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New iron bis(imino)pyridyl complexes containing dendritic wedges for alkene oligomerisation†

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The synthesis, characterisation and catalytic behaviour of new iron bis(imino)pyridyl complexes containing dendritic wedges, as well as the synthesis of bis(*para*-hydroxyphenylimino)pyridines is described. The hydroxyl functionality of the bis(*para*-hydroxyphenylimino)pyridines was used to attach dendritic wedges of the carbosilane type as well as the benzylphenyl ether type. After attachment of the dendritic wedges, complexation of these ligands to iron(II) chloride was achieved. The resulting dendritically functionalised bis(imino)pyridyl iron complexes were tested in the catalytic oligomerisation of ethene.

Introduction

The oligomerisation of ethene is one of the primary industrial processes for the production of linear 1-alkenes.[1] Oligomers in the range C_6–C_{20} 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) α-diimine complexes were also reported to be effective ethene oligomerisation catalysts,[3] while iron-based bis(imino)pyridyl complexes were described as highly active compounds in the catalytic oligomerisation of ethene in combination with the co-catalyst MAO or MMAO.[4,5]

Several modifications of the bis(imino)pyridine backbone, which have already been described in the literature,[6] mostly lead to a decrease in catalytic activity. Recently, fluoro-substituted bis(imino)pyridine complexes and their catalytic reactivity in ethene oligomerisations were described,[7] as were bis(imino)-pyridine complexes containing methoxy and CF_3 groups.[8]

Since the independent reports by Gibson[4,6] and Brookhart[9,10] on iron and cobalt bis(imino)pyridyl catalysts and nickel and palladium α-diimine catalysts for the polymerisation and oligomerisation of 1-alkenes, 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 bis(imino)pyridyl catalysts (Fig. 1) play a crucial role in determining the selectivity of the catalyst. The *ortho* substituents (R_1) have been identified as being particularly important. If both R_1 groups on each ring are non-hydrogen substituents, and preferably bulky alkyl substituents such as *iso*-propyl groups, then the catalysts are selective for the production of high molecular weight polymers from ethene. If only one of the *ortho* substituents R_1 on each ring is an alkyl group, and the other a hydrogen, then the catalyst is selective for the oligomerisation of ethene to linear 1-alkenes with a Schultz–Flory chain length distribution, as well as for the dimerisation of longer chain 1-alkenes (such as 1-hexene).

The effect of substituents in the *para*-position (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. A catalytic site at the core of a dendrimer makes it possible to control the microenvironment around the catalytic centre and thus allows modifications of the catalytic selectivity.[12] Incorporation of a catalytically active site in a dendritic macromolecule has the added potential advantage of enabling one to separate the catalyst from the product stream by means of ultra-filtration methods.

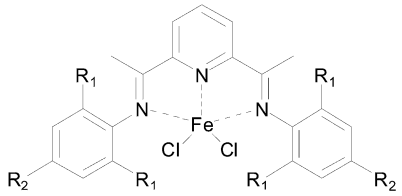

Fig. 1 Iron bis(imino)pyridyl precatalyst for the oligomerisation of 1-alkenes.

Functionalising a bis(imino)pyridyl 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 2,6-diacetylpyridine to form the bis(imino)pyridyl framework with aryl 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*-substituents (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.

Results and discussion

Preparation of ligands

Appropriate ligands would be bis(imino)pyridyl ligands with either both *ortho*-substituents (R_1) being hydrogen, or one of the substituents R_1 on each ring being a methyl group and the other a hydrogen. Substituent R_2 was chosen to be a hydroxyl group for ease of attachment of alkylbromide functionalised dendritic wedges, using the Williamson ether synthesis. Thus

† Electronic supplementary information (ESI) available: Synthetic details. See http://www.rsc.org/suppdata/dt/b4/b411884g/

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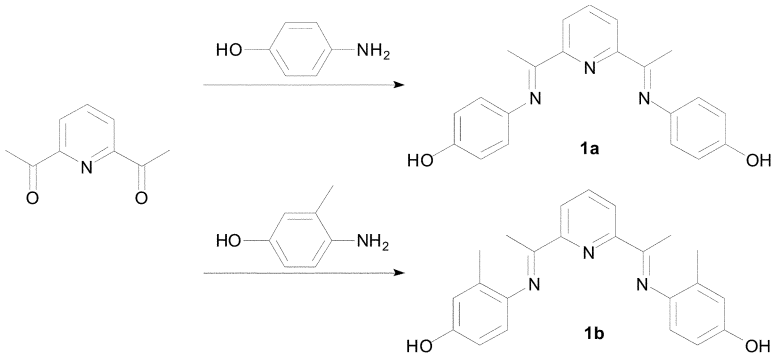
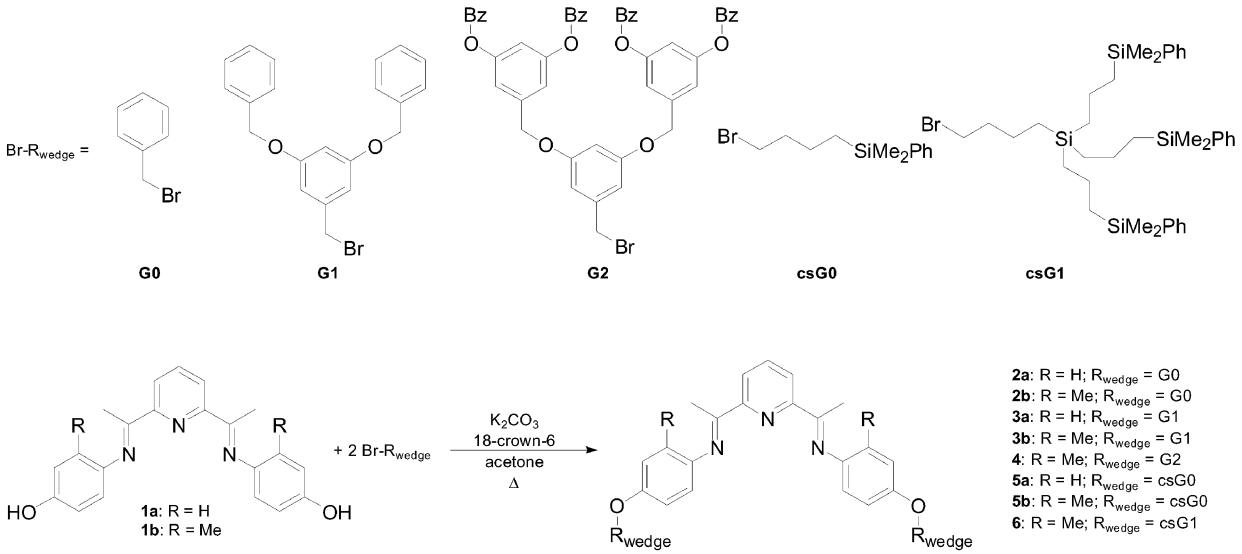


Scheme 1 Synthesis of *para*-hydroxy functionalised bis(imino)pyridyl ligands **1a** and **1b**.



Scheme 2 Synthesis of **2**–**6**.

compounds **1a** and **1b** were synthesized using simple Schiff-base condensation reactions of 2,6-diacetylpyridine and two molar equivalents of either 4-aminophenol or 4-amino-*m*-cresol (Scheme 1).

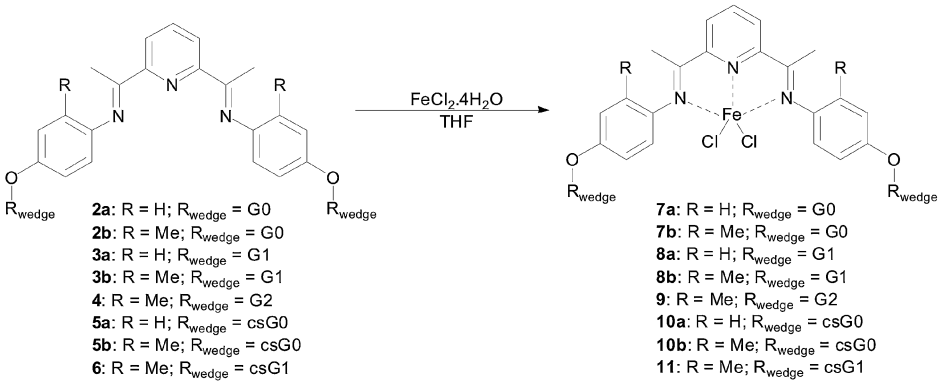
The *para*-hydroxyl group allows attachments of various dendritic wedges containing an alkylbromide functional group at the focal point. Using the Williamson ether synthesis, a quantitative yield of dendritically functionalised bis(imino)pyridyl ligands is expected, as in the synthesis of poly(benzylphenylether) dendrimers.[13] Two equivalents of the appropriate bromoalkyl wedge (see Scheme 2) were reacted with either **1a** or **1b** in acetone heated under reflux, using K_2CO_3 as the base and a sub-stoichiometric amount of 18-crown-6 (Scheme 2). The reactions typically were allowed to proceed for between 48 and 72 h. Compounds **2** to **6** were then extracted by means of an aqueous work-up. Analytically pure samples were obtained by recrystallisation from an appropriate solvent. Fréchet's poly(benzylphenylether) dendritic wedges[13] were chosen because they are easily prepared and react readily with hydroxyaryl compounds. They have previously been used as dendritic catalysts for anionic ring opening polymerisation reactions.[14] Carbosilane dendritic wedges with a bromoalkyl focal point have previously been reported,[15] and similar compounds have been prepared for this work.[16] The carbosilane wedges have the advantage of being inert and non-polar, so the influence of the ether linkages in the poly(benzylphenylether) could be evaluated. Details on the wedges employed are given in Scheme 2.

Preparation of the iron complexes

The iron precatalyst complexes, **7** to **11**, were prepared by stirring a slight excess of the bis(imino)pyridyl ligands **2** to **6** with $FeCl_2{\cdot}4H_2O$ in THF (Scheme 3), as reported in the literature.[17] The literature precatalysts **12**[10] (see Fig. 1; R_1 = Me; R_2 = H) and eight new iron complexes with dendritic substituents (**7a**–**11**) were prepared. After completion of the reaction (judged by the absence of solid particles of $FeCl_2$), the intensely coloured complexes were precipitated out of solution by the addition of diethyl ether. All new complexes were obtained as dark green powders (except **8a** and **10a**) in near quantitative yields. The compounds **8a** and **10a** may have a different structure as they are bright purple and exhibit no catalytic activity. Attempts to grow crystals suitable for X-ray crystallography were unsuccessful for all of the new compounds.

Full characterisation of the complexes proved to be difficult. High spin d^6 iron complexes are paramagnetic, and only in some instances have ^{1}H-NMR data been reported.[18] In our experience, obtaining interpretable spectra proved impossible. Many of the complexes are not soluble in readily available NMR solvents ($CDCl_3$, benzene-d_6), and the line broadening and unpredictable shifts of the peaks rendered assignment speculative at best. IR spectroscopy is of little value as a diagnostic technique for these compounds. Useful characterisation techniques were therefore limited to elemental analysis and mass spectrometry. The larger dendritic complexes are amorphous solids or oils, and may retain some solvent even after long periods of evacuation. The carbosilane substituted complexes appeared to be moderately air-sensitive, and therefore were stored under inert conditions before use in catalytic reactions.

Reasonable elemental analyses were generally obtained for the poly(benzylphenylether) substituted complexes. The FAB mass spectra were more instructive, and in all cases the parent ion and fragments involving the loss of chlorine were observed. For some of the larger complexes, the observed molecular ion was fairly



Scheme 3 Synthesis of the iron complexes **7–11**.

low in intensity, but the isotopic patterns corresponded well with the theoretical patterns for the calculated empirical formulae.

Catalytic runs

Complexes **7** to **12** were evaluated as catalysts for the oligomerisation of ethene to higher 1-alkenes. The complexes were activated using methylaluminium oxane (MAO; [Al]/[Fe] = 400) in toluene, and the active catalysts were subsequently exposed to 1 bar ethene at 30 °C. Analysis by gas chromotography was used to determine the Shultz–Flory constant α. The total yield and turnover number (T.O.N.) was calculated by removing the volatiles *in vacuo* and measuring the residual mass. The lost volatile oligomers were determined approximately by GC analysis of the involatile oligomers and extrapolation using the α-value, as described previously.[5] The catalytic data are presented in Table 1.

In order to establish reproducibility, and draw useful comparisons between the new catalysts and literature catalysts, the first two runs (entry 1 and 2) were performed using 2,6-bis-[1-(2-methylphenylimino)ethyl]pyridine iron dichloride (**12**).[5] All *para*-substituted complexes **7a–11** were active oligomerisation catalysts, with the exception of **8a** and **10a**. The effect of the *para*-ether linkage itself may be deduced from the catalytic behaviour of **7b** (entry 4). Under the conditions used in this study, both the activity and α-values were higher than that for unsubstituted analogue **12** (entries 1 and 2). The increase in α-value, relative to that for **12**, may be observed in all runs using the dendritically substituted precatalysts. This appears to be due to the *para*-ether functionality alone, as no effect of dendrimer size on the α-value is apparent. The presence of an *ortho*-methyl group made little difference to activity or selectivity in the case of **7a** and **7b**. Surprisingly, complexes **8a** and **10a** showed no catalytic activity, unlike their *ortho*-methyl substituted analogues **8b** and **10b**. The dendritically substituted catalysts **8b**, **9** and **11** displayed higher activity than their non-dendritic analogues **7b** and **10b**, and the highest activities were obtained with the **G1** poly(benzylphenylether) and carbosilane substituents (entries 6 and 10). This increased activity might be ascribed to either increased solubility of the catalysts or to a beneficial interaction between the dendritic wedges and the catalytic centre, in the case of the poly(benzylphenylether) functionalised catalysts. To test this second hypothesis, runs were carried out with **12** (entries 11 and 12) and **8b** (entry 13), in which 2 equivalents of **G1** poly(benzylphenylether) wedge were added as a catalyst promoter. The activity of the runs with **12** and 2 equivalents of **G1** was significantly higher than **12** alone, whereas the α-value remained unchanged. It appears that the poly(benzylphenylether) wedges might act as promoters in this type of catalysis, probably by stabilising the active catalyst against decomposition. The addition of two equivalents of **G1** caused no additional enhancement of catalytic activity with **8b**, which is already functionalised with a poly(benzylphenylether) wedge. It has previously been noted that aryl ether compounds can enhance catalytic activity and selectivity in ethene oligomerisation systems.[19]

Conclusions

A range of bis(imino)pyridyl iron complexes containing large dendritic wedges was successfully synthesised and characterised. The attached wedges are of both the poly(benzylphenylether) and the carbosilane type. These complexes constitute a new and exciting family of oligomerisation catalysts. It was shown that these bis(imino)pyridyl iron compounds are active in the oligomerisation of ethene, using MAO as a co-catalyst. The activity of these new catalysts is not related to the type of dendritic

Table 1 Results of the catalytic runs[a]

Entry	Precatalyst	Time/min	Yield/g	1-Alkenes (%)	α	T.O.N. ($\times 10^3$)
1	**12**	60	2.98	85	0.71	5.32
2	**12**	60	3.48	85	0.68	6.21
3	**7a**	60	4.47	89	0.75	7.98
4	**7b**	60	4.56	82	0.77	8.13
5	**8a**	60	—	—	—	Inactive
6	**8b**	60	5.85	80	0.77	10.45
7	**9**	60	4.83	83	0.76	8.62
8	**10a**	60	—	—	—	Inactive
9	**10b**	60	3.82	91	0.72	6.82
10	**11**	60	6.29	90	0.75	11.23
11	**12**[b]	60	6.62	88	0.68	11.82
12	**12**[b]	60	6.50	86	0.71	11.61
13	**8b**[b]	60	5.88	82	0.75	10.50

[a] Ethene pressure: 1 bar; catalyst loading: 20 μmol; [Al]/[Fe] = 400; initial temperature: 30 °C; solvent: toluene; total volume: 30 cm^3; time: 60 min; [b] Two equivalents of **G1** wedge added.

wedge, however the activity of the complexes shows small variations related to the size of the dendritic wedge. This opens up the possibility of using even larger dendritic wedges as substituents, without interfering with the catalytic activity. Larger dendritic substituents would make it feasible to separate the catalyst from the product stream by means of ultra-filtration methods.

Experimental

General remarks

All manipulations were carried out under purified nitrogen, using glovebox (MBraun Unilab) or standard Schlenk line techniques under pre-purified argon.[20] Diethyl ether, pentane, tetrahydrofuran (THF) and toluene were dried by passage through a column containing alumina (neutral, Brockmann grade I) and distilled from sodium/benzophenone ketyl prior to use.[21] Dichloromethane (DCM) was distilled from CaH_2; methanol and ethanol were distilled from Mg activated by I_2; and acetone was distilled from Drierite prior to use.[21] All reagents were stored under pre-purified argon. Poly(benzylphenylether) wedges **G0**, **G1**, and **G2** were prepared according to the method of Hawker and Fréchet.[13] Carbosilane wedges **csG0** and **csG1** were prepared using a method similar to that of Van Heerbeek *et al.*[15] and were reported previously.[16] Compound **12**[17] was prepared according to literature methods. All other reagents were purchased from Sigma Aldrich. NMR spectra were recorded on either a Varian Unity-400 (^{1}H, 400 MHz; ^{13}C, 100.6 MHz; ^{29}Si, 79.5 MHz) spectrometer or a Varian Mercury-300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz) spectrometer at ambient temperature. Chemical shifts were referenced to tetramethylsilane (TMS), using the residual protio impurities in the solvent (^{1}H NMR), the solvent resonances (^{13}C NMR) or external TMS (^{29}Si NMR). Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer in the range 450–4400 cm^{-1}. Spectra were recorded on solutions of samples between NaCl plates. Mass spectra were determined by Dr P. Boshoff of the mass spectrometry unit at the Cape Technikon. The selected *m*/*z* values given refer to the most abundant isotopes. In all cases, the isotopic distribution patterns were checked against the theoretical distribution. GC analyses were performed on a HP 5890 series II GC fitted with a 50 m PONA column with a film thickness of 0.5 mm. Elemental analyses were performed using a Carlo Erba EA1108 elemental analyser in the microanalytical laboratory of the University of Cape Town.

Synthesis of 2,6-bis-[1-(4-hydroxyphenylimino)ethyl]pyridine, 1a

A mixture of 2,6-diacetylpyridine (0.908 g, 5.56 mmol), 4-aminophenol (1.275 g, 11.68 mmol), toluene (30 cm^3) and a few crystals of *p*-toluenesulfonic acid was heated under reflux for 72 h, collecting the formed water in a Dean–Stark condenser. A thick, light yellow precipitate formed. After cooling, the precipitate was collected by filtration, and washed successively with dichloromethane, ether and pentane. After recrystallisation from hot methanol, **1a** was recovered as a light yellow powder. (1.812 g, 5.24 mmol, 84%); mp 245–247 °C; (Found: C, 73.1; H, 5.6; N, 12.0. $C_{21}H_{19}N_3O_2$ requires C, 73.0; H, 5.5; N, 12.1%); ν_{max}/cm^{-1} (THF) 3300 (OH), 1633 (C=N), 1568, 1506; δ_H (300 MHz; DMSO-d_6) 9.11 (2H, br s, aryl-O*H*), 9.29 (2H, d, ^3J(HH) 8 Hz, 3,5-*H*py), 7.99 (1H, t, ^3J(HH) 8 Hz, 4-*H*py), 6.82–6.76 (8H, m, *H*aryl), 2.38 (N=C*Me*); $\delta_{C\{H\}}$ (75 MHz; DMSO-d_6) 166.4 (N=*C*Me), 156.1 (4-*C*aryl), 154.7 (2,6-*C*py), 143.7 (1-*C*aryl), 137.8 (4-*C*py), 122.4, 121.7, 116.2, 16.4 (N=C*Me*); *m*/*z* (EI) 345 (M$^+$, 100), 330 (M$^+$ − Me, 5%).

Synthesis of 2,6-bis-[1-(4-hydroxy-2-methylphenylimino)ethyl]-pyridine, 1b

A solution of 2,6-diacetylpyridine (0.374 g, 2.29 mmol), 4-amino-*m*-cresol (1.127 g, 9.15 mmol) and formic acid (5 drops) in anhydrous methanol (15 cm^3) was heated to 60 °C for 4 days. After cooling, the dark yellow solution was concentrated *in vacuo* until a yellow precipitate formed. Further precipitation was allowed at −20 °C for 15 h. The precipitate was recovered by filtration and washed with cold methanol. After recrystallisation from hot methanol, **1b** was obtained as a yellow, crystalline solid. (0.690 g, 1.85 mmol, 81%); mp 212–214 °C; (Found: C, 74.0; H, 6.2; N, 11.3. $C_{23}H_{23}N_3O_2$ requires: C, 74.0; H, 6.2; N, 11.2%); ν_{max}/cm^{-1} (THF) 3314 (OH), 1635 (C=N), 1569, 1494; δ_H (400 MHz; acetone-d_6) 8.40 (2H, d, ^3J(HH) 8.0 Hz, *m*-*H*pyr), 7.99 (1H, t, ^3J(HH), *p*-*H*pyr), 7.98 (2H, s, aryl-O*H*), 6.78 (2H, m, *H*aryl), 6.72 (2H, m, *H*aryl), 6.57 (2H, d, ^3J(HH) 8.4 Hz, *H*aryl), 2.37 (6H, s, N=*C*Me), 2.08 (6H, s, aryl-*Me*); $\delta_{C\{H\}}$ (100 MHz; $CDCl_3$) 166.3 (N=*C*Me), 156.1 (4-*C*aryl), 154.1 (2,6-Cpyr), 142.4 (1-*C*aryl), 137.0 (4-*C*py), 129.2, 122.0, 119.4, 117.2, 113.0, 17.4 (aryl-*Me*), 15.6 (N=C*Me*); *m*/*z* (FAB) 374 (M$^+$ + H, 100), 358 (M$^+$ − Me, 16%).

Attachment of the wedges to the ligands

The various wedges were attached to the 2,6-bis-[1-(4-hydroxyphenylimino)ethyl]pyridines in essentially the same manner. The synthesis of a representative compound is given (for further details, see ESI†).

Synthesis of 2,6-bis-[1-(4-benzyloxyphenylimino)ethyl]pyridine, 2a

A mixture of **1a** (0.271 g, 0.784 mmol), benzyl bromide (0.72 g, 4.2 mmol), K_2CO_3 (0.325 g, 2.35 mmol), 18-crown-6 (40 mg, 0.15 mmol) and acetone (20 cm^3) was heated under reflux for 72 h. The volatiles were removed *in vacuo*, and the residue partitioned between dichloromethane and slightly alkaline water. The aqueous phase was extracted with dichloromethane (3 × 20 cm^3), and the combined organics were then washed with slightly alkaline water (3 × 20 cm^3) and slightly alkaline brine (1 × 20 cm^3). After drying over Na_2SO_4 and filtration, the volatiles were removed *in vacuo*, leaving a yellow, waxy solid. Recrystallisation from dichloromethane/methanol gave **2a** as a yellow, crystalline solid. (0.309 g, 0.588 mmol, 75%), mp 228–229 °C; (Found: C, 80.1; H, 5.9; N, 7.9. $C_{35}H_{31}N_3O_2$ requires C, 80.0; H, 5.9; N, 8.0%); ν_{max}/cm^{-1} (DCM) 1636 (C=N), 1604, 1569, 1502 (Ar), 1455, 1366, 1211 (Ar–O), 1167, 1121, 1024 (CH_2–O); δ_H (300 MHz; $CDCl_3$) 8.33 (2H, d, ^3J(HH) 8 Hz, *m*-*H*py), 7.84 (1H, t, ^3J(HH) 8 Hz, *p*-*H*py), 7.48–6.80 (18H, m, *H*aryl and *H*Ph), 5.09 (4H, s, OCH_2Ph), 2.44 (6H, s, N=C*Me*); $\delta_{C\{H\}}$ (75 MHz; $CDCl_3$) 167.3 (N=*C*Me), 155.9 (4-*C*aryl), 155.7 (2,6-*C*py), 144.9 (1-*C*aryl), 137.4, 136.7, 128.6, 127.9, 127.5, 122.2, 120.9, 115.6, 70.7 (O*C*H_2Ph), 16.1 (N=C*Me*); *m*/*z* (EI) 525 (M$^+$, 41), 434 (M$^+$ − bz, 100) 342 (M$^+$ − ArObz, 14%).

Synthesis of the iron complexes

The complexation of iron(II)chloride to the ligands (**7–12**) is performed in essentially the same way. The synthesis of a representative compound is given (For full details, see ESI†).

Synthesis of [2,6-bis-[1-(4-benzyloxyphenylimino)ethyl]-pyridine]iron dichloride, 7a

A mixture of **2a** (163 mg, 0.310 mmol) and $FeCl_2 \cdot 4H_2O$ (53 mg, 0.27 mmol) was stirred in THF (15 cm^3). A dark purple colour formed immediately. The mixture was stirred for 6 h, after which time diethyl ether (20 cm^3) was added, resulting in the precipitation of a dark purple solid. After centrifuging the mixture, the supernatant was removed, and the powder was washed with 40% THF in ether (5 × 15 cm^3) and ether (1 × 15 cm^3), centrifuging and removing the supernatant each time. After drying *in vacuo*, **7a** was obtained as a dark purple powder (154 mg, 0.236 mmol, 89%); mp >200 °C (dec); (Found: C, 63.5; H, 4.8; N, 6.2. $C_{35}H_{31}Cl_2N_3O_2Fe$ requires C, 64.4; H, 4.8; N, 6.4%); ν_{max}/cm^{-1} (DCM) 1582 (C=N), 1503 (Ph), 1465, 1454,

1379, 1238, 1171, 1110, 1014; *m/z* (FAB) 652 ($M^+ + H$, 3), 616 ($M^+ - Cl$, 29%).

Catalytic runs

A mixture of toluene (22.7 cm^3) and MAO (5.3 cm^3 of a 10% solution in toluene) was thermostatted at 30 °C. The vigorously stirred solution was saturated with ethene at 1 atm. A suspension of the catalyst precursor (20 μmol) in toluene (2.0 cm^3) was added *via* syringe. An immediate colour change occurred. The reaction was quenched after 60 min by adding 2-propanol (2 cm^3) followed by aq. HCl (0.1 M, 2 cm^3). Hexane (20 cm^3) and water (20 cm^3) were added and the organic phase was separated. The aqueous phase was extracted with hexane (2 × 20 cm^3) and the combined organic phases were washed with water (3 × 20 cm^3) and brine (3 × 20 cm^3), dried over $MgSO_4$ and filtered. The volatiles were evaporated *in vacuo* to leave the non-volatile oligomers.

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