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Inorganica Chimica Acta 358 (2005) 3491-3496

Inorganica Chimica Acta

www.elsevier.com/locate/ica

# New palladium $\alpha$ -diimine complexes containing dendritic wedges for ethene oligomerisation

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Received 30 March 2005; accepted 11 April 2005 Available online 2 June 2005

#### Abstract

The synthesis of new  $\alpha$ -diimine ligands containing zero and first generation dendritic wedges is described. These ligands were reacted with (COD)PdCl<sub>2</sub> to give the corresponding palladium  $\alpha$ -diimine complexes. The resulting palladium complexes are active in the oligomerisation of ethene and the activity was compared to a related nickel complex. © 2005 Elsevier B.V. All rights reserved.

Keywords: Palladium; α-Diimine ligand; Dendritic wedge; Oligomerisation, Ethene

#### 1. Introduction

The oligomerisation of ethene is one of the major industrial processes for the production of linear 1-alkenes [1]. Oligomers in the range C<sub>6</sub>-C<sub>20</sub> are used as co-monomers in the polymerisation of ethene to give linear low-density polyethene (LLDPE) or for the preparation of detergents and synthetic lubricants. Catalysts currently used in industry for the Shell Higher Olefin Process (SHOP) [2] contain Ni(II) complexes bearing bidentate mono-anionic ligands [1,2]. Cationic Ni(II)  $\alpha$ -diimine complexes were also reported to be effective ethene oligomerisation catalysts [3], while iron-based bis(imino)pyridine catalysts were described as highly active compounds in the oligomerisation of ethene in combination with the co-catalyst MAO or MMAO [4]. Several modifications of the bis(imino)pyridine backbone which have already been described in the literature [5] mostly lead to a

decrease in catalytic activity. Recently, related fluorosubstituted bis(imino)pyridine complexes of iron and their catalytic reactivity in ethene oligomerisations were described [6], as were bis(imino)pyridine complexes containing methoxy and CF<sub>3</sub> groups [7]. Recently we described iron bis(imino)pyridine complexes containing dendritic wedges for ethene oligomerisation [8]. Here we wish to report the related palladium  $\alpha$ -diimine systems containing wedges of the poly(benzylphenyl ether) type.

Since the independent reports by Gibson and Brookhart [9] on nickel and palladium  $\alpha$ -diimine catalysts and iron and cobalt bis(imino)pyridyl catalysts for the polymerisation and oligomerisation of 1-alkenes [9], much attention has been focused on these late transition metal catalysts as alternatives to established technologies.

It is known that the position and steric bulk of the substituents on the aryl rings of the  $\alpha$ -diimine catalysts (Fig. 1) plays a crucial role in determining the selectivity of the catalyst. In particular, the *ortho* substituents (R<sub>1</sub>) have been identified as important. If R<sub>1</sub> is a non-hydrogen substituent, and preferably a bulky substituent such as *iso*-propyl groups, then the resulting catalysts are selective for the production of high molecular weight polymers from ethene. If only one of the two *ortho* 

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Fig. 1. Palladium and nickel  $\alpha$ -diimine catalyst for the oligomerisation of 1-alkenes.

positions  $R_1$  on the aryl rings is an alkyl substituent, the catalyst is selective for the oligomerisation of ethene to linear 1-alkenes with a Schulz-Flory [10] chain length distribution, and for the dimerisation of longer chain olefins (such as 1-hexene). The effect of substituents in the *para*-position  $(\mathbf{R}_2)$  has been less studied. Our interest in dendritic molecules [11], their applications in catalysis and as new materials, led us to consider the possibility of functionalising late transition metal oligomerisation catalysts with dendritic components. This could take the form of attaching dendritic wedges to the catalysts, thus creating a catalyst at the core of a dendrimer. By having a catalytic site at the core of a dendrimer, it should be possible to control the micro-environment around the catalytic centre and thus allow modifications of the catalytic selectivity [12]. In addition to the latter, dendritically substituted homogeneous catalysts should be easily separated from the product stream by means of ultrafiltration methods.

Functionalising an  $\alpha$ -diimine ligand with dendritic wedges to create a catalytic ligand at the core of a dendrimer is likely to be synthetically achievable. The aryl components of the ligand are particularly amenable to dendritic functionalisation, as a wide range of anilines with different functionalities for substitution are commercially available. These may be reacted in standard Schiff-base type reactions with 2,3-butadione to form the  $\alpha$ -difficult framework with any rings suitable for attachment of dendritic wedges. Dendritic functionalisation at the para-position is most favourable. The direct steric control around the catalytic centre may be controlled by appropriate *ortho* substitution ( $\mathbf{R}_1$ , Fig. 1), thereby ensuring an oligomerisation catalyst. The heteroatomic functionality, for attachment of the dendritic wedges, is introduced on the *para*-position ( $R_2$ , Fig. 1) and thus removed from the active catalytic centre in order to minimise unfavourable interactions.

#### 2. Results and discussion

#### 2.1. Preparation of ligands

Appropriate ligands would be  $\alpha$ -diimine ligands with either both *ortho*-substituents (R<sub>1</sub>, Fig. 1) being hydrogen, or one of the substituents R<sub>1</sub> on each ring being a methyl group and the other a hydrogen. We chose to prepare ligands with one methyl group on the *ortho*position for this study. Substituent R<sub>2</sub> was chosen to be a hydroxyl group for ease of attachment of alkylbromide functionalised dendritic wedges, using the standard Williamson ether synthesis. Thus compound **1** was synthesised using the simple Schiff-base condensation reaction of 2,3-butadione and two molar equivalents of amino-*m*-cresol (Scheme 1).

The para-hydroxyl group allows attachments of various dendritic wedges containing an alkylbromide functionality on the focal point. Using the Williamson ether synthesis, a quantitative yield of dendritically functionalised  $\alpha$ -diimine ligands was expected. Fréchet and co-workers reported the quantitative build-up of poly(benzylphenyl ether) dendrimers [13] when applying mild reaction conditions. Applying similar conditions, we reacted two equivalents of the appropriate bromoalkyl wedge with 1 in acetone, heated under reflux, using K<sub>2</sub>CO<sub>3</sub> as the base and a sub-stoichiometric amount of 18-crown-6 as phase transfer catalyst (Scheme 2). The reactions typically were allowed to proceed for between 48 and 72 h. The compounds 2 and 3 were separated from the inorganic salts using an aqueous work-up. Analytically pure samples were obtained by recrystallisation from an appropriate solvent. Fréchets poly(benzylphenyl ether) dendritic wedges [13] were chosen because they are easily prepared and react readily with hydroxyaryl compounds. These wedges have previously been used as dendritic catalysts for anionic ring opening polymerisation reactions [14]. We reported the use of these wedges connected to iron bis(imino)pyridyl complexes [8] in alkene oligomerisation previously. Details on the wedges employed are given in Scheme 2.

The ligands **2** and **3** were characterised by <sup>1</sup>H, <sup>13</sup>C NMR spectroscopy, IR spectroscopy and satisfactory elemental analysis. For ligand **2**, satisfactory mass spectrometric was obtained and the molecular ion was observed. Ligand **3** unfortunately decomposed under MS



Scheme 1. Synthesis of 1.



Scheme 3. Synthesis of 4 and 5.

conditions and only fragments could be identified, but not the molecular ion.

#### 2.2. Preparation of the metal complexes

Palladium complexes of the  $\alpha$ -diimine ligands 2 and 3 were prepared by treating a slight excess of the ligand with (COD)PdCl<sub>2</sub> in dichloromethane (Scheme 3). The resulting yellow complexes (4 and 5) were characterised by NMR and IR spectroscopy and elemental analysis.

Preliminary attempts to prepare the analogous nickel complexes were successful [15]. Treatment of the substituted  $\alpha$ -diimine ligands with (DME)NiBr<sub>2</sub> in dichloromethane [16] led to the formation of the corresponding nickel complexes [15]. We will report on the formation of these nickel complexes in a separate communication.

#### 2.3. Catalytic ethene oligomerisation

Complexes 4 and 5 were used to investigate the catalytic behaviour in catalytic ethene oligomerisation. The catalytic runs were repeated with the literature compound 6 (see Fig. 1;  $R_1 = Me$ ;  $R_2 = H$ ; M = Pd, X = Cl) [17] as well as the corresponding NiBr<sub>2</sub> complex of ligand 2. The conditions and yields of oligomers from the catalytic runs were performed are given in Table 1. The catalytic oligomerisation reactions were quenched

by addition of *iso*-propanol, followed by addition of 1 M HCl. An aqueous work-up was used to remove aluminium salts, and the organic phase was dried. An internal standard of undecene ( $C_{11}$  1-alkene) was added in order to determine the absolute amounts of each 1-alkene formed. The volatiles were removed in vacuo, leaving behind the involatile oligomers (some  $C_{10}$ , most  $C_{12}$ , all  $C_{14}$ +), along with a certain amount of residual toluene. After determining the mass of the involatile oligomers (recovered yield), they were taken up in hexane, and GC analysis was used to determine the contribution to the mass by residual toluene and the amounts of  $C_{10}$  and  $C_{12}$  still present. Detection of higher weight oligomers ( $C_{20}$ +) and polymers is not possible using GC.

Table 1 Yields of non-volatile ethene-oligomers

Entry <sup>a</sup>	Catalyst precursor	Yield (mg)
1 <sup>b</sup>	6	25
2	6	148
3	4	112
5°	5	66
6	<b>2</b> –NiBr <sub>2</sub> complex	1605

<sup>a</sup> Conditions: 1 bar ethylene,  $[cat] = 20 \mu mol$ , [Al]/[cat] = 400, T: 40 °C, solvent: toluene, volume: 30 cm<sup>3</sup>, t: 60 min.

<sup>b</sup> Run at 25 °C.

<sup>c</sup> Run conducted using 50% of normal amounts.

From the data in Table 1, there appears to be no real correlation between the activity of the complexes and the size (i.e. generation) of the dendritic wedges on the complexes. It is therefore concluded that the dendritic wedges do not sterically interfere with the cationic metal centre. Since even the large MAO oligomers can activate the metal centre, it is suggested that dendritic wedges on the 4-position of the phenyl rings do not constitute any steric hindrance. Similar conclusions were previously drawn for the related iron bis(imino)pyridyl complexes [8]. The nickel complex of ligand 2 [15] is clearly more active than the corresponding palladium complexes – which was expected from literature analogues [17]. We suggest that the present palladium  $\alpha$ -diimine complexes can be used as models for the more active (but harder to characterise) nickel complexes.

Due to the nature of the work-up, low molecular weight oligomers in the  $C_4$ - $C_{10}$  range were lost. Subsequent GC analysis was therefore only performed on the higher molecular weight oligomers. Although a Schulz-Flory [10] distribution of oligomers was expected, GC analysis did not show such a distribution.

### 3. Conclusions

New *a*-diimine ligands containing dendritic wedges were successfully synthesised and characterised. The attached wedges are of the poly(benzylphenyl ether) type. These ligands were used successfully to synthesise new  $\alpha$ -diimine palladium complexes, and the resulting complexes were fully characterised. These complexes constitute a new and exciting family of oligomerisation catalysts, which have the potential of being separated by ultra-filtration methods. It was shown that these  $\alpha$ diimine palladium complexes are active in the oligomerisation of ethene when using MAO as a co-catalyst. The activity of the complexes is not related to the size (generation) of the dendritic wedges. This opens up the possibility for using even larger dendritic wedges as substituents, without interfering with the catalytic activity. Larger dendritic substituents could make feasible the separation of the catalyst from the product stream by means of ultra-filtration methods.

### 4. Experimental

#### 4.1. General remarks

All manipulations were carried out under purified nitrogen, using glovebox (MBraun Unilab) or standard Schlenk line techniques under pre-purified argon [18]. Dichloromethane was dried by passage through a column containing alumina (neutral, Brockmann grade I) and distilled from CaH<sub>2</sub> [19]. Methanol was distilled from Mg activated by I<sub>2</sub>, and acetone was distilled from Drierite prior to use [19]. All reagents were stored under pre-purified argon. Poly(benzylphenylether) wedge G1 was prepared according to the method of Hawker and Fréchet [13]. Compound 6, [2,3-bis(2-methylphenylimino)butane]palladium dichloride, was prepared according to the method of Brookhart and Svejda [17]. All other reagents were purchased from Sigma Aldrich. NMR spectra were recorded on either a Varian Unity-400 (<sup>1</sup>H, 400 MHz; <sup>13</sup>C, 100.6 MHz) spectrometer or a Varian Mercury-300 (<sup>1</sup>H, 300 MHz; <sup>-13</sup>C, 75.5 MHz) spectrometer at ambient temperature. Chemical shifts were referenced to tetramethylsilane (TMS), using either the residual protio impurities in the solvent (<sup>1</sup>H NMR) or the solvent resonances (<sup>13</sup>C NMR). Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer in the range  $450-4400 \text{ cm}^{-1}$ . Spectra were recorded on solutions of samples between NaCl plates. Mass spectra were recorded on a Finnigan MAT GCQ GC/MS. The selected m/z values given refer to the most abundant isotopes. In all cases the isotopic distribution pattern was checked against the theoretical distribution. Oligomer samples were analysed by GC, using a Carlo-Erba 4200 machine equipped with a Zebron ZB-1 column and an hydrogen flame ionization detector. The GC was coupled to a Columbia Supergrator 3A integrator. Elemental analyses were performed using a Carlo-Erba EA1108 elemental analyser in the microanalytical laboratory of the University of Cape Town.

# *4.2.* Synthesis of 2,3-bis(2-methyl-4-hydroxylphenylimino) butane (1)

A mixture of 2,3-butadione (912 mg, 10.6 mmol), 2methyl-4-hydroxyaniline (3.25 g, 26.4 mmol) and formic acid (a few drops) was stirred in MeOH (35 ml) at room temperature for 24 h. The mixture was concentrated until a yellow precipitate formed. After allowing further precipitation at -20 °C for 16 h, the precipitate was recovered by filtration. After recrystallisation from hot MeOH, 1 was obtained as a yellow powder. (1.56 g, 5.26 mmol, 50%); m.p. 122–126 °C;  $v_{\text{max}}/\text{cm}^{-1}$  (THF): 3310 vs (O–H), 1636 (C=N), 1607 m, 1583 m;  $\delta_{\rm H}$ (300 MHz, acetone- $d_6$ ): 8.06 (2H, broad s, aryl-OH), 6.70-6.50 (6H, m, H<sub>arvl</sub>), 2.12 (6H, s, N=CMe), 2.05 (6H, s, aryl-*Me*);  $\delta_{C\{H\}}$  (75 MHz, acetone-d<sub>6</sub>): 167.6 (N=C Me), 154.3 (4-Caryl), 142.1 (1-Caryl), 129.1 (Caryl), 119.1 (Caryl), 117.2 (Caryl), 113.0 (Caryl), 17.3 (aryl-Me), 14.8 (N=CMe); m/z (FAB) 296 (M<sup>+</sup> + H, 93), 281  $(M^+ - Me, 31\%).$ 

*4.3. Synthesis of 2,3-bis(2-methyl-4-benzyloxyphenylimino) butane* (2)

A mixture of 1 (490 mg, 1.66 mmol), 18-crown-6 (90 mg, 0.34 mmol),  $K_2CO_3$  (580 mg, 4.20 mmol), acetone

(30 ml) and benzyl bromide (0.50 ml, 4.2 mmol) was heated under reflux for 48 h. The volatiles were removed in vacuo and the residue was partitioned between  $CH_2Cl_2$  and slightly alkaline (pH ~ 7.5) water. The aqueous phase was extracted with  $CH_2Cl_2$  (3 × 20 ml), and the combined organics were washed with slightly alkaline water  $(3 \times 20 \text{ ml})$  and slightly alkaline brine  $(3 \times 20 \text{ ml})$ . After drying over Na<sub>2</sub>SO<sub>4</sub> and filtration, the volatiles were removed in vacuo, leaving a yellow crystalline material. This was recrystallised from  $CH_2Cl_2/MeOH$  to give 2 as a yellow powder. (341 mg, 0.715 mmol, 43%); m.p. 130-134 °C; (Found: C, 80.1; H, 6.9; N, 6.0%.  $C_{32}H_{32}N_2O_2$  requires C, 80.6; H, 6.8; N, 5.9%); v<sub>max</sub>/cm<sup>-1</sup> (CH<sub>2</sub>Cl<sub>2</sub>): 2922 w, 2869 w, 1640 s (C=N), 1604 m, 1576 w, 1490 vs (Ar), 1379 w, 1362 m, 1241 s, 1200 vs (Ar-O), 1162 m, 1119 s, 1028 s (CH<sub>2</sub>–O);  $\delta_{\rm H}$  (300 MHz, CDCl<sub>3</sub>): 7.46–6.58 (16H, m, H<sub>arvl</sub>), 5.07 (4H, s, OCH<sub>2</sub>Ph), 2.16 (6H, s, Me), 2.14 (6H, s, Me);  $\delta_{C{H}}$  (75 MHz, CDCl<sub>3</sub>): 168.0 (N=CMe), 155.6 (4- $C_{aryl}$ ), 143.1 (1- $C_{aryl}$ ), 137.3 (1- $C_{Ph}$ ), 129.0, 128.5, 127.9, 127.5, 118.8, 117.1, 112.4, 70.3 (OCH<sub>2</sub>Ph), 18.1 (aryl-Me) 15.5 (N=CMe).

# *4.4. Synthesis of 2,3-bis[2-methyl-4-(3,5-dibenzyloxy) benzyloxyphenylimino]butane (3)*

A mixture of 1 (219 mg, 0.739 mmol), G1 (559 mg, 1.46), 18-crown-6 (40 mg, 0.15 mmol) and  $K_2CO_3$ (261 mg, 1.90 mmol) in acetone (20 ml) was heated under reflux for 48 h. The volatiles were removed in vacuo and the residue was partitioned between CH<sub>2</sub>Cl<sub>2</sub> and slightly alkaline water. The aqueous phase was extracted with  $CH_2Cl_2$  (3 × 20 ml), and the combined organics were washed with slightly alkaline water  $(3 \times 20 \text{ ml})$ and slightly alkaline brine  $(3 \times 20 \text{ ml})$ . After drying over Na<sub>2</sub>SO<sub>4</sub> and filtration, the volatiles were removed in vacuo, leaving a yellow solid. Recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>/MeOH gave **3** as a yellow powder. (380 mg, 0.422 mmol, 57%); m.p. 143-146 °C; (Found: C, 79.6; H, 6.0; N, 3.5%. C<sub>60</sub>H<sub>56</sub>N<sub>2</sub>O<sub>6</sub> requires C, 80.0; H, 6.3; N, 3.1);  $v_{\text{max}}/\text{cm}^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub>): 2922 w, 2876 w, 1639 m (C=N), 1597 vs (Ar), 1490 s (Ar), 1452 m, 1376 m, 1202 s (Ar–O), 1160 vs, 1119 m, 1028 m (CH<sub>2</sub>–O);  $\delta_{\rm H}$  $(300 \text{ MHz}, \text{ CDCl}_3)$ : 7.42–6.64  $(32\text{H}, \text{m}, H_{\text{arvl}})$ , 5.05 (8H, s,  $OCH_2Ph$ ), 5.00 (4H, s,  $OCH_2$ -aryl wedge), 2.14 (6H, s, Me), 2.12 (6H, s, Me);  $\delta_{C\{H\}}$  (100 MHz, CDCl<sub>3</sub>): 167.9 (N=CMe), 160.2 (3,5- $C_{arylwedge}$ ), 155.5 (4-Carvlcore), 143.1, 139.8, 136.9, 136.7, 128.9, 128.5, 127.9, 127.4, 118.7, 117.8, 112.4, 106.4, 70.2 (OCH<sub>2</sub>-aryl wedge), 70.1 (OCH<sub>2</sub>Ph), 17.9 (aryl-Me), 15.4 (N=CMe).

## 4.5. Synthesis of [2,3-bis(2-methyl-4-benzyloxyphenylimino)butane]palladium dichloride (4)

A mixture of (COD)PdCl<sub>2</sub> (113 mg, 0.396 mmol) and **2** (261 mg, 0.548 mmol) was stirred in  $CH_2Cl_2$  (15 ml)

for 24 h. The thick yellow precipitate that had formed was recovered by filtration and washed with CH<sub>2</sub>Cl<sub>2</sub> and hexanes to give **4** as a yellow–orange powder. (142 mg, 0.217 mmol, 55%); m.p. (dec) > 220 °C; (Found: C, 58.6; H, 4.8; N, 4.2%. C<sub>32</sub>H<sub>32</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>Pd requires C, 58.8; H, 4.9; N, 4.3);  $v_{max}/cm^{-1}$  (CH<sub>2</sub>Cl<sub>2</sub>): 2929 w, 2856 w, 1602 s, 1579 w (C=N), 1495 s (Ar), 1352 m, 1233 m (Ar–O), 1170 m;  $\delta_{H}(300 \text{ MHz}, \text{DMSO-d}_{6})$ : 7.45–6.91 (16H, m,  $H_{aryl}$ ), 5.09 4H, s, OCH<sub>2</sub>Ph), 2.30 (6H, s, N=CMe), 2.06 (6H, s, aryl-Me);  $\delta_{C}$ (H)(75 MHz, DMSO-d<sub>6</sub>): 181.2 (N=CMe), 157.2 (6-C<sub>aryl</sub>), 138.1 (1-C<sub>aryl</sub>), 136.8 (1-C<sub>Ph</sub>), 131.6, 128.2, 127.6, 127.5, 122.7, 115.9, 111.9, 69.4 (OCH<sub>2</sub>Ph), 20.0 (Me), 17.9 (Me).

# 4.6. Synthesis of {2,3-bis[2-methyl-4-(3,5-dibenzyloxy) benzyloxyphenylimino [butane} palladium dichloride (5)

A mixture of (COD)PdCl<sub>2</sub> (12 mg, 0.042 mmol) and 3 (50 mg, 0.055 mmol) was stirred in  $CH_2Cl_2$  (10 ml) for 24 h. The volatiles were removed in vacuo and the residue was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/hexanes to give 5 as a glassy red solid. (30 mg, 0.028 mmol, 66%); m.p. 170-173 °C (dec.); (Found: C, 66.5; H, 5.1; N, 2.6%. PdC<sub>60</sub>H<sub>56</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>6</sub> requires C, 66.8; H, 5.2; N, 2.6%);  $v_{\text{max}}/\text{cm}^{-1}$  (KBr): 2360 w, 1670 w, 1570 w (C=N), 1474 s (Ar), 1445 m, 1360 m, 1022 m (CH<sub>2</sub>-O);  $\delta_{\rm H}(300 \text{ MHz}, \text{ CDCl}_3)$ : 7.34–6.81 (32H, m,  $H_{\rm arvl}$ ), 4.97 (8H, s, OCH<sub>2</sub>Ph), 4.83 (4H, s, OCH<sub>2</sub>-aryl wedge), 2.38 (6H, s, N=CMe), 2.09 (6H, s, aryl-Me);  $\delta_{C{H}}$ (75 MHz, CDCl<sub>3</sub>): 181.0 (N=CMe), 160.1 (3,5-Carylwedge), 158.1 (4-Carylcore), 139.3, 138.5, 136.9, 131.7, 128.5, 127.9, 127.6, 123.0, 116.9, 106.5, 101.7, 70.1(OCH<sub>2</sub>-aryl wedge), 69.9(OCH<sub>2</sub>Ph), 20.3 (N=CMe), 18.0 (aryl-Me).

#### 4.7. Catalytic ethene oligomerisation

A mixture of toluene (22.7 cm<sup>3</sup>) and MAO (5.3 cm<sup>3</sup> of a 10% solution in toluene) was thermostatted at 40 °C. The vigorously stirred solution was saturated with ethene at 1 atm for 30 min. A suspension of the catalyst precursor (20 µmol) in toluene (2.0 cm<sup>3</sup>) was added via syringe. An immediate colour change occurred. The reaction was quenched after 60 min by adding 2-propanol (2 cm<sup>3</sup>) followed by aq. HCl (0.1 M, 2 cm<sup>3</sup>). Hexane (20 cm<sup>3</sup>) and water (20 cm<sup>3</sup>) were added and the organic phase was separated. The aqueous phase was extracted with hexane (2 × 20 cm<sup>3</sup>). The combined organic phases were washed with water (3 × 20 cm<sup>3</sup>) and brine (3 × 20 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and filtered. The volatiles were evaporated in vacuo to leave the non-volatile oligomers.

#### Acknowledgements

Financial assistance from Sasol Technology, Sasol Polymers and the Research Fund of the University of

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