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## New nickel(II) diimine complexes bearing phenyl and *sec*-phenethyl groups: synthesis, characterization and ethylene polymerization behaviour

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A series of nickel(II) catalysts containing phenyl and chiral *sec*-phenethyl groups, {[(4-R<sub>1</sub>-2-R<sub>2</sub>C<sub>6</sub>H<sub>2</sub>N=C)<sub>2</sub>Nap]NiBr<sub>2</sub>} (Nap: 1,8-naphthdiyl, R<sub>1</sub> = Me, R<sub>2</sub> = Ph (3a); R<sub>1</sub> = Me, R<sub>2</sub> = *sec*-phenethyl (3b); R<sub>1</sub> = Cl, R<sub>2</sub> = *sec*-phenethyl (3c); R<sub>1</sub> = Me, R<sub>2</sub> = Me (3d) were synthesized and characterized. All organic compounds were fully characterized by FT-IR and NMR spectroscopy and elemental analysis. The single crystal for X-ray crystallography was isolated from 3a in CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane under air; the crystal structure showed a binuclear complex 3a', in which each nickel atom was six-coordinate. The two nickel atoms together with two bromine atoms form a planar four-membered ring, with a bromine and H<sub>2</sub>O axial ligands. These complexes, activated by diethylaluminum chloride and chiral nickel pre-catalysts *rac*-3c, exhibited good activities (up to  $2.85 \times 10^6$  g PE (mol Ni h bar)<sup>-1</sup>) for ethylene polymerization, and produced polyethylene products with a high degree of branching (up to 117 branched per 1000 carbons) at high temperature. The type and amount of branches of the polyethylenes obtained were determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: Ni(II) complexes; sec-phenethyl; ethylene polymerization; crystal structure

#### Introduction

The polymerization/oligomerization of ethylene and  $\alpha$ -olefins play pivotal roles in today's polyolefin industry production, and the polyethylene materials are tremendously important in our daily life.<sup>[1]</sup> Bulky ortho-position aryl substituents  $\alpha$ -diimine Ni(II) complexes that show high catalytic activity for  $\alpha$ -olefin polymerization have been successfully developed by Brookhart and his collaborators.<sup>[2-7]</sup> The key feature of these complexes lies in the bulky  $\alpha$ -difficult diamond that has steric hindrance in the axial direction of the metal coordination plane to suppress the associative chain transfer.<sup>[2]</sup> Since the earlier studies, investigations have increasingly focused on improvement of the catalytic properties through modification of the structures of catalysts,<sup>[8-26]</sup> especially on changes of the backbone substituents on the carbon atoms of imine groups and replacement of the aniline moiety as well as the resultant influence on ethylene polymerization. For instance, Rhinehart et al. reported a robust 2,6-bis(diphenylmethyl) substituted Ni(II)  $\alpha$ -diimine catalyst,<sup>[13]</sup> which was highly active, produced well-defined polyethylene and demonstrated remarkable thermal stability in high-temperature ethylene polymerization. Recently, a series of nickel(II) bromide catalysts with 2-{2,6-bis[di(4fluorophenyl)methyl]-4-chlorophenylimino}-3-aryliminobutane ligands have been prepared and showed very high activity toward ethylene polymerization, with activities of up to  $10^7$  g (PE) mol<sup>-1</sup> (Ni)  $h^{-1}$ , and afforded highly branched polyethylene with a bimodal distribution according to the result of Redshaw et al.<sup>[14]</sup> Moreover, a series of nickel(II) complexes with three-dimensional

geometry 9,10-dihydro-9,10-ethanoanthracene-11,12-diimine ligands were successfully prepared and exhibited very high activity for norbornene (NB) homopolymerization with only  $B(C_6F_5)_3$  as co-catalyst.<sup>[15]</sup> In particular, recent examples of ethylene polymerization, especially using 'sandwich' (8-*p*-tolyl naphthyl  $\alpha$ -diimine)nickel (II) catalysts,<sup>[16]</sup> have yielded the most highly branched polyethylene produced by Ni catalysts seen to date. However, the effect of a *para*-position substituent of the styrene aniline group, especially a *para*-position bulky electron-donating substituent of the styrene aniline group, on the catalytic behaviour of  $\alpha$ -diimine–nickel(II) complexes and the property of resultant polymers has only been reported in a limited number of cases.<sup>[27–29]</sup>

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In previous work, using  $\alpha$ -diimine nickel catalysts, we reported that 2,6-diphenyl-substituted<sup>[30]</sup> and bulky chiral 2,6-sec-diphenethylsubstituted<sup>[31]</sup>  $\alpha$ -diimine–Ni(II) complexes showed excellent activity for ethylene polymerization upon activation with diethylaluminum chloride (DEAC). In order to study the steric and electronic effects at the metal centre on the catalyst activity, catalyst thermostability and, in particular, on the microstructure of polyethylene, herein we report the synthesis and characterization of three new α-diimine-Ni (II) complexes of the type  $[NiBr_2(Ar-BIAN)]$  (Ar-BIAN = bis(arylimino) acenaphthene) bearing a phenyl or chiral sec-phenethyl or methyl group in the ortho-aryl position with a methyl group in the para-aryl position of the arylimino group. These nickel(II) complexes exhibit good activity towards ethylene polymerization and produce highly branched polyethylene. Furthermore, the impact of the polymerization parameters and the nature of the ligands present on the observed catalytic activity, as well as the properties of the polyethylene produced, have been investigated.

#### **Experimental**

#### **General Procedures and Materials**

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Methylene chloride and *o*-dichlorobenzene were pre-dried with 4 Å molecular sieves and distilled from CaH<sub>2</sub> under dry nitrogen. Toluene, diethyl ether and 1,2dimethoxyethane (DME) were distilled from sodium/benzophenone under nitrogen atmosphere. Anhydrous NiBr<sub>2</sub> (99%), phenylboronic acid (97%), Pd(OAc)<sub>2</sub> and DEAC (0.9 M solution in toluene) were obtained from Acros. 1,2-Acenaphthylenedione (98%), 4-methylaniline (98%), 4-chloroaniline (97%), 2,4-dimethylaniline (98%) and Br<sub>2</sub> (98%) were purchased from Alfa Aesar and used without further purification. [NiBr<sub>2</sub>(DME)] was synthesized according to the literature.<sup>[32]</sup>

NMR spectra were recorded at 400 MHz on a Varian Mercury Plus-400 instrument, using TMS as internal standard. FT-IR spectra were recorded on a Digilab Merlin FTS 3000 FT-IR spectrophotometer on KBr pellets. The molecular weights and molecular weight distributions ( $M_w/M_n$ ) of the polymers were determined by gel permeation chromatography–size-exclusion chromatography (GPC–SEC) with a Waters Alliance GPCV2000 chromatograph, using 1,2,4-trichlorobenzene as eluent, at a flow rate of 1.0 ml min<sup>-1</sup> and operated at 140 °C.

#### Synthesis of Aniline Derivatives

#### Synthesis of 2-bromo-4-methylaniline a

2-Bromo-4-methylaniline **a** was synthesized according to the literature.<sup>[33]</sup>

Synthesis of 4-methyl-2-phenylaniline 1a

# NH<sub>2</sub>

 $Pd(OAc)_2$  (0.01 g, 0.04 mmol), 2-bromo-4-methylaniline (0.37 g, 2.00 mmol),  $K_2CO_3$  (0.55 g, 4.00 mmol) and phenylboronic acid (0.26 g, 2.10 mmol) were placed in a 100 ml flask and allowed to stir at 25 °C for 24 h in the presence of 10 ml PEG-400. The mixture was extracted three times with 10 ml diethyl ether. The combined organic phase was dried over MgSO<sub>4</sub> and filtered,

and the solvent was removed. The residue was purified by chromatography on silica gel with petroleum ether/ethyl ester (v/v, 20:1) to give 4-methyl-2-phenylaniline **1a** (0.24 g, 66% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.33–7.38 (m, 4H, protons of C5, C10 and C11), 7.23–7.27 (m, 1H, proton of C9), 6.88–6.90 (m, 2H, proton of C3), 6.61 (d, *J* = 8.0 Hz, 1H, proton of C2), 3.42 (s, 2H, —NH<sub>2</sub>), 2.20 (s, 3H, proton of C7). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  140.75 (C1), 139.60 (C8), 130.93 (C5), 129.04 (C10), 128.97 (C4), 128.70 (C3), 127.92 (C9), 127.78 (C11), 127.03 (C6), 115.85 (C2), 20.39 (C7). Anal. Calcd for C<sub>13</sub>H<sub>13</sub>N: C, 85.21; H, 7.15; N, 7.64%. Found: C, 85.15; H, 7.17; N, 7.59%.

Synthesis of rac-4-methyl-2-sec-phenethylaniline 1b

*rac*-4-Methyl-2-*sec*-phenethylaniline **1b** was synthesized according to the literature.<sup>[31]</sup>

Synthesis of rac-4-chloro-2-sec-phenylethylaniline 1c

<code>rac-4-Chloro-2-sec-phenylethylaniline 1c</code> was synthesized according to the literature.<sup>[31]</sup>

#### Synthesis of Ligand

Synthesis of bis[N,N'-(4-methyl-2-phenylphenyl)imino]acenaphthene 2a



Formic acid (0.2 ml) was added to a stirred solution of 1,2acenaphthylenedione (0.091 g, 0.50 mmol) and 4-methyl-2phenylbenzenamine (0.20 g, 1.10 mmol) in ethanol (10 ml). The mixture was refluxed for 24 h, then cooled, and the precipitate was separated by filtration. The solid was recrystallized from EtOH/CH<sub>2</sub>Cl<sub>2</sub> (v/v, 18:1), washed with cold ethanol and dried under vacuum (0.22 g, 85% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.72 (d, J=8.2 Hz, 2H, proton of C14), 7.46 (m, 4H, protons of C16 and C15), 7.28 (s, 2H, proton of C5), 6.09-7.13 (m, 10H, protons of C8, C9 and C10), 6.77 (d, J=7.2 Hz, 2H, proton of C2), 6.69 (d, J = 7.2 Hz, 2H, proton of C3), 2.44 (s, 6H, proton of C11). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  160.43 (C12), 145.70 (C1), 139.65 (C18), 133.44 (C4), 130.65 (C7), 129.80 (C5), 129.56 (C6), 129.35 (C17), 129.03 (C16), 128.86 (C13), 128.66 (C9), 128.46 (C3), 127.88 (C8), 127.72 (C10), 127.41 (C15), 126.25 (C14), 122.53 (C2), 20.80 (C11). Anal. Calcd for C<sub>38</sub>H<sub>28</sub>N<sub>2</sub>: C, 89.03; H, 5.51; N, 5.46%. Found: C, 88.95; H, 5.57; N, 5.29%. FT-IR (KBr): 1638 cm<sup>-1</sup>(v<sub>CN</sub>).

Synthesis of rac-bis[N,N'-(4-methyl-2-sec-phenethylphenyl)imino] acenaphthene **2b** 



Using the same procedure as for the synthesis of 2a, 2b was obtained as an orange powder (0.22 g, 78% yield). <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>):  $\delta$  8.09 (d, J = 8.4 Hz, 2H, proton of C16), 7.85 (d, J = 8.4 Hz, 2H, proton of C18), 7.76 (m, 2H, proton of C17), 7.31 (s, 2H, proton of C5), 6.99 (d, J = 6.8 Hz, 4H, proton of C10), 6.74 (d, J = 7.6 Hz, 2H, proton of C2), 6.68 (m, 4H, proton of C11), 6.62 (d, J = 7.6 Hz, 2H, proton of C3), 6.48 (t, J = 7.2 Hz, 2H, proton of C12), 4.31 (q, J = 7.2 Hz, 2H, proton of C3), 6.48 (t, J = 7.2 Hz, 2H, proton of C7), 1.56 (d, J = 7.2 Hz, 2H, proton of C13). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  159.83 (C14), 146.60 (C1), 145.78 (C9), 142.99 (C20), 134.86 (C4), 131.86 (C6), 130.49 (C5), 128.65 (C19), 127.90 (C18), 127.83 (C15), 127.68 (C11), 127.56 (C10), 127.50 (C12), 124.97 (C3), 123.46 (C17), 121.71 (C16), 117.00 (C2), 40.34(C8), 21.34 (C7), 21.11 (C13). Anal. Calcd for C<sub>42</sub>H<sub>36</sub>N<sub>2</sub>: C, 88.69; H, 6.38; N, 4.93%. Found: C, 88.75; H, 6.43; N, 5.01%. FT-IR (KBr): 1640 cm<sup>-1</sup>( $\nu_{CN}$ ).

Synthesis of rac-bis[N,N'-(4-chloro-2-sec-phenethylphenyl)imino] acenaphthene **2c** 



Using the same procedure as for the synthesis of **2a**, **2c** was obtained as an orange powder (0.23 g, 76% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.78 (d, *J*=8.4 Hz, 2H, proton of C15), 7.73 (d, *J*=8.0 Hz, 2H, proton of C17), 7.43–7.48 (m, 2H, proton of C16), 7.24–7.30 (m, 4H, proton of C11), 7.05 (d, *J*=7.6 Hz, 4H, proton of C3), 6.88 (d, *J*=7.6 Hz, 2H, proton of C2), 6.53–6.78 (m, 6H, protons of C10 and C12), 4.42 (q, *J*=7.2 Hz, 2H, proton of C7), 1.58–1.63 (m, 6H, proton of C8). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  160.33 (C13), 147.62 (C1), 144.62 (C9), 143.21 (C19), 141.88 (C6), 136.94 (C4), 132.03 (C18), 130.53 (C17), 128.85 (C14), 127.90 (C5), 127.85 (C11), 127.66 (C10), 127.50 (C3), 124.97 (C16), 123.46 (C12), 118.46 (C15), 117.54 (C2), 40.19 (C7), 21.04 (C8). Anal. Calcd for C<sub>40</sub>H<sub>30</sub>Cl<sub>2</sub>N<sub>2</sub>: C, 78.81; H, 4.96; N, 4.60%. Found: C, 78.73; H, 5.02; N, 4.55%. FT-IR (KBr): 1639 cm<sup>-1</sup>( $v_{CN}$ ).

#### Synthesis of Nickel Complex 3a-d

Synthesis of {bis[N,N'-(4-methyl-2-phenylphenyl)imino]acenaphthene} dibromonickel **3a** 

[(DME)NiBr<sub>2</sub>] (0.12 g, 0.40 mmol) and ligand **2a** (0.20 g, 0.40 mmol) were combined in a Schlenk flask under a nitrogen atmosphere. CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added, and the reaction mixture was stirred at room temperature for 24 h. The resulting suspension was filtered. The solvent was removed under vacuum and the residue was washed with diethyl ether (3 × 15 ml), and then dried under vacuum at room temperature to give catalyst **3a** (0.24 g, 83% yield). Anal. Calcd for C<sub>38</sub>H<sub>28</sub>Br<sub>2</sub>N<sub>2</sub>Ni: C, 62.42; H, 3.86; N, 3.83%. Found: C, 62.31; H, 3.92; N, 3.90%. FT-IR (KBr): 1627 cm<sup>-1</sup> ( $\nu_{CN}$ ). Single crystals of complex **3a**' suitable for X-ray analysis were obtained at room temperature by dissolving the nickel complex in CH<sub>2</sub>Cl<sub>2</sub>, following by slow layering of the resulting solution with *n*-hexane in air.

Synthesis of rac-{Bis[N,N-(4-methyl-2-sec-phenethylphenyl)imino]acenaphthene} dibromonickel  ${\bf 3b}$ 

Using the same procedure as for the synthesis of **3a**, **3b** was obtained as a dark-red powder (0.26 g, 86% yield). Anal. Calcd

for  $C_{42}H_{36}Br_2N_2Ni$ : C, 64.08; H, 4.61; N, 3.56%. Found: C, 64.12; H, 4.56; N, 3.63%. FT-IR (KBr): 1629 cm<sup>-1</sup> ( $v_{CN}$ ).

### Synthesis of rac-{Bis[N,N'-(4-chloro-2-sec-phenethylphenyl)imino]acenaphthene} dibromonickel $\mathbf{3c}$

Using the same procedure as for the synthesis of **3a**, **3c** was obtained as a dark-red powder **3c** (0.28 g, 85% yield). Anal. Calcd for  $C_{40}H_{30}Br_2Cl_2N_2Ni$ : C, 58.02; H, 3.65; N, 3.38%. Found: C, 57.97; H, 3.69; N, 3.42%. FT-IR (KBr): 1628 cm<sup>-1</sup> ( $\nu_{CN}$ ).

#### Synthesis of bis[N,N'-(2,4-dimethylphenyl)imino]acenaphthene 2d

Bis[N,N'-(2,4-dimethylphenyl)imino]acenaphthene **2d** was synthesized according to the literature.<sup>[34]</sup>

Synthesis of {bis[N,N'-(2,4-dimethylphenyl)imino]acenaphthene} dibromonickel **3d** 

{Bis[*N*,*N*'-(2,4-dimethylphenyl)imino]acenaphthene}dibromonickel **3d** was synthesized according to the literature.<sup>[34]</sup>

#### **X-Ray Structure Determinations**

Single crystals of complex 3a' suitable for X-ray analysis were obtained at room temperature by dissolving nickel complex 3a in CH<sub>2</sub>Cl<sub>2</sub>, following by slow layering of the resulting solution with *n*-hexane in air. Data collections were performed at 296(2) K on a Bruker SMART APEX diffractometer with a charge-coupled device (CCD) area detector, using graphite monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). The determination of crystal class and unit cell parameters was carried out using the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on  $F^2$  anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and refinement parameters are listed in Table 1.

#### **Ethylene Polymerization**

The polymerization of ethylene was carried out in a flame-dried 250 ml crown-capped pressure bottle sealed with neoprene septa. After drying the polymerization bottle under nitrogen atmosphere, 50 ml dry toluene was added to the polymerization bottle. The resulting solvent was then saturated with a prescribed ethylene pressure. The co-catalyst (DEAC) was then added in Al/Ni molar ratios in the range of 200-1000 to the polymerization bottle via a syringe. At this time, the solutions were thermostated to the desired temperature and allowed to equilibrate for 15 min. Subsequently, an o-dichlorobenzene solution of Ni catalyst was added to the polymerization reactor. The polymerization, conducted under a dynamic pressure of ethylene (0.2 bar), was terminated with 100 ml of a 5% HCI-MeOH solution. The precipitated polymer was filtered, washed with methanol and dried under vacuum at 60 °C to constant weight.

Table 1.	Crystal data	and structure	refinements of	f complex <b>3a</b> '
<b>C</b> 1			-	,

Complex	3a′
Empirical formula	C <sub>76</sub> H <sub>56</sub> Br <sub>4</sub> N <sub>4</sub> Ni <sub>2</sub> .2(H <sub>2</sub> O).2.5(CH <sub>2</sub> Cl <sub>2</sub> ).O
Formula mass	1728.67
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal size (mm <sup>3</sup> )	$0.2 \times 0.08 \times 0.06$
Crystal system	Triclinic
Space group	P -1
a (Å)	13.8380(7)
b (Å)	16.3253(5)
c (Å)	16.9637(7)
α (°)	73.208(3)
β (°)	87.828(4)
γ (°)	86.488(3)
V (Å <sup>3</sup> )	3661.1(3)
Ζ	2
Density (calcd) (mg cm <sup>-3</sup> )	1.568
Absorption coefficient (mm <sup>-1</sup> )	2.93
<i>F</i> (000)	1742
Theta range for data collection (°)	2.9 – 28.6
Limiting indices	$-17 \le h \le 10; -21 \le k \le 21;$
	-22≤1≤22
Reflections collected	32 291
Independent reflections	16 463
R <sub>int</sub>	0.044
Completeness to $\theta = 25.05^{\circ}$	99.00%
Final R indices $[I > 2\theta(I)]$	$R_1 = 0.0640, \ wR_2 = 0.1550$
R indices (all data)	$R_1 = 0.0976, wR_2 = 0.1766$
Refinement method	Full-matrix least-squares on $F^2$
Goodness of fit on $F^2$	1.06
Max. and min. transmission	1.000 and 0.868
Largest diff. peak and hole (e.Å <sup><math>-3</math></sup> )	2.50 and -1.99

#### **Results and Discussion**

## Synthesis and Characterization of Ligands 2a–d and complexes 3a–d

After the protection of the amino group by acetic acid, 4methylaniline was brominated to form 2-bromo-4-methylaniline (**a**). The Suzuki coupling reaction of **a** and phenylboronic acid catalysed by Pd(OAc)<sub>2</sub> in PEG-400 led to the desired amine 4methyl-2-phenylaniline (**1a**), in 66% yield (Scheme 1). Reaction of the *p*-substituted anilines with styrene at elevated temperature (160 °C) in the presence of CF<sub>3</sub>SO<sub>3</sub>H catalyst resulted in the corresponding *o-sec*-phenethylanilines, *rac*-**b** and *rac*-**c** (Scheme 1). The  $\alpha$ -diimine ligands **2a–d** were prepared by the condensation of 2 equiv. of the aniline with 1 equiv. of 1,2acenaphthylenedione, usually in the presence of a formic acid catalyst. Compounds **2a–d** were characterized by elemental analysis, and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy.

The reaction of equimolar amounts of NiBr<sub>2</sub>(DME) and the  $\alpha$ diimine ligands **2a-d** in CH<sub>2</sub>Cl<sub>2</sub> led to the displacement of 1,2dimethoxyethane and afforded the catalyst precursors **3a-d** as moderately air-stable microcrystalline solids in high yields.

#### X-ray Crystallographic Studies

Suitable crystals of complex **3a**' for X-ray diffraction was obtained at room temperature by double layering a  $CH_2Cl_2$  solution of the complex **3a** with *n*-hexane in air.

The molecular structure of complex **3a**' is shown in Figure 1. Selected bond distances and angles are summarized in Table 2. In the solid state, complex 3a' clearly shows the dimeric structure of **3a** with two Ni centres connected by two bromide bridges. In each unit, the two imine N atoms in Ar-DAB, three Br atoms and a H<sub>2</sub>O molecule from the moisture coordinated to a Ni atom in a six-coordinated distorted octahedral geometry. The two Br bridges and the two imine groups bonded to the Ni centre in cis configuration and the isolated Br ions and the coordinated water linked to the same Ni atom in trans configuration. Both aryl rings bonded to the iminic nitrogens of the  $\alpha$ -diimine lie nearly perpendicular to the plane formed by the nickel and coordinated nitrogen atoms. The phenyl groups in the 2-position of the benzenamine fragments in 3a' point toward each other above and below the plane, thus shielding the apical positions of the Ni(II) centre.

The structure of 3a' is similar to those reported in the literature for other similar [NiBr<sub>2</sub>( $\alpha$ -diimine)] compounds characterized by X-ray diffraction, {bis[*N*,*N*'-4-bromo-2,6-dimethylphenyl)imino] acenaphthene}dibromonickel<sup>[35]</sup> and {bis[N,N'-(2,4,6trimethylphenyl)imino]acenaphthene}dibromonickel.<sup>[36]</sup> In fact, the Ni1-N1 bond distances in complex 3a' (2.086 Å) are similar to those determined for these compounds (2.026 and 2.021 Å, respectively), as well as the Ni1-Br1 bond distances (2.5422 Å for complex 3a' vs. 2.329 and 2.323 Å, respectively). However, the N1—Ni1—Br1 angles (92.33° for complex 3a') are very different from that determined for those compounds (113.32 and 114.4°, respectively) due to the great steric hindrance of the ortho benzene rings of complex 3a' around the Ni(II) centre. The two imino C-N bonds have a typical double bond character, with C-N bond lengths of 1.276–1.288 Å. The aryl rings of each of the  $\alpha$ diimines lie nearly perpendicular to the plane formed by the nickel and the coordinated nitrogen atoms, and face each other in a staggered conformation. In addition, there are two and a half CH<sub>2</sub>Cl<sub>2</sub> molecules and a crystallized H<sub>2</sub>O molecule in a asymmetric unit in the 3a' molecule.

#### Polymerization of Ethylene with Nickel Complexes 3a-d

The four  $\alpha$ -diimine nickel(II) complexes **3a–d**, activated by DEAC, were tested as catalyst precursors for the polymerization of ethylene, under the same reaction conditions. The results of the polymerization experiments are shown in Table 3. Blank experiments were carried out with DEAC alone under the same conditions, to confirm the inability of DEAC for ethylene polymerization.

At 0 °C, the activity of complex **3a** increased slightly with the increase of [Al]/[Ni] ratio (runs 1–3), reached a maximum around an [Al]/[Ni] ratio of 600 (run 3), and then decreased slightly (runs 3–5). For a [Al]/[Ni] ratio of 600, the highest activities of complex **3a** (runs 3, 6–8) appeared around 20 °C, and an increase in the polymerization temperature form 20 to 60 °C slightly decreased the activity (runs 6–8). The molecular weight of polymer decreased as the polymerization temperature increased from 0 to 60 °C.

The performance of the  $\alpha$ -diimine–Ni(II) complexes are significantly affected by *o*-position substituents on the aniline rings (Table 3). Complex *rac*-**3c**, bearing a chlorine substituent in the



**Scheme 1.** Syntheses of  $\alpha$ -diimine ligands **2a**-d (\*chiral carbon) and their corresponding  $\alpha$ -diimine nickel(II) dibromide complexes **3a**-d.

*para*-aryl position and one bulky chiral *sec*-phenethyl group in the *ortho*-aryl positions of the ligand, displayed the highest catalytic activity of  $2.85 \times 10^6$  g PE (mol Ni h bar)<sup>-1</sup>, and produced the highest-molecular-weight polymer (run 13,



Figure 1. Molecular structure of the catalyst precursor **3a**'. Hydrogen atoms have been omitted for clarity.

 $M_n = 21.06 \times 10^4 \text{ g mol}^{-1}$ , 0 °C, [Al]/[Ni] = 600) among our four complexes.

Complexes **3a** (bearing a phenyl group in the *ortho*-aryl position), *rac*-**3b** (bearing a chiral *sec*-phenethyl group in the *ortho*-aryl position) and **3d** (bearing a methyl group in the *ortho*-aryl position) exhibit significantly lower catalytic activity highest activity: **3a**, run 6,  $1.96 \times 10^6$  g PE (mol Ni h bar)<sup>-1</sup>; *rac*-**3b**, run 11,  $2.76 \times 10^6$  g PE (mol Ni h bar)<sup>-1</sup>; and **3d**, run 18,  $0.94 \times 10^6$  g PE (mol Ni h bar)<sup>-1</sup>.

Compared with complexes **3a** and **3d**/DEAC systems, which showed the highest catalytic activity at 20 °C (such as **3d**, run 18, activity:  $0.94 \times 10^6$  g PE (mol Ni h bar)<sup>-1</sup>), complexes *rac*-**3b** and *rac*-**3c**/DEAC systems showed the highest catalytic activity at 40 °C (such as *rac*-**3b**, run 11,  $2.76 \times 10^6$  g PE (mol Ni h bar)<sup>-1</sup>); thus chiral nickel pre-catalysts *rac*-**3b** and *rac*-**3c** have better thermal stability, even at 60 °C, and the *rac*-**3b** and *rac*-**3c**/DEAC systems still maintain good activity and produce higher-molecular-weight polyethylene.

It is known that ligand electronics have a dramatic effect on catalytic activity and polymer molecular weight.<sup>[19-24]</sup> The properties of resulting polyethylenes showed halide and polymerization temperature effects in that the polyethylenes produced with the chloride pre-catalyst *rac*-**3c** (runs 13–16 in Table 3) had slightly higher molecular weights than those produced with the methyl pre-catalyst *rac*-**3b** (runs 9–12 in Table 3).

These results indicate that the rate of chain propagation is greatly promoted by the bulky *ortho-sec*-phenethyl groups of the ligand's aryl rings. As a result, the following activity trend can be summarized for our substituted pre-catalysts under low ethylene pressure (0.2 bar), in the range 0–60 °C: 3c > 3b > 3a > 3d.

The type and amount of branches in the polyethylene obtained by  $\alpha$ -diimine nickel pre-catalysts depend not only on the ligand structure but also on the reaction conditions, such as reaction temperature end ethylene pressure.<sup>[2]</sup> Gener-

Table 2. Select	ed bond length	s (Å) and angles (°) f	for complex <b>3a</b> '
Bond length	(Å)	Bond angle	(°)
Ni1–N1	2.086(4)	Ni2-Br1-Ni1	88.15(3)
Ni1–N2	2.149(4)	Ni1-Br2-Ni2	88.52(3)
Ni2–N3	2.135(4)	N1-Ni1-O1	91.73(16)
Ni2–N4	2.100(5)	N1-Ni1-N2	79.67(17)
Ni1-01	2.126(4)	01-Ni1-N2	91.95(15)
Ni2-02	2.141(4)	N1-Ni1-Br2	173.18(12)
Br1–Ni1	2.5422(9)	O1-Ni1-Br2	82.92(11)
Br2–Ni1	2.4989(9)	N2-Ni1-Br2	96.22(12)
Br3–Ni1	2.5548(9)	N1-Ni1-Br1	92.33(12)
Br1–Ni2	2.5068(9)	N2-Ni1-Br1	171.94(12)
Br2–Ni2	2.5332(9)	Br2-Ni1-Br1	91.65(3)
Br4–Ni2	2.5391(9)	N1-Ni1-Br3	91.12(12)
N1-C1	1.439(7)	N2-Ni1-Br3	89.76(12)
N1-C14	1.276(7)	Br2–Ni1–Br3	94.33(3)
N2-C25	1.285(7)	Br1-Ni1-Br3	91.39(3)
N2-C26	1.440(7)	N4-Ni2-N3	79.83(17)
N3-C51	1.288(7)	N4-Ni2-Br2	92.15(12)
N3-C39	1.432(7)	Br1-Ni2-Br2	91.68(3)
N4-C62	1.280(7)	Br1-Ni2-Br4	91.29(3)
N4-C63	1.434(7)	Br2–Ni2–Br4	92.85(3)

Table 3. Polymerization of ethylene with complexes 3a-d/DEAC <sup>a</sup>										
Run	Complex	[Al]/[Ni]	T (℃)	t (min)	Yield (g)	Activity <sup>b</sup>	TOF <sup>c</sup> (h bar) <sup>-1</sup>	$M_{\rm n}$ g mol <sup>-1</sup> d	$M_{\rm w}/M_{\rm n}^{\rm d}$	Branches <sup>e</sup> / 1000 C
1	3a	200	0	10	0.89	1.24	0.44	20.35	1.69	_
2	3a	400	0	10	1.19	1.65	0.59	20.22	1.73	—
3	3a	600	0	10	1.31	1.82	0.65	19.13	1.72	—
4	3a	800	0	10	1.25	1.74	0.62	18.45	1.78	—
5	3a	1000	0	10	0.93	1.29	0.46	9.63	1.79	—
6	3a	600	20	10	1.41	1.96	0.7	12.93	1.83	84
7	3a	600	40	10	0.89	1.24	0.44	9.13	1.9	88
8	3a	600	60	10	0.49	0.68	0.24	7.67	2.02	108
9	rac- <b>3b</b>	600	0	10	1.1	1.53	0.55	20.41	1.72	—
10	rac- <b>3b</b>	600	20	10	1.74	2.42	0.86	14.05	1.75	89
11	rac- <b>3b</b>	600	40	10	1.99	2.76	0.99	10.93	1.81	102
12	rac- <b>3b</b>	600	60	10	0.78	1.08	0.39	4.6	1.96	110
13	rac- <b>3c</b>	600	0	10	1.01	1.4	0.5	21.06	1.71	—
14	rac- <b>3c</b>	600	20	10	1.89	2.63	0.94	18.81	1.73	93
15	rac- <b>3c</b>	600	40	10	2.05	2.85	1.02	16.05	1.85	106
16	rac- <b>3c</b>	600	60	10	0.86	1.19	0.43	5.47	1.98	117
17	3d	600	0	10	0.6	0.83	0.3	16.68	1.75	—
18	3d	600	20	10	0.68	0.94	0.34	10.13	1.79	73
19	3d	600	40	10	0.45	0.63	0.22	8.15	1.94	82
20	3d	600	60	10	0.23	0.32	0.11	2.67	2.13	99

<sup>a</sup>Polymerization conditions: *n*(Ni)=3.60 μmol; ethylene relative pressure=0.2 bar, ethylene absolute pressure=1.2 bar; *t*=polymerization time; solvent = toluene (50 ml); *T* = polymerization temperature.

<sup>b</sup>Activity in 10<sup>6</sup> g PE (mol Ni h bar)<sup>-1</sup>.

<sup>c</sup>Turnover frequency in  $10^5$  mol ethylene (mol Ni h bar)<sup>-1</sup>.

 $^{d}M_{\rm n}$  in 10<sup>4</sup> g mol<sup>-1</sup>, determined by GPC.

<sup>e</sup>Branching density, branches/1000 C = (CH<sub>3</sub>/3)/[(CH + CH<sub>2</sub> + CH<sub>3</sub>)/2] × 1000. CH<sub>3</sub>, CH<sub>2</sub>, CH refer to the intensities of the methyl, methylene and methine resonances in <sup>1</sup>H NMR spectra.<sup>[24]</sup>

ally, low ethylene pressure and high polymerization temperature favour chain walking and afford highly branched polyethylenes.<sup>[2]</sup> However, the effect of ligand structure on polyethylene branching is much more complicated. As shown in Table 3 and Figure 2, the catalyst system *rac*-**3c**/DEAC, bearing one bulky *sec*-phenethyl in the *ortho*-aryl position and an electron-withdrawing Cl substituent group in the *para*-aryl position, generated polyethylene with high degrees of branching. The total branching degrees of the polymer samples prepared with *rac*-**3c**/DEAC (runs 14–16;

 Complex 3a Run 7:
 Complex 3b Run 11:
 Complex 3c Run 15:
 Complex 3d Run 19:

 88 branches\1000 C
 102 branches\1000 C
 106 branches\1000 C
 82branches\1000 C



**Figure 2.** <sup>1</sup>H NMR (CDCl<sub>3</sub>/o-dichlorobenzene, v/v = 1:3) spectra of the nanosized dendritic polyethylene catalysed by **3a**, **3b**, **3c** and **3d**/DEAC at 40 °C (Table 3, runs 7, 11, 15, 19):  $I_{CH3}$ , integrated intensity between 0.8 and 1.0 ppm;  $I_{CH2} + I_{CH}$ , integrated intensity between 1.0 and 1.5 ppm.



**Figure 3.** <sup>13</sup>C NMR (CDCl<sub>3</sub>/o-dichlorobenzene, v/v = 1:3) spectrum of polyethylene catalysed by *rac*-**3c**/DEAC at 40 °C (Table 3, run 15). Note on labels: for xB<sub>y</sub> B<sub>y</sub> is a branch of length *y* carbons, *x* is the carbon being discussed, and the methyl at the end of the branch is numbered 1. Thus, the second carbon from the end of a butyl branch is 2B<sub>4</sub>. xB<sub>y+</sub> refers to branches of length *y* and longer. The methylenes in the backbone are labelled with Greek letters, which determine how far from a branch point methine each methylene is;  $\alpha$  denotes the first methylene next to the methine. Thus  $\gamma B_{1+}$  refers to methylenes  $\gamma$  from a branch of length 1 or longer.

branching degree: 93, 106 and 117 branches/1000 C at 20, 40 and 60 °C, respectively) are higher than those observed for *rac*-**3b**/DEAC (runs 10–12; branching degree: 91, 102 and 107 branches/1000 C at 20, 40 and 60 °C, respectively), **3a**/DEAC (runs 6–8; branching degree: 84, 88 and 108 branches/1000 C at 20, 40 and 60 °C, respectively) and **3d**/DEAC systems (runs 18–20; branching degree: 73, 82 and 99 branches/1000 C at 20, 40 and 60 °C, respectively).

The <sup>13</sup>C NMR spectrum of the polyethylene prepared with *rac*-**3c**/DEAC at 40 °C is shown in Figure 3. The number of branches was calculated according to the literature,<sup>[37]</sup> and it was found that polyethylene with 106 branches/1000 carbons (74 methyl, 11 ethyl, 9 propyl and 12 butyl or longer branches/1000 C) was obtained at 40 °C (run 15 in Table 3). This result was consistent with that calculated from the <sup>1</sup>H NMR spectrum. The rationale for the formation of the major types of branches (methyl, ethyl and butyl) in the polyethylene obtained in this work (run 15) is shown in Figure 3.

#### Conclusions

A series of new  $\alpha$ -diimine ligands and their Ni(II) complexes have been prepared and characterized. Ligands **2a**–**c** were modified in an attempt to change steric effects and the electronic density of the metal centre and eventually to improve activity in the polymerization of ethylene and control the microstructure of polyethylene. The results obtained show that the chiral complex *rac*-**3c** bearing one bulky *sec*phenethyl in the *ortho*-aryl position and an electron-withdrawing CI substituent group in the *para*-aryl position, activated by DEAC, produces a highly active catalyst system for the polymerization of ethylene and highly branched polyethylene at high temperature. Interestingly, the crystal structure of **3a**' showed a binuclear complex in which each nickel atom is six-coordinate. The two nickel atoms together with two bromine atoms form a planar four-membered ring.

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#### **Supporting Information**

Additional supporting information may be found in the online version of this article at the publisher's web-site.

CCDC 971546 contains the supplementary crystallographic data for complex **3a**'. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. **a**, **1b**, **1c**, **2d** and **3d** are known compounds and characterization data can be seen in the supporting information.