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### Nickel metallodendrimers as catalyst precursors in the tandem oligomerization of ethylene and Friedel–Crafts alkylation of its olefinic products

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### ABSTRACT

The synthesis and catalytic activity of nickel metallodendrimers (**C1–C6**) are reported. The metallodendrimers were synthesized by the coordination of the metal precursors, Ni(OAc)<sub>2</sub> and Ni(DME)Br<sub>2</sub>, to the periphery of salicylaldimine and iminopyridyl modified dendritic ligands, **DL1–DL6**, based on the generation 1 to generation 3 diaminobutane polypropylene imine (DAB–PPI) dendrimers. The metallodendrimers were tested in the oligomerization of ethylene and were found to be active catalysts. When using this catalyst system, it was found that a tandem process occurred in which ethylene oligomerization was followed by Friedel–Crafts alkylation of the reaction solvent, toluene. The latter process is mediated by the aluminium co-catalyst, EtAlCl<sub>2</sub>.

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### 1. Introduction

 $\alpha$ -Olefins can undergo many transformations depending on the reagents, the catalyst and the reaction conditions employed. Some of these transformations include hydrogenation, cracking, cyclization, isomerization, oligomerization and polymerization reactions [1]. Ethylene oligomers are the primary source of  $\alpha$ -olefins, which find application in the preparation of detergents, synthetic lubricants, plasticizers, alcohols and some copolymers. Therefore this process is of great interest to industrial and academic researchers in the field. Major commercial processes for ethylene oligomerization using homogeneous catalysts have been developed by companies like Shell (SHOP) and IFP (Dimersol and Alfabutol) [2–8].

Dendrimers are hyperbranched macromolecules that are monodisperse in nature and are characterized by a high density of peripheral groups. They possess three distinguishing architectural components, mainly (a) an initiator core, (b) an interior layer or branching points and (c) an exterior (surface groups or periphery). The very first synthesis of dendrimers was described by Vögtle et al. in 1978 who used the term "cascade macromolecules" [9]. This was followed closely by the parallel and independent development of the divergent, macromolecular synthesis of "starburst polymers" by Tomalia et al. in 1985, first using the term "dendrimer" and describing in great detail the preparation of poly(amidoamine) (PAMAM) dendrimers [10]. In the same year a communication by Newkome et al. reported the synthesis of arborols (a synonym for dendrimers) [11]. Dendrimer molecules that incorporate metal ions into their infrastructure either as cores, branching centres, arm connectors, termini or by metal incorporation at specific loci within the preassembled dendritic framework, are termed metallodendrimers [12,13]. Metallodendrimers have applications in a large number of areas such as drug delivery, molecular electronics, sensors and catalysis.

We previously reported the synthesis of dendritic nickel complexes derived from generation 1 (G1) and generation 2 (G2) dendrimeric salicylaldimine ligands based poly(propyleneimine) dendrimer scaffolds of the type, DAB-(NH<sub>2</sub>)<sub>n</sub> (n = 4 or 8, DAB = diaminobutane). These complexes are referred to as **C1** and **C2** respectively (Fig. 1). The complexes evaluated were previously found to be active in norbornene polymerization, yielding polymers with moderate to high molecular weights and low polydispersity indices [14–15].

In this paper we report the evaluation of some nickel metallodendrimer complexes based on dendrimeric Schiff base ligands as catalyst precursors in the oligomerization of ethylene. The diaminobutane polypropylene imine (DAB-PPI) dendrimer range was used as dendritic scaffolds. The G1–G3 amino functionalized PPI dendrimers were modified via Schiff base condensation reactions to produce salicylaldimine as well as iminopyridyl functionalized dendrimers. These functionalized dendrimers were then complexed to nickel salts to form dendritic complexes.

### 2. Experimental

### 2.1. General

Toluene was dried by refluxing over sodium/benzophenone. Methanol was dried by refluxing over magnesium turnings and







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Fig. 1. Structures of DAB G1 and G2 salicylaldimine nickel metallodendrimers, C1 and C2 [14].

iodine. Dichloromethane was dried by refluxing over phosphorus pentoxide. The DAB dendrimer range was obtained from Symochem, Netherlands, and used without any further purification. Salicylaldehyde, pyridine-2-carboxyaldehyde, Ni(OAc)<sub>2</sub>·XH<sub>2</sub>O, NiBr<sub>2</sub>, dimethoxyethane (DME) and EtAlCl<sub>2</sub> (25% w/v solution in toluene), were purchased from Sigma Aldrich and used without any further purification. Ethylene (99.9%) was obtained from Afrox. Infrared spectra were recorded on a Nicolet Avatar 330 FT-IR spectrophotometer, using an ATR accessory with a ZnSe crystal. <sup>1</sup>H NMR (300 MHz and 400 MHz) or <sup>13</sup>C NMR (75 MHz) spectra were recorded on a Varian VNMRS 300 MHz and a Varian Unity Inova 400 MHz spectrometer, using tetramethylsilane as an internal standard. Magnetic susceptibility was measured with a Sherwood Scientific MK-1 magnetic susceptibility balance at 298 K. Magnetic data were corrected for the magnetization of diamagnetic contributions, which were estimated from Pascal constants. UV-Vis absorption spectroscopy was conducted using a GBC UV-Vis 920 spectrometer at room temperature. TGA data were determined with a Q500 Thermogravimetric analyzer, in which the TGA scans were recorded at 10 °C/min under a nitrogen atmosphere from 30 to 590 °C. Melting points were recorded on a Stuart Scientific Melting Point apparatus SMP3, and are uncorrected. ESI Mass spectra were recorded on a Waters API Q-TOF Ultima instrument in Vmode. The source temperature was 100 °C and the desolvation temperature was 350 °C. The capillary voltage used was 3.5 kV. Microanalyses were done at the University of Cape Town. All work involving moisture and air sensitive compounds was carried out using standard Schlenk techniques. The GC analysis was done using a Varian CP-3800 gas chromatograph equipped with a HP PONA column (50 m  $\times$  0.2 mm  $\times$  0.5  $\mu$ m). The internal standard used for GC analysis was o-Xylene. MALDI-TOF spectra were recorded on a Voyager-DE FTR spectrometer.

#### 2.2. Synthesis

Ligands and complexes **DL1**, **DL2**, **DL4**, **C1**, **C2**, and **C4** were synthesized according to literature procedures [14,15].

# 2.2.1. Synthesis of ligand **DL3**, DAB-PPI G3 salicylaldimine modified dendrimer

DAB-G3 dendrimer (0.53 g, 0.31 mmol) was added to dry toluene (15 ml), in a Schlenk tube, under nitrogen. Salicylaldehyde (0.54 ml, 5 mmol) was added to the solution. The mixture was allowed to stir under reflux, for 96 h. The solvent was evaporated on a rotary evaporator, and a yellow oil was obtained. Dichloromethane (20 ml) was added to the residue and the product was washed with water (5  $\times$  30 ml). The dichloromethane layer was dried over potassium carbonate after which the latter was filtered off. The filtrate was evaporated to produce a yellow oil. Yield: 80%. IR (cm<sup>-1</sup>): v(O–H) 2941 (m); v(C=N) 1629 (s); v(C–O) 1277 (s). <sup>1</sup>H NMR in CDCl<sub>3</sub> ( $\delta$  ppm): 1.37 (-NCH<sub>2</sub>CH<sub>2</sub> DAB core), 1.54 (CH<sub>2</sub> alkyl), 1.78 (CH<sub>2</sub> alkyl), 2.36 (CH<sub>2</sub> tert amine), 2.40 (CH<sub>2</sub> tert amine), 2.48 (CH2 tert amine), 3.56 (HC=NCH2), 8.27 (N=CH imine), 6.82-7.56 (aryl). <sup>13</sup>C NMR in CDCl<sub>3</sub> (δ ppm): 24.6; 28.7; 31.2; 51.7; 52.5; 57.7; 117.2; 118.6; 131.4; 132.3; 161.5; 165.1. Anal. Calc. for C<sub>200</sub>H<sub>272</sub>N<sub>30</sub>O<sub>16</sub>: C, 71.38; H, 7.86; N, 11.30. Found: C, 71.19; H, 7.85; N, 11.13%. MS (MALDI-TOF)  $(C_{200}H_{272}N_{30}O_{16})$  [M]<sup>+</sup> at m/ z = 3352 m/z. ESI: [M]<sup>2+</sup>at m/z = 1676.5.

### 2.2.2. Synthesis of ligand **DL5**, DAB-PPI G2 iminopyridyl modified dendrimer

DAB-G2 dendrimer (0.523 g, 0.676 mmol) was added to dry toluene (20 ml) in a Schlenk tube, under nitrogen. 2-Pyridine carboxyaldehyde (0.51 ml, 0.541 mmol) was added to the solution. The mixture was allowed to stir for 48 h at room temperature. The solvent was evaporated on a rotary evaporator and a dark brown oil was obtained. Dichloromethane (20 ml) was added to the oil and the product was washed with water (5  $\times$  30 ml). The dichloromethane layer was dried over potassium carbonate after which the latter was filtered off. The filtrate was evaporated to give a brown oil. Yield: 85%. IR (cm<sup>-1</sup>): v(C=N) aliphatic 1647 (s); v(C=N) pyr 1586 (s); v(C=C) pyr 1562 (m). <sup>1</sup>H NMR in CDCl<sub>3</sub> ( $\delta$ ppm): 1.36 (-NCH<sub>2</sub>CH<sub>2</sub> DAB core), 1.57 (CH<sub>2</sub> alkyl), 1.84 (CH<sub>2</sub> alkyl), 2.41 (CH<sub>2</sub> tert amine), 2.52 (CH<sub>2</sub> tert amine), 3.58 (HC=NCH<sub>2</sub>), 8.36 (N=CH *imine*), 7.28–7.96 (CH *aryl*), 8.61 (CH *pyridine*). <sup>13</sup>C NMR in CDCl<sub>3</sub> (*b* ppm): 24.6; 28.3; 51.7; 59.5; 121.2; 124.5; 128.9; 136.4; 149.3; 154.5; 161.8. Anal. Calc. for C<sub>88</sub>H<sub>120</sub>N<sub>22</sub>: C, 69.62; H, 7.93; N, 20.13. Found: C, 69.61; H, 8.13; N, 20.58%. ESI-MS  $(C_{88}H_{120}N_{22})$  [M+H]<sup>+</sup>at m/z = 1487.

### 2.2.3. Synthesis of ligand **DL6**, DAB-PPI G3 iminopyridyl modified dendrimer

The same synthetic approach was used to prepare the generation 3 DAB iminopyridyl analogue **DL6**, by using the generation 3 DAB dendrimer with 16 mol equivalents of 2-pyridine carboxyal-dehyde to yield a brown oil as a product. Yield: 80%. IR (cm<sup>-1</sup>): v(C=N) aliphatic 1648 (s); v(C=N) pyr 1587 (s); v(C=C) pyr 1567 (m). <sup>1</sup>H NMR in CDCl<sub>3</sub> ( $\delta$  ppm): 1.38 (-NCH<sub>2</sub>C<u>H<sub>2</sub></u> DAB core), 1.59 (C<u>H<sub>2</sub></u> alkyl), 2.14 (C<u>H<sub>2</sub></u> tert amine), 2.40 (C<u>H<sub>2</sub></u> tert amine), 2.52 (C<u>H<sub>2</sub></u> tert amine), 3.67 (HC=NCH<sub>2</sub>), 8.37 (N=C<u>H</u> imine), 7.29–7.97 (C<u>H</u> aryl), 8.62 (C<u>H</u> pyridine). <sup>13</sup>C NMR in CDCl<sub>3</sub> ( $\delta$  ppm): 24.3; 28.2; 30.9; 51.7; 59.5; 121.2; 124.6; 136.5; 149.3; 154.6; 161.7. Anal. Calc. for C<sub>184</sub>H<sub>256</sub>N<sub>46</sub>: C, 67.41; H, 7.86; N, 19.39. Found: C, 67.02; H, 7.28; N, 20.60%. ESI-MS (C<sub>184</sub>H<sub>256</sub>N<sub>46</sub>) [M]<sup>5+</sup>at m/z = 622.16.

### 2.2.4. Synthesis of DAB-PPI G3 salicylaldimine nickel metallodendrimer, **C3**

To a solution of the DAB-G3 salicylaldimine ligand, **DL3** (1.36 g, 0.41 mmol) in ethanol (20 ml) was added nickel acetate tetra hydrate (0.82 g, 3.20 mmol) and the reaction mixture was allowed to stir under reflux for 24 hours, forming a green precipitate. The precipitate was filtered off by vacuum filtration and washed extensively with ethanol to give a green solid. Dichloromethane (15 ml) was added to the solid, and the solution was then filtered. The filtrate was evaporated to give **C3** as a green solid. Yield = 75%. m.p.: 199-201 °C. IR (cm<sup>-1</sup>): v(C=N) 1629 (s) and v(C-O) 1344 (s). Anal. Calc. for C<sub>200</sub>H<sub>256</sub>N<sub>30</sub>Ni<sub>8</sub>O<sub>16</sub>: C, 59.10; H, 6.42; N, 10.14. Found: C, 59.84; H, 7.73; N, 9.41%. MALDI-TOF MS (C<sub>200</sub>H<sub>256</sub>N<sub>30</sub>Ni<sub>8</sub>O<sub>16</sub>) [M+H]<sup>3+</sup> at m/z = 1269.

# 2.2.5. Synthesis of G1 Ni(DME)Br<sub>2</sub> using triethylorthoformate as a dehydrating agent

This was prepared as previously reported in the literature [16]. NiBr<sub>2</sub> (0.50 g, 2.30 mmol), a yellow solid, was added to a mixture of ethanol (20 ml) and triethylorthoformate (1.2 ml) and refluxed for 3 h to give a clear green solution. The solvent was then concentrated to 1 ml, after which excess dimethoxyethane (30 ml) was added. The mixture was allowed to crystallize and then filtered to give a bright orange solid. Yield = 84%. IR (cm<sup>-1</sup>): v(C–H) *aliphatic* at 2935 (s) and v(C–O) at 1049 (s).

# 2.2.6. Synthesis of DAB-PPI G2 iminopyridyl nickel metallodendrimer, C5

 $Ni(DME)Br_2$  (0.33 g, 1.10 mmol) was added to a solution of **DL5** (0.20 g, 0.14 mmol) in dry ethanol (15 ml). There's an immediate

colour change from orange to brown, and all reagents dissolved to give a clear brown solution. The reaction mixture was refluxed for 24 h. The solvent was evaporated to give a brown solid residue. Dichloromethane (10 ml) was added to the residue and then triturated, after which a brown solid precipitates. The precipitate was filtered to give **C5** as a brown solid which was washed several times with CH<sub>2</sub>Cl<sub>2</sub>. Yield = 80%. m.p.: 225–231 °C. IR (cm<sup>-1</sup>): v(C=N) at 1640 (s); v(C=C) *pyr* at 1597 (s) and v(C=N) *pyr* at 1568 (s). ESI–MS (C<sub>88</sub>H<sub>120</sub>Br<sub>16</sub>N<sub>22</sub>Ni<sub>8</sub>), found [M+Na]<sup>4+</sup>at *m*/*z* = 814, calcd. 3234 g/mol.

# 2.2.7. Synthesis of DAB-PPI G3 iminopyridyl nickel metallodendrimer, C6

Ni(DME)Br<sub>2</sub> (0.31 g, 1.0 mmol) was added to a solution of **DL6** (0.20 g, 0.062 mmol) in dry ethanol (20 ml). There's an immediate colour change from orange to brown, and all reagents dissolved to give a clear brown solution. The reaction mixture was refluxed for 24 h. The solvent was evaporated to give a brown solid residue. Dichloromethane (10 ml) was added to the residue and then triturated, after which a brown solid precipitates. The precipitate was filtered to give **C6** as a brown solid. Yield = 78%. m.p.: 201–204 °C. IR (cm<sup>-1</sup>): v(C=N) 1642 (s); v(C=C) pyr at 1598 (s) and v(C=N) pyr at 1571 (s). ESI-MS ( $C_{184}H_{256}Br_{32}N_{46}Ni_{16}$ ), found [M+Na]<sup>5+</sup> at m/z = 1326, calcd 6688 g/mol.

### 2.3. Ethylene oligomerization

The catalyst amounts were varied to ensure a constant amount of Ni in the system at 5  $\mu$ mol. EtAlCl<sub>2</sub> was employed as a co-catalyst. The reaction time was one hour at room temperature. The ethylene pressure was maintained at 5 atm. and the solvent employed was toluene (50 ml). Acidic ethanol (10 ml) was used to quench the reaction. The Al:Ni ratios ranged from 1000:1 to 5000:1.

#### 2.3.1. Typical ethylene oligomerization procedure

The ethylene oligomerization reactions were carried out in a 300 ml stainless steel autoclave equipped with an overhead stirrer and internal cooling coil. The autoclave was loaded in a nitrogenpurged glove box. The appropriate amount of catalyst corresponding to 5 µmol of nickel was suspended in dry toluene (50 ml) in a stainless steel PARR reactor. The required amount of EtAlCl<sub>2</sub> was added to the solution using a glass syringe. The reactor was sealed and removed from the glove-box. The reactor was flushed with ethylene 3 times. The ethylene pressure was set at 5 atm. and maintained at this pressure throughout the oligomerization procedure. The reaction was conducted at room temperature for 1 h. The oligomerization was stopped by quenching the reaction mixture with 10 ml of acidic ethanol (ethanol:HCl, 95:5). A GC aliquot was taken after which the solvent from the remaining sample was evaporated via rotary evaporation and dried on the vacuum line for 24 h. Any remaining non-volatile product was weighed and subjected to analysis by MALDI-TOF spectrometry.

### 3. Results and discussion

#### 3.1. Synthesis of DAB polypropylene imine based Schiff-base ligands

#### 3.1.1. Modification and characterization of the generation 1–3 DAB-PPI salicylaldimine ligands **DL1–DL3**

We have previously reported the synthesis of ligands **DL1** and **DL2** via Schiff base condensation of the G1 and G2 DAB-PPI dendrimers respectively with salicylaldehyde [14]. The same synthetic approach was used to prepare the generation 3 DAB salicylaldimine analogue **DL3** (Scheme 1). Due to the greater number of surface groups, the G3 ligand **DL3** needed longer reaction time than its

lower generation analogues, DL1 and DL2, to ensure complete reaction of all the peripheral amino groups with the aldehydes. The progress of the reaction was monitored by FTIR using the v(C=N) band. This band is clearly visible in the FTIR spectra of all three ligands in the region 1629–1632 cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy was also used to monitor the formation of the imine group. For example in the <sup>1</sup>H NMR spectra of the ligands, the signal for the imine proton occurs around  $\delta$  8.32–8.37 ppm while in the case of the <sup>13</sup>C NMR, the peak for the imine carbon is observed around 161 ppm for all three generations of dendrimer ligands. This thus confirms the successful surface modification of the DAB-PPI dendrimer with salicylaldimine units. The G3 dendritic ligand **DL3** has several empty cavities that can potentially trap unreacted salicylaldehyde molecules. This is indeed what we observe. Several attempts to remove the excess aldehvde from the products proved to be unsuccessful. Solvent extraction did not work since the salicylaldehyde and the dendritic ligand have similar solubility properties. The presence of the salicylaldehyde entrapped within the dendrimer cavities was confirmed by the presence of a weak but sharp singlet in the <sup>1</sup>H NMR spectrum of **DL3** at 9.91 ppm. When complexing this ligand to nickel, the pure product is obtained without the salicylaldehyde impurity.

# 3.1.2. Preparation and characterization of the generation 1–3 DAB Iminopyridyl ligands **DL4–DL6**

The synthesis of the iminopyridyl modified dendrimer ligands **DL4** and **DL5** have previously been reported by Smith et al. [17] and Mketo [18]. The generation 3 iminopyridyl analogue, **DL6**, was synthesized in a similar manner to its lower generation analogues i.e. via the Schiff base condensation of the DAB-G3 dendrimer with pyridine-2-carboxyaldehyde. The lower generation ligands require only 48 h for complete reaction, whereas the preparation of the generation 3 iminopyridyl ligand is performed over at least 72 h due to the large number of surface groups. All three ligands were isolated as dark brown oils. FTIR spectroscopy shows the  $\nu(C=N)$  band around 1645 cm<sup>-1</sup> which confirms the reaction of the adehyde with the amino groups on the periphery of the DAB-dendrimer. The  $\nu(C=N)$  bands associated with the pyridine ring are



Scheme 1. Synthesis of the DAB G3 salicylaldimine modified dendrimer, DL3.

also observed in the product spectrum and are around 1586 cm<sup>-1</sup>. In the <sup>1</sup>H NMR spectra of the ligands, the signal for the imine proton occurs around 8.37 ppm and the <sup>13</sup>C NMR spectra, show a peak assigned to the carbon atom of the imine of ligands **DL4–DL6** in the range  $\delta$  161.4–161.8 for the G1–G3 iminopyridyl ligands. Mass spectrometry analysis for **DL4** and **DL5** show a singly charged molecular ion peak at m/z = 672.80 and m/z = 1487.0 respectively. **DL6** however shows a multiply charged (+5) parent ion [M]<sup>5+</sup> at m/z 622.12. Microanalyses of the ligands **DL5** and **DL6** suggest solvent (CH<sub>2</sub>Cl<sub>2</sub>) entrapment within the cavities of the dendrimers. This was confirmed by <sup>1</sup>H NMR spectroscopy which shows a peak at 5.37 ppm assigned to the methylene chloride protons. Attempts to completely remove the entrapped solvent molecules were not successful.

# 3.2. Synthesis of DAB polypropylene imine based nickel metallodendrimers

## 3.2.1. Synthesis and characterization of the generation 1–3 DAB salicylaldimine nickel metallodendrimers, **C1–C3**

We have previously reported the synthesis of the G1 and G2 nickel salicylaldimine complexes, **C1** and **C2** by reacting the salicylaldimine modified dendrimer ligands **DL1** and **DL2** with Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O [14]. We subsequently synthesized the generation 3 salicylaldimine nickel complex, **C3**, using the same synthetic procedure as that employed for **C1** and **C2**, using the generation 3 salicylaldimine ligand, **DL3**. Fig. 2 shows the structure of the Generation 3 salicylaldimine nickel metallodendrimer, **C3**. All three complexes were isolated as green solids, with yields ranging from 75% to 85%. All complexes were characterized by FTIR spectroscopy, magnetic susceptibility measurements, mass spectrometry and elemental analysis. From the IR spectra, we observe a shift in the v(C=N) band from around 1645 cm<sup>-1</sup> to 1630 cm<sup>-1</sup> and the



Fig. 3. UV–Vis spectra of the G1 DAB salicylaldimine ligand, DL1, and nickel metallodendrimer complex, C1.

v(C-O) stretching frequencies from around 1277 cm<sup>-1</sup> to 1324 cm<sup>-1</sup> when comparing the ligand and complex spectra. These shifts are due to the coordination of the ligand to the metal via both the nitrogen and the oxygen donor sites. These effects are also observed in the FTIR spectra of other salicylaldimine-type nickel complexes reported in the literature [19–21].

All the complexes are paramagnetic thus no NMR analysis was done. The magnetic moments of these nickel salicylaldimine metallodendrimers range from 2.95 BM for the G1 complex salicylaldimine, **C1**, to 3.38 BM for the G3 pyridine–imine complex, **C6**. Tetrahedral nickel(II) complexes commonly have a magnetic moment of 3.1–4.0 BM as reported in literature. [22–23]. The ESI mass spectra for **C1** and **C2** show peaks that correspond to [M+H]<sup>+</sup> at m/z 848 and m/z 1833 respectively. The mass spectrum for **C3** shows a triply charged peak molecular ion peak at m/z 1269. The melting points for **C1–C3**, decrease when going from the G1 complex to the



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Fig. 2. Structure of DAB G3 salicylaldimine nickel metallodendrimer, C3.

G3 complex, indicating that the G1 complex, C1, is the most thermally stable of the three salicylaldimine complexes. The UV–Vis spectra of the DAB G1 salicylaldimine ligand, DL1, and the DAB G1 salicylaldimine nickel complex, C1, in a dichloromethane solution are shown in Fig. 3. The G2 and G3 analogues of these ligands (DL2 and DL3) and complexes (C2 and C3) gave similar UV–Vis spectra, hence only the G1 spectra are discussed.

The electronic spectra of the salicylaldimine ligands in the solution phase show three absorption bands at 330, 260 and 225 nm, involving  $\pi \rightarrow \pi^*$  transitions. Similar absorption bands were observed by Fan et al. [22] who reported the synthesis of salen-type Schiff base ligands. The UV–Vis spectra of the salicylaldimine Ni complexes show two bands at 240 nm and 380 nm which is assigned to the transition of  $n \rightarrow \pi^*$  of the imine ligand and d-d transitions in the metal, respectively. The latter is very weak but resembles what is normally seen for other salen type complexes [23].

# 3.2.2. Synthesis and characterization of the generation 1–3 DAB iminopyridyl nickel metallodendrimer complexes, **C4–C6**

The G1-G3 DAB iminopyridyl nickel complexes, C4-C6, were synthesized by reacting the iminopyridyl modified dendritic ligands, DL4-DL6, with Ni(DME)Br2 as a metal precursor. We recently reported the synthesis of the generation 1 iminopyridyl nickel metallodendrimer, C4[15]. The generation 2 (C5) and generation 3 (C6) (Fig. 4) iminopyridyl nickel metallodendrimers are novel complexes. The reaction of ligands, **DL4–DL6** with Ni(DME)Br<sub>2</sub>, resulted in brown solids being isolated as products with yields ranging from 78% to 85%. The iminopyridyl complexes are all fairly hygroscopic and consequently have to be stored under an inert atmosphere and handled in a nitrogen-purged glove-box. This is in contrast to the salicylaldimine complexes which are quite air stable in the solid state, as well as in solution. Another major difference between the salicylaldimine complexes C1-C3 and the iminopyridyl complexes C4-C6, is that the latter complexes have double the amount of nickel centres than the former for each corresponding dendrimer generation. Thus for example the G1 iminopyridyl complex, C4, has four nickel centres whereas the G1 salicylaldimine complex, C1, has only 2 nickel centres.

From the IR spectra of the complexes, we observe a shift in the v(C=N) stretching frequency from around 1647–1648 cm<sup>-1</sup> to 1639–1641 cm<sup>-1</sup> when comparing spectra of the ligands and complexes. The v(C=N) stretching frequency of the pyridine ring shifted from around 1586–1587 cm<sup>-1</sup> to around 1596–1598 cm<sup>-2</sup> for complexes, C4-C6. The magnetic moments of these nickel iminopyridyl metallodendrimers also gives some information regarding the geometry of the complexes. The magnetic moments of the iminopyridyl complexes are in a similar range as that of the salicylaldimine complexes, ranging from 3.23 BM for the G1 complex, C4, to 3.38 BM for the G3 complex, C6. It is believed that these complexes therefore have a tetrahedral geometry, although the magnetic moments of our complexes are slightly lower than what is expected for conventional tetrahedral nickel complexes. The melting points for C4-C6 also decrease when going from the G1 complex to the G3 complex, again indicating that the G3 complex. **C6**, has the lowest thermal stability. On the whole, the iminopyridyl complexes are less thermally stable than the corresponding salicylaldimine complexes, C1-C3. The ESI mass spectrum for C4 shows a molecular ion peak at m/z 1592 which can be assigned to an adduct of the parent ion containing two sodium ions. The mass spectra of the G2 and G3 complexes, C5 and C6, show multiply charged ions. This is not unusual since high molecular weight complexes commonly tend to form multiply charged ions. The spectrum for C5 shows a quadruply charged molecular ion peak as a Na<sup>+</sup> adduct at m/z = 814. The MS for **C6** shows a peak at m/zz = 1326 which can be assigned to a molecular ion carrying a +5 charge and detected as sodium adduct. Due to the highly hygroscopic nature of the iminopyridyl complexes, we were unable to obtain satisfactory microanalysis results.

#### 3.3. Ethylene oligomerization studies

## 3.3.1. Catalytic activity and selectivity of nickel metallodendrimers, C1–C6, at a constant Al/Ni ratio of 2000:1

Catalysts **C1–C6** were evaluated in the oligomerization of ethylene, keeping the metal loading as well as the co-catalyst: metal ratio constant. The results are shown in Table 1. The Turn-Over-Frequency (TOF) values range from 629 to 2582 kg



 $[M] = NiBr_2$ 

Fig. 4. Structure of DAB G3 iminopyridyl nickel metallodendrimer, C6.

Table 1	
TOF <sup>a</sup> of catalysts ( <b>C1-C6</b> ) at 2000:1 Al/Ni ratio.	

Dendrimer generation	TOF	TOF values <sup>a</sup>				
	DAB Ni Salicylaldimine catalysts	DAB NiBr <sub>2</sub> Iminopyridyl catalysts				
1	2417.2 ( <b>C1</b> )	2274.8 ( <b>C4</b> )				
2	2018.0 ( <b>C2</b> )	629.0 ( <b>C5</b> )				
3	2582.0 ( <b>C3</b> )	971.6 ( <b>C6</b> )				

<sup>a</sup> TOF = Kg of oligomer per mol of Ni per hour.

product  $mol^{-1}Nih^{-1}$ . The highest activity is observed for the generation 3 salicylaldimine complex, **C3**. When comparing the salicylaldimine catalysts (**C1–C3**) to the iminopyridyl catalysts (**C4–C6**), it is evident that the salicylaldimine complexes generally exhibit higher activity for all generations of dendrimers evaluated (Fig. 5). This could be related to the higher stability of the salicylaldimine complexes.

The selectivity of catalysts C1-C6 is shown in Table 2. The generation 1 catalysts (C1 and C4) tend to form mostly short chain oligomers (C<sub>4</sub>-C<sub>16</sub>). This is also the case for the other Ni salicylaldimine catalysts (C2-C3). The higher generation G2 and G3 Ni pyridine-imine catalysts (C5 and C6) on the other hand form predominantly long chain oligomers (C<sub>22+</sub>). Thus the pyridine-imine catalysts seem to be favouring chain propagation over chain termination processes. This could be due to the high degree of congestion on the dendrimer periphery of C5 and C6 which could play a role in the retardation of chain termination by sterically preventing β-hydride transfer, thus leading to longer chain products. These products of longer chain length were analyzed by MALDI-TOF mass spectrometry. It was found that the length of these oligomers typically ranged from  $C_{22}$ - $C_{60}$ , with the average chain length being around C<sub>44</sub>. A typical MALDI-TOF mass spectrum showing the distribution of oligomers formed in one of the reactions can be seen in Fig. 6.

Closer examination of the products leads to an interesting observation in which the presence of uneven carbon number compounds was detected in the product mix. For all the catalysts evaluated, a  $C_{11}$  product is formed in relatively high amounts and in the case of DAB G3 salicylaldimine catalyst (**C3**), a  $C_{13}$  product is also formed. Further investigation into the nature of these odd-carbon numbered hydrocarbon products revealed these to be alkylated benzenes. It was found that these products were the result of a Friedel–Crafts alkylation of the solvent toluene in the presence of

Table 2 Selectivity of catalysts, C1–C6 at 2000:1 Al/Ni ratio.

Catalyst	%C <sub>4</sub>	% C <sub>6</sub>	% C <sub>8</sub>	% C <sub>11</sub> <sup>a</sup>	% C <sub>13</sub> <sup>a</sup>	% C <sub>14</sub>	% C <sub>16</sub>	$% C_{22}^{+}$
C1	24.2	5.1	4.2	31.6	-	11.8	8.4	14.7
C2 C3	16.8	_	_	42.4 46.0	- 3.5	6.8 17.8	7.5 14.0	26.5 18.7
C4	55.6	6.4	0	18.0	-	-	-	20.0
C5	-	-	-	17.3	-	5.2	1.5	76.0
C6	4	-	-	21.5	-	-	-	74.5

<sup>a</sup> Friedel-Crafts alkylation products.

short chain alkenes ( $C_4-C_6$ ) formed during the ethylene oligomerization reaction. Thus for example the  $C_{11}$  products observed are isomers of butyl toluene and the  $C_{13}$  product isomers of hexyl toluene. The distribution of the oligomerization and the Friedel– Crafts alkylation products obtained using the different catalysts are shown in Table 2. No ethyl toluenes are observed indicating that direct Friedel–Crafts alkylation of toluene by ethylene does not take place under the reaction conditions employed. The Friedel–Crafts reaction was proven independent by carrying out a test reaction in which 1-hexene was reacted with EtAlCl<sub>2</sub> in the absence of any metal catalyst. This produced hexyl toluenes as the sole products.

Darkwa et al., described similar observations when evaluating their (pyrazol-1-ylmethyl) pyridine-nickel catalysts in the oligomerization of ethylene, using EtAlCl<sub>2</sub> as a co-catalyst [24]. However, they reported that their catalysts exclusively produce Friedel–Crafts products **A–C** (Scheme 2), whereas in our case even numbered ethylene oligomers in addition to the Friedel–Crafts alkylation products are observed in the product stream. This indicates that the Ni/EtAlCl<sub>2</sub> active species catalyzes the oligomerization of ethylene, while the EtAlCl<sub>2</sub> is primarily responsible for the Friedel–Crafts alkylation and that the two processes occur simultaneously. With our dendritic catalyst systems, the oligomerization reaction appears to proceed faster than the Friedel–Crafts alkylation reaction, hence the presence of ethylene oligomers in the product mix.

In the case of the reactions reported by Darkwa et al., it seems the Friedel–Crafts alkylation occurs faster than the oligomerization process, leading to the oligomeric products being consumed as soon as they are produced. Therefore no traces of oligomeric products are observed directly in this case.

It should be noted that in our systems, a fair amount of the butene produced initially subsequently becomes consumed in the



Fig. 5. Catalyst activity of C1-C6 at Al/Ni 2000:1.



Fig. 6. Representative MALDI-TOF spectrum of long chain oligomer products ( $C_{22}$ - $C_{60}$ ).



Scheme 2. Friedel-Crafts alkylation products reported by Darkwa et al. [23].

Friedel–Crafts alkylation reaction to produce the  $C_{11}$  product. In fact, in almost all cases more than half of the butene produced reacts with the solvent in a subsequent reaction. In the case of catalysts **C3** and **C5**, all the butene produced is converted as none is detected in the final product mix. Catalyst **C4** interestingly shows the lowest percentage of butene produced being converted to the alkylated toluene product. It also seems that when using the lower generation catalysts **(C1** and **C4)** lower levels of Friedel–Crafts alkylation occur when compared to the higher generation catalysts, as shown by the higher amounts of butene still present in the product mix for the former catalysts. Thus it would appear that the transition metal catalyst has some impact on the process. At this stage the precise role of the transition metal is not entirely understood.

## 3.3.2. Catalytic activity and selectivity of the generation 3 DAB nickel catalyst, **C3**

Since we've previously reported the evaluation of **C1** and **C2** in the oligomerization of ethylene [25], at various Al/Ni ratio's, we found it apt to also evaluate **C3** at different Al/Ni ratio's. The results are shown in Table 3. As expected, the DAB generation 3 salicylaldimine catalyst (**C3**) needed a much higher Al/Ni ratio than its lower generation counterparts (**C1** and **C2**) to reach optimum activity at 5000:1, with the TOF reaching up to 3582.8 kg mol<sup>-1</sup> -

Table 3						
TOF <sup>a</sup> of generation	3	DAB	nickel	catalyst,	<b>C3</b> .	

Al:Ni	DAB G3 Ni Sal
1000	1796.2
2000	2582.0
3000	2568.4
4000	2714.6
5000	3582.8
7000	2963.2

<sup>a</sup> TOF = Kg of oligomer per mol of Ni per hour.

Ni  $h^{-1}$ . The optimum Al/Ni ratios for **C1** and **C2** were previously found to be 500:1 and 2000:1 respectively [25]. These results further support our theory that the tertiary amine units present in these polypropyleneimine based dendritic systems act as Lewis base donor sites, and therefore are potential positions for coordinating to the Lewis acidic organoaluminium co-catalyst. The G1 catalyst has only two tertiary amine units within its internal structure, while the G2 catalyst has six tertiary amine units and the G3 catalyst has fourteen. It is thought that the co-catalyst, EtAlCl<sub>2</sub>, first coordinates to these Lewis basic sites before activation of the metal centre occurs. It is well known that N-donor molecules form adducts with Lewis acidic Al complexes [26]. Since the G3 catalyst

Table 4			
Selectivity of C3	at various	Al/Ni	ratios

<sup>a</sup> Friedel-Crafts products.

has the most N-donor sites it will need to react with a larger amount of the aluminium alkyl than its lower generation counterparts therefore requiring larger amounts of co-catalyst before the optimum activity is reached.

Table 4 shows the selectivity obtained at the different Al/Ni ratio's ranging from 1000:1 to 7000:1. The results indicate that irrespective of the Al/Ni ratio, the major product remains short chain oligomers.  $C_4$  is only present at an Al/Ni ratio of 1000:1. Uneven carbon number products  $C_{11}$ ,  $C_{13}$ ,  $C_{15}$  and  $C_{17}$  are also present in the product mixture. This, as discussed earlier, is due to Friedel– Crafts alkylation of the solvent, toluene. In all cases, except at Al/ Ni ratio of 1000:1, all the butenes formed is converted to  $C_{11}$  Friedel–Crafts alkylation products. Furthermore, all the hexenes formed is converted to  $C_{13}$  Friedel–Crafts alkylation products.

It is also noted that an increase in the Al/Ni ratio leads to a decrease in the production of  $C_4$  and subsequently a decrease in the formation of  $C_{11}$  Friedel–Crafts alkylation products. Since all catalytic reactions formed  $C_{11}$  as a product, we thought it best to run a blank reaction, containing no metallodendrimer catalyst, with only EtAlCl<sub>2</sub> present under the same reaction conditions. After one hour, the reaction mixture was worked-up as described earlier, and no product was observed. This proves that without our dendritic catalyst systems, neither ethylene oligomerization nor Friedel–Crafts alkylation of toluene using ethylene occurs. It is clear

that the Friedel–Crafts alkylation only occurs after the formation of butene and other even carbon number olefins, as a result of ethylene oligomerization by the metallodendritic catalysts. Therefore, the two processes occur in tandem. First we have the oligomerization of the ethylene to even numbered olefins, followed by the Friedel–Crafts alkylation of the toluene by olefins mediated by EtAlCl<sub>2</sub>.

In addition, the EtAlCl<sub>2</sub> does not mediate the alkylation of toluene in the presence of only ethylene to produce ethyl benzene. Hence, the alkylation only occurs with butene and longer chain olefins. This theory was tested by using 1-hexene as a substrate instead of ethylene. No metallodendritic catalyst was included in the reaction mixture, only EtAlCl<sub>2</sub>. Under similar reaction conditions, the EtAlCl<sub>2</sub> converted the 1-hexene to the alkylated toluene products within 10 minutes, with 100% conversion. From GC-MS analysis, we observed the selective formation of  $C_{13}$  and  $C_{19}$ compounds, which can be assigned to the Friedel–Crafts products formed via single- and di-alkylation of toluene with the  $C_6$  oligomer respectively. We also observed a  $C_{25}$  species which can be assigned to tri-alkylated Friedel–Crafts products (Fig. 7).

It can thus be concluded that even though EtAlCl<sub>2</sub> on its own does not promote the alkylation of toluene in the presence of ethylene, it does mediate the alkylation of toluene with 1-hexene in the absence of any transition metal catalyst system. Reactions with



Fig. 7. The GC-MS chromatogram indicating F/C alkylation with 1-hexene and toluene.

1-pentene and 1-octene were also evaluated and similar results were obtained where the toluene was alkylated to produce pentyland octyl-toluenes respectively. Most of the Friedel-Crafts products obtained are largely mono alkylated toluenes instead of dior tri-alkylated products, since C<sub>11</sub> (butyl-toluene) and C<sub>13</sub> (hexyl-toluene) Friedel-Crafts products are observed as major products rather than C<sub>15</sub> (dibutyl-toluenes) and/or C<sub>19</sub> (tributyl toluenes) Friedel-Crafts products. Therefore we can conclude that toluene undergoes Friedel-Crafts single-alkylation with oligomers of ethylene. When a different solvent such as hexane, is used under similar reaction conditions, no Friedel-Crafts alkylation products are observed as expected, only small amounts of short chain oligomers  $(C_4 \text{ and } C_8)$  were detected. The catalyst system shows quite low activity in hexane as solvent with the result that we did not pursue this any further.

#### 4. Conclusion

A range of metallodendritic catalysts were synthesized and evaluated in ethylene oligomerization reactions. The synthesized nickel catalysts produced a range of short-medium chain ethylene oligomers  $(C_4 - C_{18})$ , as well as some longer chained oligomers when employing EtAlCl<sub>2</sub> as a co-catalyst. An interesting observation was the presence of products due to Friedel-Crafts alkylation of the solvent, in addition to the ethylene oligomers. This was due to the reaction of the ethylene oligomers produced with the solvent, toluene. While the more active DAB G1-G3 salicylaldimine catalysts (C1-C3) form mainly short chain oligomers, the less active higher generation iminopyridyl catalysts (C5-C6) form mainly longer chain oligomers. Changing the solvent to hexane does prevent the Friedel-Crafts alkylation reaction from occurring, however we wanted to study the effect of toluene as a solvent in this catalyst system.

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