

## Research paper

# Iron, cobalt and nickel complexes bearing hyperbranched iminopyridyl ligands: Synthesis, characterization and evaluation as ethylene oligomerization catalysts



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## ABSTRACT

A series of hyperbranched iminopyridyl ligands [ethylenediamine as terminal groups (L1), 1,4-butanediamine as terminal groups (L2), 1,6-hexamethylenediamine as terminal groups (L3)] were prepared. Ligands L1–L3 were reacted with  $MCl_2 \cdot nH_2O$  ( $M = Fe, Co, Ni$ ) to form three types of complexes (C1–C5). Both L1–L3 and C1–C5 were fully characterized by FT-IR,  $^1H$  NMR, UV and ESI-MS. The nickel complexes exhibited better catalytic properties than iron and cobalt complexes for ethylene oligomerization. On activation with methylaluminoxane (MAO), the nickel complex C1 exhibited moderate catalytic activities up to  $1.56 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$  for ethylene oligomerization and the oligomers showed Schulz-Flory distribution. However, on activation with  $EtAlCl_2$ , the nickel complex C1 exhibited higher catalytic activity up to  $8.94 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1}$  for ethylene oligomerization, but the products were mainly alkylated-toluenes. The influence of the solvent and reaction parameters such as reaction temperature, ethylene pressure and Al/Ni molar ratio on the catalytic behavior of the nickel complex C1 was also investigated. Moreover, in comparison with the catalytic activity and the distribution of oligomers obtained with related hyperbranched salicylaldimine nickel complex and other non-hyperbranched iminopyridyl nickel complexes, the catalytic activity and the content of low carbon number olefins ( $C_4$  and  $C_6$ ) obtained in this work possessed relatively higher.

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## 1. Introduction

For the past two decades, late transition metal catalysts have attracted much attention as ethylene oligomerization catalysts to synthesize the linear  $\alpha$ -olefins [1–5], which are important intermediates for a variety of products as detergents, polymers, lubricants, surfactants, etc, and notable achievements are reflected in a number of review articles [6–10]. In particular, recent examples of ethylene oligomerization, especially using iron, cobalt and nickel complexes are well known and sparked academics and industrialists for exploring the novel catalytic systems and improving industrial process to obtain the oligomers with desired carbon number. A large number of research effects have focused on the design and development of late transition metal catalysts with improved catalytic performance since the Higher Olefins Process (SHOP) nickel

based catalysts were discovered [11–15]. In general, it has proved possible to control the catalytic performance of late transition metal catalysts in ethylene oligomerization through modifying the catalyst structure, choice of co-catalyst or reaction conditions. In this design, catalyst structure has been shown to play a significant role in regulating both the ligand backbones and the active species. Iminopyridyl ligands are well known in the area of ethylene oligomerization, and the results of study have indicated that the iminopyridyl iron, cobalt and nickel catalysts exhibited excellent catalytic activity and products selectivity [16–18]. For example, Su et al. [19] reported a series of 2,6-bis(imino)pyridyl iron, cobalt and nickel complexes as ethylene oligomerization catalysts. The results showed that when activated with MAO, the cobalt and nickel complexes showed catalytic activities of  $3.98 \times 10^5 \text{ g (mol Co)}^{-1} \text{ h}^{-1}$  and  $5.13 \times 10^3 \text{ g (mol Ni)}^{-1} \text{ h}^{-1}$  for ethylene oligomerization, and the iron complex showed catalytic activity of  $1.25 \times 10^5 \text{ g (mol Fe)}^{-1} \text{ h}^{-1}$  for ethylene polymerization. Xie et al. [20] synthesized a series of asymmetric 2,6-bis

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(imino) pyridyl iron complexes with alkyl and halogen substituents. These iron complexes were highly active ( $1.84 \times 10^6$  g mol<sup>-1</sup> h<sup>-1</sup>) for ethylene oligomerization with high selectivity for linear  $\alpha$ -olefins (98.7%). In addition, The monometallic nickel complexes containing N,N'-iminopyridine chelating ligands with dendritic substituents were reported by Flores et al. [21]. The catalytic activity of ethylene oligomerization reached up to  $1.34 \times 10^4$  g mol<sup>-1</sup> h<sup>-1</sup> and the oligomers presented Schulz-Flory distribution.

Hyperbranched macromolecules are a relatively new class of molecules [22] which have gained significant attention from both academia and industry since Flory's seminal theoretical report in 1952. Because the hyperbranched macromolecules have similar properties with dendritic macromolecules, for example, their three-dimensional architecture, low polydispersity and high functionality, therefore the hyperbranched macromolecules have been utilized in application in various fields ranging from additives to coating and in more advanced technologies [23] such as sensors, high loading supports in combinatorial chemistry studies and homogeneous catalysts [24]. To exploit the catalytic properties of hyperbranched homogeneous late transition metal catalysts, our group has also developed some novel iron, cobalt and nickel complexes bearing the hyperbranched salicylaldimine ligands. These resultants iron, cobalt and nickel complexes precatalysts mostly exhibited moderate catalytic activities towards ethylene oligomerization and the products were mainly low carbon number olefins [25–29].

In order to further investigate the effect of the hyperbranched macromolecules fused to iminopyridyl on the catalytic properties of the complex, we designed and prepared a series of iron, cobalt and nickel complexes with hyperbranched iminopyridyl ligands and investigated their catalytic behavior towards ethylene oligomerization in detail.

## 2. Experimental section

### 2.1. Materials and general considerations

All synthetic manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Toluene, cyclohexane and methylcyclohexane were analytical grade and dried by refluxing over sodium/benzophenone and distilled under nitrogen prior to use. MAO (10 wt% in toluene) was purchased from Sigma-Aldrich. EtAlCl<sub>2</sub> (25 wt% in toluene), Et<sub>2</sub>AlCl (25 wt% in hexane) and 2-pyridinecarboxaldehyde were obtained from Aladdin and used as received. NiCl<sub>2</sub>·6H<sub>2</sub>O was purchased from Tianjin Jizhun chemical reagent co., Ltd. CoCl<sub>2</sub>·6H<sub>2</sub>O and FeCl<sub>2</sub>·4H<sub>2</sub>O were provided by Tianjin Damao Chemical Reagent Factory. Ethylenediamine, 1,4-butanediamine and 1,6-hexamethylenediamine were obtained from Tianjin Kermel Chemical Reagent co., Ltd. The above reagents were used without any further purification. 1.0 G hyperbranched macromolecules were synthesized according to the literature procedures [30] and the yields of them were above 80%.

Infrared spectra were recorded on a Bruker Vector 22 IR spectrophotometer with a KBr disc matrix. <sup>1</sup>H NMR spectra were recorded on a Bruker-400 MHz NMR. Chemical shifts were reported in  $\delta$  (ppm) and referenced to the appropriate peak in CDCl<sub>3</sub> used as NMR solvent. The UV–visible spectra were carried out on a UV-1700 ultraviolet–visible spectrophotometer by using methanol as a solvent. Electrospray ionization mass spectrometry (ESI-MS) data were collected on a microTOF-Q II mass spectrometer. Gas chromatography (GC) analyses of oligomers were conducted on a Fuli GC9720 equipped with a flame ionization detector (FID) and a 50 m (0.2 mm i.d., 0.5  $\mu$ m film thickness) HP-PONA column.

### 2.2. Synthesis of hyperbranched iminopyridyl ligands

#### 2.2.1. Synthesis of hyperbranched iminopyridyl ligand with ethylenediamine as terminal groups (L1)

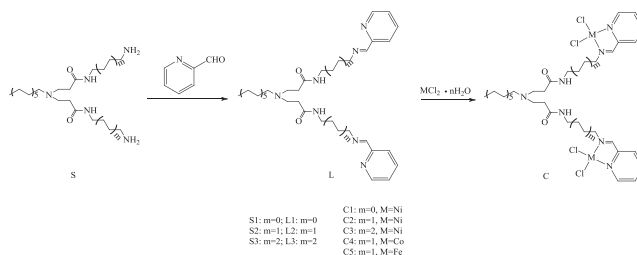
Methanol (25 mL) was added to the mixture of 1.0 G hyperbranched macromolecule S1 (2.06 g, 0.005 mol) and Na<sub>2</sub>SO<sub>4</sub> (2 g) under nitrogen atmosphere and the mixture was stirred for 15 min. 2-pyridinecarboxaldehyde (2.0 mL, 0.02 mol) was added drop-wise into the solution after the mixture was cooled to 0 °C. After 30 min of stirring, the reaction mixture was allowed to heat to 25 °C and stir for 24 h. The mixture was filtered to remove Na<sub>2</sub>SO<sub>4</sub> and the hyperbranched iminopyridyl ligand solution was obtained. The solvent was removed by vacuum distillation and a dark brown oil was obtained. Dichloromethane (30 mL) was added to the oil and the product was washed five times with distilled water. The dichloromethane layer was dried over sodium sulfate after which the latter was filtered off. The filtrate was evaporated to give a brown oil. Yield: 1.68 g (57%) (Scheme 1). IR (KBr, cm<sup>-1</sup>): 3413 (s), 3055 (w), 2926 (m), 1714 (s), 1650 (s), 1585 (m), 1211 (m), 767 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$ : 0.857 (CH<sub>3</sub>, alkyl), 1.227 (CH<sub>2</sub>, alkyl), 1.443 (CH<sub>2</sub>, alkyl), 1.577 (CH<sub>2</sub>, alkyl), 1.747 (CH<sub>2</sub>, alkyl), 2.355 (CH<sub>2</sub>C=O), 2.454 (CH<sub>2</sub>, *tert* amine), 2.772 (CH<sub>2</sub>, *tert* amine), 3.452 (CH<sub>2</sub>NH), 3.548 (HC=NCH<sub>2</sub>), 7.307 (NH), 7.580 (CH, pyridine), 7.782 (CH, pyridine), 7.986 (CH, pyridine), 8.550 (N=CH<sub>2</sub>), 8.798 (CH, pyridine).  $\lambda_{\max}$  (nm): 202, 252, 259, 265.

#### 2.2.2. Synthesis of hyperbranched iminopyridyl ligand with 1,4-butanediamine as terminal groups (L2)

Ligand L2 was prepared from 1.0 G hyperbranched macromolecule S2 (2.35 g, 0.005 mol) and 2-pyridinecarboxaldehyde (2.0 mL, 0.02 mol) following the procedure described for L1. A brown oil was obtained. Yield: 1.91 g (59%) (Scheme 1). IR (KBr, cm<sup>-1</sup>): 3410 (s), 3051 (w), 2927 (m), 1711(s), 1650 (s), 1585 (m), 1211 (m), 766 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$ : 0.852 (CH<sub>3</sub>, alkyl), 1.227 (CH<sub>2</sub>, alkyl), 1.433 (CH<sub>2</sub>, alkyl), 1.577 (CH<sub>2</sub>, alkyl), 1.748 (CH<sub>2</sub>, alkyl), 2.347 (CH<sub>2</sub>C=O), 2.449 (CH<sub>2</sub>, *tert* amine), 2.776 (CH<sub>2</sub>, *tert* amine), 3.400 (CH<sub>2</sub>NH), 3.511 (HC=NCH<sub>2</sub>), 7.297 (NH), 7.577 (CH, pyridine), 7.776 (CH, pyridine), 7.977 (CH, pyridine), 8.516 (N=CH<sub>2</sub>), 8.772 (CH, pyridine).  $\lambda_{\max}$  (nm): 204, 253, 259, 265.

#### 2.2.3. Synthesis of hyperbranched iminopyridyl ligand with 1,6-hexamethylenediamine as terminal groups (L3)

Ligand L3 was prepared from 1.0 G hyperbranched macromolecule S3 (2.63 g, 0.005 mol) and 2-pyridinecarboxaldehyde (2.0 mL, 0.02 mol) following the procedure described for L1. A brown oil was obtained. Yield: 1.90 g (54%) (Scheme 1). IR (KBr, cm<sup>-1</sup>): 3417 (s), 3060 (w), 2926 (m), 1712 (s), 1659 (s), 1587 (m), 1213 (m), 765 (m). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$ : 0.865 (CH<sub>3</sub>, alkyl), 1.230 (CH<sub>2</sub>, alkyl), 1.433 (CH<sub>2</sub>, alkyl), 1.580 (CH<sub>2</sub>, alkyl), 1.741 (CH<sub>2</sub>, alkyl), 2.343 (CH<sub>2</sub>C=O), 2.448 (CH<sub>2</sub>, *tert* amine), 2.764 (CH<sub>2</sub>, *tert* amine), 3.422 (CH<sub>2</sub>NH), 3.517 (HC=NCH<sub>2</sub>), 7.300



Scheme 1. Synthetic routes of the hyperbranched iminopyridyl metal complexes.

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