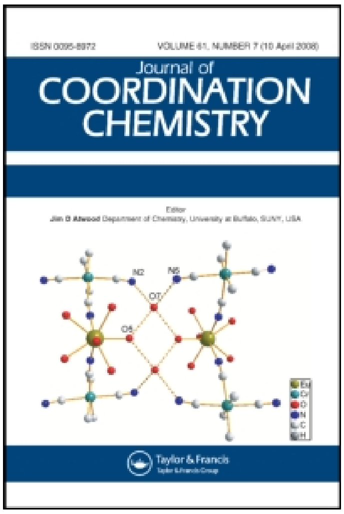

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Synthesis, crystal structure and catalytic performance of <i>bis</i>(imino)pyridyl nickel complexes

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Synthesis, crystal structure and catalytic performance of *bis*(imino)pyridyl nickel complexes

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Two new Ni(II) complexes of 2,6-*bis*[1-(2,6-diethylphenylimino)ethyl]pyridine (L^1), 2,6-*bis*[1-(4-methylphenylimino)ethyl]pyridine ($\mathbf{L^2}$) have been synthesized and structurally characterized. Complex $Ni(L^1)Cl_2 \cdot CH_3CN$ (**1**), exhibits a distorted trigonal bipyramidal geometry, whereas complex $Ni(L^1)(CH_3CN)Cl_2$ (**2**), is six-coordinate with a geometry that can best be described as distorted octahedral. The catalytic activities of complexes **1**, **2**, Ni{2,6-*bis*[1-(2,6-diisopropylphenylimino)ethyl]pyridine} $Cl_2 \cdot CH_3CN$ (**3**), and Ni{2,6-*bis*[1-(2,6-dimethylphenylimino)ethyl]pyridine}$Cl_2 \cdot CH_3CN$ (**4**), for ethylene polymerization were studied under activation with MAO.

Keywords: *bis*(Imino)pyridyl nickel complexes; Crystal structure; Ethylene polymerization

1. Introduction

Since Brookhart *et al*. [1–3] found that α-diimine nickel complexes have good catalytic properties for homopolymerization of ethylene and copolymerization of ethylene with polar monomers, design and synthesis of novel late transition metal diimino-complexes for olefin polymerization has been an active field [4–6]. In 1998, Brookhart *et al*. [7, 8] reported ethylene polymerization catalyzed by the *bis*(imino)pyridyl iron(II) and cobalt(II) complexes. These complexes, activated with MAO, MMAO or alkyl aluminium/boron cocatalyst, demonstrate good catalytic properties for ethylene polymerization [9–15]. Nickel complexes with α-diimine, β-diimine or salicylaldimine complexes show that α-diimine nickel complexes [1–3] catalyze olefin polymerization, β-diimine nickel complexes [16] activated by MAO had lower activity to ethylene polymerization and neutral salicylaldimine nickel complexes reported by Grubbs *et al*. [17, 18] had higher activity to ethylene polymerization. Hence, research on *bis*(imino)pyridyl metal catalysts has focused on nickel complexes not the iron(II) and cobalt(II) complexes. Considering structures and electronic properties of the metal,

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bis(imino)pyridyl nickel(II) complexes should have similar properities to those of *bis*(imino)pyridyl iron(II) and cobalt(II), so we are very interested in research on the syntheses, structures and catalytic properties of *bis*(imino)pyridyl nickel(II) complexes. The synthesis and catalytic properties of Ni{2,6-*bis*[1-(2-methylphenylimino) ethyl]pyridine}$Cl_2 \cdot CH_3CN$, and Ni{2,6-*bis*[1-(phenylimino)ethyl]pyridine}Cl_2 have been reported [19]. However, up to now, no reports on the catalytic properties of nickel(II) with bulky aryl substituted *bis*(imino)pyridyl ligands have appeared. Although these *bis*(imino)pyridyl nickel catalysts have lower activity for olefin polymerization, it is important for the further design and synthesis of late transition metal catalysts with better performances for olefin polymerization to understand the difference between *bis*(imino)pyridyl nickel catalysts and the iron as well as cobalt complexes in structures and properties to clarify the relation between the structures and performances of these series of catalysts.

We reported synthesis and structure of bulky aryl substituted *bis*(imino)pyridyl nickel(II) complexes **3** and **4** [20]. Here we describe the synthesis and crystal structure of *bis*(imino)pyridyl nickel(II) complexes **1** and **2**. Complexes **1**–**4** exhibit low catalytic activities for ethylene polymerization under activation with MAO.

2. Experimental

2.1. *Reagents and general techniques*

All manipulations of air and moisture-sensitive compounds were performed under nitrogen using standard Schlenk techniques. ^1H NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Elemental analyses were performed on a Perkin-Elmer 240C element analyzer. Gel permeation chromatographs (GPC) were obtained using a Waters 150CV (columns supplied by Shodex (807, 806 and 804)) (BP Chemicals Ltd.) at 135°C. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Complexes **3** and **4** were prepared according to literature methods [20]. 2,6-Diisopropylaniline, 2,6-dimethylaniline, 2,6-diethylaniline and 4-methylaniline were purchased from Aldrich Chemical Co. and used as received. 2,6-Diacetylpyridine was prepared according to a published procedure [21].

2.2. *Syntheses of ligands*

2.2.1. 2,6-*bis*[1-(2,6-diethylphenylimino)ethyl]pyridine (L^1). 2,6-Diethylaniline (4.8 mL, 28.9 mmol) was added to a solution of 2,6-diacetylpyridine (1.57 g, 9.6 mmol) in absolute methanol (40 mL). After addition of several drops of formic acid, the reaction mixture was refluxed for 24 h and then allowed to cool to room temperature. Crude product precipitated as yellow powder. Pure $\mathbf{L^1}$ was obtained in 84% yield (3.43 g) by recrystallization from methanol. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 8.54 (d, 2H, $J = 7.5$ Hz, Py–H_m), 7.95 (t, 1H, $J = 7.5$ Hz, Py–H_p), 7.16–7.04 (m, 6H, Ar–H), 2.41 (q, 4H, $J = 7.2$ Hz, CH_2CH_3), 2.28 (s, 6H, N=CMe), 1.17 (t, 6H, $J = 7.2$ Hz, CH_2CH_3). IR (KBr, cm^{-1}): 3063w, 2969m, 2931m, 2873w, 1639vs, 1589w, 1568w, 1454s, 1366s, 1326m, 1299m, 1246s, 1199s, 1122s, 1102m, 1074m, 992m, 964m, 877m, 826s, 770s, 740w, 685w, 630 w, 532w, 416w. Anal. Calcd for $C_{29}H_{35}N_3$: C, 81.84; H, 8.29; N, 9.87%. Found: C, 82.00; H, 8.31; N, 9.65%.

2.2.2. 2,6-*bis*[1-(4-methylphenylimino)ethyl]pyridine ($\mathbf{L^2}$). $\mathbf{L^2}$ was prepared by the same procedure as $\mathbf{L^1}$. Yield: 88%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.43 (d, 2H, $J = 7.8$ Hz, Py–Hm), 7.92 (t, 1H, $J = 7.8$ Hz, Py–Hp), 7.26-6.96 (m, 8H, Ar–H), 2.39 (s, 6H, N=CMe), 2.15 (s, 6H, CMe). IR (KBr, cm^{-1}): 3074w, 3025w, 2915w, 2860w, 1642vs, 1605w, 1569m, 1501s, 1452w, 1361m, 1320w, 1293w, 1220s, 1074w, 841s, 828s, 751m, 630w, 519s, 471w. Anal. Calcd for $C_{23}H_{23}N_3$: C, 80.90; H, 6.79; N, 12.31%; Found: C, 80.98; H, 6.83; N, 12.16%.

2.3. *Syntheses of complexes*

2.3.1. 2,6-*bis*[1-(2,6-diethylphenylimino)ethyl]pyridine$NiCl_2 \cdot 0.5CH_3CN$ (1). A mixture of $\mathbf{L}^1$ (180 mg, 0.42 mmol) and $NiCl_2 \cdot 6H_2O$ (100 mg, 0.42 mmol) in CH_3CN (35 mL) was stirred under nitrogen at room temperature for 12 h. Evaporation of the solvent gave the crude product as yellow powder. Pure product **1** was obtained in 76% yield (184 mg) by recrystallization from CH_3CN/CH_2Cl_2 (2 : 1 by volume). IR (KBr, cm^{-1}): 3070w, 2966s, 2934m, 2874m, 1621m, 1582s, 1444s, 1373s, 1320w, 1268s, 1210s, 1111w, 1033w, 981w, 863w, 811s, 779s, 744m, 647w, 560w, 436w. Anal. Calcd for $C_{30}H_{36.5}N_{3.5}Cl_2Ni$: C, 62.59; H, 6.39; N, 8.52%; Found: C, 62.66; H, 6.62; N, 8.85%.

2.3.2. 2,6-*bis*[1-(4-methylphenylimino)ethyl]pyridine$Ni(CH_3CN)Cl_2$ (2). This complex was prepared by the same procedure as **1**. Yield: 80%. IR (KBr, cm^{-1}): 3327m, 3058w, 3025w, 2921w, 1624m, 1587s, 1507vs, 1373m, 1264s, 1236s, 1101w, 1013w, 850. m, 820m, 773w, 745w, 707w, 668w, 526w, 488w. Anal. Calcd for $C_{25}H_{26}N_4Cl_2Ni$: C, 58.64; H, 5.12; N, 10.94%; Found: C, 58.98; H, 5.40; N, 10.96%.

2.4. *X-ray crystallography*

The data were collected with a Rigaku R-AXIS RAPID IP (complex **1**) or a Siemens SMART 1000 CCD diffractometer (complex **2**) equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 ± 2 K. The structure was solved by direct methods and refined by full-matrix least squares based on F^2 using the SHELXTL 5.1 software package [22]. The nickel and chlorine atoms in complexes **1** and **2** were first located, and carbon, nitrogen atoms were found in difference Fourier maps. The hydrogen atoms residing in the carbon atoms were located geometrically. C27 in complex **1** was disordered and occupied two sites. The complex **1** contains 0.5 CH_3CN based on chemical analysis. Crystallographic data are given in table 1.

2.5. *General ethylene polymerization procedure*

All polymerization reactions were performed in a 250 mL stainless steel autoclave with magnetic stirrer. After drying autoclave was vacuated, ethylene gas with 1 atm pressure

Table 1. Crystal data and details of structure refinement parameters for complexes **1** and **2**.

Data	**1**	**2**
Formula	$C_{30}H_{36.5}N_{3.5}Cl_2Ni$	$C_{25}H_{26}N_4Cl_2Ni$
F.W.	575.7	512.1
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	12.708(3)	13.332(4)
b (Å)	15.607(3)	14.731(4)
c (Å)	15.952(3)	14.388(4)
β (°)	96.80(3)	91.85(1)
Volume (Å^3)	3141.6(11)	2623.7(11)
Z	4	4
D_{Calcd} (g cm^{-3})	1.217	1.296
$F(000)$	1212	1064
θ range for data collection (°)	3.15–27.41	2.01–28.76
Limiting indices	$-16 \le h \le 16$, $-20 \le k \le 20$, $-18 \le l \le 20$	$-17 \le h \le 13$, $-12 \le k \le 19$, $-18 \le l \le 18$
Absorption correction	Semi-empirical	Semi-empirical
Data/restraints/parameters	6988/24/353	6209/17/289
Goodness-of-fit on F^2	1.041	1.025
Final R indices [$I > 2\sigma(I)$]		
R_1[a]	0.0588	0.0592
wR_2[b]	0.1543	0.1616
R indices (all data)		
R_1[a]	0.1026	0.0951
wR_2[b]	0.1797	0.1809
Largest diff. peak and hole (e A^{-3})	0.538 and −0.319	0.817 and −0.625

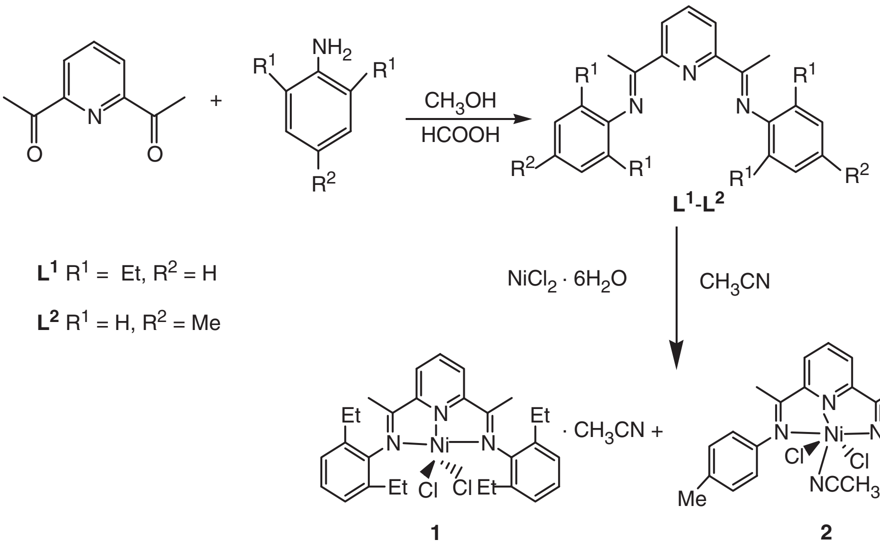
[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]]^{1/2}$.

was introduced and an appropriate amount of toluene was added through the sample-inlet valve with rapid stirring. After the system was at constant temperature, a solution of complex and MAO in toluene reacting in an ampoule in suitable ratio was added to the reaction autoclave through the sample-inlet valve and the pressure of ethylene was increased to the desired value. During the reaction the pressure of ethylene was kept constant. After some time, the polymerization was quenched by injecting acidified methanol [HCl(3M) : methanol = 1 : 1].

3. Results and discussion

3.1. *Synthesis and characterization*

The 2,6-*bis*[1-(2,6-diethylphenylimino)ethyl]pyridine ($\mathbf{L^1}$) and 2,6-*bis*[1-(4-methylphenylimino)ethyl]pyridine ($\mathbf{L^2}$) [23, 24] were synthesized according to modified published procedures in good yield and high purity by condensation of 2,6-diacetylpyridine with the corresponding aniline in refluxing absolute methanol and in the presence of formic acid (scheme 1). The ligands were characterized using ^{1}H NMR, IR spectroscopy and elemental analysis. Nickel complexes of these ligands have been prepared by reaction of $NiCl_2 \cdot 6H_2O$ with the stoichiometric amount of corresponding 2,6-*bis*(imino)pyridyl



Scheme 1. The synthetic route of complexes **1** and **2**.

ligand in CH_3CN at room temperature (scheme 1). Complexes **1** and **2** were isolated as dark red crystals in good yield and characterized using IR spectroscopy and elemental analysis. Single-crystal X-ray diffraction analyses are carried out for **1** and **2**.

The IR spectra of the free ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ show that the C=N stretching frequencies appear at 1639 and $1642\,cm^{-1}$. In the two complexes, the C=N stretching vibrations shift toward lower frequencies appear at 1621 and $1624\,cm^{-1}$, respectively, and were greatly reduced in intensity, which indicated coordination of the imino nitrogen atoms to the metal.

3.2. *Description of structures*

Crystals of **1** and **2** suitable for X-ray structural determination were grown from acetonitrile/dichloromethane (2 : 1) solution. The molecular structures of complexes **1** and **2** are given in figures 1 and 2, respectively, and selected distances and bond angles are listed in tables 2 and 3.

There are one independent molecule and 0.5 CH_3CN molecule in the asymmetric unit of **1**. Complex **1** has a structure with approximate C_s symmetry about a plane bisecting the central pyridine ring and containing the nickel atom and the two chlorine atoms. The central nickel atom is coordinated to five groups and the geometry about the nickel atom is a distorted trigonal bipyramidal with the equatorial plane defined by the N(2)(pyridyl), Cl(1) and Cl(2) atoms and the N(1) and N(3)(imino) atoms in the axial positions. The nickel atom deviates by 0.236 Å from the coordination plane. The mean deviation of the nickel atoms from the equatorial plane is 0.011 Å, and the axial Ni–N(imino) bonds subtend the angle of 151.4(2)°. The angles between the planes of phenyl rings and the plane of three coordinated nitrogen atoms are close to each other and approximate perpendicular (80.0(1) and 83.5(2)°, respectively). The dihedral angle

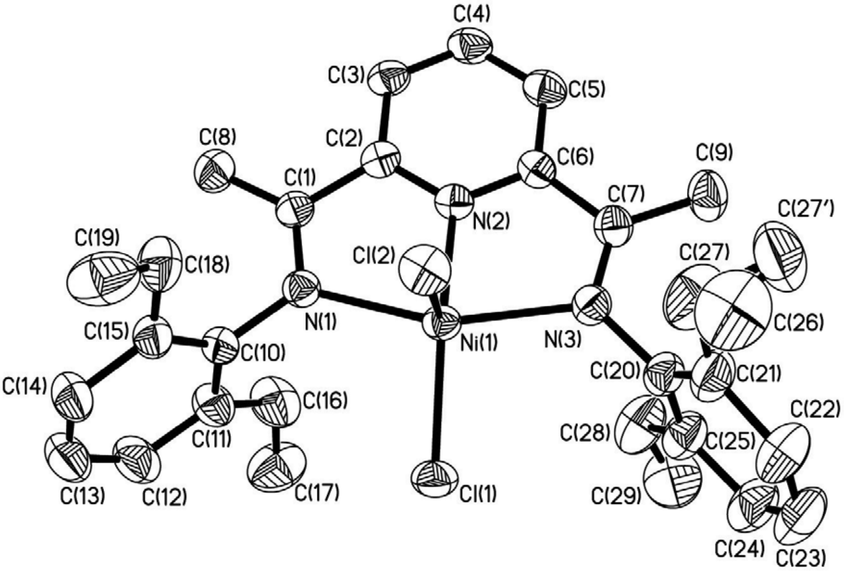


Figure 1. The molecular structure of **1** (0.5 CH_3CN molecule is omitted for clarity).

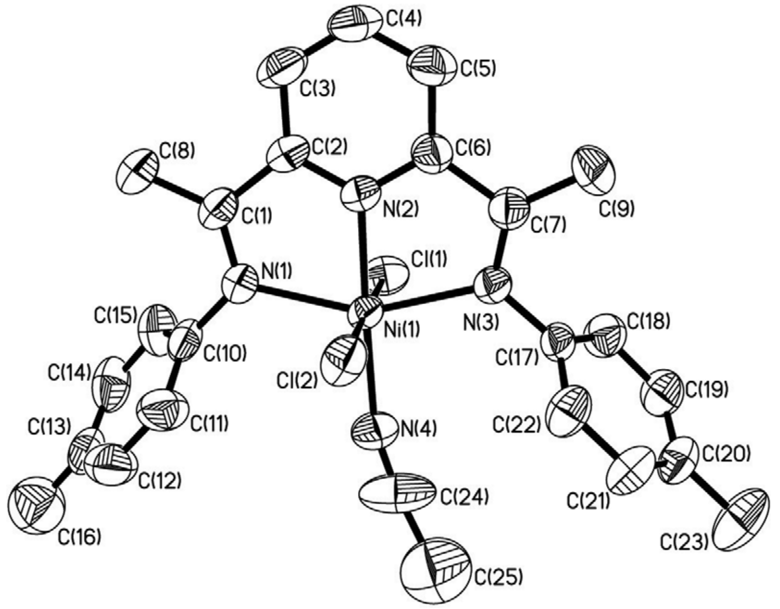


Figure 2. The molecular structure of **2**.

between the phenyl rings is also almost perpendicular to each other (81.7(2)°). In one independent molecule of complex **1**, the Ni–N(pyridyl) bond is significantly shorter than the Ni–N(imino) bonds. The two imino C=N bonds have typical double-bond character with C=N bond lengths of 1.292(9) and 1.299(8) Å.

Table 2. Selected bond distances (Å) and angles (°) in complex **1**.

Ni(1)–N(2)	1.995(5)	Ni(1)–Cl(2)	2.275(2)
Ni(1)–N(1)	2.191(5)	N(1)–C(1)	1.299(8)
Ni(1)–Cl(1)	2.256(2)	N(3)–C(7)	1.292(9)
Ni(1)–N(3)	2.174(5)		
N(2)–Ni(1)–N(1)	76.2(2)	Cl(1)–Ni(1)–N(3)	98.9(2)
N(2)–Ni(1)–Cl(1)	147.8(2)	N(2)–Ni(1)–Cl(2)	99.1(2)
N(1)–Ni(1)–Cl(1)	98.9(2)	N(1)–Ni(1)–Cl(2)	95.7(2)
N(2)–Ni(1)–N(3)	76.7(2)	Cl(1)–Ni(1)–Cl(2)	113.2(8)
N(1)–Ni(1)–N(3)	151.4(2)	N(3)–Ni(1)–Cl(2)	97.7(2)

Table 3. Selected bond distances (Å) and angles (°) in complex **2**.

Ni(1)–N(2)	1.975(3)	Ni(1)–Cl(2)	2.411(1)
Ni(1)–N(1)	2.124(3)	Ni(1)–N(4)	2.043(4)
Ni(1)–Cl(1)	2.407(1)	N(1)–C(1)	1.292(5)
Ni(1)–N(3)	2.129(3)	N(3)–C(7)	1.292(5)
N(2)–Ni(1)–N(1)	77.1(1)	Cl(1)–Ni(1)–Cl(2)	177.9(4)
N(2)–Ni(1)–Cl(1)	90.7(1)	N(3)–Ni(1)–Cl(2)	90.6(10)
N(1)–Ni(1)–Cl(1)	88.9(1)	N(2)–Ni(1)–N(4)	177.9(2)
N(2)–Ni(1)–N(3)	77.7(1)	N(4)–Ni(1)–N(1)	105.0(2)
N(1)–Ni(1)–N(3)	154.7(1)	N(4)–Ni(1)–N(3)	100.2(1)
Cl(1)–Ni(1)–N(3)	89.9(1)	N(4)–Ni(1)–Cl(1)	89.7(1)
N(2)–Ni(1)–Cl(2)	91.4(1)	N(4)–Ni(1)–Cl(2)	88.2(1)
N(1)–Ni(1)–Cl(2)	91.5(1)		

Complex **2** exhibits approximate C_s symmetry and distorted octahedral geometry for Ni(II), with the pyridyl nitrogen atom, nitrogen atom of acetonitrile and two chlorine atoms forming the equatorial plane. This structure is different than **1**, **3** and **4** [19], in which nitrogen of acetonitrile is coordinated in metal center. The equatorial and axis angles are all oriented closely orthogonally to each other, in which bond angles are in the range between 88.2(1) and 91.4(1)°. The dihedral angles between the phenyl rings and the plane formed by four coordinated nitrogen atoms are 67.6(2) and 71.3(1)°. The dihedral angle between two phenyl rings is also oriented approximately orthogonally to each other (87.5(1)°). The Ni atom lies 0.009 Å out of the plane of the four coordinated nitrogen atoms. The mean deviation of the nickel from the equatorial plane is 0.018 Å. The two imino C=N bonds have typical double-bond character with C=N both bond lengths of 1.292(5) Å. There are no intermolecular packing features of interest in either complex.

Among the complexes **1**–**4**, complexes **1**, **3** and **4** are all five-coordinated with distorted trigonal bipyramidal geometry, while complex **2** is six-coordinated with distorted octahedral geometry. The different configuration may be caused by the size and position of substituents on the phenyl ring. Complexes **1**, **3** and **4** have larger *o*-substituents on the aryl ring resulting in bigger steric hindrance, while complex **2** has no *p*-substituent on the aryl ring which makes it have less steric hindrance and allows coordination of acetonitrile to form a six-coordinated structure. When the crystal structures of these four nickel complexes were compared to those of iron and cobalt complexes $2,6\text{-}(2,6\text{-}\mathrm{Pr}^{i}_{2}\mathrm{C_6H_4N{=}CMe})_2\mathrm{C_5H_3NMCl_2}$ (M = Fe or Co) [14] with similar

Table 4. Results of polymerization for complexes **1–4**.[a,b]

Catalyst	Loading (μmol)	Yield (g)	Activity (g PE /mmol cat. h)	M_w[c]	T_m[d] (°C)
1	3.0	0.12	40	3730	118
2	3.0	0.06	20	3181	115
3	3.0	0.15	50	3782	118
4	3.0	0.10	33	3530	117

[a] Conditions: cat/MAO, 1 : 1000; polymerization time 1 h; temperature, 30°C; solvent (toluene 200 mL).

[b] The polymeric results are closely to above corresponding data for per catalyst under other conditions (Conditions: cat/MAO, 1 : 2000, 1 : 3000; polymerization time 2 h, 3 h; temperature, 40°C, 50°C, 60°C, respectively).

[c] Determined by GPC.

[d] Determined by DSC.

structures, the bond lengths of M–N(pyridyl) (2.088(4) and 2.051(3) Å, respectively) and M–N(imino) (in the range of 2.211(3)–2.250(4) Å) in *bis*(imino)pyridyl iron(II) and cobalt(II) complexes are longer than the corresponding values in the four *bis*(imino)-pyridyl nickel complexes, while the angles of N(imino)–M–N(imino) (140.1(1) and 141.3(1)°) in *bis*(imino)pyridyl iron(II) and cobalt(II) complexes are much smaller than those in the four *bis*(imino)pyridyl nickel complexes, thus the space on the central metal in *bis*(imino)pyridyl iron(II) and cobalt(II) complexes for coordination of olefin molecules is larger than that in the *bis*(imino)pyridyl nickel complexes benefiting the coordination and insertion of olefin molecules.

3.3. *Polymerization results*

To investigate the reaction parameters affecting the ethylene polymerization, we carried out the polymerization at 30, 40, 50, and 60°C, for every catalyst. The ratio of each catalyst to MAO(Cat/MAO) was 1 : 1000, 1 : 2000 and 1 : 3000. The polymerization time is 1, 2, and 3 h, respectively. The polymerization results shown in table 4 indicate that complexes **1**–**4** are less active catalyst precursors compared to the high catalytic activity of *bis*(imino)pyridyl iron(II) and cobalt(II) complexes. Two reasons may result in these nickel complexes having lower catalytic activity: (1) the electronegativity of nickel is larger than that of iron and cobalt which makes the central nickel bonded to the three electron-donating nitrogen atoms of *bis*(imino)pyridyl readily reduced to the low valence nickel when activated by MAO, (2) the radius of nickel is smaller than that of iron and cobalt which makes the central nickel have less space for coordination of olefin molecules, hindering the coordination and insertion of olefin molecules.

4. Conclusion

In conclusion, two new nickel complexes with 2,6-*bis*(imino)pyridyl ligands have been synthesized. Four complexes activated with MAO exhibit low catalytic activity for ethylene polymerization. The influence of polymerization conditions and the structures of complexes on catalytic performance are in progress.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 293334 for complex **1**, CCDC No. 293335 for complex **2**. Copies of this information may be obtained free of charge from The Director, CCDC 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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