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Communication

Dramatic Effect of Heteroatom Backbone Substituents on the Ethylene Polymerization Behavior of Bis(imino)pyridine Iron Catalysts

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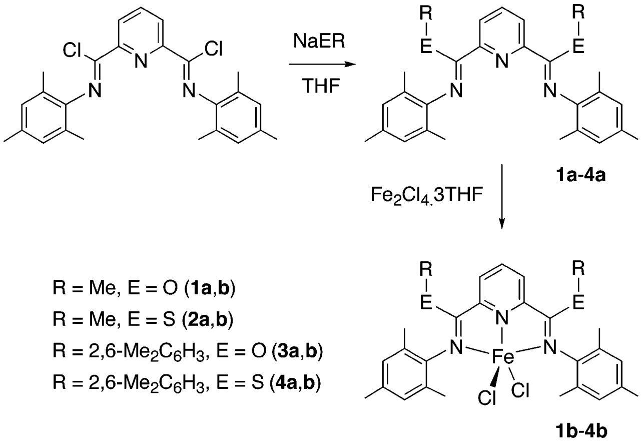
Bis(imino)pyridine iron complexes bearing ether and thioether backbone substituents have been synthesized and evaluated for the polymerization of ethylene. The methoxy derivative is inactive whereas bulky phenoxides or thioether derivatives afford activities as high as the most active systems reported to date.

The discovery of highly active olefin polymerization catalyts based on bis(imino)pyridine complexes of iron and cobalt[1] provided a significant impetus to the search for polymerization systems based on the late transition metals.[2] While many modifications to the ligand aryl substituents and central donor moiety have been described,[3] relatively little attention has been given to the effect of changes to the substituents at the imine carbon atoms. Here, we describe iron catalysts that incorporate ether and thioether groups and the surprising finding that small ether units afford catalytically inactive systems whereas large ether and thioether substituents give catalysts with very high productivities.

Scheme 1



R = Me, E = O (**1a**,**b**)
R = Me, E = S (**2a**,**b**)
R = 2,6-Me$_2$C$_6$H$_3$, E = O (**3a**,**b**)
R = 2,6-Me$_2$C$_6$H$_3$, E = S (**4a**,**b**)

The ether and thioether derivatized proligands **1a**−**4a** were prepared by treatment of pyridine-2,6-dicarboxyimidoyl dichloride with NaER according to Scheme 1. Their subsequent treatment with anhydrous iron(II)chloride afforded the heteroatom-derivatized precatalysts **1b**−**4b**.

The starting point for our catalytic studies was the methoxy derivative **1b** whose molecular structure was found to be closely related to its ketimine relative, **5b** (ER = Me),[1c] with a distorted trigonal bipyramidal geometry at the iron center (Figure 1).

Contrastingly, though, **1b** was found to be inactive for ethylene polymerization under a variety of conditions of temperature, pressure, and activator. A possible explanation for this is attack on the ligand backbone by the Lewis acid activator of a type seen in vanadium catalyst systems.[4] However, this seems to be ruled out by the finding that free ligand **1a** is recovered quantitatively after treatment of **1b** with MAO. An alternative explanation is reversible binding of the activator at the heteroatom leading to destabilization of the catalyst, possibly via ligand dissociation, or decomposition of the active iron−alkyl propagating species. In order to probe the possibility of the activator binding to the heteroatom, we targeted the 2,6-dimethylphenyl ether derivative **3b** where it was envisaged that the increased steric

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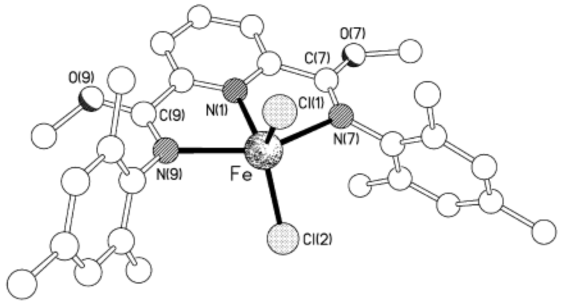

Figure 1. Molecular structure of **1b**. Selected bond lengths (Å): Fe−Cl(1) 2.301(2), Fe−Cl(2) 2.245(2), Fe−N(1) 2.096(6), Fe−N(7) 2.373(6), Fe−N(9) 2.297(6), C(7)−N(7) 1.275(9), C(9)−N(9) 1.264(9).

Table 1. Ethylene Polymerizations Using **1b**−**5b**[a]

run	precat (μmol)	polymer yield (g)	activity g/(mmol h bar)	M_n[b]	M_w[b]	M_w/M_n
	1b (10.0)	0	0			
2	**2b** (1.0)	11.0	2750	6300	79 000	12.5
3	**3b** (1.0)	14.0	3500	50 8000	432 000	8.5
4	**4b** (0.5)	70.0	35 000	24 000	398 000	16.6
5	**5b** (0.5)	60.0	30 000	34 400	212 000	6.2

[a] General conditions: 1-L stainless steel autoclave; precatalysts activated with 100 equiv MAO prior to injection; 2 mmol MAO used as scavenger; isobutane solvent; 1 h run; 4 bar of ethylene; 40 °C. [b] Determined by GPC.

demands of the aryl ether moiety would disfavor activator binding at the ether oxygen atom. An ethylene polymerization test in a 1-L stainless steel autoclave at 4 bar ethylene pressure revealed an activity of 3500 g mmol^{-1} h^{-1} bar^{-1} (Table 1), affording linear polyethylene (by NMR) with a M_w of 432,000 Da and a relatively broad molecular weight distribution, typical of iron-based catalysts.

An alternative approach to disfavoring binding at the heteroatom backbone substituent is to use a soft atom such as sulfur which would be expected to bind much less strongly to the hard aluminum activator centers. The methylthioether derivative **2b** was synthesized and found, unlike its ether relative **1b**, to be active for ethylene polymerization, giving an activity of 2750 g mmol^{-1} h^{-1} bar^{-1}, and with a substantially lower molecular weight than for **3b**.

In order to combine the electronic effect of a soft donor atom with steric protection of the heteroatom, the 2,6-dimethylphenyl thioether complex **4b** was then targeted. Its molecular structure, which has approximate C_s symmetry, is substantially different to that of **1b**, having a distorted square pyramidal geometry at iron (Figure 2). The metal lies 0.41 Å out of the N_3 plane and 0.47 Å out of the basal plane (the atoms of which are coplanar to within 0.04 Å). A particularly unusual feature of the structure is the substantial inclination of ca. 22° of the pyridine ring to the basal coordination plane. This out of plane tilt is accompanied by a pyramidalization of the N(1) center, the nitrogen atom lying 0.29 Å out of the plane of its substituents, and there is a significant lengthening of the Fe−N(1) bond [2.165(4) Å], cf. those in **1b** [2.096(6) Å] and the ketimine analogue **5b** [2.110(6) Å]. These distortions are attributed to the effect of accommodating the sterically demanding thioether groups.

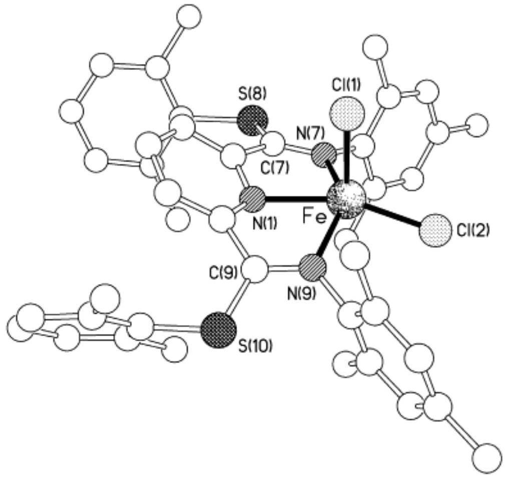

Figure 2. Molecular structure of **4b**. Selected bond lengths (Å): Fe−Cl(1) 2.3300(14), Fe−Cl(2) 2.2490(14), Fe−N(1) 2.165(4), Fe−N(7) 2.216(4), Fe−N(9) 2.191(3), C(7)−N(7) 1.282(6), C(9)−N(9) 1.287(6).

In an ethylene polymerization test under similar conditions, **4b** gave an activity of 35 000 g mmol^{-1} h^{-1} bar^{-1}, a value that compares favorably with the ketimine standard **5b** (run 5, Table 1). Examination of plots of ethylene uptake versus time over 60 min runs (see Supporting Information) reveals the contrasting behavior of the aryl ether and methylthioether derivatives **3b** and **2b**, which possess very short catalyst lifetimes, to the relatively long-lived nature of the bulky arylthioether catalyst **4b**. These results suggest that catalyst deactivation is most probably enhanced by binding of activator at the heteroatom within the ligand backbone. Interestingly, **4b** is found to have a longer catalyst lifetime than the ketimine standard **5b** and augurs well for the use of the bulky thioether ligands to improve the performance of iron-based polymerization catalysts.

The effect of these heteroatom containing ligand systems on the performance of catalysts based on other transition metals will be reported in due course.

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Supporting Information Available: Crystallographic information (in CIF format) and synthetic procedures and characterization data for the ligands and complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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