefin polymerization [36–47]. It is noteworthy that catalytic products in ethylene polymerization are much dependent on catalyst structure. For example, for β-diimine nickel complexes (Scheme 1, I) [36], the products were polyethylenes, while for β-diketiminate [39–42] and anilido-imine nickel complexes(II) [43,44], both polyethylenes and oligomers were found. As to nickel complexes bearing quinolylimine(III) [45], β-pyridylimine(IV) [46], and dipyridylamine(V) ligands [47], only ethylene oligomers were obtained. Although pyridylformamidines and pyridylamidines(VI) were synthesized and investigated in metal–metal interactions [48], they have rarely been applied in olefin polymerization.

In this contribution, syntheses of a series of novel [N,N] 2-pyridylbenzamidine nickel(II) complexes was reported. Molecular structures of the nickel complexes were also characterized by X-ray single-crystal analyses. Furthermore, ethylene oligomerization catalyzed by these nickel complexes after activation with MAO was investigated.

2. Experimental

2.1. General procedures

All manipulations were performed under nitrogen atmosphere using glove box and Schlenk techniques. Polymerization-grade ethylene and extra-pure-grade nitrogen were further purified before feeding into the reactor by passing through a DC-IB gas purification instrument.

2.2. Materials

Tetrahydrofuran, hexane and toluene were refluxed over metallic sodium for 24 h. Dichloromethane was refluxed over phosphorus pentoxide for 6 h, and then distilled under nitrogen atmosphere before being used. 2,6-Diisopropylaniline and 2,6-dimethylaniline were purchased from Aldrich Chemical Co. and distilled under reduced pressure before being used. *p*-Toluoyl

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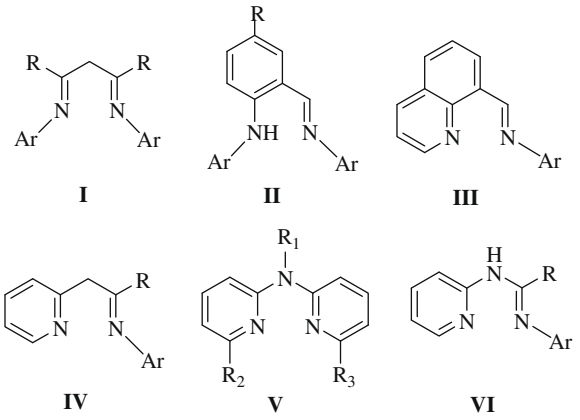


Scheme 1. Types of [N,N] six-membered ring ligands.

chloride, *p*-anisoyl chloride, 2-amino-6-methylpyridine and 2-amino-5-nitropyridine were purchased from Aldrich Chemical Co. and used as received. Benzoyl chloride was purchased from Guangzhou Chemical Reagent Factory and used without further purification. 2-Aminopyridine was purchased from Shanghai Chemical Reagent Factory and used after recrystallization from ethanol. Methylaluminoxane (MAO) was prepared by partial hydrolysis of trimethylaluminum (TMA) in toluene at 0–60 °C with $Al_2(SO_4)_3 \cdot 18H_2O$ as the water source. The initial $[H_2O]/[Al]$ in molar ratio was 1.3.

2.3. Measurement

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-Plus 300 MHz NMR spectrometer and referenced versus TMS as standard. Elemental analyses were determined with a Vario EL Series Elemental Analyzer from Elementar. The GC–MS data were recorded with a Finnigan Voyager GC-8000 Top Series GC–MS System with DB-5MS GC column. The following temperature program of the oven was adopted: keeping 40 °C for 2 min, increasing the temperature by 5 °C/min heating to 110 °C, and then by a 15 °C/min heating until 250 °C which was kept constant for a further 2 min.

2.4. X-ray structure determination

The X-ray diffraction data of single crystals were obtained with the $\omega-2\theta$ scan mode on a Bruker SMART 1000 CCD diffractiometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173 K. The structure was solved using direct methods, and further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

2.5. Ethylene oligomerization

Ethylene oligomerization reactions were performed in a 50 mL glass flask equipped with a magnetic stirrer, and continuous feed of ethylene was used. A typical reaction was performed by adding proper amount of MAO solid and solvent (19 mL) into the reactor under ethylene atmosphere. The catalyst in dichloromethane solution (1 mL, Ni = 5 μmol) was injected into the reactor *via* syringe. Ethylene was continuously fed in order to maintain the ethylene pressure at 0.5 atm. After 30 min, the reaction was terminated by addition of cold acidic ethanol (ethanol–HCl, 95:5). The organic layer was analyzed quickly by gas chromatography (GC) for determining the composition and mass distribution of the oligomers.

2.5.1. Synthesis of 2,6-$iPr_2C_6H_3$–N=C(Ph)–NH–Py (**L1**)

Benzoyl chloride (1.1 mL, 10 mmol) and triethylamine (1.6 mL, 11 mmol) were added to a vigorously stirred solution of 2,6-diisopropylaniline (1.9 mL, 10 mmol) in CH_2Cl_2 (45 mL). After 3 h, the precipitate of $(C_2H_5)_3N \cdot HCl$ was filtrated, and white solid powder benzamide was obtained by evaporating the solvent. Then excess of thionyl chloride (2.0 mL, 28 mmol) was added to the benzamide and the reaction mixtures were stirred for 2 h at 80 °C. The remainder thionyl chloride was distilled off under reduced pressure, to give the imidoyl chloride as yellow and slowly solidifying oil. Successively, toluene (40 mL), triethylamine (1.6 mL, 11 mmol) and 2-aminopyridine (0.94 g, 10 mmol) were added to the reaction system. The mixtures were heated to reflux for 24 h under the protection of nitrogen atmosphere. $(C_2H_5)_3N \cdot HCl$ was removed by filtration, and toluene was evaporated from the filtrate. After recrystallization of the product from ethanol, **L1** was obtained as light yellow crystal in 48% yield (1.72 g, 4.83 mmol). Melting point: 156 °C. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm) [an isomer (*E-syn* and *E-anti*) ratio of 1.2:1] major isomer: 13.31(s, 1H, N*H*), 8.25 (br, 1H, pyridyl α-H), 7.66–6.92 (m, 11H, pyridyl and phenyl protons), 3.26 (m, 2H, C*H*$(CH_3)_2$), 1.14 (d, 12H, CH(C*H*$_3)_2$). Minor isomer: 13.31 (s, 1H, N*H*), 8.25 (br, 1H, pyridyl α-H), 7.66–6.92 (m, 11H, pyridyl and phenyl protons), 3.04 (m, 2H, C*H*$(CH_3)_2$), 0.94 (d, 12H, CH(C*H*$_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm) major isomer: 162.79, 144.99, 144.56, 137.27, 136.04, 134.41, 129.12, 128.80, 128.29, 127.47, 127.10, 123.30, 117.47, 113.26, 28.65, 25.19. Major isomer: 160.53, 144.99, 144.56, 137.27, 136.04, 134.41, 129.12, 128.80, 128.29, 127.47, 127.10, 123.30, 117.47, 113.26, 28.27, 21.83. EI-MS (*m*/*z*): 358 $[M]^+$; 264 $[M-C_5H_5N_2]^+$. Elemental *Anal.* Calc. for $C_{24}H_{27}N_3$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.47; H, 7.59; N, 11.64%.

2.5.2. Synthesis of 2,6-$iPr_2C_6H_3$–N=C(Ph)–NH–(5-NO_2–Py) (**L2**)

L2 was prepared according to the method described for **L1**, the mixtures were purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10/1) as eluent, and then recrystallized from ethanol in 31% yield. Melting point: 140 °C. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) [an isomer ratio of 2.3:1] major isomer: 13.12 (s, 1H, N*H*), 9.13 (br, 1H, pyridyl α-H), 8.38 (br, 1H, pyridyl γ-H), 7.40–7.06 (m, 9H, pyridyl and phenyl protons), 3.13 (m, 2H, C*H*$(CH_3)_2$), 1.13 (d, 12H, CH(C*H*$_3)_2$). Minor isomer: 13.12 (s, 1H, N*H*), 9.13 (br, 1H, pyridyl α-H), 8.38 (br, 1H, pyridyl γ-H), 7.40–7.06 (m, 9H, pyridyl and phenyl protons), 2.94 (m, 2H, C*H*$(CH_3)_2$), 0.92 (d, 12H, CH(C*H*$_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm) major isomer: 163.38, 144.08, 142.95, 138.56, 134.92, 132.01, 130.18, 129.04, 128.54, 128.50, 127.99, 122.70, 123.65, 122.35, 28.49, 25.12. Minor isomer: 163.05, 144.08, 142.95, 138.56, 134.92, 132.01, 130.18, 129.04, 128.54, 128.50, 127.99, 122.70, 123.65, 122.35, 28.39, 21.79. EI-MS (*m*/*z*): 403 $[M]^+$; 264 $[M-C_5H_4N_2O_2]^+$. Elemental *Anal.* Calc. for $C_{24}H_{26}N_4O_2$: C, 71.62; H, 6.51; N, 13.92. Found: C, 71.40; H, 6.61; N, 14.08%.

2.5.3. Synthesis of 2,6-$iPr_2C_6H_3$–N=C(4-$CH_3OC_6H_4$)–NH–Py (**L3**)

L3 was prepared according to the method described for **L1** in 46% yield. Melting point: 169 °C. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) [an isomer ratio of 1.3:1] major isomer: 13.25 (s, 1H, N*H*), 8.23 (br, 1H, pyridyl α-H), 7.64 (br, 1H, pyridyl γ-H), 7.38–6.68 (m, 9H, pyridyl and phenyl protons), 3.72 (s, 3H, OC*H*$_3$), 3.24 (m, 2H, C*H*$(CH_3)_2$), 1.13 (d, 12H, CH(C*H*$_3)_2$). Minor isomer: 13.25 (s, 1H, N*H*), 8.23 (br, 1H, pyridyl α-H), 7.64 (br, 1H, pyridyl γ-H), 7.38–6.68 (m, 9H, pyridyl and phenyl protons), 3.72 (s, 3H, OC*H*$_3$), 3.02 (m, 2H, C*H*$(CH_3)_2$), 0.94 (d, 12H, CH(C*H*$_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm) major isomer: 162.82, 144.97, 144.47, 137.19, 134.72, 130.50, 128.56, 126.98, 123.56, 122.41, 117.20, 113.67, 113.21, 112.85, 55.15, 28.65, 25.12. Minor isomer:

160.25, 144.97, 144.47, 137.19, 134.72, 130.50, 128.56, 126.98, 123.56, 122.41, 117.20, 113.67, 113.21, 112.85, 55.15, 28.25, 21.94. EI-MS (*m*/*z*): 388 $[M]^+$; 294 $[M-C_5H_4N_2]^+$. Elemental *Anal.* Calc. for $C_{25}H_{29}N_3O$: C, 77.48; H, 7.54; N, 10.84. Found: C, 77.55; H, 7.64; N, 10.76%.

*2.5.4. Synthesis of 2,6-iPr$_2$C$_6$H$_3$–N=C(4-CH$_3$C$_6$H$_4$)–NH–(6-CH$_3$–Py) (**L4**)*

L4 was prepared according to the method described for **L1**. The mixtures were purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10/1) as eluent, and then recrystallized from ethanol in 63% yield. Melting point: 119 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) [an isomer ratio of 1.5:1] major isomer: 13.35 (s, 1H, N*H*), 7.56–6.80 (m, 10H, pyridyl and phenyl protons), 3.30 (m, 2H, C*H*$(CH_3)_2$), 2.45 (s, 3H, methyl protons on pyridyl), 2.50 (s, 3H, CH_3), 1.15 (d, 12H, CH(CH_3)$_2$). Minor isomer: 13.35 (s, 1H, N*H*), 7.56–6.80 (m, 10H, pyridyl and phenyl protons), 3.04 (m, 2H, C*H*$(CH_3)_2$), 2.45 (s, 3H, methyl protons on pyridyl), 2.50 (s, 3H, CH_3), 0.99 (d, 12H, CH(CH_3)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm) major isomer: 162.39, 153.65, 152.72, 144.70, 139.00, 137.50, 134.56, 133.31, 128.76, 128.08, 126.97, 123.20, 119.41, 116.62, 28.53, 25.43, 24.29, 21.81. Minor isomer: 160.50, 153.65, 152.72, 144.70, 139.00, 137.50, 134.56, 133.31, 128.76, 128.08, 126.97, 123.20, 119.41, 116.62, 28.23, 24.29, 21.81, 21.36. EI-MS (*m*/*z*): 386 $[M]^+$; 278 $[M-C_6H_7N_2]^+$. Elemental *Anal.* Calc. for $C_{26}H_{31}N_3$: C, 81.00; H, 8.10; N, 10.90. Found: C, 80.93; H, 8.05; N, 10.91%.

*2.5.5. Synthesis of [2,6-iPr$_2$C$_6$H$_3$–N=C(Ph)–NH–Py]NiBr$_2$ (**1**)*

L1 (358 mg, 1.0 mmol) was dissolved in 40 mL anhydrous dichloromethane under nitrogen atmosphere. (DME)$NiBr_2$ (308 mg, 1.0 mmol) was added under room temperature. The light yellow solution changed into purple quickly, and the solution was stirred for another 12 h. Then the reaction mixture was filtrated and 20 mL hexane was added. After being filtrated from Celite, the solid was washed by hexane (2 × 10 mL). Drying in vacuum, 532 mg of complex **1** was obtained in 92% yields. Decomposition temperature: 289 °C. FAB$^+$-MS: *m*/*z*: 575, 576, 577, 578 $[M]^+$; 495, 496, 497 $[M-Br]^+$; 415, 416, 417 $[M-2Br]^{2+}$; 264, 265 $[L1-C_5H_5N_2]^+$. Elemental *Anal.* Calc. for $C_{24}H_{27}Br_2N_3Ni$: C, 50.05; H, 4.72; N, 7.30. Found: C, 49.72; H, 4.83; N, 7.16%.

*2.5.6. Synthesis of [2,6-iPr$_2$C$_6$H$_3$–N=C(Ph)–NH–(5-NO$_2$–Py)]NiBr$_2$ (**2**)*

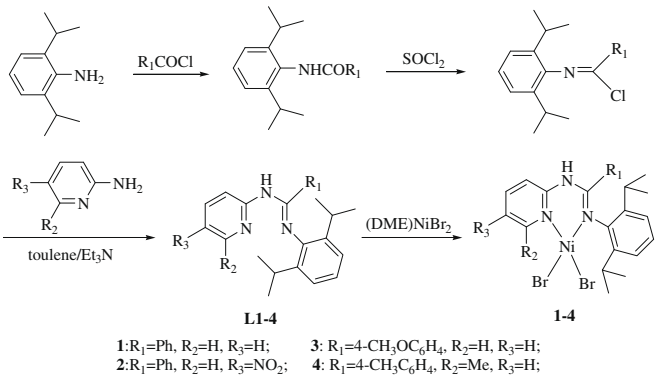
Complex **2** was prepared according to the method described for **1** in 77% yields as brown solid. Decomposition temperature: 277 °C. FAB$^+$-MS: *m*/*z*: 619, 620, 621, 622 $[M]^+$; 539, 541, 542 $[M-Br]^+$; 460, 461, 462 $[M-2Br]^{2+}$; 264, 265 $[L2-C_5H_4N_2O_2]^+$. Elemental *Anal.* Calc. for $C_{24}H_{26}Br_2N_4NiO_2$: C, 46.42; H, 4.22; N, 9.02. Found: C, 46.15; H, 4.13; N, 8.89%.

*2.5.7. Synthesis of [2,6-iPr$_2$C$_6$H$_3$–N=C(4-CH$_3$OC$_6$H$_4$)–NH–Py]NiBr$_2$ (**3**)*

Complex **3** was prepared according to the method described for **1** in 89% yields as purple solid. Decomposition temperature: 302 °C. FAB$^+$-MS: *m*/*z*: 605, 606, 607, 608 $[M]^+$; 525, 526, 527 $[M-Br]^+$; 445, 446, 447 $[M-2Br]^{2+}$; 294, 295 $[L3-C_5H_4N_2]^+$. Elemental *Anal.* Calc. for $C_{25}H_{29}Br_2N_3NiO$: C, 49.55; H, 4.82; N, 6.93. Found: C, 49.34; H, 4.91; N, 6.86%.

*2.5.8. Synthesis of [2,6-iPr$_2$C$_6$H$_3$–N=C(4-CH$_3$C$_6$H$_4$)–NH–(6-CH$_3$–Py)]NiBr$_2$ (**4**)*

Complex **4** was prepared according to the method described for **1** in 76% yields as purple solid. Decomposition temperature: 305 °C. FAB$^+$-MS: *m*/*z*: 603, 604, 605, 606, 607 $[M]^+$; 523, 524, 525, 526 $[M-Br]^+$; 443, 444, 445 $[M-2Br]^{2+}$; 278, 279 $[L4-C_6H_7N_2]^+$. Elemental *Anal.* Calc. for $C_{26}H_{31}Br_2N_3Ni$: C, 51.70; H, 5.17; N, 6.96. Found: C, 51.51; H, 5.34; N, 6.83%.



Scheme 2. Preparation of nickel complexes **1**–**4**.

3. Results and discussion

3.1. Ligand and nickel complex syntheses

Four new 2-pyridylbenzamidine ligands with various steric and electronic substituents were synthesized following a classical route for *N*,*N*-disubstituted amidines [49,50]. The synthetic procedures are outlined in Scheme 2, and the particulars of each step were detailed in the Section 2. Benzamide could be easily available from 2,6-diisopropylaniline and substituted benzoyl chloride in high yield with triethylamine as the precipitator. Imidoyl chloride could be produced by the dehydration reaction between benzamide and excess of thionyl chloride. After distilling the residue of thionyl chloride, the 2-pyridylbenzamidine ligands were obtained by the reaction between the quantitative 2-aminopyridine derivatives and imidoyl chlorides in refluxing toluene. Pure **L1** and **L3** were obtained as light yellow crystals by recrystallization in ethanol, while **L2** and **L4** were purified using silica chromatography and then recrystallized in ethanol. All of these ligands were proved by ^{1}H and ^{13}C NMR, MS and elemental analyses. A single crystal of **L2** grown from ethanol solution also assuredly confirmed the ligand structure.

The nickel complexes **1**–**4** were synthesized by mixing (DME)-$NiBr_2$ and corresponding ligand in anhydrous dichloromethane in high yield. Because of paramagnetism, nickel complexes **1**–**4** were

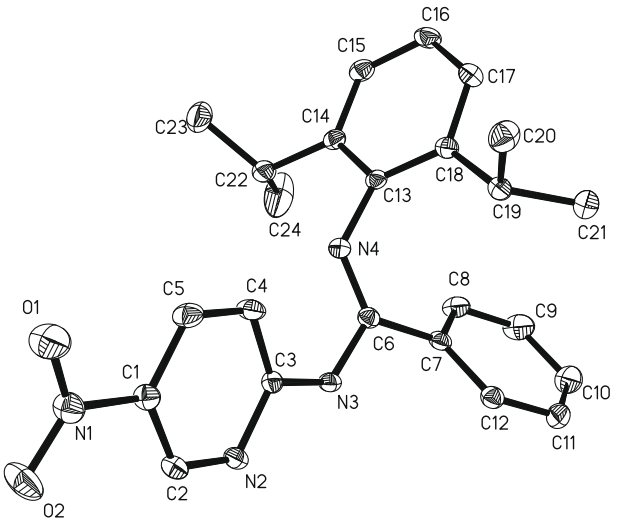


Fig. 1. Molecular structure of **L2** depicted with 30% thermal ellipsoids and with hydrogen atoms omitted. Selected bond lengths (Å): C(3)–N(3) 1.371(2), C(6)–N(3) 1.393(2), C(6)–N(4) 1.276(2), C(13)–N(4) 1.416(2).

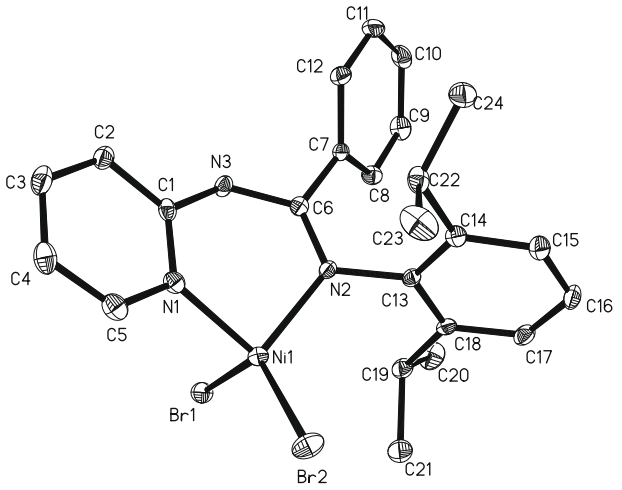


Fig. 2. Molecular structure of **1** depicted with 30% thermal ellipsoids and with hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): C(1)–N(3) 1.402(5), C(6)–N(3) 1.375(4), C(6)–N(2) 1.291(4), C(13)–N(2) 1.449(4), Ni(1)–N(1) 1.985(3), Ni(1)–N(2) 1.974(3), Ni(1)–Br(1) 2.3911(7), Ni(1)–Br(2) 2.3263(7), N(1)–Ni(1)–N(2) 92.6(1), N(1)–Ni(1)–Br(1) 101.21(9), N(1)–Ni(1)–Br(2) 110.30(9), N(2)–Ni(1)–Br(1) 105.14(9), N(2)–Ni(1)–Br(2) 115.22(9), Br(1)–Ni(1)–Br(2) 126.38(3).

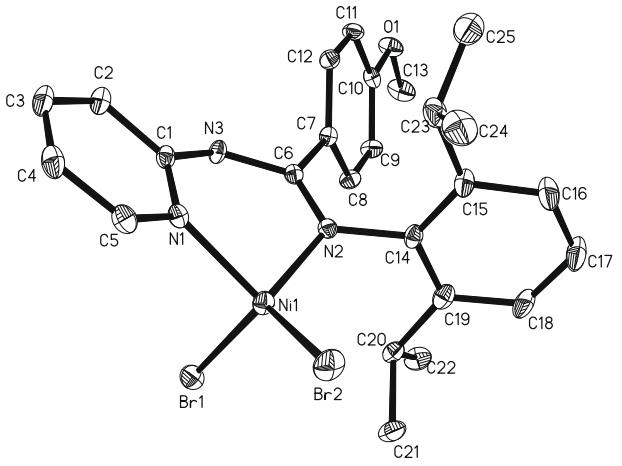


Fig. 3. Molecular structure of **3** depicted with 30% thermal ellipsoids and with hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): C(1)–N(3) 1.397(4), C(6)–N(3) 1.370(4), C(6)–N(2) 1.298(4), C(14)–N(2) 1.453(5), Ni(1)–N(1) 1.984(3), Ni(1)–N(2) 1.968(3), Ni(1)–Br(1) 2.4006(7), Ni(1)–Br(2) 2.3342(7), N(1)–Ni(1)–N(2) 92.7(1), N(1)–Ni(1)–Br(1) 99.90(10), N(1)–Ni(1)–Br(2) 112.70(9), N(2)–Ni(1)–Br(1) 103.89(9), N(2)–Ni(1)–Br(2) 118.01(9), Br(1)–Ni(1)–Br(2) 123.94(3).

not characterized by ^{1}H NMR but were characterized by MS, elemental analysis, and X-ray crystallography.

3.2. Molecular structure

A previous reference [48] reported that the *N*,*N*-phenylpyridylbenzamidine forms a dimer in the solid state which results from the presence of weak inter-molecular hydrogen bond involving the hydrogen atom in the amidine nitrogen atom and the pyridyl groups. In contrast, the X-ray structure of ligand **L2** (Fig. 1) shows that the 2-pyridylbenzamidine ligand exhibits a monomer structure, and adopts *E-syn* rather than *E-anti* geometry. In addition, the bond lengths of N(4)–C(6) and N(3)–C(6) are 1.276(2) and 1.393(2) Å, indicative of double and single bonds, respectively.

Nickel complexes suitable for X-ray diffraction determination were grown from dichloromethane/hexane or tetrahydrofuran/hexane at ambient temperature under a nitrogen atmosphere. ORTEP diagrams are given in Figs. 2–4 along with selected bond

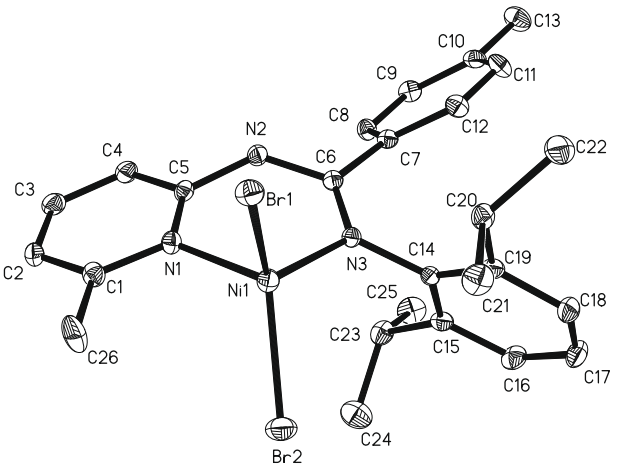


Fig. 4. Molecular structure of **4** depicted with 30% thermal ellipsoids and with hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): C(5)–N(2) 1.399(4), C(6)–N(2) 1.368(3), C(6)–N(3) 1.299(3), C(14)–N(3) 1.458(3), Ni(1)–N(1) 1.997(2), Ni(1)–N(3) 1.989(2), Ni(1)–Br(1) 2.3997(5), Ni(1)–Br(2) 2.3483(5), N(1)–Ni(1)–N(3) 95.8(1), N(1)–Ni(1)–Br(1) 100.79(7), N(3)–Ni(1)–Br(2) 104.98(7), N(3)–Ni(1)–Br(1) 114.28(7), N(3)–Ni(1)–Br(2) 104.98(7), Br(1)–Ni(1)–Br(2) 126.25(1).

lengths and bond angles, respectively. The data collection and structure refinement parameters are summarized in Table 1.

Similar to the β-diimine nickel complexes [36], all of the nickel complexes reveal a distorted tetrahedral geometry around the nickel metal center and the [N,N] six-membered chelating rings exhibit a boat conformation with metal atom. The nickel atom is surrounded by a pyridyl nitrogen atom, an imine N atom, and two terminal Br atoms. In addition, there is no *intra-* or *inter*-molecular hydrogen bonding (Ni···H) between the hydrogen on the amidine nitrogen atom and nickel metal atom. Bearing the similar steric hindrance of ligand, the Ni–$N_{pyridine}$ and Ni–N_{imine} bond lengths of **1** and **3** are nearly the same. In contrast, the Ni–$N_{pyridine}$ and Ni–N_{imine} bond lengths of **4** are 1.997(2) and 1.989(2) Å, respectively, which are longer than those of **1** and **3**. The result indicates that the introduction of methyl on the *ortho* position of pyridyl decreases the bonding ability between pyridine, imine and nickel metal. Moreover, the N–Ni–N bite angles of **1** and **3** are 92.6(1)° and 92.7(1)°, respectively, which are smaller than that of **4** (95.8(1)°), well in accordance with those observed for nickel complexes bearing bulky substituents oriented in a more open environment [46–47,51].

3.3. Ethylene oligmerization

Ethylene oligomerizations were carried out with the nickel complexes in the presence of MAO in order to study their catalytic properties. Initially, toluene was used as the reaction media for ethylene oligomerization, and consumption of ethylene was observed. However, it was surprising that the obtained liquid mixtures were complicated and only small amount of ethylene oligomers was detected by GC–MS (Fig. 5). According to the GC–MS analysis, peak **A** and **B** can be assigned to butene and hexene, respectively, while peaks **C**–**G** can be attributed to alkylated toluene and the collected peaks **H** should be ascribed to ditolylmethanes. The existence of oligomers of ethylene, alkylated toluene and ditolylmethanes in the products means that there are multiple catalytic processes in the system, involving ethylene oligomerization and toluene alkylations by either ethylene or the oligomers by a Friedel–Crafts process [52–55] and disproportionation [56]. Very recently, nickel complexes bearing [N,P] five-membered chelating ring were reported to catalyze reactions with ethylene producing oligomers and alkylated toluene [57].

Table 1
Crystallographic data for **L2**, **1**, **3** and **4**.

Compound	**L2**	**1**	**3**	**4**
Formula	$C_{24}H_{25}N_4O_2$	$C_{24}H_{27}Br_2N_3Ni$	$C_{25}H_{29}Br_2N_3NiO$	$C_{26}H_{31}Br_2N_3Ni$
Formula weight	401.48	576.02	606.04	604.07
Crystal size (mm)	0.12 × 0.09 × 0.01	0.09 × 0.07 × 0.05	0.10 × 0.08 × 0.06	0.10 × 0.08 × 0.05
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2(1)/n$	$P2(1)/n$	$P2(1)/n$
a (Å)	8.2857(15)	9.4357(12)	9.3676(12)	9.7549(10)
b (Å)	11.834(2)	18.215(2)	19.349(2)	18.1652(18)
c (Å)	12.549(2)	14.0164(18)	13.9412(19)	14.5490(14)
α (°)	110.520(3)	90	90	90
β (°)	107.437(3)	101.021(3)	98.471(2)	91.968(2)
γ (°)	90.894(3)	90	90	90
Z	2	4	4	4
Volume (Å^3)	1089.4(3)	2364.6(5)	2499.3(6)	2576.6(4)
D_{calc} (g cm^{-3})	1.224	1.618	1.611	1.557
$F(000)$	426	1160	1224	1224
μ (mm^{-1})	0.080	4.216	3.996	3.873
No. of observed reflections	8533	11 162	12 445	12 028
No. of unique reflections	4230	5031	5357	5024
R_{int}	0.0263	0.0347	0.0472	0.0224
Data/parameters	4230/271	5031/271	5357/289	5024/289
Goodness of fit	1.038	1.099	0.986	1.029
R_1/wR_2 ($I > 2\sigma(I)$)	0.0449, 0.1166	0.0344, 0.0760	0.0398, 0.0824	0.0267, 0.0672
R_1/wR_2 (all data)	0.0732, 0.1348	0.0653, 0.0993	0.0805, 0.0975	0.0388, 0.0732

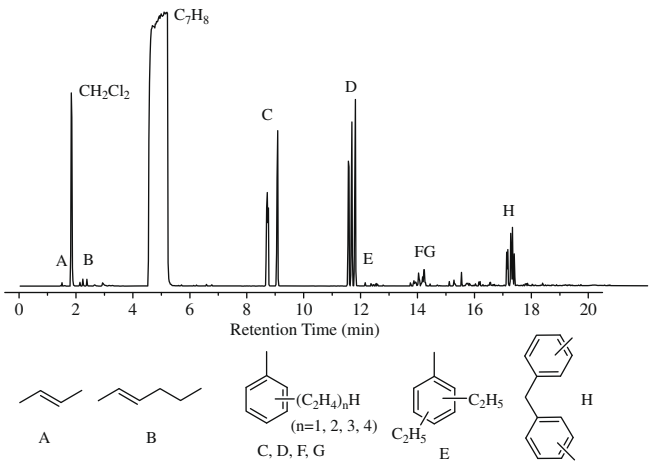


Fig. 5. GC–MS analysis of the products obtained from **2**/MAO in toluene at 0 °C.

In order to obtain the onefold oligomers, dichloromethane was used as solvent instead of toluene and the results of the catalytic reactions are summarized in Table 2. It was shown that four complexes exhibited moderate catalytic activities (TOF *ca.* 10^3–10^4 mol ethylene/mol Ni h). To evaluate the effect of the catalyst structure on TOF, **1**–**4** complexes were screened under the same conditions of T = 20 °C and Al/Ni = 600. In comparison to **1**, **4** with methyl on the *ortho* position of pyridine, and **3** containing electron-donating methoxy on the *para* position of the phenyl exhibited a lower TOF. Meanwhile, **2** containing electron-withdrawing nitro group on the *meso* position of pyridine showed the highest TOF up to 10.5 × 10^3 mol ethylene/(mol Ni h). A reasonable explanation for the TOF enhancement is that the introduction of an electron-withdrawing group would generate a more electrophilic nickel center, resulting in reduction of activation energy for ethylene insertion and favoring ethylene monomer coordination and insertion [9,58].

Furthermore, the structure of the complexes also affects the distribution of oligomers. GC–MS analyses confirmed that the oligomers obtained by **1**, **3** and **4**/MAO at 20 °C mainly contained butene and hexene. Besides butene and hexene, the products obtained by **2**/MAO also contained higher oligomers such as octene and decene (Fig. 6).

Compared with other nickel complexes with [N,N] six-membered chelating ring, it revealed that complexes **1**–**4** show higher

Table 2
The data of ethylene oligomerizations with **1**–**4**/MAO in CH_2Cl_2.

Run	Complex	Al/Ni	T (°C)	TOF[a]	Distribution of oligomers (mol%)			
					C4	C6	C8	C10
1	**1**	600	20	4.5	55.7	44.3	–[b]	–
2	**2**	600	20	10.5	31.8	38.7	25.4	4.1
3	**3**	600	20	2.3	76.2	23.8	–	–
4	**4**	600	20	3.6	69.6	20.4	–	–
5	**2**	600	−10	3.2	17.8	26.3	46.2	9.7
6	**2**	600	0	7.9	19.9	30.1	42.4	7.6
7	**2**	400	20	8.1	34.7	42.5	15.6	7.2
8	**2**	800	20	11.7	28.3	34.9	27.7	9.1
9	**2**	1200	20	9.8	35.6	49.2	12.0	3.2
10[c]	**1**–**4**	600	0	2.1–5.6	alkylated toluene and ditolylmethanes			

Reaction conditions: Ni complex, 5 μmol; t_p, 0.5 h; CH_2Cl_2, 20 mL; ethylene pressure, 0.5 atm.
[a] 10^3 mol ethylene/(mol Ni h).
[b] Not detected or in trace.
[c] Toluene was used instead of CH_2Cl_2 as solvent.

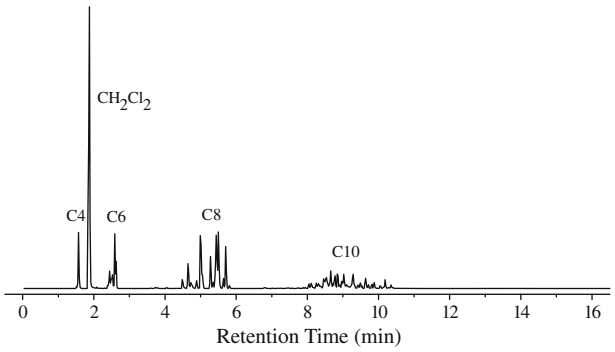


Fig. 6. GC–MS analysis of ethylene oligomers obtained by **2**/MAO in CH_2Cl_2 at 0 °C (run 6 in Table 2).

activity than that of quinolylimine nickel complex(III) [45]. It is supposed that the hydrogen atom on the amidine nitrogen may lose in the presence of MAO. In this case, the neutral amidine ligand transfers to anionic ligand, resulting in a stronger strength of the Ni–N_{imine} bond. As a result, it may stabilize the transition state for ethylene insertion, and increase the activity of the ethylene oliogmerization [26,19,40]. However, they are one or two orders of magnitude lower than those of β-pyridylimine(IV) [46] and dipyridylamine(V) nickel complexes [47]. Moreover, the carbon lengths of oligomers produced by **1**–**4**/MAO are shorter than those by dipyridylamine(V) nickel complexes. Considering the hydrogen atom on the amidine nitrogen atom is being replaced by one bulky alkyl substituent in dipyridylamine(V) nickel complexes, there is increased steric hindrance in the axial position in the dipyridylamine(V) nickel complexes, which could protect the active species, thus enhancing the catalytic activity and obtaining higher oligomers in the process of oligomerizaion.

To test the role of reaction parameters in catalytic properties, further studies were performed with **2**/MAO system as the representative. The reaction temperature greatly influenced the TOF. With an increase in the reaction temperature from −10 to 20 °C, the TOF increased consistently. Meanwhile, the distribution of oligomers changed with the increase of temperature. In general, increasing temperature led to a decrease in the proportions of higher oligomers, which suggested that the process of β-H elimination accelerates in ethylene oligomerization at high temperature.

Besides, the amount of cocatalyst also influenced the catalytic performances. The enhancement of Al/Ni molar ratio from 400 to 800 resulted in an increase of TOF up to 11.7×10^3 mol ethylene/(mol Ni h). However, a further increase of the Al/Ni molar ratio showed a slightly negative effect on TOF. The oligomers were confirmed as olefins, and no alkanes were observed, which indicated that the termination of propagation chain is via β-H elimination rather than transferring to MAO.

4. Conclusion

Four 2-pyridylbenzamidine nickel complexes with different steric and electronic substituents (**1**–**4**) have been synthesized and characterized. The solid state structures of **1**, **2** and **4** confirmed that the nickel complexes adopt distorted tetrahedral geometry, forming a six-membered chelating ring. All of these nickel complexes showed a moderate TOF for ethylene oligomerization after activated with MAO. The solvent had a great influence on products of the catalytic reactions. In toluene, ethylene oligomers, alkylated toluene and ditolylmethanes were detected. In contrast, only ethylene oligomers were obtained in dichloromethane. Moreover, the catalyst structure showed important effects on TOF and distribution of oligomers. Bearing an electron-withdrawing substituent, complex **2** exhibited the highest TOF and obtained higher order oligomers. Besides, the reaction temperature and Al/Ni molar ratio also proved to affect the catalytic properties.

Supplementary data

CCDC 713921, 713922, 713923 and 713924 contains the supplementary crystallographic data for **L2**, **1**, **3** and **4**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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