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Review

Carbocyclic-fused *N*,*N*,*N*-pincer ligands as ring-strain adjustable supports for iron and cobalt catalysts in ethylene oligo-/polymerization

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ABSTRACT

Recent progress in the application of homogeneous iron and cobalt catalysts in ethylene oligo-/polymerization is reviewed with particular emphasis placed on the tuning of catalyst performance through the introduction of controlled amounts of ring strain to the ligand frame. While new examples of catalysts bearing the prototypical bis(arylimino)pyridine continue to emerge in the literature, the last decade has witnessed a number of key advances concerned with the fusion of carbocyclic units to the *N*,*N*,*N*-pincer manifold with a view to enhancing both the catalytic activities and thermal stablility of their resultant catalysts. Some notable examples include iron complexes containing aryl-fused imino-phenanthroline ligands, which have proved highly active catalysts for ethylene oligomerization and indeed have shown considerable industrial promise on the pilot plant scale. Elsewhere, bis(arylimino)pyridines incorporating singly or doubly fused cycloalkyl units with the ring sizes anywhere between five- and eight-membered have been systematically developed and have proved versatile supports for both metal centers. More significantly, clear correlations between structure and activity as well as oligo-/polymer properties are a feature of these strain-adjustable catalysts. In many cases, linear vinyl-polyethylenes are accessible which are in demand for the production of long-chain branched copolymers, functional polymers as well as coating materials.

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1. Introduction

Over recent years there have been some notable advances in the development of well-defined homogeneous catalysts based on earth-abundant base metals [1–12]. In particular, iron and cobalt complexes supported by pincer ligands have been shown to promote a wide variety of important transformations including, (i) the hydrogenation of olefins, carbonyl compounds, carboxylic acid derivatives and CO_2 [10,13–28], (ii) the dehydrogenation of alcohols, amines and alkanes [29–34], (iii) transfer hydrogenation reactions [35] and (iv) dehydrogenative cross-coupling [36–38]. Perhaps more significantly, iron and cobalt complexes have proved potent catalysts for not only olefin polymerization [39–50] but also for shorter chain oligomerization reactions [42,45,50]. Indeed, the recent integration of iron catalyst technology into a five-hundred ton process for making α-olefins in China highlights the vast industrial significance of such catalysts [45].

In order to explore the full scope and versatility of these industrially promising polymerization catalysts we have, over the last decade or so, been concerned with a systematic exploration of the structural features of the pre-catalyst and in particular the auxiliary ligand that dictates catalyst performance. The first examples of iron and cobalt catalysts displaying high activity were first disclosed some twenty years ago [51–55]. Indeed, these first generation systems based on bis(arylimino)pyridine pincer ligands (**A**, Fig. 1) were capable of generating either oligomers (mainly α-olefins) or highly linear polyethylene depending on the steric properties of the N-aryl groups. Subsequently, a second generation of catalysts incorporating both subtle and more dramatic changes to the parent *N,N,N*-bis(arylimino)pyridine framework have emerged that not only allow exceptional performance and high thermal stabilities but are also capable of promoting a broad range of oligomer and polymer properties [42,45,50]. While catalysts bearing the prototypical **A** (Fig. 1) continue to see some important developments as symmetrical and unsymmetrical derivatives [42–50], the disclosure of carbocyclic-fused *N,N,N*-pincer ligands (**B** and **C**, Fig. 1) represents a notable recent advance in the field [42,45,50]. In particular, the central pyridine donor of an *N,N,N* ligand can be fused by either aryl or saturated cycloalkyl rings, the latter being amenable to their introduction as singly (**B**, Fig. 1) or doubly (**C**, Fig. 1) fused units with the alkyl ring sizes anywhere from five- to eight-membered [42,45,50]. The net effect of these ring variations is to influence the strain and chelation properties of the tridentate ligand which in-turn affects the catalytic performance, thermal robustness, polymer properties and oligomeric distributions.

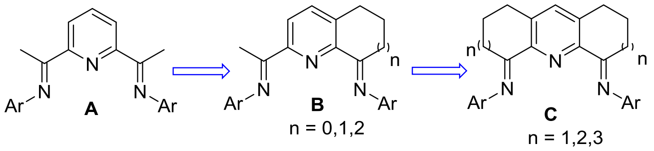


Fig. 1. Evolution of the bis(arylimino)pyridine ligand frame (**A**) through incorporation of carbocyclic-fused units to give **B** and **C** [42,45,50–53].

In this review it is the objective to cover key developments in iron and cobalt catalyst technology that have occurred in the last decade with a focus on making correlations between pre-catalyst/ligand, co-catalyst, thermal stability and the microstructure of the resulting polymers and oligomers. For reviews and book chapters covering the first decade since the initial discovery of such catalysts, the reader is directed towards a number of leading references [43,44,46–49].

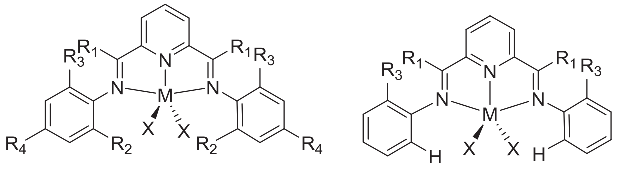
2. Fe/Co pre-catalysts bearing bis(arylimino)pyridines

In 1998, the Brookhart [51] and Gibson [52,53] groups independently disclosed bis(arylimino)pyridine–iron and –cobalt pincer complexes as catalysts for ethylene oligo-/polymerization. These initial studies found that activation of **1** (M = Fe, Co; X = Cl, Br) (Fig. 2), incorporating alkyl groups at the *ortho*- and *para*-positions of the N-aryl groups, with methylalumoxane (MAO) [52,53] or modified methylaluminoxane (MMAO) [51] resulted in high activity in ethylene polymerization (up to 206.0×10^6 g PE mol^{-1}(Fe) h^{-1} and 17.0×10^6 g PE mol^{-1}(Co) h^{-1} for Ar = 2,4,6-tri methylphenyl; reaction conditions: isobutane as solvent, 10 bar of ethylene, reaction time 1 h, 50 °C). More importantly, these catalysts promoted the formation of high density/highly linear polyethylene with high molecular weight ($M_w \sim 10^5$ g mol^{-1}) [53]. By contrast, catalysts containing N-aryl groups substituted by less bulky substituents at the *ortho*-positions (**2**, Fig. 2) generated oligomers displaying Schulz-Flory distributions (with activities up to 10^6 g (oligomer) $mmol^{-1}$ (Fe) h^{-1}at 90 °C) [54,55].

In subsequent years considerable efforts have been devoted to modifying the bis(arylimino)pyridine pincer framework with the purpose of enhancing the catalytic activities and thermal stability of their complexes. These efforts have mainly concentrated on varying the substituents on the N-aryl group with the aim to affect the steric hindrance and electronic properties of the complexes and in-turn the polymerization activities and polymer microstructure [42–50]. In addition, studies directed to modifying the imine-N and imine-C substituents as well as the central pyridine unit have seen some developments.

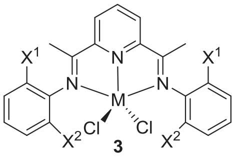
The Qian group in 2002 investigated the use of bis(arylimino) pyridine–iron and cobalt complexes **3** bearing 2,6-dihalide substituted N-aryl groups (Fig. 3) [56,57]. Examples bearing fluoride substituents exhibited by far the highest activity amongst this series while the fluoride-substituted iron complexes exhibited high selectivity (>93%) for linear α-olefins [56,57]. On the other hand, derivatives bearing chloride or bromide substituents at both *ortho*-positions afforded relatively lower activities but produced highly linear polyethylene with high molecular weight (≈10^6 g mol^{-1}). Moreover, the introduction of iodide substituents led to increased activity [57].

The influence of the *para*-substituent on the N-aryl rings in bis (arylimino)pyridine–iron complexes **4** (Fig. 4) has been studied by



1 M = Fe, Co; X = Cl, Br 2

Fig. 2. First generation bis(arylimino)pyridine–iron(II) and –cobalt(II) pre-catalysts **1** and **2** [51–55].



3

X^1, X^2 = F, Cl, Br, I
M = Fe, Co

Fig. 3. Halide-substituted bis(arylimino)pyridine–iron and –cobalt complexes **3** [56,57].