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Synthesis and characterization of 2-(2-benzhydrylnaphthyliminomethyl)pyridylnickel halides: formation of branched polyethylene

Erlin Yue,†,‡ Qifeng Xing,‡ Liping Zhang,‡ Qisong Shi,‡ Xiao-Ping Cao,*,† Lin Wang,‡ Carl Redshaw,*,§ and Wen-Hua Sun,*,†,‡

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Abstract: A series of 2-(2-benzhydrylnaphthyliminomethyl)pyridine derivatives (L1–L3) was prepared and used to synthesize the corresponding bis-ligated nickel(II) halide complexes (Ni1–Ni6) in good yield. The molecular structures of representative complexes, namely the bromide Ni3 and the chloride complex Ni6, were confirmed by single crystal X-ray diffraction, and revealed a distorted octahedral geometry at nickel. Upon activation with either methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), all nickel complex pre-catalysts exhibited high activities (up to $2.02 \times 10^7$ g(PE)·mol$^{-1}$(Ni)·h$^{-1}$) towards ethylene polymerization, producing branched polyethylene of low molecular weight and narrow polydispersity. The influence of the reaction parameters and the nature of the ligands on the catalytic behavior of the title nickel complexes were investigated.

Introduction

Polyolefin materials are extensively used in our daily life and the annually consumption amounts to over 130 million tonnes. In order to produce advanced polyolefins using new catalytic systems, attention has switched to late-transition metal complex pre-catalysts in both the industrial and academic arenas.\(^1,2\) Since the discovery of the $\alpha$-diiminometal (Ni or Pd) complexes\(^3\) and bis(imino)pyridylmetal (Fe or Co) complexes,\(^4\) the characteristic features of the polyethylene obtained have been shown to rely on the metal employed: highly linear polyethylene was generally produced from either iron or cobalt complex pre-catalysts,\(^1,2a\) whereas branched polyethylene was commonly observed from catalytic systems based on nickel complex pre-catalysts.\(^1,2b\) The polymerization mechanism operating within nickel systems is an illustration of how hydrogen-elimination facilitates chain-transfer to produce branched polymers.\(^5\) Currently, industrial processes for accessing branched polyethylenes mostly rely on the copolymerization of ethylene with $\alpha$-olefins. Nickel pre-catalysts are providing new approaches to highly branched polyethylene, and the resulting new polymers can potentially exhibit new properties and may yield a new family of advanced polyolefins.\(^2b\) Therefore, the syntheses of nickel complexes have extensively been conducted through designing new ligands with modification via the use of different substituents.\(^6\) As an example, the 2-iminopyridylnickel complex pre-catalysts (A, Scheme 1) exhibited high activities towards ethylene polymerization or oligomerization,\(^7\) whilst the methyl-bridged binuclear complex pre-catalysts (B, Scheme 1) performed ethylene oligomerization and polymerization.\(^5,9\) Recently, progress has been made through the use of benzhydryl-substituted anilines,\(^10–12\) and the 2-iminopyridylnickel complex model (C, Scheme 1) was revisited to reveal high activities solely for ethylene polymerization.\(^13\)

Subsequently, new benzhydryl-substituted naphthylamines were designed and were used to prepare 2-(1-(2-benzhydrylnaphthylimino)ethyl)pyridylnickel complexes (D, Scheme 1), which revealed high activities of up to $1.22 \times 10^7$ g(PE)·mol$^{-1}$(Ni)·h$^{-1}$ towards ethylene polymerization.\(^14\) Given this, the 2-(2-benzhydrylnaphthyliminomethyl)pyridyl nickel halide complexes are bis-ligated complexes (E, Scheme 1), which according to literature would be expected to be inactive in...
catalysis polymerization.\textsuperscript{15} However, the title nickel complexes were found to exhibit even higher activities toward ethylene polymerization than did their 2-(1-(2-benzhydrylnaphthylimino)ethyl)pyridyl-nickel analogues.\textsuperscript{14} Herein, the synthesis and characterization of the 2-(2-benzhydrylnaphthyliminomethyl)pyridine derivatives and their nickel complexes are reported, and the catalytic performances of these nickel complexes, as well as the properties of the resulting polyethylene, are investigated.

Results and discussion

Synthesis and characterization

The series of 2-(2-benzhydrylnaphthyliminomethyl)pyridine derivatives (L1–L3, Scheme 2) was readily synthesized by the condensation reaction of picolin aldehyde with benzhydryl-substituted naphthylamines in moderate yields following the reported procedure.\textsuperscript{14} All organic compounds were characterized by FT–IR, \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy as well as by elemental analysis.

Trials of the reaction of the 2-(2-benzhydrylnaphthyliminomethyl)pyridine in dichloromethane solution with different molar ratios of NiCl\textsubscript{2}·6H\textsubscript{2}O or (DME)NiBr\textsubscript{2} in ethanol were conducted, and the bis-ligated nickel halide (chloride or bromide) complexes (Ni1–Ni6) were best isolated when using two equivalents of organic compound to nickel halide (Scheme 2). According to the FT–IR spectra, the C=N stretching vibrations in complexes Ni1–Ni6 were shifted to lower frequencies in the region 1622–1634 cm\textsuperscript{-1} with weaker intensity compared to the peaks at 1642–1643 cm\textsuperscript{-1} for the free organic compounds, indicating the effective coordination between the imino-group and the cationic nickel center. Elemental analysis data was consistent with these nickel complexes having the formula \textit{L}$_2$Ni\textit{X}$_2$ (X = Br, Cl). Crystal structures of a representative bromide (Ni3) and chloride (Ni6) complexes were determined.

Single-crystal X-ray diffraction studies

Single crystals of Ni3 and Ni6 suitable for X-ray diffraction analysis were obtained by laying diethyl ether onto their dichloromethane solutions at room temperature. Both complexes Ni3 and Ni6 are bis-ligated mononickel(II) complexes possessing a distorted octahedral geometry at the nickel center. The molecular structures of Ni3 and Ni6 are shown in Fig. 1 and 2, respectively, and their selected bond lengths and angles are tabulated in Table 1.

\begin{table}[h]
\centering
\begin{tabular}{lccc}
\hline
 & Ni3 & Ni6 \\
\hline
Bond lengths (Å) & \\
Ni(1)–N(1) & 2.068(3) & Ni(1)–N(1) & 2.083(3) \\
Ni(1)–N(2) & 2.234(3) & Ni(1)–N(2) & 2.234(3) \\
Ni(1)–N(1’1) & 2.068(3) & Ni(1)–N(1’) & 2.083(3) \\
N(1)–N(1)–N(2) & 101.87(10) & N(1)–N(1′)–N(2) & 101.87(10) \\
N(1)–N(1)–N(1′1) & 180.00(13) & N(1)–N(1′)–N(1′1) & 180.00(13) \\
N(1)–N(1′1)–N(2) & 101.87(10) & N(1)–N(1′)–N(2) & 101.87(10) \\
N(1)–N(1′1)–N(1′1) & 180.00(13) & N(1)–N(1′1)–N(1′1) & 180.00(13) \\
N(1′)–N(1)–N(2) & 87.98(8) & N(1′)–N(1)–Cl(1) & 91.33(8) \\
N(1′)–N(1)–N(1′1) & 92.02(8) & N(1′)–N(1′1)–Cl(1) & 88.67(8) \\
N(2)–N(1)–Br(1) & 83.74(10) & N(2)–N(1)–Cl(1) & 96.68(7) \\
N(2)–N(1)–N(1′1) & 83.74(10) & N(2)–N(1′1)–Cl(1) & 96.68(7) \\
\hline
\end{tabular}
\caption{Selected bond lengths (Å) and angles (°) for Ni3 and Ni6}
\end{table}

As shown in Fig. 1, the nickel center is coordinated by four nitrogens (N1, N2, N1′ and N2′) of the two chelate ligands and two bromides (Br1 and Br1′), which is similar to the aniline-based bis[(iminopyridyl)nickel dibromide].\textsuperscript{13,16} There is a five-membered hetero-nickel plane with N1, Ni1, N2, C1 and C6...
Various co-catalysts such as MAO, MMAO and Et₂AlCl were used to activate the nickel pre-catalyst Ni2 for ethylene polymerization (runs 1–3 in Table 2), which indicated that higher catalytic activities in ethylene polymerization were achievable when employing either MAO or MMAO.

### Table 2 Ethylene polymerization by Ni2 using various co-catalysts

<table>
<thead>
<tr>
<th>Run</th>
<th>Co-catalyst</th>
<th>Al/Ni</th>
<th>Yield/g</th>
<th>Activity (^{a})</th>
<th>(M_w/M_n)</th>
<th>(T_m/°C)</th>
<th>(M_w/gmol(^{-1}))</th>
<th>(M_n/gmol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>11.3</td>
<td>2817</td>
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<td>109.3</td>
<td>122.4</td>
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<tr>
<td>2</td>
<td>MMAO</td>
<td>1000</td>
<td>4.88</td>
<td>4.88</td>
<td>2251</td>
<td>2.24</td>
<td>111.7</td>
<td>117.1</td>
</tr>
<tr>
<td>3</td>
<td>Et₂AlCl</td>
<td>300</td>
<td>3.14</td>
<td>3.14</td>
<td>1425</td>
<td>1.88</td>
<td>101.2</td>
<td>101.2</td>
</tr>
</tbody>
</table>

\(^{a}\) General conditions: 2 \(μ\)mol of Ni; 30 min; 30 °C; 100 mL of toluene for 10 atm of ethylene.  \(^{b}\) Determined by GPC.  \(^{c}\) Determined by DSC.

### Table 3 Ethylene polymerization by Ni1–Ni6/MMAO

<table>
<thead>
<tr>
<th>Run</th>
<th>Pre-cat.</th>
<th>Al/Ni</th>
<th>(T/°C)</th>
<th>Yield/g</th>
<th>Activity (^{a})</th>
<th>(M_w/M_n)</th>
<th>(T_m/°C)</th>
<th>(M_w/gmol(^{-1}))</th>
<th>(M_n/gmol(^{-1}))</th>
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</thead>
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<tr>
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<td>Ni2</td>
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<td>30</td>
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<td>11.5</td>
<td>2434</td>
<td>2.34</td>
<td>107.5</td>
<td>107.5</td>
</tr>
<tr>
<td>4</td>
<td>Ni2</td>
<td>1500</td>
<td>30</td>
<td>14.5</td>
<td>14.5</td>
<td>1718</td>
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<td>30</td>
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<td>1700</td>
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<td>118.7</td>
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<td>Ni2</td>
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<td>30</td>
<td>10.7</td>
<td>10.7</td>
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<td>84.9</td>
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\(^{a}\) General conditions: 2 \(μ\)mol of Ni; 30 min; 100 mL of toluene for 1 atm of ethylene.  \(^{b}\) Determined by GPC.  \(^{c}\) Determined by DSC.

At 30 °C and 10 atm of ethylene, the Al/Ni ratio was changed from 750 to 2250 (runs 1–7, Table 3), and the highest activity was observed with the Al/Ni ratio 1500 (run 4, Table 3) at 1.45 \(×\) 107 g(PE) mol⁻¹(Ni) h⁻¹. In general, the molecular weights of the resultant polyethylene slightly decreased on increasing the Al/Ni ratio (runs 1–5, Table 3), which was ascribed to faster chain transfer on increasing the Al concentration. However, the catalytic system with the Al/Ni ratio of 2000 (run 6, Table 3) revealed a higher activity than did the system with the Al/Ni ratio of 1750 (run 5, Table 3). Therefore there are two maximum activities for such catalytic systems at different Al/Ni ratios of 1500 and 2000. As seen in the GPC curve (Fig. 3), all catalytic systems generally exhibited single-site catalysis with narrow polydispersity for all the obtained polyethylene.

On fixing the Al/Ni molar ratio at 1500, the reaction temperature was changed from 20 to 60 °C (runs 4, and 8–11, Table 3); the highest activity observed, namely 1.45 \(×\) 107 g(PE) mol⁻¹(Ni) h⁻¹, was at 30 °C (run 4 in Table 3). The GPC data indicated that higher molecular weight polyethylene was obtained at lower temperatures, and the GPC curves are shown in Fig. 4. These phenomena were consistent to previous observations for 2-iminopyridylnickel pre-catalysts, and are ascribed to increased chain-transfer and termination at higher temperature. As well as the GPC measurements, the melting points of resultant polyethylenes were measured by differential scanning calorimetry (DSC). The \(T_m\) values of the polyethylene dramatically decreased on elevating the reaction temperature (runs 4, and 8–11, Table 3), and are slightly higher than those of their analogs bearing 2-(1-(2-benzhydrylnaphthylimino)ethyl) pyridines, probably reflecting less branches in the current systems.

At 30 °C and 10 atm of ethylene, the Al/Ni ratio was changed from 750 to 2250 (runs 1–7, Table 3), and the highest activity was observed with the Al/Ni ratio 1500 (run 4, Table 3) at 1.45 \(×\) 107 g(PE) mol⁻¹(Ni) h⁻¹. In general, the molecular weights of the resultant polyethylene slightly decreased on increasing the Al/Ni ratio (runs 1–5, Table 3), which was ascribed to faster chain transfer on increasing the Al concentration. However, the catalytic system with the Al/Ni ratio of 2000 (run 6, Table 3) revealed a higher activity than did the system with the Al/Ni ratio of 1750 (run 5, Table 3). Therefore there are two maximum activities for such catalytic systems at different Al/Ni ratios of 1500 and 2000. As seen in the GPC curve (Fig. 3), all catalytic systems generally exhibited single-site catalysis with narrow polydispersity for all the obtained polyethylene.
in trans positions, which is not favorably for coordination insertion; the transformation of these bis-ligated nickel species into mono-ligated active species is assumed to occur during the ethylene polymerization. It is noteworthy that the nickel pre-catalysts (Ni3 and Ni6) bearing more benzhydryl substituents exhibited relatively higher activities than did their analogues, which is different to the catalytic performances by the analogues ligated by 2-(1-(2-benzhydrylnaphthylimino)ethyl) pyridines in the presence of Et3AlCl.

The 13C NMR spectrum for the polyethylene obtained from the Ni2/MMAO at 60 °C (run 11 in Table 3) is shown in Fig. 5. Interpreted according to the literature, there are 182 branches per 1000 carbons, and the signals are presented in Table 4, which indicates that the main branches include methyl (26.88 %), some long chains (35.18 %) and amyl chains (17.00 %), which is consistent to the observations for the analogue system comprising the 2-(1-(2-benzhydrylnaphthylimino)ethyl)pyridyl nickel halide complexes.14

![Fig. 5 13C NMR spectrum of the polyethylene by Ni2/MMAO at 60 °C (run 11 in Table 3)](image)

### Table 4 Percentage of branches for the polyethylene (run 11 in Table 3)

<table>
<thead>
<tr>
<th>Peak no.</th>
<th>Chem. Shifts</th>
<th>Integral exp.</th>
<th>Branch content</th>
<th>Percentage over total branching</th>
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<td>Mn</td>
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<tr>
<td>2</td>
<td>11.39</td>
<td>0.73</td>
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<td>3</td>
<td>14.09</td>
<td>6.41</td>
<td>N(n1,5)</td>
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</tr>
<tr>
<td>4</td>
<td>19.97</td>
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<td>N(n1,6)</td>
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</tr>
<tr>
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<td>20.29</td>
<td>0.55</td>
<td>Ne</td>
<td>0.147</td>
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<td>[R]</td>
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<td>Branches/1000C</td>
<td></td>
</tr>
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<td>Long branches</td>
<td>35.18 %</td>
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</table>

### Ethylene polymerization in the presence of MMAO

In a similar manner, the pre-catalyst Ni2 in the presence of MMAO was explored (runs 1–9, Table 5), and the highest activity of 8.99 × 104 g(Pe):mol⁻¹(Ni) h⁻¹ was obtained with the Al/ Ni ratio of 1750 at 30 °C (run 4 in Table 5). On comparison with the system using MAO, the system with MMAO is less thermally stable, whilst the resultant polyethylene exhibited relatively lower molecular weights and narrower PDI, but slightly higher melting points suggestive of less branching.

### Table 5 Ethylene polymerization by Ni1–Ni6/ MMAO

<table>
<thead>
<tr>
<th>Run</th>
<th>Pre-catalyst</th>
<th>Al/Ni</th>
<th>T/°C</th>
<th>t/min</th>
<th>Yield/%</th>
<th>Act/10⁴ g(Pe):mol⁻¹(Ni) h⁻¹</th>
<th>Mw/Mn</th>
<th>Tm/°C</th>
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</thead>
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<tr>
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* General conditions: 2 μmol of Ni; 100 mL of toluene for 10 atm of ethylene. ¹ 10⁴ g(Pe):mol⁻¹(Ni) h⁻¹ Determined by GPC. ² Determined by DSC.

Regarding the lifetime of the active species, the polymerization was conducted over different periods from 10 to 40 min (runs 4, and 10–12, Table 5). On prolonging the reaction time, the catalytic activities slightly decreased, whilst the obtained polyethylene revealed higher molecular weight and wider polydispersity (Fig. 6). These results are consistent to the observations for the reported nickel analogues bearing the 2-iminopyridine ligand system.10, 13-14

![Fig. 6 GPC curves of polyethylene obtained using the Ni2/ MMAO system over different times (runs 4, 10–12 in Table 5)](image)

All the other nickel pre-catalysts were investigated in the presence of MMAO, and were found to perform with good activities in ethylene polymerization under the optimum conditions of Al/Ni molar ratio 1750 at 30 °C (runs 13–17, Table 5). Regarding to the influences of reaction parameters and the nature of ligands, the tendency of catalytic performance of the Ni/MMAO systems is highly similar to the observation of the Ni/MAO; however, the system with MMAO exhibited slightly lower activity and produced lower molecular weight polyethylene than did the system using MAO.
Conclusion

The series of 2-(2-benzhydrylnaphthyliminomethyl)pyridine derivatives and their nickel halide complexes were synthesized and fully characterized, and single crystal X-ray diffraction revealed the complexes Ni3 and Ni6 to contain bis-ligated mononickel with a distorted octahedral geometry at the metal. All the nickel complex pre-catalysts, activated by either MAO or MMAO, exhibited high activities (up to 2.02 × 107 g(PE)·mol−1·h−1) towards ethylene polymerization, and produced polyethylene of lower molecular weight and narrow molecular polydispersity. This is a rare example of bis-ligated nickel halides performing with high activities towards ethylene polymerization, especially given that the two halides are trans. The nickel complexes bearing 2-(arylimino)ethyl)pyridines showed slightly higher activity than their analogues bearing 2-(1-aryliminomethyl)pyridine derivatives.14

Experimental Section

General consideration. All manipulations involving air- and moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were prepared as yellow solids in 64 % yield. Mp: 110–111 °C. 1H NMR (400 MHz, CDCl3, TMS): δ 8.68 (d, 1H, J = 4.4 Hz, Py–H), 8.00 (d, 1H, J = 7.6 Hz, Py–H), 7.95 (s, 1H, –CH=N), 7.87 (d, 1H, J = 8.8 Hz, Py–H), 7.78 (t, 1H, J = 7.6 Hz, Py–H), 7.40–6.88 (m, 33H, Ar–H), 6.64 (s, 1H, –CHPh2), 6.12 (s, 1H, –CHPh2), 5.65 (s, 1H, –CHPh2), 5.57 (s, 1H, –CHPh2). 13C NMR (100 MHz, CDCl3, TMS): 165.6, 154.1 (–CH=N), 149.7, 145.6, 143.9, 143.8, 143.7, 140.9, 136.8, 136.6, 135.6, 130.0, 129.6, 129.5, 129.4, 128.6, 128.4, 128.2, 127.5, 126.3, 126.2, 126.1, 125.5, 124.3, 124.2, 121.9, 53.0 (–CHPh2), 51.7 (–CHPh2). FT–IR (KBr, disk, cm−1): 1643 (ν(C=N)), 1543, 1499, 1457, 1438, 1348, 1367, 1336, 1182, 1074, 1032, 920, 779, 746, 95.

Synthesis of nickel Complexes

General procedure. NiCl2·6H2O (0.25 mmol) or (DMENi)Br2 (0.25 mmol) was dissolved in 5 mL ethanol and added to the solution of the ligands (0.5 mmol) in 5 mL CH2Cl2. The mixture was stirred for 12 h, and then diethyl ether was poured into the mixture to precipitate the complex. The precipitant was collected by filtration, washed with diethyl ether (3 × 5 mL), and dried under vacuum at 60 °C.

Synthesis of ligands

2-(2-Benzhydrylnaphthyliminomethyl)pyridine (L1). A solution of picolinaldehyde (0.221 g, 2.06 mmol), 2-benzhydrylaniline (0.670 g, 2.17 mmol) and a catalytic amount of p-toluenesulfonic acid (0.079 g, 0.41 mmol) in toluene (80 mL) was refluxed for 8 h. The solvent was evaporated under reduced pressure, and then the residue was purified by column chromatography on basic alumina with the eluent of petroleum ether–ethyl acetate (v : v = 20 : 1) to afford a yellow solid in 76 % isolated yield. Mp: 108–109 °C. 1H NMR (400 MHz, CDCl3, TMS): δ 8.71 (d, 1H, J = 4.8 Hz, Py–H), 8.19 (d, 1H, J = 8.0 Hz, Py–H), 8.05 (s, 1H, –CH=N), 7.87–7.82 (m, 2H, Py–H), 7.76 (d, 1H, J = 8.4 Hz, Ar–H), 7.59 (d, 1H, J = 8.4 Hz, Ar–H), 7.48–7.37 (m, 3H, Ar–H), 7.24–7.09 (m, 1H, Ar–H), 5.84 (s, 1H, –CHPh2). 13C NMR (100 MHz, CDCl3, TMS): 165.7, 154.2 (–CH=N), 149.9, 146.9, 143.9, 136.8, 133.1, 129.8, 128.7, 128.4, 128.0, 127.6, 126.4, 126.1, 125.9, 125.7, 125.6, 124.1, 123.5, 122.0, 51.8 (–CHPh2). FT–IR (KBr, disk, cm−1): 3052, 3024, 1642 (ν(C=N)), 1576, 1466, 1302, 1275, 1089, 748, 736, 698. Anal. Calcd for C35H32N2O2Cl2 (598.78): C, 84.71; H, 5.56; N, 7.03 %; Found: C, 84.76; H, 5.79; N, 6.93 %.

2-(2-Benzhydrylnaphthyliminomethyl)pyridine (L2). Using the same procedure as for the synthesis of L1, L2 was prepared as a yellow solid in 72 % yield. Mp: 147–148 °C. 1H NMR (400 MHz, CDCl3, TMS): δ 8.70 (d, 1H, J = 4.8 Hz, Py–H), 8.20 (d, 1H, J = 8.0 Hz, Py–H), 8.09 (s, 1H, –CH=N), 7.96 (d, 1H, J = 8.4 Hz, Py–H), 7.86–7.79 (m, 2H, Py–H and Ar–H), 7.42–6.90 (m, 23H, Ar–H), 6.68 (s, 1H, Ar–H), 6.17 (s, 1H, –CHPh2), 5.71 (s, 1H, –CHPh2). 13C NMR (100 MHz, CDCl3, TMS): 165.6, 154.2 (–CH=N), 149.9, 145.7, 143.8, 143.7, 136.8, 133.6, 131.4, 131.3, 130.4, 129.6, 129.5, 128.8, 128.4, 128.2, 127.6, 126.3, 126.2, 126.1, 125.5, 124.3, 124.2, 121.9, 53.0 (–CHPh2), 51.7 (–CHPh2). FT–IR (KBr, disk, cm−1): 3053, 3024, 1643 (ν(C=N)), 1578, 1491, 1440, 1384, 1342, 1252, 1155, 1075, 1030, 991, 948, 915, 753, 736, 698. Anal. Calcd for C35H32N2O2Cl2 (598.78): C, 66.18; H, 5.79; N, 7.49 %; Found: C, 68.66; H, 4.37; N, 5.52 %.
studies were carried out on a Rigaku Saturn 724 + CCD with SQUEEZE option of the crystallographic program PLATON 20 on the geometry of the main compounds. Therefore, the Ni₆ chloride (Ni₄, yellow, 91 % yield): FT–IR (KBr, disk, cm⁻¹): ν(C=N), 1634; ν(C-Br), 567. Anal. Calcd for C₁₁₀H₈₄Br₂N₄Ni, C, 57.22; H, 3.48; N, 4.28 %. Found: C, 57.02; H, 3.38 %. 19

Bis(2-(2-benzhydrylnaphthyliminomethyl)pyridyl)nickel chloride (Ni₄, yellow, 91 % yield): FT–IR (KBr, disk, cm⁻¹): ν(C=N), 1634; ν(C-Br), 567. Anal. Calcd for C₁₁₀H₈₄Br₂N₄Ni, C, 57.22; H, 3.48; N, 4.28 %. Found: C, 57.02; H, 3.38 %.

Bis(2-(4,7-tribenzhydrylnaphthyliminomethyl)pyridyl)nickel chloride (Ni₆, yellow, 84 % yield): FT–IR (KBr, disk, cm⁻¹): ν(C=N), 1597; ν(C-Br), 540. Anal. Calcd for C₁₁₀H₈₄Br₂N₄Ni, C, 57.22; H, 3.48; N, 4.28 %. Found: C, 57.02; H, 3.38 %.

X-ray crystallographic studies

Single crystals of Ni₃ and Ni₆ suitable for X-ray diffraction analyses were obtained by slow diffusion of diethyl ether onto the respective dichloromethane solution at room temperature. X-ray studies were carried out on a Rigaku Saturn 724 CCD with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 173(2) K (Ni₃) and 100(2) K (Ni₆), cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F². All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.19 Within structure refinement of Ni₃ and Ni₆, there were free solvent molecules which have no influence on the geometry of the main compounds. Therefore, the SQUEEZE option of the crystallographic program PLATON was used to remove these free solvents from the structure. Details of the X-ray structure determinations and refinements are provided in Table 6.

General procedure for ethylene polymerization

A 250 mL stainless steel autoclave equipped with a mechanical stirrer and a temperature controller was used to perform ethylene polymerization. The autoclave was evacuated by a vacuum pump and back-filled twice with N₂ and once with ethylene. When the desired reaction temperature was reached, 30 mL toluene was added under ethylene atmosphere, and the nickel pre-catalyst in 20 mL toluene was injected. The required amount of co-catalysts (MAO, MMAO or Et₂AlCl) and additional toluene (maintaining total volume as 100 mL in reactor) were added by syringe. The reaction mixture was intensively stirred for the desired time under 10 atm of ethylene and maintained at this level by constant feeding of ethylene. The reaction was quenched by addition of acidic ethanol. The precipitated polymer was washed with ethanol several times and dried in vacuo.


Graphical Abstract

for

Synthesis and characterization of 2-(2-benzhydrylnaphthyliminomethyl)pyridyl nickel halides: Formation of branched polyethylene

Erlin Yue, Qifeng Xing, Liping Zhang, Xiao-Ping Cao, Lin Wang, Carl Redshaw, and Wen-Hua Sun

The 2-((2-benzhydrylnaphthyl)iminomethyl)pyridylnickel halide complexes, activated by MAO or MMAO, showed high activities (up to $2.02 \times 10^7$ g(PE) mol$^{-1}$(Ni) h$^{-1}$) towards ethylene polymerization.