

Synthesis, characterization, and ethylene polymerization behaviors of late-transition metal complexes coordinated with chlorinated bis(arylimino)pyridine ligand



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ABSTRACT

A series of late-transition metal complexes supported with chlorinated bis(arylimino)pyridine ligands [2,6-(ArN=CCl)₂C₅H₃N]MtCl₂ (Ar = 2,4,6-Me₃C₆H₂, Mt = Fe (**1a**), Co (**2a**), Ni (**3a**); Ar = 2,6-ⁱPr₂C₆H₃, Mt = Fe (**1b**), Co (**2b**); Ar = 2,6-Et₂C₆H₃, Mt = Co (**1c**), Ni (**3c**); Ar = 2,6-Me₂C₆H₃, Mt = Fe (**1d**), Co (**2d**); Ar = 4-Cl-2,6-Me₂C₆H₂, Mt = Fe (**1e**), Co (**2e**); Ar = 4-Br-2,6-Me₂C₆H₂, Mt = Fe (**1f**), Co (**2f**)) were synthesized. At the presence of methylaluminoxane (MAO), Fe(II)- and Co(II)- based complexes were highly active towards ethylene polymerization, affording polymers with bimodal and unimodal molar mass distributions, respectively, while the Ni(II)-based complexes gave no polymer products. Moreover, the obtained polyethylenes were predominately saturated and vinyl-terminated for Fe(II)- and Co(II)-based complexes, respectively. Changing the ligand environment, polymerization parameters also posed a great influence on the catalytic activities and the properties of the resulting polymers.

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1. Introduction

The molecular parameters of polymeric materials including molecular weight, molecular weight distribution, and chain structure play a crucial role in determining their physical and chemical properties. Polyethylenes (PEs) possessing well-controlled molecular weight distribution are of particular interest. PEs with bimodal molecular weight distribution display good processing behaviors and excellent mechanical properties due to the coexistence of low and high molecular weight moieties. Many methodologies have been developed to prepare bimodal PEs, but the key point still relies on the revolutionary development of novel catalytic systems [1,2].

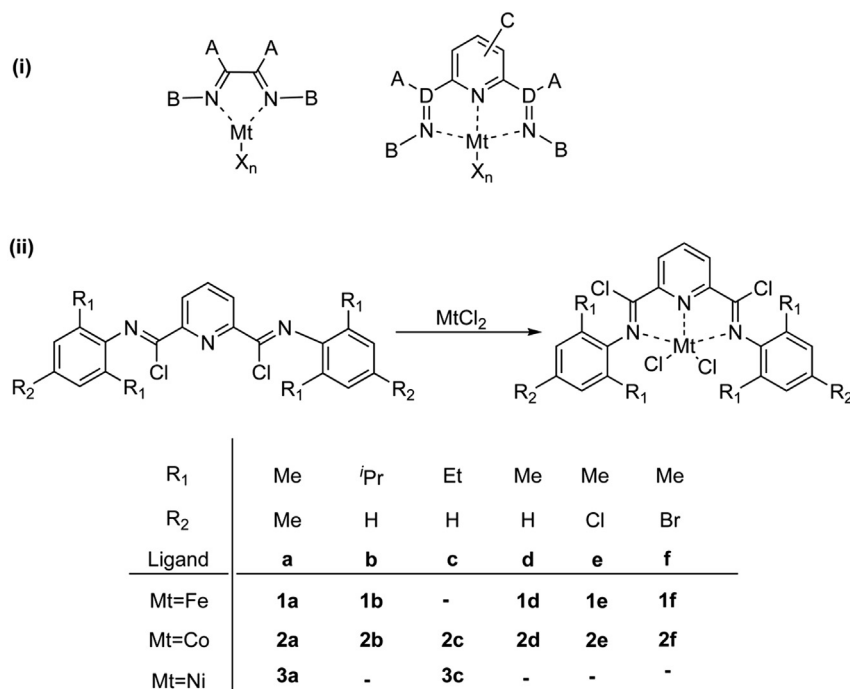
Colossal acceleration has been made in tapping new catalysts for ethylene polymerization during the past few decades. One of the most noticeable advances is the advent of catalysts bearing imine-based ligands including bulky neutral α -diimine and bis(arylimino)

pyridine (Scheme 1(i)) [3–6]. Since these catalysts afford polyethylenes with novel polymer architectures, e.g., highly branched chain structure and bimodal molecular weight distribution, extensive researches have been focused on these two systems. The easy-varied framework of such type ligands has attracted considerable research interests, which allows synthesis of numerous complexes bearing distinct skeleton structures. A myriad of modifications either on position “A” [7–9](α -diimine), “B” [10–13](both two), “C” [14–16](both two), or “D” [17](bis(arylimino)pyridine) have been studied (shown in Scheme 1(i)). From the general structures of α -diimine and bis(arylimino)pyridine, an open-and-shut conclusion is made that the electronic effect of substituents on the position “A”, “B”, and “D” directly influence the coordinating ability of nitrogen atom, so to influence the electronic characteristic of the metal centre, which in turn affect the catalytic behaviors of the active species. Position “B”, “C” and “D” had been studied previously, in contrast, for bis(arylimino)pyridine catalysts, relatively fewer reports were related to position “A”. In our previous study, chlorine atom was introduced to position “A” and a series of bis-(N-arylimino)pyridine cobalt(II) complexes were prepared [18]. In this study, Fe(II), Co(II), and Ni(II) complexes

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Scheme 1. (i): General structures of α -diimine and bis(arylimino)pyridine; (ii): Synthetic procedures of Fe(II), Co(II), and Ni(II) complexes.

supported by bis(*N*-arylcaboximidoylchloride)pyridine ligands were synthesized, and their catalytic behaviors in ethylene polymerization was investigated. Within expectation, these complexes behaved much differently in ethylene polymerization and strictly depended on nature of the central metal, yielding polyethylenes with distinct molecular weight and molecular weight distribution, the variation of polymerization conditions on ethylene polymerization behavior and the resulting polymers were examined and discussed as well.

2. Results and discussion

2.1. Synthesis and characterization of ligands and complexes

Bis(arylcaboximidoylchloride)pyridine ligands (**a–f**) bearing different substituents were synthesized according to previous reports [18]. The Co(II), Fe(II), and Ni(II) complexes were prepared by stoichiometric reactions of FeCl₂, CoCl₂, and NiCl₂ with the corresponding ligands in tetrahydrofuran (Scheme 1(ii)). All the ligands and complexes were fully characterized by NMR, FT-IR spectra and elemental analysis. In the FT-IR spectra, C=N stretching frequencies of the complexes shift to lower values (1613–1627 cm⁻¹) comparing with the corresponding ligands (1655–1661 cm⁻¹). Ligand **e** and complexes **2f** and **3a** were further characterized by single crystal X-ray diffraction analysis, the molecular structures were shown in Figs. 1–4 and the crystallographic data together with the collection and refinement parameters are summarized in Tables S1 and S2 (in supporting information).

The solid structure of the ligand **e** had a similar structure as previous report [19], which has a (*E,E*) conformation with typical imino C=N double bond character, 1.255(3) Å and 1.251(3) Å. The two phenyl rings are approximately orthogonal to the pyridinyl plane (81.15° and 77.29°).

The structures of **2f** and **3a** (Figs. 2 and 3) are isomorphous, and they perform approximate C_s symmetry about a plane containing

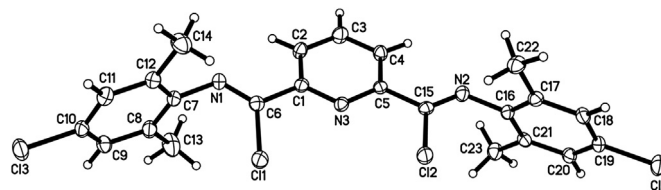


Fig. 1. Molecular structure of **e**, drawn at 35% of probability.

the metal centre, the two chlorine atoms, and the pyridyl nitrogen atom. The deviations of the metal ion from the N₃ plane are 0.213 and 0.159 Å, respectively. The geometries around the cobalt(II) and nickel(II) centers are *penta*-coordinated and can be best described as distorted trigonal bipyramidal with the equatorial plane formed

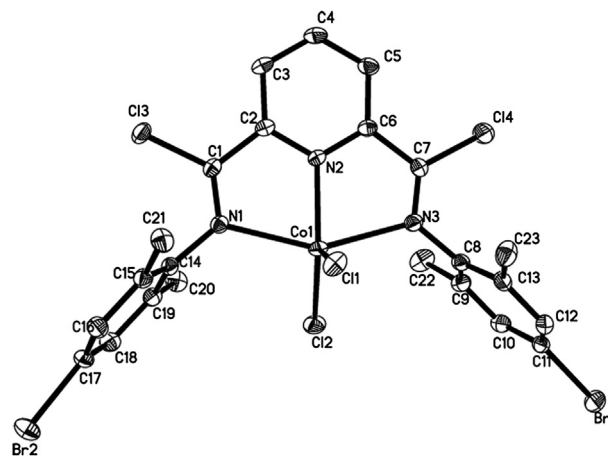


Fig. 2. Molecular structure of **2f**, drawn at 35% of probability. Hydrogen atoms and CH₂Cl₂ molecule were omitted for clarity.

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