

# Moderately branched ultra-high molecular weight polyethylene by using *N,N'*-nickel catalysts adorned with sterically hindered dibenzocycloheptyl groups

Muhammad Zada,<sup>a,b</sup> Liwei Guo,<sup>a,c</sup> Randi Zhang,<sup>a</sup> Wenjuan Zhang,<sup>c,\*</sup> Yanping Ma,<sup>a</sup> Gregory A. Solan,<sup>a,d,\*</sup> Yang Sun,<sup>a</sup> Wen-Hua Sun<sup>a,b,\*</sup>

<sup>a</sup> Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: whsun@iccas.ac.cn

<sup>b</sup> CAS Research/Education Center for Excellence in Molecular Sciences, University of Chinese Academy of Sciences, Beijing 100049, China.

<sup>c</sup> Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing Engineering Research Center of Textile Nanofiber, School of Materials Science and Engineering, Beijing Institute of Fashion Technology, Beijing 100029, China. E-mail: zhangwj@bift.edu.cn

<sup>d</sup> Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, UK. E-mail: gas8@leicester.ac.uk.

## ABSTRACT

Five examples of unsymmetrical 1,2-bis(arylimino)acenaphthene (**L1** – **L5**), each containing one *N*-2,4-bis(dibenzocycloheptyl)-6-methylphenyl group and one sterically and electronically variable *N*-aryl group, have been used to prepare the *N,N'*-nickel(II) halide complexes, [1-[2,4- $\{(C_{15}H_{13})_2$ -6-MeC<sub>6</sub>H<sub>2</sub>N]-2-(ArN)C<sub>2</sub>C<sub>10</sub>H<sub>6</sub>]NiX<sub>2</sub> (X = Br: Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Ni1**, 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Ni2**, 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Ni3**, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> **Ni4**, 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub> **Ni5**) and (X = Cl: Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Ni6**, 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Ni7**, 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Ni8**, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> **Ni9**, 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub> **Ni10**), in high yield. The molecular structures **Ni3** and **Ni7** highlight the extensive steric protection imparted by the *ortho*-dibenzocycloheptyl group and the distorted tetrahedral geometry conferred to the nickel center. On activation with either Et<sub>2</sub>AlCl or MAO, **Ni1** – **Ni10** exhibited very high activities for ethylene polymerization with the least bulky **Ni1** the most active (up to  $1.06 \times 10^7$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup> with MAO). Notably, these sterically bulky catalysts have a propensity towards generating very high molecular weight polyethylene with moderate levels of branching and narrow dispersities with the

most hindered **Ni3** and **Ni8** affording ultra-high molecular weight material (up to  $1.5 \times 10^6$  g mol<sup>-1</sup>). Indeed, both the activity and molecular weights of the resulting polyethylene are among the highest to be reported for this class of unsymmetrical 1,2-bis(imino)acenaphthene-nickel catalyst.

*Keywords:* nickel(II), 1,2-bis(imino)acenaphthene, dibenzocycloheptyl substitution, high molecular weight, moderately branched polyethylene.

## 1 INTRODUCTION

Ever since the first report of  $\alpha$ -diimino-nickel(II) complexes as effective catalysts for ethylene polymerization over two decades ago, their capacity to generate polyethylene with various levels of branching and molecular weight has been recognized.<sup>[1,2]</sup> These findings have in turn help motivate numerous studies directed towards improving the performance of the catalyst and influencing the polymer properties.<sup>[3]</sup> Moreover, these branched polymers have been attracting growing interest due to their connection to thermoplastic elastomers (TPEs).<sup>[4]</sup> With regard to catalyst structure, steric and electronic effects imparted by the chelating  $\alpha$ -diimine ligand are vital to the catalytic performance and properties of the polyethylene.<sup>[3a,5,6]</sup> In particular, the degree of steric hindrance exerted by the *N*-aryl *ortho*-substituents is known to impact on the molecular weight of the polymer by suppressing chain termination in the case of more bulky derivatives.<sup>[4a,b,5b,f,6b-g]</sup> However, it is important to emphasize that too much steric bulk can hamper productivity by impeding ethylene coordination and more than likely the level of chain walking leading to polymer branching.<sup>[4,6c-d,g,7]</sup> Hence, there can be considered a fine balance between the level of steric hindrance and good catalytic performance along with desirable polymer properties.

As part of an on-going program, our group and others have been interested in nickel catalysts bearing 1,2-bis(arylimino)acenaphthenes and have demonstrated a variety of beneficial effects on ethylene polymerization by introducing *N*-aryl groups appended with sterically encumbered benzhydryl (CHPh<sub>2</sub>)<sup>[5a-g,6b-g,8]</sup> and its substituted derivatives (*e.g.*, (4-FPh)<sub>2</sub>CH).<sup>[6f,9]</sup> In particular, our efforts have been focused on unsymmetrical examples in which the benzhydryl substitution is limited to one *N*-aryl group while the other can be systematically varied.<sup>[9,10]</sup> For example, the 2,6-(CHPh<sub>2</sub>)<sub>2</sub>-substituted precatalysts of type **A** (Figure 1) are highly active and form polymers displaying high to ultra-high molecular weights ( $> 1 \times 10^6$  g mol<sup>-1</sup>) and a range of branching contents that can be influenced by the nature of the *para*-R group (*e.g.*, NO<sub>2</sub>, *t*-Bu).<sup>[4b,6b]</sup> On the other hand, the 2,4-

(CHPh<sub>2</sub>)<sub>2</sub>-substituted systems **B** (Figure 1), exhibited good thermal stability while the degree of branching was less but affected by the *ortho*-R group (Me vs. Cl) with the Cl derivative generating relatively more branches per 1000 Cs.<sup>[10c,11]</sup> Interestingly, the remote fluorenyl derivative **C** (Figure 1), in which the two phenyl groups of a benzhydryl have been effectively tethered, gives rise to higher productivity, relatively high molecular weight and lower branching contents, highlighting the indirect influence of a large *para*-substituent.<sup>[12]</sup>

< Figure 1 >

In this paper we report the use of a dibenzocycloheptyl group as an alternative sterically bulky *ortho*-substituent. In particular, we disclose a series of unsymmetrical 1,2-bis(imino)acenaphthene-nickel(II) halides complexes (**D**, Figure 1), in which one N-2,4-(dibenzocycloheptyl)-6-methylphenyl group remains fixed while the second aryl group can be modified in terms of its steric and electronic properties. We reasoned that the tethered phenyl groups in the *ortho*-dibenzocycloheptyl unit would lead to a more rigid bulky substituent when compared to its more flexible benzhydryl counterpart; the presence of a remote dibenzocycloheptyl substituent serves as an additional point of interest. A detailed catalytic evaluation of bromide and chloride examples of **D** is then undertaken to determine how the structural features of the precatalyst, type of co-catalyst, temperature and run time, influence catalyst activity as well as the polymer molecular weight, dispersity and branching; comparisons with **A** – **C** are also developed. Full details of the synthetic protocols employed for ligand synthesis and complexation are also described.

## 2 EXPERIMENTAL

### 2.1 General Considerations

All manipulations of moisture and/or air sensitive compounds were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. All the solvents prior to use were heated to reflux and distilled under a nitrogen atmosphere. Methylaluminoxane (MAO, 1.46 M in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane) were purchased from Akzo Nobel Corp while diethylaluminum chloride (Et<sub>2</sub>AlCl, 0.79 M in toluene) and ethylaluminum sesquichloride [EASC (Et<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>, 0.87 M in toluene)] were purchased from Acros Chemicals. High purity ethylene was purchased from Beijing Yanshan Petrochemical Co. and used as received. All other reagents were purchased from Aldrich, Acros or local suppliers. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the free ligands, complexes and precursors were recorded on Bruker DMX (400 MHz or 600 MHz instrument) at ambient temperature using TMS as an internal standard; the  $\delta$  values are given in ppm and *J* values in Hz. The FT-IR spectra were recorded on a Perkin Elmer System 2000 FT-IR

spectrometer and elemental analysis were performed using a Flash EA 1112 microanalyzer. The molecular weight ( $M_w$ ) and molecular weight distribution ( $M_w/M_n$ ) of the polyethylene were determined using PL-GPC220 at instrument at 150 °C using 1,2,4-trichlorobenzene as a solvent. The melt temperatures of the polyethylenes were obtained using differential scanning calorimetry (DSC, TA2000) under a nitrogen atmosphere. Typically, the polyethylene sample (4.5 – 5.5 mg) was heated up to 150 °C at a heating rate of 20 °C per minute for 5 minutes at the same temperature to remove its thermal history and then cooled to -20 °C at the same heating rate. For the  $^{13}\text{C}$  NMR spectra of the polyethylenes, a weighed amount of polyethylene (80 - 100 mg) was combined with 1,1,2,2-tetrachloroethane- $d_2$  (2 mL) with TMS as an internal standard. Inverse gated  $^{13}\text{C}$  spectra recorded on a Bruker DMX 300 spectrometer at 75.47 MHz in 5 mm standard glass tubes at 100 °C with the number of scans between 3537 and 4352. Operating conditions used: spectral width 17986 kHz; acquisition time 1.8 s; relaxation delay 2.0 s; pulse width 15.5  $\mu\text{s}$ . An estimation of the branching content was made by integration of the corresponding peaks in the  $^{13}\text{C}$  NMR spectra using approaches described in the literature.<sup>[13]</sup> The procedure for the synthesis of bis(dibenzocycloheptyl)-6-methylaniline is given in the supporting information.

## 2.2 Synthesis and characterization

### 2.2.1 Synthesis of 2-((2,4-bis(dibenzocycloheptyl)-6-methylphenylimino)acenaphthylen-1-one.

2,4-Bis(dibenzocycloheptyl)-6-methylaniline (8.10 g, 16.50 mmol), acenaphthalen-1,2-dione (3.01 g, 16.50 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.47 g, 15 mol%) were added to a mixture of dichloromethane (200 mL) and ethanol (50 mL). The reaction mixture was stirred for 24 h at room temperature. After completion of the reaction, all volatiles were removed under reduced pressure. The resulting solid was recrystallized from dichloromethane and ethanol to afford the product as a purple solid (8.40 g, 78%). Mp: 224 – 226 °C. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3060 (w), 3015 (w), 2920 (w), 2889 (w), 2863 (w), 2829 (w), 1727 ( $\nu(\text{C}=\text{O})$ , m), 1651 ( $\nu(\text{C}=\text{N})$ , m), 1601 (m), 1490 (m), 1490 (m), 1431 (m), 1360 (w), 1305 (w), 1274 (m), 1225 (m), 1170 (w), 1130 (w), 1150 (w), 1016 (m), 945 (w), 941 (w), 908 (m), 880 (w), 829 (m), 800 (w), 752 (s), 712 (m), 653 (w).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  8.04 (d,  $J = 7.6$  Hz, 2H, An-H), 7.83 (d,  $J = 8.0$  Hz, 1H, An-H), 7.72 (t,  $J = 7.4$  Hz, 1H, An-H), 7.28–7.02 (m, 13H, Ar-H), 6.75 (d,  $J = 5.6$  Hz, 1H, Ar-H), 6.66 (s, 1H, Ar- $H_m$ ), 6.50 (s, 1H, Ar- $H_m$ ), 6.41 (d,  $J = 6.8$  Hz, 1H, Ar-H), 6.12 (t,  $J = 7.4$  Hz, 1H, Ar-H), 6.01 (d,  $J = 7.6$  Hz, 1H, An-H), 5.80 (t,  $J = 7.4$  Hz, 1H An-H), 5.16 (d,  $J = 3.6$  Hz, 2H, -CH-), 3.15–3.01 (m, 4H, -CH<sub>2</sub>-), 2.67–2.50 (m, 4H, -CH<sub>2</sub>-), 1.88 (s, 3H, -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  190.1,

162.2, 145.8, 142.6, 141.5, 141.5, 140.1, 140.0, 139.8, 139.5, 139.4, 138.9, 137.6, 131.7, 131.4, 131.2, 131.1, 131.0, 130.9, 130.7, 130.2, 129.1, 129.0, 128.8, 127.9, 127.8, 127.2, 127.2, 127.0, 126.5, 126.1, 126.0, 125.9, 125.2, 125.2, 124.2, 121.8, 121.5, 57.7, 56.1, 32.7, 31.8, 29.9, 17.7.

### 2.2.2 Synthesis of 1-[2,4- $\{(C_{15}H_{13})_2$ -6-MeC<sub>6</sub>H<sub>2</sub>N]-2-(ArN)C<sub>2</sub>C<sub>10</sub>H<sub>6</sub>

(a) Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**L1**). To a mixture of 2-((2,4-bis(dibenzocycloheptyl)-6-methylphenylimino)acenaphthylen-1-one (1.01 g, 1.54 mmol) and catalytic amount of *p*-toluenesulfonic acid (0.04 g, 15 mol%) in dry toluene (30 mL) was added dropwise 2,6-dimethylaniline (0.186 g, 1.54 mmol). The mixture was stirred and heated to reflux for 14 h using a Dean-Stark trap. On cooling to room temperature, all the volatiles were removed under reduced pressure and the residue purified by alumina (basic) column chromatography with petroleum ether/ethyl acetate (25:1) as the eluent to afford **L1** as an orange powder (0.30 g 26%). Mp: 224 – 226 °C. FT-IR (KBr, cm<sup>-1</sup>): 3050 (w), 3016 (w), 2951 (w), 2920 (w), 2885 (w), 2835 (w), 1660 (ν(C=N), m), 1635 (ν(C=N), m), 1591 (m), 1493 (m), 1463 (m), 1431 (m), 1378 (w), 1356 (w), 1302 (w), 1276 (w), 1254 (w), 1230 (w), 1204 (w), 1157 (w), 1130 (w), 1098 (w), 1040 (w), 948 (w), 922 (w), 880 (w), 848 (w), 828 (w), 778 (m), 773 (m), 766 (s), 705 (w), 676 (w), 656 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.76 (d, *J* = 8.3 Hz, 1H, An-H), 7.69 (d, *J* = 8.2 Hz, 1H, An-H), 7.32 – 7.03 (m, 17H, An/Ar-H), 6.78 (t, *J* = 4.0 Hz, 1H, Ar-H), 6.65 (s, 1H, Ar-H<sub>m</sub>), 6.62 (d, *J* = 7.1 Hz, 1H, Ar-H<sub>m</sub>), 6.56 (s, 1H, Ar-H<sub>m</sub>), 6.34 (d, *J* = 7.1 Hz, 1H, Ar-H<sub>m</sub>), 6.17 (d, *J* = 7.3 Hz, 1H, Ar-H), 6.05 (t, *J* = 7.4 Hz, 1H Ar-H), 5.86 (t, *J* = 7.4 Hz, 1H Ar-H), 5.33 (s, 1H, -CH-), 5.19 (s, 1H, -CH-), 3.22–2.21 (m, 2H, -CH<sub>2</sub>-), 3.14–3.10 (m, 2H, -CH<sub>2</sub>-), 2.86–2.83 (m, 2H, -CH<sub>2</sub>-). 2.61–2.53 (m, 2H, -CH<sub>2</sub>-), 2.46 (s, 3H, -CH<sub>3</sub>), 2.02 (s, 3H, -CH<sub>3</sub>), 1.90 (s, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 163.3, 161.6, 149.3, 146.5, 141.8, 141.4, 140.5, 140.3, 139.9, 139.5, 139.2, 139.1, 137.9, 131.7, 131.4, 131.1, 131.0, 130.9, 130.3, 130.2, 129.4, 129.3, 129.2, 128.6, 128.4, 128.3, 128.2, 127.8, 127.3, 127.1, 127.0, 126.9, 126.4, 125.3, 125.2, 124.6, 124.5, 124.4, 123.7, 121.9, 57.7, 56.2, 32.9, 32.7, 31.8, 30.0, 18.0, 17.8, 17.7. Anal. calcd for C<sub>57</sub>H<sub>46</sub>N<sub>2</sub> (759.00): C, 90.20; H, 6.11; N, 3.69. Found: C, 90.15; H, 6.14; N, 3.65%.

(b) Ar = 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**L2**). Using a similar procedure and molar ratios to that described for the synthesis of **L1**, **L2** was isolated as an orange powder (0.47 g, 39%). Mp: 213 – 215 °C. FT-IR (KBr, cm<sup>-1</sup>): 3053 (w), 3015 (w), 2963 (w), 2921 (w), 2883 (w), 2838 (w), 1657 (ν(C=N), m), 1635 (ν(C=N), w), 1591 (m), 1492 (m), 1464 (m), 1437 (m), 157 (w), 1335 (w), 1307 (w), 1275 (w), 1234

(w), 1196 (w), 1156 (w), 1133 (w), 1101 (w), 1044 (w), 1025 (w), 971 (w), 927 (w), 878 (w), 846 (w), 722 (m), 747 (s), 707 (m), 676 (w).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  7.75 (d,  $J = 8.4$  Hz, 1H, An-H), 7.68 (d,  $J = 8.4$  Hz, 1H, An-H), 7.30 – 7.04 (m, 17H, An/Ar-H), 6.79 (t,  $J = 4.2$  Hz, 1H, Ar-H), 6.65 (s, 1H, Ar- $H_m$ ), 6.61 (d,  $J = 6.8$  Hz, 1H, Ar- $H_m$ ), 6.57 (s, 1H, Ar- $H_m$ ), 6.34 (d,  $J = 7.2$  Hz, 1H, Ar- $H_m$ ), 6.20 (d,  $J = 7.2$  Hz, 1H, Ar-H), 6.06 (t,  $J = 7.4$  Hz, 1H, Ar-H), 5.88 (t,  $J = 7.4$  Hz, 1H, Ar-H), 5.36 (s, 1H, -CH-), 5.20 (s, 1H, -CH-), 3.27–3.21 (m, 1H, -CH<sub>2</sub>-), 3.18–3.04 (m, 2H, -CH<sub>2</sub>-), 2.99–2.88 (m, 1H, -CH<sub>2</sub>-), 2.86–2.80 (m, 1H, -CH<sub>2</sub>-), 2.76–2.71 (m, 1H, -CH<sub>2</sub>-), 2.69–2.52 (m, 2H, -CH<sub>2</sub>-), 2.50–2.42 (m, 1H, -CH<sub>2</sub>-), 2.37–2.29 (m, 1H, -CH<sub>2</sub>-), 2.05–2.01 (m, 1H, -CH<sub>2</sub>-), 1.89 (s, 3H, -CH<sub>3</sub>), 1.37 (t,  $J = 7.4$  Hz, 3H, -CH<sub>2</sub>CH<sub>3</sub>), 1.03 (t,  $J = 7.4$  Hz, 3H, -CH<sub>2</sub>CH<sub>3</sub>).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  163.3, 161.2, 148.5, 146.6, 141.4, 140.5, 140.3, 139.9, 139.5, 139.5, 139.2, 139.1, 137.9, 131.7, 131.4, 131.2, 131.1, 131.0, 130.9, 130.8, 130.1, 130.3, 130.2, 129.4, 129.3, 129.2, 129.2, 128.6, 128.4, 128.3, 127.6, 127.4, 127.1, 127.0, 126.9, 126.6, 126.4, 126.0, 125.4, 124.6, 124.3, 124.0, 122.4, 122.0, 57.7, 56.1, 32.9, 32.7, 31.7, 30.0, 24.8, 24.4, 17.7, 13.7. Anal. calcd for  $\text{C}_{59}\text{H}_{50}\text{N}_2$  (787.04): C, 90.04; H, 6.40; N, 3.56. Found: C, 89.94; H, 6.50; N, 3.53%.

(c) Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**L3**). Using a similar procedure and molar ratios to that described for the synthesis of **L1**, **L3** was isolated as an orange powder (0.42 g, 32%). Mp: 212 – 214 °C. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3059 (w), 3013 (w), 2958 (w), 2925 (w), 2871 (w), 1668 ( $\nu(\text{C}=\text{N})$ , m), 1640 ( $\nu(\text{C}=\text{N})$ , m), 1592 (m), 1490 (m), 1462 (m), 1229 (m), 1382 (w), 1276 (w), 1250 (w), 1231 (w), 1201 (w), 1160 (w), 1132 (w), 1197 (w), 1040 (w), 976 (w), 924 (m), 879 (w), 828 (w), 750 (s), 706 (m), 660 (w).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  7.75 (d,  $J = 8.0$  Hz, 1H, An-H), 7.68 (d,  $J = 8.4$  Hz, 1H, An-H), 7.35 – 7.04 (m, 17H, An/Ar-H), 6.80 (t,  $J = 4.0$  Hz, 1H, Ar-H), 6.65 (s, 1H, Ar- $H_m$ ), 6.61 (d,  $J = 7.2$  Hz, 1H, Ar- $H_m$ ), 6.57 (s, 1H, Ar- $H_m$ ), 6.33 (d,  $J = 7.2$  Hz, 1H, Ar- $H_m$ ), 6.24 (d,  $J = 7.6$  Hz, 1H, Ar-H), 6.02 (t,  $J = 7.4$  Hz, 1H, Ar-H), 5.90 (t,  $J = 7.2$  Hz, 1H, Ar-H), 5.37 (s, 1H, -CH-), 5.19 (s, 1H, -CH-), 3.41–3.23 (m, 2H, -CH<sub>2</sub>-), 3.15–3.03 (m, 2H, -CH<sub>2</sub>-), 3.91–2.79 (m, 2H, -CH<sub>2</sub>-), 2.71–2.63 (m, 2H, -CH<sub>2</sub>-), 2.60–2.50 (m, 1H, -CH-), 2.07–2.04 (m, 1H, -CH-), 1.87 (s, 3H, -CH<sub>3</sub>), 1.40 (d,  $J = 6.8$  Hz, 3H, -CH<sub>3</sub>), 1.25 (d,  $J = 6.8$  Hz, 3H, -CH<sub>3</sub>), 1.18 (d,  $J = 6.8$  Hz, 3H, -CH<sub>3</sub>), 0.83 (d,  $J = 6.8$  Hz, 3H, -CH<sub>3</sub>).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  163.2, 161.6, 147.2, 146.5, 141.9, 141.4, 140.7, 140.4, 139.9, 139.5, 139.5, 139.1, 137.9, 135.6, 135.4, 131.7, 131.4, 13.2, 131.1, 131.0, 130.7, 130.3, 129.4, 129.2, 128.6, 128.5, 128.2, 127.4, 127.1, 127.0, 126.9, 126.4, 126.1, 126.0, 125.4, 124.5, 124.3, 124.2, 123.6, 123.2, 122.7, 122.0, 57.7, 56.1, 33.0, 32.7, 31.7, 30.1, 28.6, 28.5, 23.7,

23.1, 22.9, 17.6. Anal. calcd for C<sub>61</sub>H<sub>54</sub>N<sub>2</sub> (815.10): C, 89.89; H, 6.68; N, 3.44. Found: C, 89.67; H, 6.76; N, 3.40%.

(d) Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**L4**). Using a similar procedure and molar ratios to that described for the synthesis of **L1**, **L4** was isolated as an orange powder (0.42 g, 35%). Mp: 216 – 218 °C. FT-IR (KBr, cm<sup>-1</sup>): 3055 (w), 3018 (w), 2929 (w), 2833 (w), 1675 (ν(C=N), m), 1651 (ν(C=N), m), 1598 (w), 1572 (w), 1489 (m), 1468 (m), 1430 (m), 1378 (w), 1357 (w), 1308 (w), 1276 (w), 1232 (m), 1208 (w), 1158 (w), 1099 (w), 1038 (m), 974 (w), 950 (w), 923 (w), 886 (w), 848 (w), 827 (w), 804 (w), 758 (s), 707 (m), 660 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.75 (d, *J* = 8.3 Hz, 1H, An-H), 7.68 (d, *J* = 8.2 Hz, 1H, An-H), 7.31–7.04 (m, 14H, An/Ar-H), 7.03 (s, 1H, Ar-H<sub>m</sub>), 6.95 (s, 1H, Ar-H<sub>m</sub>), 6.78 (t, *J* = 4.4 Hz, 1H, Ar-H), 6.68 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.64 (s, 1H, Ar-H<sub>m</sub>), 6.55 (s, 1H, Ar-H<sub>m</sub>), 6.34 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.17 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.04 (t, *J* = 7.4 Hz, 1H, Ar-H), 5.86 (t, *J* = 7.4 Hz, 1H, Ar-H), 5.32 (s, 1H, -CH-), 5.18 (s, 1H, -CH-), 3.24–2.05 (m, 4H, -CH<sub>2</sub>-), 2.87–2.79 (m, 2H, -CH<sub>2</sub>-), 2.60–2.48 (m, 2H, -CH<sub>2</sub>-), 2.42 (s, 3H, -CH<sub>3</sub>), 2.39 (s, 3H, -CH<sub>3</sub>), 1.98 (s, 3H, -CH<sub>3</sub>), 1.89 (s, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 163.4, 161.7, 146.7, 146.5, 141.8, 141.4, 140.4, 140.2, 139.9, 139.5, 139.2, 139.1, 137.9, 132.9, 131.7, 131.4, 131.2, 131.1, 131.0, 130.9, 130.3, 130.2, 129.4, 129.3, 129.1, 128.9, 128.5, 128.2, 127.7, 127.3, 127.1, 127.0, 126.9, 126.4, 126.1, 126.0, 125.2, 125.0, 124.5, 124.4, 122.0, 121.9, 57.7, 56.2, 32.9, 32.7, 31.7, 30.0, 20.9, 18.0, 17.7. Anal. calcd for C<sub>61</sub>H<sub>54</sub>N<sub>2</sub> (773.02): C, 90.12; H, 6.26; N, 3.62. Found: C, 89.72; H, 6.30; N, 3.51%.

(e) Ar = 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub> (**L5**). Using a similar procedure and molar ratios to that described for the synthesis of **L1**, **L5** was isolated as an orange powder (0.33 g, 28%). Mp: 210 – 212 °C. FT-IR (KBr, cm<sup>-1</sup>): 3057 (w), 3015 (w), 2927 (w), 2871 (w), 1669 (ν(C=N), w), 1638 (ν(C=N), w), 1595 (w), 1489 (m), 1455 (m), 1435 (m), 1273 (w), 1229 (w), 1207 (w), 1156 (w), 1135 (w), 1099 (w), 1037 (w), 972 (w), 920 (m), 859 (w), 830 (m), 780 (m), 748 (s), 705 (w). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.74 (d, *J* = 8.4 Hz, 1H, An-H), 7.68 (d, *J* = 8.0 Hz, 1H, An-H), 7.32–7.03 (m, 15H, An/Ar-H), 6.98 (s, 1H, Ar-H<sub>m</sub>), 6.78 (t, *J* = 4.4 Hz, 1H, Ar-H), 6.71 (d, *J* = 6.8 Hz, 1H, Ar-H), 6.64 (s, 1H, Ar-H<sub>m</sub>), 6.56 (s, 1H, Ar-H<sub>m</sub>), 6.32 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.19 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.04 (t, *J* = 7.4 Hz, 1H, Ar-H), 5.87 (t, *J* = 7.4 Hz, 1H, Ar-H), 5.35 (s, 1H, -CH-), 5.19 (s, 1H, -CH-), 3.27–3.04 (m, 2H, -CH<sub>2</sub>-), 2.95–2.79 (m, 2H, -CH<sub>2</sub>-), 2.71–2.61 (m, 2H, -CH<sub>2</sub>-), 2.58–2.45 (m, 2H, -CH<sub>2</sub>-), 2.43 (s, 3H, -CH<sub>3</sub>), 2.40–2.25 (m, 2H, -CH<sub>2</sub>-), 2.05–1.79 (m, 2H, -CH<sub>2</sub>-), 1.88 (s, 3H,

–CH<sub>3</sub>), 1.34 (t,  $J = 7.6$  Hz, 3H, –CH<sub>2</sub>CH<sub>3</sub>), 1.01 (t,  $J = 7.4$  Hz, 3H, –CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  163.4, 161.6, 146.6, 145.9, 141.8, 141.4, 140.5, 140.2, 139.9, 139.5, 139.1, 137.9, 131.7, 131.4, 131.1, 131.0, 130.9, 130.7, 130.4, 130.2, 129.4, 129.3, 128.4, 128.3, 128.2, 127.6, 127.3, 127.2, 126.9, 126.7, 126.4, 126.1, 126.0, 125.8, 125.3, 124.5, 124.3, 122.4, 121.9, 57.7, 56.1, 32.9, 32.7, 31.7, 30.0, 24.8, 24.4, 21.2, 17.7, 14.3, 13.7. Anal. calcd for C<sub>61</sub>H<sub>54</sub>N<sub>2</sub> (801.07): C, 89.96; H, 6.54; N, 3.50. Found: C, 89.78; H, 6.64; N, 3.47%.

### 2.2.3 Synthesis of [1-[2,4-{(C<sub>15</sub>H<sub>13</sub>)<sub>2</sub>-6-MeC<sub>6</sub>H<sub>2</sub>N]-2-(ArN)C<sub>2</sub>C<sub>10</sub>H<sub>6</sub>]NiBr<sub>2</sub>

(a) Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**Ni1**). **L1** (0.20 g, 0.26 mmol) and (DME)NiBr<sub>2</sub> (0.08 g, 0.26 mmol) were combined in a mixture of dichloromethane (10 mL) and ethanol (10 mL) and stirred under an atmosphere of nitrogen at room temperature. After 12 h all the volatiles were evaporated under reduced pressure. An excess of diethyl ether was added to the residue to induce precipitation. The precipitate was filtered and washed with diethyl ether (3 × 15 mL) to afford **Ni1** as a dark red solid (0.23 g, 92%). FT-IR (KBr, cm<sup>-1</sup>): 3057 (w), 3021 (w), 2932 (w), 2872 (w), 1656 (ν(C=N), w), 1626 (ν(C=N), m), 1585 (m), 1489 (m), 1463 (m), 1425 (m), 1379 (w), 1356 (w), 1292 (m), 1223 (w), 1187 (w), 1160 (w), 1132 (w), 1104 (w), 1041 (w), 952 (w), 920 (w), 888 (w), 848 (w), 829 (w), 762 (s), 709 (m), 653 (w). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, TMS):  $\delta$  56.45 (1H, –CH–), 28.78 (3H, –CH<sub>3</sub>), 27.22 (3H, –CH<sub>3</sub>), 26.78 (3H, –CH<sub>3</sub>), 25.55 (1H, An–H), 25.13 (1H, Ar–H<sub>m</sub>), 25.06 (1H, Ar–H<sub>m</sub>), 23.80 (1H, Ar–H<sub>m</sub>), 23.13 (1H, An–H), 22.38 (1H, Ar–H<sub>m</sub>), 17.06 (1H, An–H), 16.46 (1H, An–H), 8.56 (1H, Ar–H), 8.45 (1H, –CH–), 8.05 (1H, Ar–H), 7.91 (1H, Ar–H), 7.73–7.66 (4H, –CH<sub>2</sub>–), 7.17 (1H, –CH<sub>2</sub>–), 6.97 (2H, –CH<sub>2</sub>–), 6.87 (1H, –CH<sub>2</sub>–), 6.20 (1H, Ar–H), 5.88 (1H, Ar–H), 5.77 (1H, Ar–H), 5.59 (1H, An–H), 5.46 (1H, Ar–H), 4.90 (1H, An–H), 4.69 (2H, Ar–H), 4.35 (1H, Ar–H), 3.57 (1H, Ar–H), 3.43 (1H, Ar–H), 3.31 (1H, Ar–H), 3.13 (1H, Ar–H), 2.59 (1H, Ar–H), 1.14 (1H, Ar–H), –16.60 (1H, Ar–H<sub>p</sub>). Anal. calcd for C<sub>57</sub>H<sub>46</sub>Br<sub>2</sub>N<sub>2</sub>Ni·H<sub>2</sub>O (995.51): C, 68.77; H, 4.86; N, 2.81. Found: C, 68.48; H, 4.76; N, 2.82%.

(b) Ar = 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**Ni2**). Using a similar procedure and molar ratios to that described for the synthesis of **Ni1**, **Ni2** was isolated as a dark red solid (0.24 g, 92%). FT-IR (KBr, cm<sup>-1</sup>): 3057 (w), 3017 (w), 2967 (w), 2933 (w), 2874 (w), 1653 (ν(C=N), w), 1624 (ν(C=N), m), 1583 (m), 1490 (m), 1461 (m), 1427 (m), 1379 (w), 1356 (w), 1293 (w), 1243 (w), 1224 (w), 1187 (w), 1161 (w), 1133 (w), 1106 (w), 1045 (w), 954 (w), 918 (w), 882 (w), 849 (w), 829 (m), 759 (s), 711 (m), 654 (w). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, TMS):  $\delta$  56.51 (1H, –CH–), 30.21 (1H, –CH<sub>2</sub>CH<sub>3</sub>), 28.51 (1H, –CH<sub>2</sub>CH<sub>3</sub>),

26.97 (3H, -CH<sub>3</sub>), 25.73 (1H, -CH<sub>2</sub>CH<sub>3</sub>), 25.02 (1H, -CH<sub>2</sub>CH<sub>3</sub>), 24.46 (1H, An-H), 23.68 (1H, Ar-H<sub>m</sub>), 23.32 (1H, Ar-H<sub>m</sub>), 22.52 (1H, Ar-H<sub>m</sub>), 16.96 (1H, An-H), 16.45 (1H, An-H), 8.54 (1H, Ar-H), 8.47 (1H, -CH-), 8.07 (1H, Ar-H<sub>m</sub>), 7.93 (1H, An-H), 7.75–7.65 (4H, -CH<sub>2</sub>-), 7.17 (1H, -CH<sub>2</sub>-), 7.22 (1H, An-H), 7.10–6.94 (4H, -CH<sub>2</sub>-), 6.45 (1H, Ar-H), 6.05 (1H, Ar-H), 5.84 (1H, Ar-H), 5.67 (1H, An-H), 5.47 (1H, Ar-H), 4.96 (1H, Ar-H), 4.75–4.72 (2H, Ar-H), 4.38 (1H, Ar-H), 3.51–3.29 (3H, Ar-H), 2.72 (1H, Ar-H), 1.26 (1H, Ar-H), 0.73 (3H, -CH<sub>2</sub>CH<sub>3</sub>), 0.08 (1H, Ar-H), -0.20 (3H, -CH<sub>2</sub>CH<sub>3</sub>), -16.29 (1H, Ar-H<sub>p</sub>). Anal. calcd for C<sub>59</sub>H<sub>50</sub>Br<sub>2</sub>N<sub>2</sub>Ni·H<sub>2</sub>O (1023.56): C, 69.23; H, 5.12; N, 2.74. Found: C, 68.96; H, 5.05; N, 2.78%.

(c) Ar = 2,6-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**Ni3**). Using a similar procedure and molar ratios to that described for the synthesis of **Ni1**, **Ni3** was isolated as a dark red solid (0.26 g, 96%). FT-IR (KBr, cm<sup>-1</sup>): 3057 (w), 3015 (w), 2965 (w), 2928 (w), 2869 (w), 1651 (ν(C=N), w), 1623 (ν(C=N), m), 1581 (m), 1491 (m), 1428 (m), 1383 (m), 1358 (w), 1325 (w), 1294 (m), 1245 (w), 1226 (w), 1184 (w), 1157 (w), 1133 (w), 1105 (w), 1048 (m), 943 (w), 879 (w), 831 (m), 806 (w), 755 (s), 710 (m), 654 (w). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, TMS): δ 57.18 (1H, -CH-), 27.82 (3H, -CH<sub>3</sub>), 25.32 (2H, -CH(CH<sub>3</sub>)<sub>2</sub>), 23.87–23.64 (3H, An-H), 23.35 (1H, Ar-H<sub>m</sub>), 17.23 (1H, An-H), 16.53 (1H, An-H), 8.56 (1H, Ar-H), 8.49 (1H, -CH-), 8.12 (1H, Ar-H<sub>m</sub>), 7.94 (1H, Ar-H<sub>m</sub>), 7.75–7.68 (5H, -CH<sub>2</sub>-), 7.35 (1H, Ar-H<sub>m</sub>), 7.25 (1H, -CH<sub>2</sub>-), 7.03 (1H, -CH<sub>2</sub>-), 6.96 (1H, -CH<sub>2</sub>-), 6.60 (1H, Ar-H), 6.23 (1H, Ar-H), 5.82 (1H, An-H), 5.60–5.53 (3H, Ar-H), 5.01 (1H, Ar-H), 4.88 (1H, Ar-H), 4.76 (1H, Ar-H), 4.45 (1H, Ar-H), 3.70–3.43 (5H, Ar-H), 2.90 (1H, Ar-H), 2.02 (3H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.57 (3H, -CH(CH<sub>3</sub>)<sub>2</sub>), 1.40 (3H, -CH(CH<sub>3</sub>)<sub>2</sub>), 0.76 (3H, -CH(CH<sub>3</sub>)<sub>2</sub>), -15.56 (1H, Ar-H<sub>p</sub>). Anal. calcd for C<sub>61</sub>H<sub>54</sub>Br<sub>2</sub>N<sub>2</sub>Ni·H<sub>2</sub>O (1051.61): C, 69.67; H, 5.37; N, 2.66. Found: C, 69.83; H, 5.38; N, 2.73%.

(d) Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**Ni4**). Using a similar procedure and molar ratios to that described for the synthesis of **Ni1**, **Ni4** was isolated as a dark red solid (0.24 g, 92%). FT-IR (KBr, cm<sup>-1</sup>): 3058 (w), 3016 (w), 2930 (w), 2872 (w), 1655 (ν(C=N), w), 1626 (ν(C=N), m), 1586 (m), 1489 (m), 1451 (m), 1426 (m), 1380 (w), 1357 (w), 1293 (w), 1241 (w), 1208 (w), 1188 (w), 1160 (w), 1133 (w), 1099 (w), 1041 (w), 948 (w), 921 (w), 884 (w), 853 (w), 828 (m), 801 (w), 765 (s), 709 (m), 655 (w). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, TMS): δ 56.19 (1H, -CH-), 33.95 (3H, Ar-*p*-CH<sub>3</sub>), 28.62 (3H, -CH<sub>3</sub>), 26.79 (6H, -CH<sub>3</sub>), 24.95 (1H, Ar-H<sub>m</sub>), 24.86 (1H, Ar-H<sub>m</sub>), 24.58 (1H, An-H), 24.15 (1H, Ar-H<sub>m</sub>), 22.86 (1H, An-H), 21.90 (1H, Ar-H<sub>m</sub>), 16.85 (1H, An-H), 16.23 (1H, An-H), 8.67 (1H, Ar-H), 8.44 (1H, -CH-), 8.12 (1H, Ar-H), 7.91 (1H, An-H), 7.65 (5H, -CH<sub>2</sub>-), 7.16 (1H, An-H), 6.92–6.82

(3H,  $-\text{CH}_2-$ ), 6.25 (1H, Ar-H), 5.97 (1H, Ar-H), 5.70 (1H, Ar-H), 5.33 (1H, Ar-H), 4.90 (1H, Ar-H), 4.68 (3H, Ar-H), 4.34 (1H, Ar-H), 3.63 (1H, Ar-H), 3.23 (1H, Ar-H), 2.45 (1H, Ar-H), 1.24 (1H, Ar-H), 1.09 (1H, Ar-H). Anal. calcd for  $\text{C}_{58}\text{H}_{48}\text{Br}_2\text{N}_2\text{Ni}\cdot 3\text{H}_2\text{O}$  (1045.56): C, 66.63; H, 5.21; N, 2.68. Found: C, 66.95; H, 4.87; N, 2.76%.

(e) Ar = 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub> (**Ni5**). Using a similar procedure and molar ratios to that described for the synthesis of **Ni1**, **Ni5** was isolated as a dark red solid (0.23 g, 85%). FT-IR (KBr,  $\text{cm}^{-1}$ ): 3055 (w), 3014 (w), 2967 (w), 2928 (w), 2874 (w), 2833 (w), 1653 ( $\nu(\text{C}=\text{N})$ , w), 1625 ( $\nu(\text{C}=\text{N})$ , m), 1582 (m), 1490 (m), 1449 (m), 1423 (m), 1380 (w), 1356 (w), 1295 (m), 1230 (w), 1202 (w), 1159 (w), 1133 (w), 1098 (w), 1045 (w), 959 (w), 920 (w), 884 (w), 859 (m), 829 (m), 795 (w), 757 (s), 711 (m), 656 (w). <sup>1</sup>H NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ , TMS):  $\delta$  56.36 (1H,  $-\text{CH}-$ ), 33.90 (3H, Ar-*p*-CH<sub>3</sub>), 29.96 (1H,  $-\text{CH}_2\text{CH}_3$ ), 28.39 (1H,  $-\text{CH}_2\text{CH}_3$ ), 26.66 (3H,  $-\text{CH}_3$ ), 25.54 (1H,  $-\text{CH}_2\text{CH}_3$ ), 25.34 (1H, An-H), 24.92 (1H, An-H), 24.23 (1H, Ar-H<sub>m</sub>), 24.11 (1H, Ar-H<sub>m</sub>), 23.24 (1H, Ar-H<sub>m</sub>), 22.22 (1H, Ar-H<sub>m</sub>), 22.02 (1H,  $-\text{CH}_2\text{CH}_3$ ), 16.90 (1H, An-H), 16.42 (1H, An-H), 8.53 (1H,  $-\text{CH}-$ ), 8.47 (1H, Ar-H), 8.07 (1H, Ar-H), 7.92 (1H, An-H), 7.69–7.64 (5H,  $-\text{CH}_2-$ ), 7.22 (1H, An-H), 7.04 (2H,  $-\text{CH}_2-$ ), 6.93 (1H,  $-\text{CH}_2-$ ), 6.51 (1H, Ar-H), 5.94 (1H, Ar-H), 5.62 (1H, Ar-H), 5.41 (1H, Ar-H), 4.96 (1H, Ar-H), 4.69 (1H, Ar-H), 4.35 (1H, Ar-H), 3.57 (1H, Ar-H), 3.36 (1H, Ar-H), 3.22 (1H, Ar-H), 2.67 (1H, Ar-H), 2.02 (1H, Ar-H) 1.26 (3H,  $-\text{CH}_2\text{CH}_3$ ), 0.77 (3H,  $-\text{CH}_2\text{CH}_3$ ), -0.14 (2H, Ar-H). Anal. calcd for  $\text{C}_{60}\text{H}_{52}\text{Br}_2\text{N}_2\text{Ni}\cdot 3\text{H}_2\text{O}$  (1073.62): C, 67.12; H, 5.45; N, 2.61. Found: C, 67.33; H, 5.13; N, 2.73%.

#### 2.2.4 Synthesis of [1-[2,4- $\{(\text{C}_{15}\text{H}_{13})_2$ -6-MeC<sub>6</sub>H<sub>2</sub>N]-2-(ArN)C<sub>2</sub>C<sub>10</sub>H<sub>6</sub>]NiCl<sub>2</sub>

(a) Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**Ni6**). Under a nitrogen atmosphere,  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  (0.06 g, 0.26 mmol) was added to a solution of **L1** (0.20 g, 0.26 mmol) in dichloromethane (10 mL) and ethanol (10 mL) and the reaction mixture stirred at room temperature for 24 h. After removal of the volatiles under reduced pressure, an excess of diethyl ether was added to induce precipitation. The precipitate was filtered, washed with diethyl ether (3 × 15 mL) and dried under reduced pressure to afford **Ni6** as a light orange solid (0.21 g, 91%). FT-IR (KBr,  $\text{cm}^{-1}$ ): 3058 (w), 3016 (w), 2926 (w), 1659 ( $\nu(\text{C}=\text{N})$ , w), 1628 ( $\nu(\text{C}=\text{N})$ , m), 1586 (m), 1490 (w), 1464 (w), 1446 (m), 1426 (m), 1381 (w), 1357 (w), 1295 (w), 1231 (w), 1192 (w), 1160 (w), 1134 (w), 1094 (w), 1043 (w), 953 (w), 920 (w), 887 (w), 830 (w), 765 (s), 709 (w). Anal. calcd for  $\text{C}_{57}\text{H}_{46}\text{Cl}_2\text{N}_2\text{Ni}\cdot 3\text{H}_2\text{O}$  (942.63): C, 72.63; H, 5.56; N, 2.97. Found: C, 72.69; H, 5.17; N, 3.01%.

(b) Ar = 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**Ni7**). Using a similar procedure and molar ratios to that described for the synthesis of **Ni6**, **Ni7** was isolated as a light orange solid (0.21 g, 88%). FT-IR (KBr, cm<sup>-1</sup>): 3059 (w), 3016 (w), 2967 (w), 2928 (w), 2875 (w), 1656 (ν(C=N), w), 1626 (ν(C=N), m), 1585 (m), 1491 (m), 1445 (m), 1427 (m), 1381 (w), 1358 (w), 1296 (m), 1244 (w), 1227 (w), 1190 (w), 1160 (w), 1134 (w), 1099 (w), 1045 (w), 954 (w), 922 (w), 876 (w), 831 (m), 754 (s), 654 (w). Anal. calcd for C<sub>59</sub>H<sub>50</sub>Cl<sub>2</sub>N<sub>2</sub>Ni·3H<sub>2</sub>O (952.67): C, 74.38; H, 5.71; N, 2.94. Found: C, 74.66; H, 5.44; N, 2.99%.

(c) Ar = 2,6-i-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**Ni8**). Using a similar procedure and molar ratios to that described for the synthesis of **Ni6**, **Ni8** was isolated as a light orange solid (0.22 g, 88%). FT-IR (KBr, cm<sup>-1</sup>): 3057 (w), 3014 (w), 2968 (w), 2870 (w), 1658 (ν(C=N), w), 1626 (ν(C=N), m), 1589 (m), 1492 (m), 1465 (m), 1439 (m), 1384 (w), 1359 (w), 1327 (w), 1295 (m), 1246 (w), 1229 (w), 1184 (w), 1159 (w), 1133 (w), 1100 (w), 1049 (m), 953 (w), 879 (w), 833 (m), 807 (w), 757 (s), 711 (w). Anal. calcd for C<sub>61</sub>H<sub>54</sub>Cl<sub>2</sub>N<sub>2</sub>Ni·H<sub>2</sub>O (962.71): C, 76.10; H, 5.86; N, 2.91. Found: C, 75.64; H, 5.76; N, 2.89%.

(d) Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (**Ni9**). Using a similar procedure and molar ratios to that described for the synthesis of **Ni6**, **Ni9** was isolated as a light orange solid (0.20 g, 87%). FT-IR (KBr, cm<sup>-1</sup>): 3058 (w), 3018 (w), 2932 (w), 2871 (w), 1660 (ν(C=N), w), 1629 (ν(C=N), m), 1588 (m), 1488 (m), 1464 (m), 1448 (m), 1426 (m), 1380 (w), 1356 (w), 1294 (w), 1243 (w), 1224 (w), 1188 (w), 1160 (w), 1133 (w), 1101 (w), 1040 (w), 954 (w), 919 (w), 886 (w), 853 (w), 827 (w), 801 (w), 766 (s), 711 (m), 656 (w). Anal. calcd for C<sub>58</sub>H<sub>48</sub>Cl<sub>2</sub>N<sub>2</sub>Ni·3H<sub>2</sub>O (956.66): C, 72.82; H, 5.69; N, 2.93. Found: C, 73.11; H, 5.38; N, 2.90%

(e) Ar = 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub> (**Ni10**). Using a similar procedure and molar ratios to that described for the synthesis of **Ni6**, **Ni10** was isolated as a light orange solid (0.20 g, 83%). FT-IR (KBr, cm<sup>-1</sup>): 3056 (w), 3014 (w), 2968 (w), 2929 (w), 2876 (w), 1656 (ν(C=N), w), 1626 (ν(C=N), m), 1585 (m), 1491 (m), 1450 (m), 1425 (m), 1380 (w), 1357 (w), 1295 (m), 1232 (w), 1204 (w), 1160 (w), 1134 (w), 1099 (w), 1046 (w), 957 (w), 882 (w), 859 (w), 830 (m), 796 (w), 771 (s), 758 (s), 711 (m), 656 (w). Anal. calcd for C<sub>60</sub>H<sub>52</sub>Cl<sub>2</sub>N<sub>2</sub>Ni·2H<sub>2</sub>O (966.70): C, 74.55; H, 5.84; N, 2.90. Found: C, 74.31; H, 5.47; N, 2.92%.

### 2.3 X-Ray Crystallographic Studies

Crystals of **Ni3** and **Ni7** suitable for the single crystal X-ray diffraction studies were grown by the slow diffusion of heptane into dichloromethane solutions of the corresponding complex at room temperature. The X-ray determinations were conducted on Rigaku Saturn 724+ CCD diffractometer with graphite monochromatic Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 173(2) K and the cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and an empirical absorption was applied. The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$ . All hydrogen atoms were placed in calculated positions. The structural solution and refinement were performed by using the Olex2 1.2 package.<sup>[14]</sup> In the structural refinement free solvent molecules, which have no effect on the geometry of the main compound, were squeezed with PLATON software.<sup>[15]</sup> All details of crystal data and structural refinements for **Ni3** and **Ni7** are summarized in Table 1.

< Table 1 >

## 2.4 Typical Ethylene Polymerization Procedure

A typical ethylene polymerization at 10 atm was carried out in a stainless steel autoclave (250 mL) equipped with a pressure control system, temperature controller and mechanical stirrer. The autoclave was evacuated and back-filled three times with nitrogen and once with ethylene. When the required temperature was reached, the precatalyst (2.0  $\mu\text{mol}$ ) dissolved in toluene (25 mL), was injected into the autoclave containing ethylene (*ca.* 1 atm) followed by the addition of more toluene (25 mL). The required amount of co-catalyst ( $\text{Et}_2\text{AlCl}$ , EASC, MAO, or MMAO) and additional toluene were successively added by syringe taking the total volume to 100 mL. The autoclave was immediately pressurized to the pre-determined ethylene pressure and the stirring commenced (400 rpm). After the required reaction time, the reactor was cooled with a water bath and the ethylene pressure vented. Following quenching of the reaction with 10% hydrochloric acid in ethanol, the polymer was collected and washed with ethanol and dried under reduced pressure at 50  $^\circ\text{C}$  and weighed.

## 3 RESULTS AND DISCUSSIONS

### 3.1 Synthesis and Characterization

The nickel(II) halide complexes, [1-[2,4- $\{(\text{C}_{15}\text{H}_{13})_2$ -6-MeC $_6$ H $_2$ N]-2-(ArN)C $_2$ C $_{10}$ H $_6$ ]NiBr $_2$  (Ar = 2,6-Me $_2$ C $_6$ H $_3$  **Ni1**, 2,6-Et $_2$ C $_6$ H $_3$  **Ni2**, 2,6-*i*-Pr $_2$ C $_6$ H $_3$  **Ni3**, 2,4,6-Me $_3$ C $_6$ H $_2$  **Ni4**, 2,6-Et $_2$ -4-MeC $_6$ H $_2$  **Ni5**) and

[1-[2,4- $\{(\text{C}_{15}\text{H}_{13})_2$ -6-MeC<sub>6</sub>H<sub>2</sub>N]-2-(ArN)C<sub>2</sub>C<sub>10</sub>H<sub>6</sub>]NiCl<sub>2</sub> (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Ni6**, 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Ni7**, 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **Ni8**, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> **Ni9**, 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub> **Ni10**), have been synthesized in high yield by the reaction of the corresponding 1,2-bis(imino)acenaphthene (**L1** – **L5**) with either NiBr<sub>2</sub>(DME) (DME = 1,2-dimethoxyethane) or NiCl<sub>2</sub>·6H<sub>2</sub>O, respectively (Scheme 1). All ten complexes have been fully characterized by FT-IR spectroscopy, <sup>1</sup>H NMR spectroscopy, elemental analysis and in the cases of **Ni3** and **Ni7** by single crystal X-ray diffraction.

To form the unsymmetrical 1,2-bis(imino)acenaphthenes, 1-[2,4- $\{(\text{C}_{15}\text{H}_{13})_2$ -6-MeC<sub>6</sub>H<sub>2</sub>N]-2-(ArN)C<sub>2</sub>C<sub>10</sub>H<sub>6</sub> (Ar = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **L1**, 2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **L2**, 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> **L3**, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> **L4**, 2,6-Et<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub> **L5**), three steps were required (Scheme 1). Firstly, 2,4-bis(dibenzocycloheptyl)-6-methylaniline was prepared by the zinc(II) chloride catalyzed Friedel-Crafts alkylation of 2-methylaniline with dibenzocycloheptanol in reasonable yield (see SI).<sup>[6b,16]</sup> This aniline was then condensed with one molar equivalent of acenaphthalen-1,2-dione to give imine-ketone 2-((2,4-bis(dibenzocycloheptyl)-6-methylphenylimino)acenaphthylen-1-one, which could then be used in a second condensation reaction with the corresponding aniline to generate **L1** – **L5**. All new organic compounds have been fully characterized by NMR (<sup>1</sup>H and <sup>13</sup>C) and FT-IR spectroscopy as well as by elemental analysis.

< Scheme 1 >

Single crystals of **Ni3** and **Ni7** suitable for the X-ray determinations were grown by the slow diffusion of heptane into a solution of the corresponding complex in dichloromethane at ambient temperature. Perspective views of each structure are shown Figures 2 and 3; selected bond distances and angles are collected in Table 2. Two independent molecules (A and B) were generated during the structural refinement of **Ni7**, which are essentially the same differing only in the relative disposition of the NiX<sub>2</sub> unit with respect to the acenaphthene plane; only molecule A is displayed in Figure 3 while bond lengths and angles for both are listed in Table 2. The structures of **Ni3** and **Ni7** are similar and are both composed of a single nickel center bound by an unsymmetrical *N,N*-chelating 1,2-bis(arylimino)acenaphthene and two halide ligands resulting in a distorted tetrahedral geometry. The two structures differ in the type of bidentate nitrogen donor ligand, with **L3** bound in **Ni3** and **L2** in **Ni7**, as well as the nature of the halide (Br (**Ni3**), Cl (**Ni7**)). The N(1)–Ni(1)–N(2) bite angles in each complex are comparable at 82.85(14)° (**Ni3**), 82.29(8)<sub>A</sub>°, 82.31(8)<sub>B</sub>°, (**Ni7**) while there is some variation in the X(1)–Ni(1)–X(2) angles [121.62(3)° (**Ni3**), 127.76(9)<sub>A</sub>°, 126.19(4)<sub>B</sub>° (**Ni7**)]. The N-aryl rings are inclined almost perpendicularly with respect to their neighboring imine vectors while the imine bond lengths for both complexes fall in the range 1.272(3) – 1.291(5) Å, which are

quite typical of this functional group.<sup>[6b-g,8,17,18]</sup> Despite the differences in N-aryl groups, the Ni–N distances in each complex show little difference [2.024(4) Å vs. 2.043(4) Å (**Ni3**); 2.0326(18)<sub>A</sub>, 2.0265(17)<sub>B</sub> Å vs. 2.048(2)<sub>A</sub>, 2.0291(19)<sub>B</sub> Å (**Ni7**)]. Within each *ortho*-/*para*-substituted dibenzocycloheptyl group the central seven-membered ring is puckered on account of the three sp<sup>3</sup>-hybridized carbon atoms. There are no intermolecular contacts of note.

< Figure 2 >

< Figure 3 >

< Table 2 >

The <sup>1</sup>H NMR spectra of the nickel complexes, recorded in CD<sub>2</sub>Cl<sub>2</sub> at ambient temperature, display broad and highly shifted resonances as a result of the presence of the paramagnetic nickel(II) center (Figures S3 – S7). Nevertheless, some assignment has been made on the basis of a comparison with related Ni(II) complexes and proximity to the paramagnetic center. Taking **Ni1** as an example, the chemical shifts fall in the range δ 56.45 to -16.0 with the acenaphthene protons being identified as six independent signals at δ 25.55, 23.13, 17.06, 16.46, 5.59 and 4.90 in agreement with the presence of the two inequivalent *N*-aryl groups. A single *para*-aryl proton on the 2,6-dimethylphenyl group can be seen as the most upfield signal at δ -16.0 whilst the most downfield signal at δ 56.45 has been attributed to the CH proton of the *ortho*-substituted dibenzocycloheptyl group, a value that is considerably more downfield shifted than that seen in related benzhydryl-containing nickel complexes.<sup>[4a,4b,5b,6b,6e,f,9,10,11,16]</sup> The FT-IR spectra of **Ni1** – **Ni10** each reveal two ν(C=N)<sub>imine</sub> absorption bands in the range 1660 – 1623 cm<sup>-1</sup> which compares to 1675 – 1635 cm<sup>-1</sup> in the corresponding free ligands. Such shifts toward lower wavenumbers are supportive of the effective coordination between the nickel metal center and imine nitrogen donors.<sup>[17, 18]</sup>

### 3.2 Catalytic Testing for Ethylene Polymerization

(a) *Co-catalyst screen*. To ascertain the most suitable co-catalyst, **Ni1** was selected as the test precatalyst and four different alkyl-aluminums were assessed namely, EASC (ethylaluminum sesquichloride), Et<sub>2</sub>AlCl (diethylaluminum chloride), MAO (methylaluminoxane) and MMAO (modified methylaluminoxane). In a typical polymerization, a run was conducted over 30 minutes in toluene under 10 atm C<sub>2</sub>H<sub>4</sub> and at a temperature of 30 °C; the results of the screening are summarized in Table 3. Inspection of the data reveals the catalytic activities as a function of the co-catalyst

decrease in the order: MAO > Et<sub>2</sub>AlCl > EASC > MMAO. Therefore, based on the level of activity as well as the distinct chemical nature of the aluminum activators, Et<sub>2</sub>AlCl and MAO were chosen for more in-depth studies.

<Table 3>

(b) *Ethylene polymerization using Ni1 – Ni10/Et<sub>2</sub>AlCl*. To facilitate the catalyst optimization, Ni1 was again employed as the test precatalyst with Et<sub>2</sub>AlCl as the co-catalyst and the Al:Ni molar ratio, temperature and run time all investigated. Initially, with the temperature fixed at 30 °C, the Al:Ni molar ratio was gradually increased from 200 to 700 (entries 1 – 6, Table 4). At a relatively low ratio of 400 the activity reached a maximum of  $6.54 \times 10^6$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup> (entry 3, Table 4). Above 400 the catalytic activity steadily decreased and by 700 it had dropped by nearly a half (entry 6, Table 3). In a similar way, the molecular weight reached a maximum of  $5.5 \times 10^5$  g mol<sup>-1</sup> with the molar ratio at 400 (entry 3, Table 4) and then gradually decreased to  $3.8 \times 10^5$  g mol<sup>-1</sup> at a ratio of 700 (entry 6, Table 4); the corresponding GPC curves are shown in Figure 4. This latter drop in molecular weight can be attributed to a greater rate of chain transfer with respect to chain propagation at a higher molar ratio of co-catalyst.<sup>[6b,9b,11,12,18b,19]</sup> Across the molar Al:Ni ratio range the molecular weight distribution remained relatively narrow between 3.2 and 4.0 indicative of a well behaved catalytic species.

<Table 4>

<Figure 4>

To study the thermal stability of Ni1/Et<sub>2</sub>AlCl, the reaction temperature was varied from 20 to 60 °C with the Al:Ni ratio retained at 400. A peak in activity of  $6.54 \times$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup> was observed at 30 °C (entry 3, Table 4) and then steadily decreased reaching its lowest level of  $3.08 \times$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup> at 60 °C (entry 10, Table 4). This loss in activity can be attributed to a combination of partial deactivation of the active species and a lower solubility of the ethylene monomer in toluene at elevated temperature.<sup>[4a,6e,f,9b,10c-e,11,18b]</sup> On the other hand, the molecular weight of the polyethylene initially increased from 20 to 30 °C and then decreased from  $5.5$  to  $1.5 \times 10^5$  g mol<sup>-1</sup> as the temperature was raised from 30 to 60 °C as the rate of chain termination increased (entries 3, 7-10, Table 4); the corresponding GPC curves are shown in Figure 5.

<Figure 5>

To explore the effect of time, the polymerization runs using Ni1/Et<sub>2</sub>AlCl were conducted at intervals of 5, 15, 30, 45 and 60 minutes with the Al:Ni molar ratio retained at 400 and the reaction temperature of 30 °C. The results indicate that highest activity of  $1.76 \times 10^7$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup> was

achieved after 5 minutes (entry 11, Table 4). Afterwards the value gradually decreased in line with partial deactivation of the active species over longer reaction times (entries 3 and 12 – 14, Table 4). This result indicates that a short induction period is required to generate the active species following the addition of co-catalyst. Although the activity drops, it still remains relatively high even after 60 minutes [ $3.59 \times 10^6$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup>], highlighting the appreciable lifetime of this catalyst. As expected, the molecular weight of the polyethylene increased over longer run times reaching a maximum of  $5.8 \times 10^5$  g mol<sup>-1</sup> after 60 minutes (Figure 6).

<Figure 6>

Using the favored operating conditions established using **Ni1**/Et<sub>2</sub>AlCl (Al:Ni = 400, temp = 30 °C, run time = 30 min), the remaining precatalysts, **Ni2** – **Ni10**, were all evaluated using Et<sub>2</sub>AlCl (Table 5). According to the data, all the bromide complexes (**Ni1** – **Ni5**) exhibited activities in the range of  $5.67 – 6.54 \times 10^6$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup> (entries 1 – 5, Table 5) which are generally higher when compared to the chlorides (**Ni6** – **Ni10**:  $5.37 – 5.64 \times 10^6$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup>). The origin of these differences between the halides remains unclear but it may relate to the different stability of the active species, the activation process and the nature of the resultant counter-ion.<sup>[4b,6b,18a-c]</sup> Nevertheless, similar trends in activity exist in each halide series with, **Ni1** [2,6-di(Me)] > **Ni4** [2,4,6-tri(Me)] > **Ni2** [2,6-di(Et)] > **Ni5** [2,6-di(Et)-4-Me] > **Ni3** [2,6-di(i-Pr)] for the bromides and, **Ni6** [2,6-di(Me)] > **Ni9** [2,4,6-tri(Me)] > **Ni7** [2,6-di(Et)] > **Ni10** [2,6-di(Et)-4-Me] > **Ni8** [2,6-di(i-Pr)] for the chlorides. Evidently, the steric and electronic effects of the second N-aryl group greatly influence the catalytic activities. With regard to electronic properties, the presence of a *para*-methyl group appears to have a negative effect which is highlighted by **Ni1** being more active than **Ni4** and **Ni2** more than **Ni5**. In terms of steric properties, the least sterically bulky **Ni1** and **Ni6** are the most productive while the most bulky (**Ni3**, **Ni8**) the least. Conversely, **Ni3** and **Ni8** generate the highest molecular weight polyethylene and indeed their values enter the ultra-high molecular weight range ( $10.4 – 11.4 \times 10^5$  g mol<sup>-1</sup>; entries 3, 8, Table 5). Similar steric/molecular weight correlations with related nickel catalysts have been previously reported.<sup>[6b]</sup> The GPC curves of all the polymers generated using **Ni1** – **Ni10**/Et<sub>2</sub>AlCl are shown in Figures S8 and S9.

<Table 5>

(c) *Ethylene polymerization using Ni1 – Ni10/MAO*. With MAO as co-catalyst a similar optimization procedure was followed to that described using Et<sub>2</sub>AlCl once again using **Ni1** as the precatalyst; the results are collected in Table 6. On varying the Al:Ni molar ratio between 1000 and 3000, the highest

activity of  $10.56 \times 10^6$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup> was achieved when the polymerization was conducted with an Al:Ni ratio of 2250 and at 30 °C (entry 4, Table 6). Furthermore, the molecular weight of the polyethylene reached its highest value of  $5.9 \times 10^5$  g mol<sup>-1</sup> with the same ratio and then slowly dropped to  $3.8 \times 10^5$  g mol<sup>-1</sup> as the molar ratio was increased to 3000 (entries 1 – 7, Table 6); the corresponding GPC curves are shown in Figure 7.

<Table 6>

<Figure 7>

Monitoring the activity of **Ni1**/MAO, whilst the temperature of polymerization was increased from 20 to 60 °C, revealed a peak in activity at 30 °C ( $10.56 \times 10^6$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup>, entry 4, Table 6); a similar thermal stability was also exhibited by **Ni1**/Et<sub>2</sub>AlCl though the peak activity was lower ( $6.54 \times 10^6$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup>). On raising the temperature of the run to 60 °C, the activity dropped to  $3.12 \times 10^6$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup> (entry 11, Table 6). Likewise, the molecular weight of the polyethylene reached a maximum at 30 °C [ $5.9 \times 10^7$  g mol<sup>-1</sup>] then gradually lowered on raising the temperature (entries 4 and 8 – 11, Table 6); these temperature effects on molecular weight are further illustrated by their GPC curves (Figure 8).

<Figure 8>

With the Al:Ni molar ratio maintained at 2250 and the temperature at 30 °C, the activity of **Ni1**/MAO was recorded at selected times between 5 and 60 minutes. The highest activity was observed after 5 minutes ( $1.88 \times 10^7$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup>: entry 12, Table 6) and is indeed comparable with that obtained when using **Ni1**/Et<sub>2</sub>AlCl ( $1.76 \times 10^7$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup>: entry 11, Table 4). After this initial spike in activity, the value progressively dropped over longer periods of time reaching its lowest value of  $5.51 \times 10^6$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup> after 60 minutes (entries 4, 13-15, Table 6). In terms of the molecular weight of the resulting polyethylenes, these gradually increased as the time was prolonged achieving the highest value of  $7.2 \times 10^5$  g mol<sup>-1</sup> after 60 minutes, this trend is also borne out in their GPC curves (Figure 9).

<Figure 9>

With the optimal conditions determined using **Ni1**/MAO namely, Al:Ni ratio = 2250, temperature = 30 °C and run time = 30 minutes, the remaining nine nickel precatalysts, **Ni2** – **Ni10**, were also screened; the results are compiled in Table 7 alongside those for **Ni1**. As seen with the Et<sub>2</sub>AlCl study, all the bromide precatalysts generally exhibited higher activities by comparison to the chlorides [range:  $7.03 - 10.56 \times 10^6$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup> (**Ni1** – **Ni5**) vs.  $6.91 - 8.34 \times 10^6$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup> (**Ni6** – **Ni10**): entries 1 – 10, Table 7]. Indeed, for each halide series the relative performance

of precatalysts mirrors that seen in the Et<sub>2</sub>AlCl study with **Ni1** [2,6-di(Me)] > **Ni4** [2,4,6-tri(Me)] > **Ni2** [2,6-di(Et)] > **Ni5** [2,6-di(Et)-4-Me] > **Ni3** [2,6-di(i-Pr)] for the bromides and **Ni6** [2,6-di(Me)] > **Ni9** [2,4,6-tri(Me)] > **Ni7** [2,6-di(Et)] > **Ni10** [2,6-di(Et)-4-Me] > **Ni8** [2,6-di(i-Pr)] for the chlorides. Evidently, the same type of steric/electronic arguments can be used to explain the variations in activity with the upshot that the least sterically bulky **Ni1** and **Ni6** of each series display the best catalytic performance. Moreover, these MAO-activated catalysts in general display higher activities than that seen earlier with **Ni1** – **Ni10**/Et<sub>2</sub>AlCl highlighting the importance of the aluminoxane activator.

With respect to the molecular weight of polyethylene (see Figures S10 and S11), the bulkier precatalysts **Ni3** and **Ni8** once again produced the highest molecular weight polymer with the *M<sub>w</sub>*'s entering the ultra-high molecular-weight window [10.3 – 14.8 × 10<sup>5</sup> g mol<sup>-1</sup>: entries 3 and 8, Table 7]. Furthermore, the molecular weights of the polymers generated using **Ni1** – **Ni10**/MAO are in general higher than that seen with **Ni1** – **Ni10**/Et<sub>2</sub>AlCl. It is unclear as the origin of this co-catalyst-promoted molecular weight enhancement, but it may be due to the sterically bulky methylaluminoxane counter-anions undergoing slow polymer chain transfer relative to chain propagation.<sup>[9b,18a-c, 10d]</sup>

To allow a comparison of these current precatalysts (**D**) with the previously reported nickel systems, **A** – **C** (Figure 1), Figure 10 depicts the optimum molecular weight and activity observed for each class of precatalyst; all tests were performed using MAO or MMAO at 10 atm C<sub>2</sub>H<sub>4</sub> and at their optimized temperature.<sup>[4b,11,12]</sup> Several points emerge from inspection of the figure. Firstly, the catalytic activity seen using **D** is the highest of all four classes and hence highlights the beneficial effect of dibenzocycloheptyl substitution on productivity. Secondly, the molecular weight of the polyethylene formed using **D** is second only to that seen with the 2,6-benzhydryl-substituted **A**. Furthermore, in comparison to 2,4-benzhydryl **B**, the 2,4-dibenzocycloheptyl groups in **D** have an enhancement effect on the molecular weight. By contrast, the least sterically bulky **C** is the least active and forms lower molecular weight polyethylene than that seen using **D**.

<Figure 10>

### 3.3 Structural Properties of the Polyethylenes

Examination of the melt temperatures (*T<sub>m</sub>*) reveals that for the polymers obtained using **Ni1** - **Ni10** with either Et<sub>2</sub>AlCl or MAO fall in the range 91.9 – 113.3 °C with little difference observed between activator [91.9 – 108.7 °C (Et<sub>2</sub>AlCl) vs. 95.0 – 113.3 °C (MAO)] (Tables 5, 7). This range in values would suggest that these polyethylenes display some level of branching. To verify this assertion,

representative samples obtained using **Ni1**/Et<sub>2</sub>AlCl (entry 3, Table 4) and **Ni1**/MAO (entry 4, Table 6) were selected for high-temperature <sup>13</sup>C NMR spectroscopy (Figures 11 and **S12**).

<Figure 11>

<Figure 12>

Both spectra, recorded in deuterated 1,1,2,2-tetrachloroethane at 100 °C, revealed a wide range of aliphatic peaks in the  $\delta$  11.0 to 40.0 region that could be assigned and interpreted on the basis of reported literature data (Tables S1 and S2).<sup>[13]</sup> For the polyethylene generated using **Ni1**/Et<sub>2</sub>AlCl, 80 branches per 1000 Cs could be determined, including methyl (52.5%), ethyl (3.1%), propyl (4.0%), butyl (6.8%), amyl (6.8%), 1,4-paired methyls (7.3%), 1,6-paired methyls (2.2%) in addition to longer chain branches (17.2%). By comparison, the polyethylene obtained with **Ni1**/MAO possessed 63 branches per 1000 Cs, including methyl (63.7%), ethyl (7.2%), propyl (3.2%), butyl (5.2%), amyl (4.8%), 1,4-paired methyl (1.4%), 1,6-paired methyl (8.4%) and longer chain branches (6.1%). This level of branching content seen with either co-catalyst in this study is lower than seen with **A** which displays 173 branches per 1000 Cs (Figure 1).<sup>[4b]</sup> On the other hand, the number of branches seen by the 2,4-benzyhydril system (**B**, Figure 1) displays 14 branches per 1000 Cs using MMAO as co-catalyst; notably this branching content could be increased with temperature.<sup>[11]</sup> As to the remote fluorenyl derivative system (**C**, Figure 1), it generated 8 branches per 1000 Cs using MAO as co-catalyst.<sup>[12]</sup> It would seem that the current system generates a moderate level of branching as opposed to the high level with **A** and lower levels with **B** and **C**. Furthermore, it is apparent that the steric properties of the *ortho*-substituents influence the degree of branching with most bulky **A** giving the most followed by **D** (**Table S3**). It is unclear how these large groups affect the relative rates of isomerization (chain walking) and monomer insertion (propagation).<sup>[7a,c]</sup>

## 4 Conclusions

The incorporation of dibenzocycloheptyl groups at the 2,4-positions of a single N-aryl group in an unsymmetrical 1,2-bis(arylimino)acenaphthene has been successfully achieved and five examples disclosed through variation of the second aryl group (**L1** – **L5**). In turn, **L1** – **L5** have been used to generate their corresponding *N,N'*-nickel(II) bromide (**Ni1** – **Ni5**) and chloride chelates (**Ni6** – **Ni10**), all of which have been fully characterized including in two cases by single crystal X-ray diffraction (**Ni3** and **Ni7**). Moreover, complexes **Ni1** – **Ni10** proved highly active for the polymerization of ethylene at 30 °C on activation with either Et<sub>2</sub>AlCl or MAO, with the least sterically encumbered **Ni1**

[2,6-di(Me)] the most active and reaching its peak performance with MAO ( $10.56 \times 10^6$  g PE mol<sup>-1</sup>(Ni) h<sup>-1</sup>). More significantly, high molecular weight polyethylene was a feature of all the polymerizations with ultra-high molecular weight obtained with the more sterically hindered precatalysts and reaching a maximum of  $14.8 \times 10^5$  g mol<sup>-1</sup> using **Ni3** [2,6-di(i-Pr)]/MAO; moderate branching contents are a feature of the materials irrespective of the co-catalyst employed.

## Supplementary data

CCDC No. 1868517 and 1868518 contain the crystallographic data for complexes **Ni3** and **Ni7**. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/>.

## ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No. 21871275 and 51473170). MZ is grateful for a CAS-TWAS president's fellowship. GAS thanks the Chinese Academy of Sciences for a President's International Fellowship for Visiting Scientists.

## REFERENCES

- [1] L. K. Johnson, C. M. Killian, and M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414.
- [2] C. M. Killian, D. J. Tempel, L. K. Johnson, and M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 11664.
- [3] a) R. Gao, W.-H. Sun, and C. Redshaw, *Catal. Sci. Technol.* **2013**, *3*, 1172. b) C. Bianchini, G. Giambastiani, L. Luconi, A. Meli, *Coord. Chem. Rev.* **2010**, *254*, 431. c) M. Delferro, and T. J. Marks., *Chem. Rev.* **2011**, *111*, 2450. d) Q. Xing, T. Zhao, Y. Qiao, L. Wang, C. Redshaw, and W.-H. Sun, *RSC Adv.* **2013**, *3*, 26184. e) S. Wang, W. Zhao, X. Hao, B. Li, C. Redshaw, Y. Li, W.-H. Sun, *J. Organomet. Chem.* **2013**, *731*, 78.
- [4] a) X. Wang, L. Fan, Y. Ma, C.-Y. Guo, G. A. Solan, Y. Sun, and W.-H. Sun, *Polym. Chem.* **2017**, *8*, 2785. b) Q. Mahmood, Y. Zeng, E. Yue, G. A. Solan, T. Liang, and W.-H., Sun, *Polym. Chem.* **2017**, *8*, 6416. c) M. Akiba, and S. A., Hashim, *Prog. Polym. Sci.* **1997**, *22*, 475. d) L. R. Kucera, Mark. R. Brei, R. F. Storey, *Polym.* **2013**, *54*, 3796. e) J. D. Arriola, E. M. Canahan, P. D. Hustad, R. L. Kuhlman, T. T. Wenzel, *Sci.* **2006**, *312*, 714.
- [5] a) W.-H. Sun, *Adv. Polym. Sci.* **2013**, *258*, 163. b) S. Wang, W.-H. Sun, C. Redshaw, *J. Organomet. Chem.* **2014**, *751*, 717. c) J. Ma, C. Feng, S. Wang, K.-Q. Zhao, W.-H. Sun, C. Redshaw,

and G. A. Solan, *Inorg. Chem. Front.* **2014**, *1*, 14. d) W. Zhang, W.-H. Sun, and C. Redshaw, *Dalton Trans.* **2013**, *42*, 8988. e) C. Carlini, A. Macinai, F. Masi, A. M. R. Galletti, R. Santi, G. Sbrana, A., Sommazzi, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2534. f) C. Popeney, and Z., Guan, *Organometallics* **2005**, *24*, 1145. g) C. S. Popeney, and Z. Guan, *Macromolecules* **2010**, *43*, 4091. h) G. Lanza, I. L. Fragalà, and T. J. Marks, *J. Am. Chem. Soc.* **2000**, *122*, 12764. i) H. Gao, Z. Ke, L. Pei, K. Song, Q. Wu, *Polym.* **2007**, *48*, 7249. j) C. S. Popeney, C. M. Levins, and Z. Guan, *Organometallics* **2011**, *30*, 2432. k) D. R. Moore, M. Cheng, E. B. Lokbkovsky, and G. W. Coaes, *Angew. Chem. Int. Ed.* **2002**, *41*, 2599.

[6] P. Kuhn, D. Semeril, C. Jeunesse, D. Matt, M. Neuburger, and A. Mota, *Chem. Eur. J.* **2006**, *12*, 5210. b) Q. Mahmood, Y. Zeng, X. Wang, Y. Sun, W.-H. Sun, *Dalton Trans.* **2017**, *46*, 6934. c) Z. Chen, K. E. Allen, P. S. White, O. Daugulis, and M. Brookhart, *Organometallics* **2016**, *35*, 1756. d) D. P. Gates, S. A. Svejda, E. Oñate, C. M. Killian, L. K. Johnson, P. S. White, and M. Brookhart, *Macromolecules* **2000**, *33*, 2320. e) S. Yuan, E. Yue, C. Wen, and W.-H. Sun, *RSC Adv.* **2016**, *6*, 7431. f) S. Du, S. Kong, Q. Shi, J. Mao, C. Guo, J. Yi, T. Liang, and W. H. Sun, *Organometallics* **2015**, *34*, 582. g) J. L. Rhinehart, L. A. Brown, and B. K. Long, *J. Am. Chem. Soc.* **2013**, *135*, 16316.

[7] a) Z. Guan, P. M. Cotts, E. F. McCord, S. J. McLain, *Science*, **1999**, *283*, 2659. b) C. M. Killian, L. K. Johnson, M. Brookhart, *Organometallics* **1997**, *16*, 2005. c) L. Gua, S. Dai, X. Sui, and C. Chen, *ACS Catal.* **2016**, *6*, 428.

[8] J. L. Rhinehart, N. E. Mitchell, and B. K. Long, *ACS Catal.* **2014**, *4*, 2501.

[9] a) X. Wang, L. Fan, Y. Yuan, S. Du, Y. Sun, G. A. Solan, C. Y. Guo, and W. H. Sun, *Dalton Trans.* **2016**, *45*, 18313. b) Y. Chen, S. Du, C. Huang, G. A. Solan, X. Hao, W.-H. Sun, *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 1971. c) Q. Liu, W. Zhang, D. Jia, X. Hao, C. Redshaw, W.-H. Sun, *Appl. Catal. A* **2014**, *475*, 195.

[10] a) S. Kong, C.-Y. Guo, W. Yang, L. Wang, W.-H. Sun, R. Glaser, *J. Organomet. Chem.* **2013**, *725*, 37. b) C. Wen, S. Yuan, Q. Shi, E. Yue, D. Liu, and W.-H. Sun, *Organometallics* **2014**, *33*, 7223. c) L. Fan, E. Yue, S. Du, C.-Y. Guo, X. Hao, and W.-H., Sun, *RSC Adv.* **2015**, *5*, 93274. d) L. Fan, S. Du, Z.; C.-Y. Guo, X. Hao, W. -H. Sun, *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 1369. e) H. Liu, W. Zhao, X. Hao, C. Redshaw, W. Huang, and W.-H. Sun, *Organometallics* **2011**, *30*, 2418. f) D. Jia, W. Zhang, W. Liu, L. Wang, C. Redshaw, and W.-H. Sun, *Catal. Sci. Technol.* **2013**, *3*, 2737.

- [11] H. Liu, W. Zhao, J. Yu, W. Yang, X. Hao, C. Redshaw, L. Chen, and W.-H. Sun, *Catal. Sci. Technol.* **2012**, *2*, 415.
- [12] V. Katla, E. Yue, N. M. Rajendran, T. Liang, W.-H. Sun, *C. R. Chim.* **2016**, *19*, 604.
- [13] G. B. Galland, R. F. de Souza, R. S. Mauler, and F. F. Nunes, *Macromolecules* **1999**, *32*, 1620.
- [14] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, and H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.
- [15] A. L. Spek, *Acta Cryst.* **2009**, D65, 148.
- [16] S. Meiries, K. Speck, D. B. Cordes, A. M. Z. Slawin, and S. P. Nolan, *Organometallics* **2012**, *32*, 330.
- [17] a) S. Dai, and C. Chen, *Angew. Chem. Int. Ed.* **2016**, *55*, 13281. b) H. Gao, X. Liu, Y. Tang, J. Pan, and Q. Wu, *Polym. Chem.* **2011**, *2*, 1398. c) D. Zhang, E. T. Nadres, M. Brookhart, and O. Daugulis, *Organometallics* **2013**, *32*, 5136.
- [18] a) J. Yu, X. Hu, Y. Zeng, L. Zhang, C. Ni, X. Hao, and W.-H. Sun, *New J. Chem.* **2011**, *35*, 178. b) Y. Zeng, Q. Mahmood, X. Hao, W.-H. Sun, *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 1910. c) J. Yu, Y. Zeng, W. Huang, X. Hao, and W.-H. Sun, *Dalton Trans.* **2011**, *40*, 8436. d) Y. Zhang, C. Huang, X. Wang, Q. Mahmood, X. Hao, X. Hu, C.-Y. Guo, G. A. Solan, and W.-H. Sun, *Polym. Chem.* **2017**, *8*, 995. e) C. Huang, Y. Zeng, Z. Flisak, Z. Zhao, T. Liang, W.-H. Sun, *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 2071. f) Y. Zeng, Q. Mahmood, T. Liang, W.-H. Sun, *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 3214. g) T. Zhang, D. Guo, S. Jie, W.-H. Sun, T. Li, X. Yang, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4765. h) S. Du, Q. Xing, Z. Flisak, E. Yue, Y. Sun, and W. H. Sun, *Dalton Trans.* **2015**, *44*, 12282. i) X. Hou, T. Liang, W.-H. Sun, C. Redshaw, X. Chen, *J. Organomet. Chem.* **2012**, *708*, 98. j) W. Chai, J. Yu, L. Wang, X. Hu, C. Redshaw, W.-H. Sun, *Inorg. Chim. Acta* **2012**, *385*, 21.
- [19] a) G. J. Britovsek, S. A. Cohen, V. C. Gibson, and M.V. Meurs, *J. Am. Chem. Soc.*, **2004**, *126*, 10701. b) E. Yue, L. Zhang, Q. Xing, X.-P. Cao, X. Hao, C. Radshaw, and W.-H. Sun, *Dalton Trans.* **2014**, *43*, 423.

## Captions of Tables, Figures and Scheme

**Table 1** Crystal data and structure refinement of **Ni3** and **Ni7**

**Table 2** Selected bond lengths (Å) and angles (°) for **Ni3** and **Ni7**

**Table 3** Catalytic evaluation of **Ni1** with four different co-catalysts

**Table 4** Optimization of the polymerization conditions using **Ni1**/Et<sub>2</sub>AlCl

**Table 5** Ethylene polymerization using **Ni1** - **Ni10**/Et<sub>2</sub>AlCl under optimized conditions

**Table 6** Optimization of the polymerization conditions using **Ni1**/MAO

**Table 7** Ethylene polymerization using **Ni1** - **Ni10**/MAO under optimized conditions

**Figure 1** Benzhydryl and its tethered counterparts as N-aryl substituents in unsymmetrical 1,2-bis(arylimino)acenaphthene-nickel(II) halide precatalysts (**A** – **D**)

**Figure 2** ORTEP representation of **Ni3** with the thermal ellipsoids set at a probability level of 30%. All hydrogen atoms and solvent molecules have been omitted for clarity.

**Figure 3** ORTEP representation of **Ni7** (molecule A) with the thermal ellipsoids set at a probability level of 30%. All hydrogen atoms and solvent molecules have been omitted for clarity.

**Figure 4** GPC curves of the polyethylene obtained using **Ni1**/Et<sub>2</sub>AlCl with different Al:Ni molar ratios (entries 1 – 6, Table 4).

**Figure 5** GPC curves of the polyethylene obtained using **Ni1**/Et<sub>2</sub>AlCl at different run temperatures (entries 3 and 7 – 10, Table 4).

**Figure 6** GPC curves of the polyethylene obtained using **Ni1**/Et<sub>2</sub>AlCl over different run times (entries 3 and 11 – 14, Table 4).

**Figure 7** GPC curves of the polyethylene obtained using **Ni1**/MAO with different Al:Ni molar ratios (entries 1 – 7, Table 6).

**Figure 8** GPC curves of the polyethylene obtained using **Ni1**/MAO at different temperatures (entries 8 – 11, Table 6).

**Figure 9** GPC curves of the polyethylene obtained using **Ni1**/MAO over different reaction times (entries 4, 12 – 15, Table 6).

**Figure 10** Comparison of activity and  $M_w$  of the polyethylene generated using **A**, **B** and **C** with that obtained using the current system **D**; all tests performed using either MAO or MMAO at 10 atm C<sub>2</sub>H<sub>4</sub> at their optimized temperature.

**Figure 11** <sup>13</sup>C NMR spectrum of the polyethylene obtained using **Ni1**/Et<sub>2</sub>AlCl (entry 3, Table 3); recorded in deuterated 1,1,2,2-tetrachloroethane at 100 °C. Peak assignments are with respect to the depicted polymer backbone.

**Scheme 1** Synthesis of 1,2-bis(imino)acenaphthenes, **L1** – **L5**, and their nickel complexes, **Ni1** – **Ni10**.

**Table 1** Crystal data and structure refinement of **Ni3** and **Ni7**

	<b>Ni3</b>	<b>Ni7</b>
Empirical formula	C <sub>61</sub> H <sub>54</sub> Br <sub>2</sub> N <sub>2</sub> Ni	2 (C <sub>59</sub> H <sub>50</sub> Cl <sub>2</sub> N <sub>2</sub> Ni)
Formula weight	1033.59	916.62
Temperature/K	173.1500	173.1500
Wavelength/Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	P2(1)/c	P2(1)/n
a/Å	10.534(2)	18.248(4)
b/Å	20.031(4)	27.896(6)
c/Å	28.439(6)	21.385(4)
$\alpha/^\circ$	90	90
$\beta/^\circ$	95.95(3)	108.81(3)
$\gamma/^\circ$	90	90
Volume/Å <sup>3</sup>	5968(2)	10304(4)
Z	4	8
$D_{\text{Calcd}} \text{ g/cm}^3$	1.150	1.182
$\mu/\text{mm}^{-1}$	1.699	0.518
$F(000)$	2128.0	3840.0
Crystal size/mm <sup>3</sup>	0.418 × 0.138 × 0.071	0.933 × 0.529 × 0.507
$\theta$ range (°)	2.492 to 54.874	2.486 to 54.964
Limiting Indices	-13 ≤ h ≤ 13 -25 ≤ k ≤ 25 -36 ≤ l ≤ 36	-23 ≤ h ≤ 23 -36 ≤ k ≤ 36 -27 ≤ l ≤ 27
No. of rflns collected	63801	23539
No. of unique rflns	13595	23539
R(int)	0.0689	0.0390
No. params	600	1270
Completeness to $\theta$ (%)	99.7	99.7
Goodness of fit on $F^2$	1.207	1.056
Final R indices [ $I \geq 2\sigma(I)$ ]	R <sub>1</sub> = 0.0791 wR <sub>2</sub> = 0.1913	R <sub>1</sub> = 0.0560 wR <sub>2</sub> = 0.1565
R indices [all data]	R <sub>1</sub> = 0.0917 wR <sub>2</sub> = 0.2057	R <sub>1</sub> = 0.0597 wR <sub>2</sub> = 0.1604
Largest diff. peak, and hole/e Å <sup>-3</sup>	0.74/-0.59	0.94/-0.70

**Table 2** Selected bond lengths (Å) and angles (°) for **Ni3** and **Ni7**

X	<b>Ni3</b>	<b>Ni7</b>	
	Br	Cl	
	Bond lengths (Å)		
		<i>Molecule A</i>	<i>Molecule B</i>
Ni(1)–X(1)	2.3328(8)	2.1727(15)	2.2001(9)
Ni(1)–X(2)	2.3353(8)	2.182(3)	2.1885(9)
Ni(1)–N(1)	2.024(4)	2.0326(18)	2.0265(17)
Ni(1)–N(2)	2.043(4)	2.048(2)	2.0291(19)
N(1)–C(12)	1.291(5)	1.285(3)	1.280(3)
N(2)–C(1)	1.280(5)	1.272(3)	1.286(3)
N(1)–C(13)	1.428(5)	1.434(3)	1.439(2)
N(2)–C(50)	1.442(5)	1.451(4)	1.446(3)
	Bond angles (°)		
X(1)–Ni(1)–X(2)	121.62(3)	127.76(8)	126.19(4)
N(1)–Ni(1)–N(2)	82.85(14)	82.29(8)	82.31(7)
N(1)–Ni(1)–X(1)	105.60(10)	104.72(7)	105.97(6)
N(1)–Ni(1)–X(2)	116.80(10)	114.47(9)	112.98(6)
N(2)–Ni(1)–X(1)	109.71(10)	105.41(9)	112.22(6)
N(2)–Ni(1)–X(2)	113.53(10)	112.63(9)	108.57(6)

**Table 3** Catalytic evaluation of **Ni1** with four different co-catalysts

Entry	Co-cat.	Al:Ni	T (°C)	t (min)	Mass of PE (g)	Activity <sup>b</sup>	$M_w^c$	$M_w/M_n^c$	$T_m$ (°C) <sup>d</sup>
1	Et <sub>2</sub> AlCl	400	30	30	6.54	6.54	5.5	3.9	104.5
2	EASC	400	30	30	4.93	4.93	6.7	3.1	102.3
3	MAO	2000	30	30	6.56	6.56	5.4	4.1	110.4
4	MMAO	2000	30	30	3.28	3.28	4.3	4.1	107.0

<sup>a</sup> General conditions: 2.0 μmol of **Ni1**, 100 mL toluene, 10 atm C<sub>2</sub>H<sub>4</sub>, 30 °C, 30 min.

<sup>b</sup> × 10<sup>6</sup> g of PE mol<sup>-1</sup>(Ni) h<sup>-1</sup>.

<sup>c</sup>  $M_w$ : × 10<sup>5</sup> g mol<sup>-1</sup>, determined by GPC.

<sup>d</sup> Determined by DSC.

**Table 4** Optimization of the polymerization conditions using **Ni1**/Et<sub>2</sub>AlCl

Entry	T (°C)	t (min)	Al:Ni	Mass of PE (g)	Activity <sup>b</sup>	$M_w^c$	$M_w/M_n^c$	$T_m$ (°C) <sup>d</sup>
1	30	30	200	4.07	4.07	3.2	3.4	114.3
2	30	30	300	5.17	5.17	4.7	4.0	106.6
3	30	30	400	6.54	6.54	5.5	3.2	104.5
4	30	30	500	5.77	5.77	5.4	3.6	103.0
5	30	30	600	4.92	4.92	4.2	3.9	95.7
6	30	30	700	3.85	3.85	3.8	3.5	116.9
7	20	30	400	4.96	4.96	4.2	2.4	107.3
8	40	30	400	4.38	4.38	2.5	3.1	74.3
9	50	30	400	3.47	3.47	2.3	3.1	79.3
10	60	30	400	3.08	3.08	1.5	2.9	82.4
11	30	5	400	2.94	17.64	3.8	3.4	101.0
12	30	15	400	5.62	11.24	4.5	3.2	102.4
13	30	45	400	6.95	4.63	5.7	4.3	102.1
14	30	60	400	7.18	3.59	5.8	4.3	102.0

<sup>a</sup> General conditions: 2.0  $\mu\text{mol}$  of **Ni1**, 100 mL toluene, 10 atm C<sub>2</sub>H<sub>4</sub>.

<sup>b</sup>  $\times 10^6$  g of PE mol<sup>-1</sup>(Ni) h<sup>-1</sup>.

<sup>c</sup>  $M_w$ :  $\times 10^5$  g mol<sup>-1</sup>, determined by GPC.

<sup>d</sup> Determined by DSC.

**Table 5** Ethylene polymerization using **Ni1 - Ni10**/Et<sub>2</sub>AlCl under optimized conditions

Entry	Precat.	Mass of PE (g)	Activity <sup>b</sup>	$M_w^c$	$M_w/M_n^c$	$T_m$ (°C) <sup>d</sup>
1	<b>Ni1</b>	6.54	6.54	5.5	3.9	104.5
2	<b>Ni2</b>	6.04	6.04	6.5	3.5	93.8
3	<b>Ni3</b>	5.67	5.67	11.4	2.8	91.9
4	<b>Ni4</b>	6.21	6.21	6.2	2.6	107.8
5	<b>Ni5</b>	5.91	5.91	5.6	3.2	98.2
6	<b>Ni6</b>	5.89	5.89	6.1	4.1	100.8
7	<b>Ni7</b>	5.64	5.64	6.6	3.2	100.0
8	<b>Ni8</b>	5.37	5.37	10.4	3.5	101.7
9	<b>Ni9</b>	5.71	5.71	6.2	4.5	108.7
10	<b>Ni10</b>	5.48	5.48	10.0	3.1	100.4

<sup>a</sup> General conditions: 2.0  $\mu\text{mol}$  of precatalyst, 100 mL toluene, 10 atm C<sub>2</sub>H<sub>4</sub>, 30 °C, 30 min, Al:Ni ratio of 400;

<sup>b</sup>  $\times 10^6$  g PE mol<sup>-1</sup>(PE) h<sup>-1</sup>;

<sup>c</sup>  $M_w$ :  $\times 10^5$  g mol<sup>-1</sup>, determined by GPC;

<sup>d</sup> Determined by DSC.

**Table 6** Optimization of the polymerization conditions using **Ni1**/MAO

Entry	T (°C)	t (min)	Al:Ni	Mass of PE (g)	Activity <sup>b</sup>	$M_w^c$	$M_w/M_n^c$	$T_m$ (°C) <sup>d</sup>
1	30	30	1000	5.29	5.29	4.3	4.2	110.5
2	30	30	1500	5.54	5.54	4.5	4.3	100.6
3	30	30	2000	6.56	6.56	5.4	4.1	110.4
4	30	30	2250	10.56	10.56	5.9	3.4	113.3
5	30	30	2500	7.21	7.21	5.2	3.9	107.2
6	30	30	2750	5.34	5.34	4.8	3.7	114.1
7	30	30	3000	3.81	3.81	3.8	3.5	110.7
8	20	30	2250	6.48	6.48	5.4	3.6	114.9
9	40	30	2250	7.43	7.43	4.0	3.8	107.7
10	50	30	2250	5.51	5.51	2.8	3.0	98.3
11	60	30	2250	3.12	3.12	1.8	3.1	91.3
12	30	5	2250	3.14	18.84	4.4	3.7	104.2
13	30	15	2250	6.32	12.64	4.9	4.1	107.3
14	30	45	2250	10.81	7.21	6.0	3.3	109.9
15	30	60	2250	11.02	5.51	7.2	3.1	108.2

<sup>a</sup> General conditions: 2.0  $\mu\text{mol}$  of **Ni1**, 100 mL toluene, 10 atm  $\text{C}_2\text{H}_4$ .

<sup>b</sup>  $\times 10^6$  g of PE  $\text{mol}^{-1}(\text{Ni}) \text{h}^{-1}$ .

<sup>c</sup>  $M_w$ :  $\times 10^5$  g  $\text{mol}^{-1}$ , determined by GPC.

<sup>d</sup> Determined by DSC.

**Table 7** Ethylene polymerization using **Ni1 - Ni10**/MAO under optimized conditions

Entry	Precat.	Mass of PE (g)	Activity <sup>b</sup>	$M_w^c$	$M_w/M_n^c$	$T_m$ (°C) <sup>d</sup>
1	<b>Ni1</b>	10.56	10.56	5.9	3.4	113.3
2	<b>Ni2</b>	8.82	8.32	8.8	3.3	105.5
3	<b>Ni3</b>	7.03	7.03	14.8	3.1	101.6
4	<b>Ni4</b>	7.85	8.45	7.5	2.2	111.2
5	<b>Ni5</b>	8.53	7.57	9.3	3.5	101.7
6	<b>Ni6</b>	8.94	8.34	6.9	3.2	109.0
7	<b>Ni7</b>	8.13	7.53	9.1	4.0	105.7
8	<b>Ni8</b>	6.91	6.91	10.3	3.2	95.00
9	<b>Ni9</b>	7.26	7.76	5.6	4.1	108.5
10	<b>Ni10</b>	7.93	7.34	8.5	3.2	106.4

<sup>a</sup> General conditions: 2.0  $\mu\text{mol}$  of precatalyst, 100 mL toluene, 10 atm  $\text{C}_2\text{H}_4$ , 30 °C, 30 min, Al:Ni ratio of 2250;

<sup>b</sup>  $\times 10^6$  g of PE  $\text{mol}^{-1}(\text{Ni}) \text{h}^{-1}$ ;

<sup>c</sup>  $M_w$ :  $\times 10^5$  g  $\text{mol}^{-1}$ , determined by GPC;

<sup>d</sup> Determined by DSC.