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**Alternatives to  
Pyridinediimine  
Ligands: Syntheses  
and Structures of  
Metal Complexes  
Supported by  
Donor-Modified  
 $\alpha$ -Diimine Ligands**

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Polyethylene is a long, chain-like compound formed by linking thousands of ethylene molecules. The linking process (polymerization) is often orchestrated by a metal center that facilitates the repeated addition of ethylene to the growing polymer chain. This paper describes the preparation and characterization of a family of iron-containing compounds that serve as effective catalysts for the polymerization of ethylene. The iron center is coordinated to an organic compound (ligand) containing nitrogen, phosphorus and sulfur atoms. The structure adopted by the iron-ligand complex is suitable for the rapid and efficient polymerization of ethylene.

PAPER

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**Alternatives to pyridinediimine ligands: syntheses and structures of metal complexes supported by donor-modified  $\alpha$ -diimine ligands**

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This report describes the synthesis and characterization of metal halide complexes ( $M = Mn, Fe, Co$ ) supported by a new family of pendant donor-modified  $\alpha$ -diimine ligands. The donor (N, O, P, S) substituent is linked to the  $\alpha$ -diimine by a short hydrocarbon spacer forming a tridentate, *mer*-coordinating ligand structure. The tridentate ligands are assembled from monoimine precursors, the latter being synthesized by selective reaction with one carbonyl group of the  $\alpha$ -dione. While attempts to separately isolate tridentate ligands in pure form were unsuccessful, metal complexes supported by the tridentate ligand are readily synthesized *in-situ*, by forming the ligand in the presence of the metal halide, resulting in a metal complex which subsequently crystallizes out of the reaction mixture. Metal complexes with NNN, NNO, NNP and NNS donor sets have been prepared and examples supported by NNN, NNP and NNS ligands have been structurally characterized. In the solid state, NNN and NNP ligands coordinate in a *mer* fashion and the metal complexes possess distorted square pyramidal structures and high spin ( $S = 2$ ) electronic configurations. Compounds with NNS coordination environments display a variety of solid state structures, ranging from those with unbound sulfur atoms, including chloride bridged and solvent ligated species, to those with sulfur weakly bound to the metal center. The extent of sulfur ligation depends on the donor ability of the crystallization solvent and the substitution pattern of the arylthioether substituent.

**Introduction**

Over the past decade, ligands with imine functional groups have found wide use in olefin polymerization catalysis. For example, Brookhart demonstrated that nickel(II) and palladium(II) complexes supported by  $\alpha$ -diimine ligands are effective  $\alpha$ -olefin polymerization catalysts in the presence of methylalumoxane (MAO). Of particular note, nickel and palladium diimine catalysts polymerize ethylene to an unusual highly branched polyethylene (*via* a chain walking mechanism)<sup>1</sup> and palladium diimine catalysts are able to copolymerize  $\alpha$ -olefins and functionalized vinyl monomers.<sup>2</sup> More recently, Gibson<sup>3</sup> and Brookhart<sup>4</sup> separately showed that iron(II) halides supported by pyridinebisimine (PBI) ligands display exceptional reactivity towards ethylene, producing  $\alpha$ -olefin oligomers or high density polyethylene depending on the size and location of substituents on the imino-aryl rings. Since the initial reports by Gibson and Brookhart, which detailed the impact that imino-aryl substituents have on catalyst activity and product properties, more recent studies have examined the effect of heteroatom (*e.g.* Cl, Br, I, F, OMe, CF<sub>3</sub>) substituted imino-aryl groups on iron(II)-PBI catalyst activity and oligomer properties. Of particular relevance was the ability to alter the product distribution from high molar mass polymers to low molar mass oligomers by varying the substitution pattern of the aryl ring.

In addition, iron(II) complexes supported by asymmetric versions of PBI ligands have also been studied. These asymmetric

ligands are formed *via* sequential and selective reaction of bulky anilines with the  $\alpha$ -dione carbonyl groups; examples of such ligands are shown as **A–C**<sup>5–10</sup> in Scheme 1. Here the ability to modify the oligomer product distribution, as measured by the Schulz–Flory constant,  $K$ , has been well documented. In a rather dramatic case, the iron(II) catalyst with ligand **B** switches from producing oligomers to polyethylene by replacing the hydrogen 2,6-aryl substituents on one ring with methyl groups. Finally, PBI-related ligands, formed by placing heteroatoms in the ligand backbone, have also been explored. Selected examples are shown as ligands **D–G** in Scheme 1.<sup>11–13</sup> Such ligand modifications often have a large impact on subsequent catalyst activity and oligomer properties, particularly on the Schulz–Flory constant. The ability to vary  $K$  over a fairly wide range, with, in most cases, relatively small changes in ligand structure, has fueled our interest in this area. Control over  $K$  is particularly important in an industrial setting where the ability to modify the product distribution *via* catalyst modification can provide  $\alpha$ -olefin producers with another handle to optimize the value of the oligomeric product exiting the reactor.

We are especially interested in the use of alternative tridentate ligands that resemble the overall coordination geometry of PBI systems, but which allow for more substantial ligand (electronic and steric) variation. In particular, we wished to introduce alternative donors (O, P, S) into a tridentate ligand environment and we targeted strategies that allowed us to separately modify the donor heteroatom and its substituents. Moreover, since most PBI and  $\alpha$ -diimine ligands reported to date are comprised of arylimine functional groups, we also sought routes to more electronically diverse *alkyl*-substituted imines. This report outlines the syntheses and structures of divalent metal complexes supported by *mer*-ligating acenaphthene-diimine ligands, which have been modified

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