Remote dibenzocycloheptyl-substitution of an iminotrihydroquinoline-nickel catalyst as a route to narrowly dispersed branched polyethylene waxes with alkene functionality

Liwei Guo,^{a,b} Dongzhi Zhu,^{a,b} Wenjuan Zhang,^{a,b,*} Muhammad Zada,^b Gregory A. Solan,^{b,c,*} Xiang Hao^b and Wen-Hua Sun^{b,*}

^a 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

^b 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

^c Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, UK. E-mail: gas8@leicester.ac.uk.

Abstract

The 8-(arylimino)-5,6,7-trihydroquinoline-nickel(II) chlorides, [8-N{2,6-R₂-4-(C₁₅H₁₃)C₆H₂}C₉H₈N}]NiCl₂ (R = Me **Ni1**, Et **Ni2**, *i*-Pr **Ni3**, F **Ni4**, Cl **Ni5**), each appended with a remote *para*-dibenzocycloheptyl group, have been synthesized from either the pre-formed ligand (**Ni1** - **Ni3**) or by generating the ligand *in-situ* during complexation (**Ni4**, **Ni5**). The molecular structures of **Ni2** and **Ni3** adopt dimeric or trimeric forms in the solid state, in which the chlorides can act as doubly or triply bridging ligands. On treatment with either MMAO or Et₂AlCl, **Ni1** - **Ni5** showed low (**Ni4**, **Ni5**) to high activities (**Ni1** - **Ni3**: up to 4.58×10^6 g PE mol⁻¹ (Ni) h⁻¹) for ethylene polymerization producing unsaturated polyethylenes of low molecular weight (1.4 - 2.7 kg·mol⁻¹) and narrow dispersity (< 2.0). In the main, these polyethylene waxes are highly branched and contain relatively high levels of internal vinylenes (–CH=CH–) with respect to terminal vinyls (–CH=CH₂). The *ortho*-substituents of the precatalyst were found to not only affect the catalytic activity but also the vinylenes:vinyl ratio and the branching content. Notably, the materials generated using *ortho*-fluoro **Ni4**/Et₂AlCl possessed the least number of branches and an increased vinyl contribution. Furthermore, these unsaturated polyethylenes can be readily functionalized by epoxidation with almost quantitative conversion.

Keywords: Nickel complex; Ethylene polymerization; Unsaturated polyethylene waxes; Epoxidation

Introduction

The aptitude of α -diimine-nickel complexes to perform as highly efficient catalysts for ethylene polymerization has been the subject of continued attention since the first report in the mid-1990s [1]. Typically, the polyethylenes formed display a broad range of branching contents due to the propensity of the catalysts to mediate “chain-walking”, leading to materials displaying a wide range of promising properties [2-5]. Up to now, many nickel(II) halide precatalysts have been reported, in which the structural features of the chelating ligand have been found to greatly affect the catalytic activity and the microstructure of the polymer [6,7]. In addition to the diazabutadiene-class of nickel catalyst [8-11], many examples of nickel complexes bearing iminopyridine ligands have been investigated and their effectiveness is, in large measure, linked to steric and electronic properties of the ligand backbone and the N-aryl substituents [12-16].

Over recent years, our group has developed several classes of cycloalkyl-fused iminopyridine-nickel catalyst and explored the effect of this cycloalkyl integration on the polymerization performance. For example, the 8-arylimino-5,6,7-trihydroquinoline-nickel(II) chlorides (**A**, Chart 1) displayed very high activities (*ca.* $10^7 \text{ g(PE)} \cdot \text{mol}^{-1}(\text{Ni}) \cdot \text{h}^{-1}$) for ethylene polymerization and produced low molecular weight polyethylenes ($M_w = 3.3 - 9.2 \text{ kg} \cdot \text{mol}^{-1}$) with narrow dispersities [17]. On the other hand, by replacing the *ortho*-alkyl substituents on the *N*-aryl group (*e.g.*, Me, Et, *i*-Pr) in **A** with cyclohexyl or cyclopentyl units, the resultant **B** and **C** (Chart 1) showed lower activity ($2.53 - 3.33 \times 10^6 \text{ g(PE)} \cdot \text{mol}^{-1}(\text{Ni}) \cdot \text{h}^{-1}$) and produced polymer of reduced molecular weight ($2 - 3 \text{ kg} \cdot \text{mol}^{-1}$) [18]. Furthermore, by introducing one or two *ortho*-benzhydryl groups, the polymerization activity dropped further ($0.57 - 1.2 \times 10^6 \text{ g(PE)} \cdot \text{mol}^{-1}(\text{Ni}) \cdot \text{h}^{-1}$), but notably afforded higher molecular weight materials ($M_w = 6.8 - 9.0 \text{ kg mol}^{-1}$) [19].

More recently, it has been recognized that substituents on the remote 4-position of a cycloalkyl-fused iminopyridine-nickel catalyst can also be influential on performance. For example, studies involving 2,6-dibenzhydryl-containing **D** (Chart 1) have revealed that electron withdrawing 4-R groups (*e.g.*, Cl, F) exhibited higher activity and produced highly branched polyethylene waxes with low molecular weights and narrow molecular weight distributions [20]. Similarly, the *para*-nitro **E** displayed high activities (up to $4.05 \times 10^6 \text{ g} \cdot (\text{PE}) \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$) for ethylene polymerization [21], while its NH_2 and carboxamide (NHC(O)Ph) derivatives exhibited much lower levels [22]. With fluorenyl as the

para-substituent, the activity of **F** (Chart 1) ranged from 1.5 to $4.2 \times 10^6 \text{ g(PE)} \cdot \text{mol}^{-1}(\text{Ni}) \cdot \text{h}^{-1}$ with the steric properties of the *ortho*-substituents proving decisive [23]. Elsewhere, the effects of remote *para*-substituents on other nickel-mediated ethylene polymerization have also been noted [24, 25].

Chart 1 Examples of cyclohexyl-fused iminopyridine-nickel(II) halide precatalysts

In this article we are concerned with developing the dibenzocycloheptyl counterpart of fluorenyl **F** (Chart 1) as we suspected that the high acidity of the fluorenyl methine proton in **F** may have had some impact on the polymerization performance [26]. Specifically, we report a family of *para*-dibenzocycloheptyl-substituted 8-arylimino-5,6,7-trihydroquinoline-nickel complexes (**G**, Chart 1) in which the steric and electronic properties of the *ortho*-R groups will be varied. An in-depth catalytic evaluation of **G** is then conducted to investigate how co-catalyst, temperature and run time, influence catalyst activity as well as polymer molecular weight, dispersity, branching and type of alkenic unsaturation; comparisons with fused **A**, **E** and **F** are also developed. In addition, we explore the ability of the post-polymerization materials to undergo functionalization.

Experimental

General considerations

All manipulations of air and/or moisture sensitive compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium–benzophenone and

distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M in toluene) and modified methylaluminoxane (MMAO, 1.93 M in toluene) were purchased from Akzo Nobel Corp., while diethylaluminum chloride (Et_2AlCl , 1.17 M in toluene) and ethylaluminum sesquichloride (EASC, 0.87 M in toluene) were obtained from Acros Chemicals. High purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. Other reagents were purchased from Aldrich, Acros or local suppliers. 5,6,7-Trihydroquinolin-8-one, 4-dibenzocycloheptyl-2,6-dimethylaniline, 4-dibenzocycloheptyl-2,6-diethylaniline, 4-dibenzocycloheptyl-2,6-diisopropylaniline, 4-dibenzocycloheptyl-2,6-difluoroaniline and 4-dibenzocycloheptyl-2,6-dichloroaniline were prepared using literature procedures [10, 27]. NMR spectra were recorded on Bruker DMX 400 MHz and Bruker DMX 300 MHz instrument at ambient temperature using TMS as an internal standard. IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 microanalyzer. Weight average molecular weights (M_w) and molecular weight distributions (M_w/M_n) of the polyethylenes were determined using a PL-GPC220 at 150 °C with 1,2,4-trichlorobenzene as the eluting solvent. The melt temperatures of the polyethylenes were obtained from the second scanning run on PerkinElmer TA-Q2000 differential scanning calorimeter (DSC) under a nitrogen atmosphere. In the procedure, a sample of 4.0 – 6.0 mg was heated to 150 °C at a rate of 10 °C min^{-1} . The ^1H and ^{13}C NMR spectra of the polyethylenes were recorded on a Bruker DMX 300 MHz instrument at 100 °C in deuterated 1,1,2,2-tetrachloroethane- d_2 with TMS as the internal standard.

Synthesis of 8-N{2,6-R₂-4-(C₁₅H₁₃)C₆H₂}C₉H₈N (**L**) / 8-NH{2,6-R₂-4-(C₁₅H₁₃)C₆H₂}C₉H₇N (**L'**)

(a) R = Me **L1/L1'**. A solution of 5,6,7-trihydroquinolin-8-one (0.74 g, 5.0 mmol) 4-dibenzocycloheptyl-2,6-dimethylaniline (1.90 g, 6.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.21 g, 24 mol%) in toluene (25 mL) was stirred at reflux for 8 h. On cooling to room temperature, the solvent was removed under reduced pressure and the residue purified by column chromatography (alumina column). Elution with petroleum ether/ethyl acetate (100/1, v/v) gave **L1/L1'** (76:24) as a yellow powder (0.48 g, 22%). ^1H NMR (300 MHz, CDCl_3 , TMS): δ 8.70 (d, J = 3.0 Hz, 1H, Py *H*), 8.38 (d, J = 4.5 Hz, 1H, **L1'** - Py *H*), 7.55 (d, J = 9.0 Hz, 1H, Py *H*), 7.42 (d, J = 9.0 Hz, 1H, **L1'** - Py *H*), 7.33 - 7.27 (m, 1H - Py *H*, 2H - Ph *H*, 1H **L1'** - Py *H*), 7.23 – 7.17 (m, 4H, Ph *H*, 6H, **L1'** - Ph *H*), 7.15 – 7.12 (m, 2H, Ph *H*, 2H, **L1'** - Ph *H*), 6.58 (s, 2H, **L1'** - Ph *H*), 6.49 (s, 2H, Ph *H*), 5.16 (s, 1H,

-CH, 1H, **L1'** - CH), 4.70 (t, $J = 4.5$ Hz, 1H, **L1'** -NH), 3.23 – 3.10 (m, 2H, -CH₂, 2H, **L1'** -CH₂), 2.92 (t, $J = 6.0$ Hz, 2H, -CH₂), 2.83 – 2.66 (m, 2H, -CH₂, 4H, **L1'** -CH₂), 2.34 (t, $J = 6.0$ Hz, 2H, -CH₂), 2.28 – 2.23 (m, 2H, **L1'** -CH₂), 2.04 (s, 1H, -CH), 1.95 – 1.85 (m, 2H, -CH₂), 1.93 (t, $J = 6.0$ Hz, 2H, **L1'** -CH₂), 1.89 (s, 6H, -CH₃, 6H, **L1'** -CH₃). ¹³C NMR (75 MHz, CDCl₃, TMS): δ 164.6, 150.0, 148.9, 147.0, 146.1, 140.9, 140.6, 139.9, 139.5, 137.2, 136.9, 135.0, 134.7, 132.3, 131.5, 131.5, 130.8, 127.1, 126.6, 126.0, 124.8, 122.0, 97.9, 58.0, 57.8, 32.2, 30.5, 29.5, 28.03, 22.40, 21.5, 18.4. FT-IR (KBr, cm⁻¹): 3355 (m), 2936 (m), 2824 (s), 1642 (ν (C=N), s), 1567 (m), 1476 (s), 1412 (s), 1371 (m), 1323 (m), 1298 (m), 1268 (m), 1246 (m), 1227 (m), 1194 (m), 1135 (w), 1098 (m), 1046 (m), 1020 (m), 970 (w), 935 (w), 883 (s), 788 (s), 752 (s), 723 (w), 692 (m). Anal. calcd for C₃₂H₃₀N₂ (442.61): C, 86.84; H, 6.83; N, 6.33%. Found: C, 86.59%; H, 6.87; N, 6.58%.

(b) R = Et **L2/L2'**. A solution of 5,6,7-trihydroquinolin-8-one (0.74 g, 5.0 mmol), 4-dibenzocycloheptyl-2,6-diethylaniline (2.0 g, 6.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.20 g, 23 mol%) in toluene (25 mL) was stirred and heated to reflux for 8 h. On cooling to room temperature, the solvent was removed under reduced pressure and the residue purified by column chromatography (alumina column). Elution with petroleum ether/ethyl acetate (100/1, v/v) gave **L2/L2'** (75:25) as a yellow-green powder (0.24 g, 10%). ¹H NMR (300 MHz, CDCl₃, TMS): δ 8.70 (d, $J = 6.0$ Hz, 1H, Py *H*), 8.38 (d, $J = 6.0$ Hz, 1H, **L2'** - Py *H*), 7.54 (d, $J = 6.0$ Hz, 1H, Py *H*), 7.41 (d, $J = 3.0$ Hz, 1H, **L2'** - Py *H*, 2H, **L2'** - Ph *H*), 7.33 (t, $J = 4.5$ Hz, 1H, Py-*H*, 1H, **L2'** - Py *H*, **L2'** - Ph *H*), 7.29 - 7.25 (m, 2H, Ph *H*, **L2'** - Ph *H*), 7.21 – 7.18 (m, 4H, Ph *H*, 4H, **L2'** - Ph *H*), 7.16 – 7.11 (m, 2H, Ph *H*, 2H, **L2'** - Ph *H*), 6.63 (s, 2H, **L2'** - Ph *H*), 6.55 (s, 2H, Ph *H*), 5.21 (s, 1H, -CH, 1H, **L2'** - CH), 4.46 (t, $J = 4.5$ Hz, 1H, **L2'** -NH), 3.14 – 3.06 (m, 2H, -CH₂, 2H, **L2'** -CH₂), 2.91 (t, $J = 6.0$ Hz, 2H, -CH₂), 2.82 – 2.65 (m, 2H, -CH₂, 4H, **L2'** -CH₂, 1H, **L2'** -CH), 2.51 – 2.44 (m, 4H, **L2'** -CH₂), 2.37 (t, $J = 6.0$ Hz, 2H, -CH₂), 2.31 – 2.12 (m, 4H, CH₂, 2H, **L2'** -CH₂), 1.94 – 1.86 (m, 2H, -CH₂), 1.00 (t, $J = 3.0$ Hz, 6H, **L2'** -CH₃), 0.94 (t, $J = 7.5$ Hz, 6H, -CH₃). ¹³C NMR (75 MHz, CDCl₃, TMS): δ 164.3, 150.1, 148.9, 145.8, 141.5, 141.0, 140.8, 140.0, 139.9, 139.8, 137.2, 136.9, 131.4, 130.7, 127.6, 127.1, 127.0, 127.0, 126.0, 126.0, 125.4, 124.8, 97.6, 58.2, 58.0, 30.7, 29.5, 28.0, 24.9, 24.6, 24.5, 22.7, 22.3, 21.5. FT-IR (KBr, cm⁻¹): 3395 (m), 3333 (m), 2964 (m), 2930 (m), 2872 (m), 2838 (w), 1641 (ν (C=N), s), 1621 (w), 1569 (m), 1470 (s), 1425 (s), 1373 (m), 1330 (w), 1285 (m), 1258 (s), 1193 (m), 1094 (s), 1047 (w), 1019 (m),

887 (m), 794 (s), 761 (s), 724 (w), 682 (s). Anal. calcd for C₃₄H₃₄N₂ (470.66): C, 86.77; H, 7.28; N, 5.95%. Found: C, 86.69; H, 7.36; N, 5.87%.

(c) R = *i*-Pr **L3/L3'**. A solution of 5,6,7-trihydroquinolin-8-one (0.74 g, 5.0 mmol) 4-dibenzocycloheptyl-2,6-diisopropylaniline (2.2 g, 6.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid (0.22 g, 26 mol%) was stirred and heated to reflux in toluene (25 mL) for 8 h. On cooling to room temperature, the solvent was removed under reduced pressure and the residue purified by column chromatography (alumina column). Eluting with petroleum ether/ethyl acetate (100/1, v/v) gave **L3/L3'** (78:22) as a yellow powder (0.54 g, 27%). ¹H NMR (300 MHz, CDCl₃, TMS): δ 8.71 (d, *J* = 3.6 Hz, 1H, Py *H*), 8.39 (d, *J* = 4.5 Hz, 1H, **L3'** - Py *H*), 7.55 (d, *J* = 7.5 Hz, 1H, Py *H*), 7.42 (d, *J* = 7.2 Hz, 1H, **L3'** - Py *H*), 7.33 (t, *J* = 4.5 Hz, 2H, Ph *H*, 2H, **L3'** - Ph *H*), 7.28 (t, *J* = 4.5 Hz, 1H, Py *H*, 1H, **L3'** - Py *H*), 7.18 (t, *J* = 4.5 Hz, 4H, Ph *H*, 4H, **L3'** - Ph *H*), 7.15 – 7.07 (m, 2H, Ph *H*, 2H, **L3'** - Ph *H*), 6.71 (s, 2H, **L3'** - Ph *H*), 6.60 (s, 2H, Ph *H*), 5.22 (s, 1H, -CH, 1H, **L3'** - CH), 4.45 (t, *J* = 4.5 Hz, 1H, **L3'** -NH), 3.15 – 3.00 (m, 2H, -CH₂, 2H, **L3'** -CH₂, 2H, **L3'** -CH), 2.94 (t, *J* = 6.0 Hz, 2H, -CH₂), 2.85 – 2.65 (m, 2H, -CH₂, 2H, -CH, 4H, **L3'** -CH₂, 1H, **L3'** -CH), 2.41 (t, *J* = 6.3 Hz, 2H, -CH₂), 2.28 – 2.21 (m, 2H, **L3'** -CH₂), 1.95 – 1.87 (m, 2H, -CH₂), 0.96 (t, *J* = 4.5 Hz, 12H, **L3'** -CH₃), 0.92 (t, *J* = 4.5 Hz, 12H, -CH₃). ¹³C NMR (75 MHz, CDCl₃, TMS): δ 164.7, 150.0, 148.9, 146.4, 144.1, 141.3, 140.9, 140.2, 139.8, 137.3, 136.9, 135.5, 134.6, 134.1, 131.4, 131.3, 130.7, 127.0, 125.9, 124.8, 122.6, 122.2, 97.7, 58.4, 58.18, 32.31, 32.1, 30.9, 29.5, 28.2, 28.0, 23.5, 23.4, 22.4, 22.3, 21.5. FT-IR (KBr, cm⁻¹): 3330 (m), 2960 (s), 2932 (w), 2870 (m), 2829 (m), 1732 (w), 1644 (ν(C=N), s), 1623 (w), 1604 (w), 1573 (m), 1479 (s), 1455 (w), 1426 (s), 1380 (w), 1355 (m), 1331 (w), 1286 (m), 1251 (m), 1194 (m), 1104 (m), 1070 (m), 1045 (m), 1019 (m), 945 (m), 894 (m), 793 (s), 761 (s), 686 (s). Anal. calcd for C₃₆H₃₈N₂ (498.71): C, 86.70; H, 7.68; N, 5.62%. Found: C, 87.88; H, 7.82; N, 5.37%.

Synthesis of [8-N{2,6-R₂-4-(C₁₅H₁₃)C₆H₂Ar}C₉H₈N]NiCl₂ (Ni1 – Ni3)

General procedure. A solution of NiCl₂·6H₂O (0.12 g, 0.5 mmol) in ethanol (10 mL) was added to a solution of the corresponding **L/L'** (0.5 mmol) in CH₂Cl₂ (10 mL) at room temperature. The reaction mixture was stirred at room temperature for 12 h. Diethyl ether (50 mL) was then added to induce precipitation and the precipitate collected by filtration, washed with diethyl ether (3 × 5 mL) and dried

under reduced pressure to give the corresponding complex.

(a) R = Me **Ni1**. Green powder (0.26 g, 90%). FT-IR (KBr, cm^{-1}): 3250 (s), 3013 (w), 2930 (m), 1626 ($\nu(\text{C}=\text{N})$, s), 1586 (s), 1453 (s), 1337 (m), 1287 (m), 1214 (s), 1136 (s), 1102 (m), 1048 (w), 924 (m), 880 (w), 834 (w), 794 (s), 763 (s). Anal. calcd for $\text{C}_{32}\text{H}_{30}\text{Cl}_2\text{N}_2\text{Ni}$ (572.20): C, 67.17; H, 5.28; N, 4.90%. Found: C, 67.35; H, 5.47; N, 4.63%.

(b) R = Et **Ni2**. Green powder (0.28 g, 92%). FT-IR (KBr, cm^{-1}): 2930 (m), 2868 (w), 1620 ($\nu(\text{C}=\text{N})$, s), 1584 (s), 1490 (w), 1457 (s), 1429 (s), 1346 (w), 1334 (m), 1306 (m), 1289 (m), 1259 (w), 1221 (m), 1200 (m), 1158 (w), 1130 (m), 1099 (w), 1055 (w), 1041 (w), 927 (w), 886 (m), 822 (s), 797 (m), 763 (s), 746 (w), 729 (m), 699 (m). Anal. calcd for $\text{C}_{34}\text{H}_{34}\text{Cl}_2\text{N}_2\text{Ni}$ (600.25): C, 68.03; H, 5.71; N, 4.67%. Found: C, 68.24; H, 5.84; N, 4.53%.

(c) R = *i*-Pr **Ni3**. Green powder (0.32 g, 82%). FT-IR (KBr, cm^{-1}): 3225 (m), 2948 (m), 2865 (m), 1617 ($\nu(\text{C}=\text{N})$, m), 1582 (s), 1491 (w), 1452 (s), 1381 (m), 1354 (w), 1331 (s), 1283 (m), 1195 (m), 1163 (w), 1120 (s), 1075 (s), 1041 (s), 950 (w), 924 (m), 883 (m), 797 (s), 714 (s), 725 (m), 695 (m). Anal. calcd for $\text{C}_{36}\text{H}_{38}\text{Cl}_2\text{N}_2\text{Ni}$ (628.31): C, 68.82; H, 6.10; N, 4.46%. Found: C, 69.01; H, 6.35; N, 4.28%.

One-pot synthesis of [8-N{2,6-R₂-4-(C₁₅H₁₃)C₆H₂Ar}C₉H₈N]NiCl₂ (**Ni4**, **Ni5**)

General procedure. A suspension of 5,6,7-trihydroquinolin-8-one (0.15 g, 1.0 mmol), the corresponding aniline (1.0 mmol) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24 g, 1.0 mmol) in glacial acetic acid (10 mL) was stirred and heated to reflux for 6 h. On cooling to room temperature, an excess of diethyl ether (30 mL) was added to precipitate the product. The precipitate was then filtered and washed with diethyl ether (3×15 mL) and dried under reduced pressure to give the corresponding complex.

(a) R = F **Ni4**. Green powder (0.27 g, 47%). FT-IR (KBr, cm^{-1}): 3064 (w), 2860 (m), 1652 (s), 1623 ($\nu(\text{C}=\text{N})$, w), 1590 (s), 1576 (w), 1458 (m), 1430 (m), 1411 (w), 1332 (s), 1304 (w), 1288 (s), 1205 (s), 1132 (s), 1103 (s), 1034 (m), 912 (s), 846 (m), 827 (s), 809 (s), 769 (m), 715 (s). Anal. calcd for $\text{C}_{30}\text{H}_{24}\text{Cl}_2\text{F}_2\text{N}_2\text{Ni}$ (580.13): C, 62.11; H, 4.17; N, 4.83%. Found: C, 62.04; H, 4.39; N, 3.89%.

(b) R = Cl **Ni5**. Green powder (0.27 g, 44%). FT-IR (KBr, cm^{-1}): 3068 (w), 2935 (w), 2972 (m), 1658 (s), 1633 ($\nu(\text{C}=\text{N})$, w), 1585 (s), 1517 (s), 1493 (m), 1426 (s), 1354 (w), 1316 (s), 1288 (m), 1206 (s), 1130 (w), 1106 (s), 1032 (s), 977 (m), 914 (m), 869 (m), 797 (m), 765 (s), 713 (w), 690 (w). Anal. calcd for $\text{C}_{30}\text{H}_{24}\text{Cl}_4\text{N}_2\text{Ni}$ (613.03): C, 58.78; H, 3.95; N, 4.57%. Found: C, 59.11; H, 4.30; N, 4.22%.

Crystallographic Studies

Single crystals of **Ni2**·1/2H₂O and **Ni3**·1/3H₂O suitable for X-ray diffraction were grown by layering a dichloromethane/methanol solution of the corresponding complex with diethyl ether at room temperature. X-ray studies were carried out using a Rigaku Saturn 724 + CCD diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å) at 173(2) K. 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 F^2 . All hydrogen atoms were placed in calculated positions. Structure refinement were performed by using the SHELXL-97 package [28, 29]. The SQUEEZE option of the crystallographic program PLATON was used to remove free solvents from the structures of both **Ni2**·1/2H₂O and **Ni3**·1/3H₂O. Details of the X-ray structure determinations and refinements are provided in Table 1. CCDC numbers 1857880 (**Ni2**·1/2H₂O), 1857881(**Ni3**·1/3H₂O) contains the supplementary crystallographic data for this paper could be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table 1 Crystal data and structure refinement for **Ni2**·1/2H₂O and **Ni3**·1/3H₂O

Identification code	Ni2 ·1/2H ₂ O	Ni3 ·1/3H ₂ O
CCDC No.	1857880	1857881
Empirical formula	C ₆₈ H ₇₀ Cl ₄ N ₄ Ni ₂ O	C ₁₀₈ H ₁₁₆ Cl ₆ N ₆ Ni ₃ O
Formula weight	1218.50	1902.89
Temperature/K	173.15	173.15
Wavelength/Å	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	14.976(3)	12.2313(2)
<i>b</i> /Å	16.076(3)	16.2235(3)
<i>c</i> /Å	17.149(3)	29.7464(6)
α /°	116.07(3)	76.594(2)
β /°	90.50(3)	84.642(2)
γ /°	113.59(3)	69.987(2)
Volume/Å ³	3312.3(15)	5394.52(19)
<i>Z</i>	2	2
$D_{\text{calcd}}/(\text{g cm}^{-3})$	1.222	1.171
μ/mm^{-1}	0.772	0.713
$F(000)$	1276.0	2000.0

Crystal size/mm ³	0.157 × 0.142 × 0.064	0.19 × 0.13 × 0.11
Radiation	MoK _α (λ = 0.71073)	MoK _α (λ = 0.71073)
2θ range for data collection/°	3.332 to 52.744	3.332 to 52.744
	-19 ≤ h ≤ 19	-15 ≤ h ≤ 15
Index ranges	-20 ≤ k ≤ 20	-20 ≤ k ≤ 20
	-22 ≤ l ≤ 22	-37 ≤ l ≤ 37
Reflections collected	45200	71725
Independent reflections	15074 [R _{int} = 0.0440, R _{sigma} = 0.0471]	22010 [R _{int} = 0.0604, R _{sigma} = 0.0750]
Data/restraints/parameters	15074/19/728	22010/255/1262
Completeness to θ	0.992	0.997
Goodness-of-fit on F ²	1.107	1.040
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0557	R ₁ = 0.0725
	wR ₂ = 0.1128	wR ₂ = 0.1629
Final R indexes [all data]	R ₁ = 0.0645	R ₁ = 0.1155
	wR ₂ = 0.1175	wR ₂ = 0.1819
Largest diff. peak and hole / (e Å ⁻³)	0.92/-0.43	0.80/-0.48

General procedure for ethylene polymerization

Ethylene polymerizations were carried out in a 250 mL stainless steel autoclave equipped with a mechanical stirrer and a temperature controller. The autoclave was evacuated and back-filled three times with nitrogen and once with ethylene. When the required temperature was reached, the precatalyst (3 μmol), 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 (MMAO or Et₂AlCl) 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. 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 until of constant mass.

Polyethylene epoxidation

A sample of polyethylene wax (2.0 g), prepared using **Ni1**/Et₂AlCl at 30 °C (run 18, Table 4), was placed in 100 mL Schlenk tube containing dry toluene (50 mL). The contents of the flask was then stirred and heated to 65 °C until the polymer had completely dissolved. *m*-Chloroperbenzoic acid (1.50 g, 8.7 mmol), dissolved in toluene (10 mL), was added and the mixture stirred at 65 °C for 4 h. On cooling

to room temperature, methanol (100 mL) was added to induce precipitation and the precipitate filtered, washed with methanol and dried under reduced pressure at 50 °C for 24 h to give e-PE as a white solid (1.80 g, 90%). ¹H NMR (300 MHz, C₂D₂Cl₄, TMS): δ 3.03, 2.91, 2.75, 2.71, 2.48, 2.45, 1.56, 1.38, 0.96, 0.94. ¹³C NMR (75 MHz, C₂D₂Cl₄, TMS): δ 129.2, 128.4, 125.5, 74.5, 74.2, 73.8, 59.6, 58.7, 58.4, 58.2, 57.0, 56.9, 52.3, 52.2, 46.7, 39.4, 37.9, 37.6, 37.4, 36.9, 34.3, 33.8, 33.0, 32.0, 29.8, 29.4, 28.1, 27.6, 27.3, 27.1, 26.8, 23.1, 22.7, 21.3, 19.9, 19.4, 17.7, 14.6, 14.0, 13.3, 11.3, 11.0, 10.5.

Results and discussion

1. Synthesis and characterization of the ligands and complexes

The condensation reactions of 5,6,7-trihydroquinolin-8-one with 2,6-R₂-4-(C₁₅H₁₃)C₆H₂NH₂ (R = Me, Et, *i*-Pr) afforded the ligands as a tautomeric mixture of [8-N{2,6-R₂-4-(C₁₅H₁₃)C₆H₂}C₉H₈N] (R = Me **L1**, Et **L2**, *i*-Pr **L3**) and [8-NH{2,6-R₂-4-(C₁₅H₁₃)C₆H₂}C₉H₇N] (R = Me **L1'**, Et **L2'**, *i*-Pr **L3'**) as yellow solids (Scheme 1). All three compounds have been characterized by ¹H, ¹³C NMR and FT-IR spectroscopy as well as by elemental analysis. Treatment of **L1/L1'** - **L3/L3'** with NiCl₂·6H₂O in a mixture of ethanol and dichloromethane at room temperature gave [8-N{2,6-R₂-4-(C₁₅H₁₃)C₆H₂}C₉H₈N]NiCl₂ (R = Me **Ni1**, Et **Ni2**, *i*-Pr **Ni3**) as green solids in good yields (82 – 92%). By contrast, the nickel complexes, [8-N{2,6-R₂-4-(C₁₅H₁₃)C₆H₂}C₉H₈N]NiCl₂ (R = F **Ni4**, Cl **Ni5**), were obtained in reasonable yield by the one-pot reactions of 5,6,7-trihydroquinolin-8-one, 2,6-R₂-4-(C₁₅H₁₃)C₆H₂NH₂ (R = F, Cl) and NiCl₂·6H₂O in acetic acid owing to difficulties encountered in the free ligand synthesis. All five complexes are air stable have been characterized by FT-IR spectroscopy and by elemental analysis, while **Ni2** and **Ni3** have been the subject of single crystal X-ray diffraction studies.

Scheme 1 Synthesis of ligands **L1 – L3** and complexes **Ni1 – Ni5**

Single crystals of **Ni2** and **Ni3** suitable for X-ray determinations were grown by layering a dichloromethane/methanol solution of the corresponding complex with diethyl ether at room temperature. Perspective views of their structures are shown in Figures 1 and 2; selected bond distances and angles are collected in Table 2.

Figure 1 ORTEP representation of **Ni2·1/2H₂O**. The thermal ellipsoids are shown at the 30% probability level and the hydrogen atoms have been omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for **Ni2**·1/2H₂O and **Ni3**·1/3H₂O

Ni2			Ni3	
Bond length (Å)				
Ni⋯Ni ^a	Ni1⋯Ni2	3.473	Ni1⋯Ni2	3.584
			Ni2⋯Ni3	3.125
			Ni1⋯Ni3	4.498
Ni-N _{imine}	Ni1-N2	2.097(2)	Ni1-N2	2.054(4)
	Ni2-N4	2.065(2)	Ni2-N4	2.127(4)
Ni-N _{pyridine}	Ni1-N1	2.053(2)	Ni3-N6	2.151(3)
			Ni1-N1	2.114(4)
			Ni2-N3	2.042(4)
			Ni3-N5	2.048(3)
Ni-Cl	Ni1-Cl1	2.3902(16)	Ni1-Cl1	2.3552(15)
	Ni2-Cl4	2.3095(10)	Ni3-Cl6	2.3394(13)
Ni-μ-Cl	Ni1-Cl3	2.4700(18)	Ni1-Cl3	2.5885(11)
	Ni1-Cl2	2.4355(9)	Ni1-Cl2	2.3607(12)
	Ni2-Cl3	2.3701(8)	Ni2-Cl5	2.4554(11)
	Ni2-Cl2	2.3326(17)	Ni2-Cl2	2.3888(11)
			Ni2-Cl4	2.3612(12)
			Ni3-Cl4	2.5517(12)
			Ni3-Cl5	2.4300(12)
			Ni3-Cl3	2.4558(11)
Ni-O _{water}	Ni1-O1	2.1163(19)	Ni1-O1	2.094(3)
Bond angles (°)				
	N3-Ni2-N4	79.10(9)	O1-Ni1-Cl1	171.75(9)
	N1-Ni1-N2	78.91(8)	N1-Ni1-Cl1	87.91(12)
	Cl1-Ni1-Cl3	167.57(3)	N2-Ni1-Cl1	98.86(12)
	O1-Ni1-N2	170.12(8)	Cl1-Ni1-Cl2	95.93(5)
	N1-Ni1-Cl2	178.02(6)	Cl2-Ni2-Cl5	167.30(4)
	N3-Ni2-Cl4	90.78(7)	N4-Ni2-Cl3	172.92(11)
	N4-Ni2-Cl4	103.65(7)	Cl6-Ni3-Cl5	169.76(5)
			N5-Ni3-N6	78.33(14)

^a The Ni···Ni distances were measured using Ortep software

The structure of **Ni2**·1/2H₂O is based on a dimeric core, ClNi(μ-Cl)₂NiCl, in which one chloride per nickel center bridges the metal atoms while the remaining chlorides acts as monodentate ligands; similar structural motifs have been reported [5,13,17,19,20]. In addition, each nickel atom is bound by two nitrogen atoms belonging to the neutral chelating **L2**. Unexpectedly, a water molecule acts as monodentate ligand to Ni1 leading to a distorted octahedral geometry conferred to this metal center [O1-Ni1-N2 170.12(8), N(1)-Ni1-Cl2 178.02(6), Cl1-Ni1-Cl3 167.57(3)°]. By contrast, the geometry

around the Ni2 center can be described as square pyramidal, in which Cl12, C3, N3 and N4 form the basal plane while Cl14 occupies the axial site [N3-Ni2-Cl14 is $90.78(7)^\circ$]. In addition, the Ni-N_{imine} bond lengths [$2.065(2)$ Å, $2.097(2)$ Å] are generally longer than that the Ni-N_{pyridine} distances [$2.053(2)$ Å, $2.055(2)$ Å], reflecting the better donor ability of a pyridine nitrogen. The N-aryl groups are inclined essentially orthogonally to the neighboring imine vectors, while the central seven-membered ring within the *para*-dibenzocycloheptyl units are puckered as the result of the three sp^3 -hybridized carbon atoms. The coordinated water undergoes an intramolecular hydrogen bond interaction with Cl14 on the neighboring metal center [$\text{OH}\cdots\text{Cl14}$ 3.103 Å]. There are no intermolecular contacts of note.

Figure 2 (a) ORTEP representation of $\text{Ni}_3 \cdot 1/3\text{H}_2\text{O}$ and (b) a view with the N-aryl groups removed. The thermal ellipsoids are shown at the 30% probability level and the hydrogen atoms have been omitted for clarity.

The structure of **Ni3** • 1/3H₂O adopts an unusual trinuclear core, Ni₃Cl₂(μ₂-Cl)₃(μ₃-Cl), in which Cl3 triply bridges all three nickel centers while Cl2, Cl4 and Cl5 act as bridging ligands between two adjacent metals; monodentate Cl1 and Cl6 are additionally bound to Ni1 and Ni3, respectively. The coordination spheres of each nickel atom are each completed by a bidentate **L3** and, in the case of Ni1, additionally by a water molecule resulting in distorted octahedral geometries around all three metal centers (Figure 2b). The Ni-N_{pyridine} distances involving Ni2 and Ni3 are similar [2.042(4), 2.048(3) Å] and indeed shorter than the corresponding Ni-N_{imine} distances [2.127(4), 2.151(3) Å]. By contrast, the Ni1-N1_{pyridine} distance [2.114(4) Å] is longer than the Ni1-N2_{imine} length [2.054(4) Å], which is likely due to the steric hindrance imposed by the neighboring μ₃-Cl and water ligands. Puckering of the central seven-membered ring within the dibenzocycloheptyl units is again a feature of this *para*-substituted group. In addition, there are intramolecular hydrogen-bonding interactions between the coordinated water and Cl4 and Cl6 [OH...Cl(4) 3.117 Å, OH...Cl(6) 3.068 Å]. There are no intermolecular contacts of note.

Additional support for the composition of **Ni1** – **Ni5** was provided by the microanalytical and IR data, the latter revealing imine absorptions around 1620 cm⁻¹ which are typical of nickel(II)-coordinated imine nitrogen atoms [5].

2. Ethylene polymerization

To explore the most effective co-catalyst for the ethylene polymerizations, four different alkyl-aluminum reagents were assessed, MAO, MMAO, Et₂AlCl and EASC, with **Ni3** selected as the test precatalyst. Typically, the screening was conducted in toluene at 10 atm C₂H₄ over 30 minutes; the results are collected in Table 3. Of the four tests, **Ni3**/Et₂AlCl showed the highest activity while **Ni3**/MAO and **Ni3**/EASC were less active but comparable in value (runs 2, 4, Table 3). To allow an assessment of two distinct classes of activator, MMAO and Et₂AlCl were chosen for the subsequent more in-depth investigations.

Table 3 Ethylene polymerization using **Ni3**^a

Run	Co-cat.	Al:Ni	Mass of PE (g)	Activity ^b	<i>M_w</i> ^c	<i>M_w</i> / <i>M_n</i> ^d	<i>T_m</i> ^e (°C)
1	MAO	2000	0.84	0.56	2.29	1.52	68.2

2	MMAO	2000	4.32	2.89	2.08	1.62	63.9
3	Et ₂ AlCl	500	6.83	4.58	1.69	1.51	55.6
4	EASC	500	4.42	2.95	1.64	1.63	55.6

^a Conditions: 3.0 μmol of **Ni3**, 30 $^{\circ}\text{C}$, 30 min, 10 atm C₂H₄, total volume 100 mL;

^b Activity: $\times 10^6$ g PE mol⁻¹ (Ni) h⁻¹;

^c Weight-average molecular weight in kg mol⁻¹, as determined by GPC;

^d Polydispersity, as determined by GPC;

^e Melt temperature, as determined by DSC.

(a) *Catalytic evaluation of Ni1 – Ni5/Et₂AlCl*. Before all five precatalysts were screened with Et₂AlCl, the conditions of the polymerization were first optimized using **Ni3**. Specifically, the influence of Al:Ni molar ratio, temperature and reaction time were all evaluated; the results are compiled in Table 4.

Table 4 Ethylene polymerization using **Ni1 - Ni5** / Et₂AlCl^a

Run	Precat.	Al:Ni	T ($^{\circ}\text{C}$)	T (min)	Mass of PE (g)	Activity ^b	M_w^c	M_w/M_n^d	T_m^e ($^{\circ}\text{C}$)
1	Ni3	300	30	30	5.14	3.43	1.58	1.72	53.0
2	Ni3	400	30	30	5.32	3.55	1.44	1.59	49.6
3	Ni3	450	30	30	5.63	3.77	1.59	1.56	55.7
4	Ni3	500	30	30	6.83	4.58	1.69	1.51	55.6
5	Ni3	550	30	30	5.81	3.89	1.63	1.56	64.5
6	Ni3	600	30	30	5.74	3.83	1.68	1.62	55.8
7	Ni3	700	30	30	5.23	3.49	1.74	1.57	52.2
8	Ni3	800	30	30	3.81	2.54	1.63	1.59	51.1
9	Ni3	500	20	30	5.76	3.84	1.30	1.56	66.4
10	Ni3	500	40	30	2.69	1.80	2.11	1.77	62.1
11	Ni3	500	50	30	0.66	0.44	1.31	1.49	68.5
12	Ni3	500	30	5	0.61	2.44	1.75	1.48	53.8
13	Ni3	500	30	15	2.31	3.08	1.60	1.48	54.7
14	Ni3	500	30	45	7.59	3.53	1.63	1.66	53.9
15	Ni3	500	30	60	10.26	3.42	1.61	1.63	52.3
16 ^f	Ni3	500	30	30	0.87	0.58	1.35	1.54	66.6
17 ^g	Ni3	500	30	30	Trace	Trace	--	--	--
18	Ni1	500	30	30	5.80	3.87	1.57	1.48	67.1
19	Ni2	500	30	30	5.53	3.68	1.94	1.58	68.3
20	Ni4	500	30	30	0.07	0.05	1.54	1.66	75.7
21	Ni5	500	30	30	Trace	Trace	--	--	--

^a Conditions: 3.0 μmol of precatalyst, 30 $^{\circ}\text{C}$, 30 min, 10 atm C₂H₄, total volume 100 mL;

^b Activity: $\times 10^6$ g PE mol⁻¹ (Ni) h⁻¹;

^c Weight-average molecular weight in kg mol⁻¹, as determined by GPC;

^d Polydispersity, as determined by GPC;

^e Melting temperature, as determined by DSC;

^f 5 atm C₂H₄;

^g 1 atm C₂H₄.

Firstly, with the temperature set at 30 °C and the run time at 30 minutes, the Al:Ni molar ratio was varied between 300 and 800 (runs 1 – 8, Table 4). As the molar ratio was increased, the catalytic activity reached a maximum of 4.58×10^6 g(PE)·mol(Ni)⁻¹ h⁻¹ at a ratio of 500 (run 3, Table 4). Above 500, the activity gradually decreased reaching its lowest value of 2.54×10^6 g(PE)·mol(Ni)⁻¹ h⁻¹ at a ratio of 800 (run 8, Table 4). However, there was no clear effects shown by the amount of co-catalyst on the molecular weight with very similar values observed across the ratio range ($M_w = 1.44 - 1.74$ kg·mol⁻¹). In addition, the molecular weight distribution (M_w/M_n range = 1.51 – 1.72) remained particularly narrow and unimodal as shown by the GPC curves (Figure 3).

Figure 3 GPC curves for the polyethylene obtained using **Ni3**/Et₂AlCl at various Al:Ni ratios (runs 1 – 8, Table 4).

Secondly, with the Al:Ni molar ratio fixed at 500 and the reaction time at 30 minutes, the temperature was varied between 20 and 50 °C resulting in the highest activity of **Ni3**/Et₂AlCl being achieved at 30 °C (runs 4, 9 – 11, Table 4). Further raising the temperature up to 50 °C led to a rapid decrease in activity from 4.58 to 0.44×10^6 g(PE)·mol(Ni)⁻¹ h⁻¹ (runs 4, 9 - 11, Table 4), which can be ascribed to the deactivation of the active species and the lower solubility of ethylene at higher temperature [19-25]. As reported elsewhere, an active species of the type [LNi(II)Et]⁺[AlEt₃Cl]⁻ would seem likely that on decomposition at higher temperature would form an inactive bis-ligated Ni(I) species

[30]. In addition, the molecular weight distribution remained very narrow ($M_w/M_n < 2.0$) at various temperatures indicative of a single site catalyst.

Thirdly, with the temperature kept at 30 °C and the Al:Ni molar ratio at 500, the effect of time was investigated by conducting the polymerizations using **Ni3**/Et₂AlCl at 5, 15, 30, 45 and 60 minute intervals. Between 5 and 30 minutes the activity gradually increased reaching a peak after 30 minutes [18-19, 22, 31-35], while during the second 30 minutes it slowly decreased with the onset of catalyst deactivation. The ethylene pressure also significantly affected the performance, which was demonstrated by the much lower activity at 5 atm C₂H₄ and only trace amounts of polymer observed at 1 atm (runs 16, 17, Table 4). Additionally, the molecular weight of the polymer obtained at 5 atm was lower than that achieved at 10 atm, which can be attributed to the higher propagation rate at higher ethylene pressure (runs 4, 16, Table 4).

Finally, under the optimum conditions established for **Ni3** (Al:Ni = 500, run temperature = 30 °C, run time = 30 minutes), **Ni1** - **Ni5** were all investigated for ethylene polymerization (runs 4, 18 - 21, Table 4). The catalytic activities were found to fall in the order, **Ni3** > **Ni1** ~ **Ni2** >> **Ni4** ~ **Ni5**, highlighting the importance of both steric and electronic properties imparted by the *ortho*-R groups. In terms of steric properties, the most bulky isopropyl system **Ni3** delivered the highest activity of 4.58×10^6 g(PE)·mol(Ni)⁻¹·h⁻¹ followed closely by **Ni1** and **Ni2**. Conversely, **Ni4** and **Ni5** exhibited much lower activity due to a likely combination of the electron-withdrawing properties of F or Cl and steric differences. In general, the type of *ortho*-substituent had little effect on both the molecular weight (M_w range: 1.54 - 1.94 kg·mol⁻¹) and the dispersity of the polymer. By contrast, the melt temperature (T_m) of the polyethylene generated by *ortho*-fluoride **Ni4** was notably higher (75.7 °C) than that produced by **Ni1** - **Ni3** (55.6 – 68.3 °C); this finding is discussed in more detail later.

To explore the overall effect of *para*-dibenzocycloheptyl substitution on catalytic performance with Et₂AlCl as the co-catalyst, the activity, molecular weight and dispersity data for the structurally related iminotrihydroquinoline-complexes **A** [17], **E** [21] and **F** [23] are presented alongside that for **Ni2** in Chart 2. In terms of activity, **A** (5.20×10^6 g(PE)·mol⁻¹(Ni)·h⁻¹), proved the most active with their relative performances falling in the order: **A** > **F** > **Ni2** > **E**. On the other hand, the molecular weight of the polymer generated using **Ni2** was at the lower end ($M_w = 1.94 \times 10^3$ g mol⁻¹) and comparable with that formed by **F**. Moreover, **Ni2** delivered the polymer exhibiting the narrowest dispersity ($M_w/M_n =$

1.58) of this series. It is apparent that performance of **Ni2**/Et₂AlCl is quite different from that of **A** and **E** but bears some resemblance to that for fluorenyl-containing **F**.

Chart 2 Comparative catalytic performance of **A**, **E**, **F** and **Ni2**; all polymerizations were performed under 10 atm C₂H₄.

(b) *Catalytic evaluation of Ni1 – Ni5/MMAO*. To complement the study performed with Et₂AlCl, a parallel investigation was performed using MMAO as co-catalyst; the results are collected in Table 5. Once again, **Ni3** was chosen as the test precatalyst to allow an optimization of the polymerization parameters. On increasing the Al:Ni molar ratio from 1000 to 3000, the highest activity for **Ni3**/MMAO of 4.12×10^6 g(PE)·mol(Ni)⁻¹·h⁻¹ was observed at a ratio of 1500 (runs 1 – 7, Table 5) which compares to 4.58×10^6 g(PE)·mol(Ni)⁻¹·h⁻¹ with **Ni3**/Et₂AlCl. In terms of molecular weight, little variation was observed over the ratio range (*M_w* range: 1.80 - 2.05 kg·mol⁻¹), an observation that was also noted with Et₂AlCl. Likewise, the dispersity (*M_w*/*M_n* < 2.0) remained narrow and supportive of single site behavior.

Table 5 Ethylene polymerization using **Ni1** - **Ni5** and MMAO as co-catalyst^a

Run	Precat.	Al:Ni	T (°C)	T (min)	Mass of PE (g)	Activity ^b	<i>M_w</i> ^c	<i>M_w</i> / <i>M_n</i> ^d	<i>T_m</i> ^e (°C)
1	Ni3	1000	30	30	1.78	1.19	2.05	1.55	61.1
2	Ni3	1250	30	30	5.42	3.63	1.87	1.67	59.7

3	Ni3	1500	30	30	6.15	4.12	1.89	1.67	59.3
4	Ni3	1750	30	30	5.61	3.76	1.80	1.66	55.7
5	Ni3	2000	30	30	4.32	2.89	2.08	1.62	63.9
6	Ni3	2500	30	30	4.12	2.76	1.98	1.63	61.5
7	Ni3	3000	30	30	3.84	2.57	1.87	1.59	60.5
9	Ni3	1500	20	30	4.50	3.00	2.68	1.79	74.9
10	Ni3	1500	40	30	3.43	2.30	1.57	1.57	58.1
11	Ni3	1500	50	30	1.63	1.09	1.31	1.55	50.4
12	Ni3	1500	30	5	0.73	2.92	1.71	1.57	53.2
13	Ni3	1500	30	15	2.68	3.57	1.63	1.53	54.7
14	Ni3	1500	30	45	8.40	3.73	1.95	1.73	60.9
15	Ni3	1500	30	60	10.3	3.44	1.81	1.72	60.5
16 ^f	Ni3	1500	30	30	0.89	0.59	1.56	1.55	57.8
17 ^g	Ni3	1500	30	30	Trace	Trace	--	--	--
18	Ni1	1500	30	30	6.48	4.32	2.11	1.69	82.6
19	Ni2	1500	30	30	3.62	2.41	2.41	1.68	75.3
20	Ni4	1500	30	30	0.31	0.21	1.36	1.75	75.3
21	Ni5	1500	30	30	0.09	0.06	1.73	1.54	82.2

^a Conditions: 3.0 μmol of precatalyst, 30 $^{\circ}\text{C}$, 30 min, 10 atm C_2H_4 , total volume 100 mL;

^b Activity: $\times 10^6$ g PE mol^{-1} (Ni) h^{-1} ;

^c Weight-average molecular weight in kg mol^{-1} , as determined by GPC;

^d Polydispersity, as determined by GPC;

^e Melt temperature, as determined by DSC;

^f 5 atm C_2H_4 ;

^g 1 atm of C_2H_4 .

With the Al:Ni molar ratio kept at 1500, the temperature was increased from 20 to 50 $^{\circ}\text{C}$ (runs 3 and 9 – 11, Table 5), leading to the topmost activity for Ni3/MMAO being achieved at 30 $^{\circ}\text{C}$. As temperature was raised to 40 $^{\circ}\text{C}$, the activity started to decrease and then much more dramatically when it reached 50 $^{\circ}\text{C}$ as the result of deactivation of the active species and lower solubility of ethylene at higher temperature (runs 10, 11, Table 5). Furthermore, the molecular weight of the polyethylene lowered from 2.68 to 1.31 $\text{kg}\cdot\text{mol}^{-1}$ between 20 and 50 $^{\circ}\text{C}$, suggesting a higher rate of chain termination as compared to chain propagation at elevated temperature (runs 3, 9–11, Table 5) [17-19, 22, 32, 34]; this trend is also depicted in the GPC traces (Figure 4). The molecular weight distribution, nonetheless, remained particularly narrow despite the variations in temperature ($M_w/M_n < 2.0$). In addition, the T_m of the polymers decreased from 74.9 to 50.4 $^{\circ}\text{C}$ when the temperature was increased from 20 to 50 $^{\circ}\text{C}$, which can be ascribed to increased branching at more elevated temperatures.

By performing the polymerization at intervals between 5 and 60 minutes, with the temperature

maintained at 30 °C and the Al:Ni ratio at 1500, the polymerization activity reached a maximum at 30 minutes and then gradually decreased as the run time was extended; a similar phenomenon was noted with **Ni3**/Et₂AlCl. On the other hand, the molecular weight of the polymer remained essentially constant ($M_w = 1.63 - 1.95 \text{ kg}\cdot\text{mol}^{-1}$) and the distribution narrow ($M_w/M_n < 1.8$). As with Et₂AlCl study, decreasing the ethylene pressure from 10 to 5 and then to 1 atm saw the polymerization activity decrease to only trace quantities (runs 3, 16, 17, Table 5).

Figure 4 GPC curves of the polyethylenes obtained using **Ni1**/MMAO at different temperatures (runs 3, 9 – 11, Table 5)

Under the optimum conditions established for **Ni3**/MMAO (Al:Ni = 1500, run temperature = 30 °C, run time = 30 minutes), the remaining four nickel precatalysts were similarly evaluated (runs 18 - 21, Table 5). In terms of relative catalytic activity, they fall in the order: **Ni1** ~ **Ni3** > **Ni2** >> **Ni4** ~ **Ni5**. Once again similar trends were observed to that seen with Et₂AlCl activation, with the *ortho*-alkyl substituted **Ni1** – **Ni3** considerably more active (up to $4.32 \times 10^6 \text{ g(PE)}\cdot\text{mol(Ni)}^{-1}\cdot\text{h}^{-1}$) than their *ortho*-halide counterparts (up to $0.31 \times 10^6 \text{ g(PE)}\cdot\text{mol(Ni)}^{-1}\cdot\text{h}^{-1}$). In addition, the molecular weights of the polyethylenes generated using **Ni1** - **Ni3** ($M_w = 1.89 - 2.41 \text{ kg}\cdot\text{mol}^{-1}$) are slightly higher than that seen for **Ni4** and **Ni5** ($1.36 - 1.73 \text{ kg}\cdot\text{mol}^{-1}$). On the other hand, the T_m values fall in a similar range [59.3 – 82.6 °C (**Ni1** – **Ni3**) vs. 75.3 – 82.2 °C (**Ni4**, **Ni5**)].

3. Microstructural analysis of the polyethylenes

To investigate the effects of co-catalyst and temperature on the microstructural properties of the polyethylenes as well as to account for any unusual variations in physical data of the materials, high

temperature ^1H and ^{13}C NMR spectroscopy was carried out on selected samples. Firstly, we examined the NMR spectra of the polyethylene sample displaying the unusually high T_m (*vide supra*) prepared using *ortho*-fluoro **Ni4**/ Et_2AlCl (run 20, Table 4) and compared these data with that obtained using *ortho*-alkyl **Ni1** - **Ni3**/ Et_2AlCl (runs 4, 18, 19, Table 4).

Figure 5 ^1H NMR spectra of the polyethylenes obtained using **Ni1** - **Ni4**/ Et_2AlCl at 30 °C (runs 4, 18 – 20, Table 4); recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C.

In general, the ^1H NMR spectra of the polymers generated using **Ni1** – **Ni4** reveal the presence of both vinyl and vinylenic groups with characteristic $-\text{CH}=\text{CH}_2$ peaks at δ 5.90 (H_b) and 5.00 (H_a) (integration ratio of 1:2) and $-\text{CH}=\text{CH}-$ peaks at δ 5.5 (H_c/H_c') (Figure 5). Closer inspection of the spectra reveals that the ratio of vinylenic to vinyl ($-\text{CH}=\text{CH}-$):($\text{H}_2\text{C}=\text{CH}-$) was notably affected by the *ortho*-R group in the precatalyst and ranged from 9.1:1 to 1.2:1. Indeed, as a function of precatalyst, this vinyl group content followed the order: **Ni4**(F) > **Ni1**(Me) > **Ni2**(Et) > **Ni3**(*i*-Pr), which would suggest

the electron withdrawing fluoride group favored vinyl groups.

Figure 6 ^{13}C NMR spectrum of the polyethylene generated using **Ni3**/ Et_2AlCl at 30 °C (run 4, Table 4); recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C.

Further support for the vinylene/vinyl mixture of unsaturation highlighted in the ^1H NMR spectra was provided by the ^{13}C NMR spectrum of polyethylene sample afforded using **Ni3**/ Et_2AlCl (run 4, Table 4), in which characteristic downfield resonances are clearly observable for the corresponding alkenic carbon atoms (C_a , C_b , C_c and C_c' in Figure 6). Moreover, closer analysis of the upfield region revealed the sample to be highly branched and by using literature approaches a total of 87 branches/1000 Cs could be determined in which methyl branches accounted for 65.0%, ethyl branches accounted for 2.7%, butyl branches accounted for 4.0%, amyl branches accounted for 5.6% and longer chain branches (C_n , $n > 6$) 22.7% [36–38]. Similarly, the sample prepared using **Ni1** showed signals corresponding to vinylene and vinyl groups along with upfield saturated peaks corresponding to a branching content of 75 branches/1000 Cs (Figure S1, run 18, Table 4).

In marked contrast, the ^{13}C NMR spectrum of the polymer formed by **Ni4** indicated that it possessed a total of 20 branches/1000 Cs, which is much lower than seen using **Ni1** or **Ni3**, with methyl branches accounting for 60.6%, butyl branches 7.4% and longer chain branches 32.0% (Figure 7). In addition, the vinyl group signals (C_b , C_a) are much higher in intensity than that seen for the vinylene group (C_c), which concurs with the ^1H NMR data (vinylene:vinyl = 1.2:1). This finding suggested that

the *ortho*-F substitution suppressed chain-walking and favored β -H elimination. The explanation for this observation is uncertain but may be due to weak hydrogen bonding between the *ortho*-fluorine atoms and the coordinated ethylene during the insertion transition state; similar results have been observed elsewhere [39-41]. This lower branching content of the polyethylene formed by **Ni4** was also consistent with the higher T_m of the polymer.

Figure 7 ^{13}C NMR spectrum of the polyethylene obtained using **Ni4**/ Et_2AlCl at 30 °C (run 20, Table 4); recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C.

Since the temperature greatly affected the catalytic behavior of the nickel catalysts developed in this study, the structural properties of the polyethylenes obtained using **Ni3**/ Et_2AlCl at 30, 40 and 50 °C (runs 4, 10, 11, Table 4) were also examined by ^1H and ^{13}C NMR spectroscopy. Their ^1H NMR spectra showed that the ratio of vinylene:vinyl slightly increased from 9.14:1 to 10.4:1 on raising the temperature from 30 to 50 °C (Figure 8). This is likely due to the higher termination rate at higher temperature and hence increased likelihood of forming vinylene units within the polymer chain. In the ^{13}C NMR spectrum of the polymer obtained at 50 °C, a much higher branching content of 138 branches/1000 Cs was observed, which can be explained by increased β -H elimination at higher temperature (Figure S2, run 11, Table 4).

Figure 8 ^1H NMR spectra of the polyethylene generated using $\text{Ni3}/\text{Et}_2\text{AlCl}$ at 30, 40 and 50 $^\circ\text{C}$ (runs 4, 10, 11, Table 4); recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 $^\circ\text{C}$.

With regard to the effect of co-catalyst on the microstructure of the polymer, the ^1H and ^{13}C NMR spectra of the polymer generated using $\text{Ni3}/\text{MMAO}$ at 30 $^\circ\text{C}$ was also recorded (run 3, Table 5). Both vinyl and vinylene groups are again present with a vinylene:vinyl ratio of 4.9:1 found in the ^1H NMR spectrum (Figure 9). The ^{13}C NMR spectrum supported this vinylene:vinyl composition and also showed the sample possess 120 branches/1000 Cs that included methyl branches (77.5%), butyl branches (3.3%) as well as longer chain branches (19.2%) (Figure 10) [37]. Moreover, these results suggest that co-catalysts such as Et_2AlCl and MMAO have little effect on the microstructure of resultant polymer, which was demonstrated by the preference for highly branched polyethylene with internal double bonds being present in both cases.

Figure 9 ^1H NMR spectrum of the polyethylene obtained using **Ni3**/MMAO at 30 °C (run 3 in Table 5); recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C.

Figure 10 ^{13}C NMR spectrum of the polyethylene obtained using **Ni3**/MMAO at 30 °C (run 3 in Table 5); recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C.

4. Polyethylene epoxidation

With the view to exploring the capacity of these materials to undergo further reactivity post-polymerization, epoxidation was investigated of a wax-like sample prepared using **Ni1**/ Et_2AlCl at 30 °C (run 18, Table 4). Using a method based on previously reported approaches [42-45], the sample

was treated with *m*-chloroperbenzoic acid in toluene at reflux affording the epoxidized polyethylene (e-PE) with almost quantitatively conversion. The formation of e-PE was evidenced by the disappearance of alkenic proton peaks (δ 4.9 – 5.8) in the ^1H NMR spectrum and new peaks at δ 3.03, 2.91, 2.75, 2.71, 2.48 and 2.45 that can be assigned to the proton resonances belonging to the epoxide functional groups (Figures 11). Furthermore, the ^{13}C NMR spectrum (Figure 12) showed new peaks between δ 46.8 – 60.0 that correspond to the three-membered epoxide rings. The GPC data revealed that e-PE displayed a slightly higher molecular weight ($M_w = 1.78 \text{ kg mol}^{-1}$) and higher T_m value (69.6 $^\circ\text{C}$) than the starting polyethylene employed (run 18, Table 4, $M_w = 1.57 \text{ kg mol}^{-1}$, $T_m = 67.1 \text{ }^\circ\text{C}$).

Figure 11 ^1H NMR spectrum of the polyethylene starting material (top: run 18, Table 4) and e-PE (bottom); recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 $^\circ\text{C}$

Figure 12 ^{13}C NMR spectra of the polyethylene starting material (top: run 18, Table 4) and e-PE (bottom); recorded in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100 °C

Conclusions

The iminotrihydroquinoline-nickel(II) chlorides, **Ni1** – **Ni5**, each containing a *para*-dibenzocycloheptyl group and a selection of sterically and electronically distinct *ortho*-substituents, have been successfully synthesized and fully characterized. The molecular structure of **Ni2** adopted a chloride-bridged dimeric form, while **Ni3** possessed an unusual chloride-bridged trinuclear arrangement. Upon treatment with either MMAO or Et_2AlCl , all precatalysts showed low to high activities toward ethylene polymerization (generally: $\text{Et}_2\text{AlCl} > \text{MMAO}$), producing polyethylenes of low molecular weight ($1 - 2 \text{ kg}\cdot\text{mol}^{-1}$) and narrow dispersities. All the resultant polyethylene waxes are highly branched and unsaturated, with internal double bonds constituting, in most cases, the major class of unsaturation. The nature of the *ortho*-substituents greatly affected their catalytic activity, type of unsaturation and branching content. In particular, **Ni4** (F) and **Ni5** (Cl) containing electron withdrawing group *ortho*-groups exhibited much lower activities than *ortho*-alkyl **Ni1** - **Ni3**, while polymers generated by **Ni4**/ Et_2AlCl contained much less branches and possessed a relatively high vinyl content. Moreover, these materials can be readily epoxidized with almost quantitative conversion of the double bond.

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