

## 2-Benzoxazolyl-6-[1-(arylimino)ethyl]pyridyliron(II) Chlorides as Ethylene Oligomerization Catalysts

Rong Gao,<sup>[a]</sup> Yan Li,<sup>[a]</sup> Fosong Wang,<sup>\*[a]</sup> Wen-Hua Sun,<sup>\*[a]</sup> and Manfred Bochmann<sup>[b]</sup>

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A series of iron(II) dichloride complexes (Fe1–Fe7) ligated by 2-(2-benzoxazolyl)-6-[1-(arylimino)ethyl]pyridines was synthesized and characterized [aryl = 2,6-R<sup>1</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>; R<sup>1</sup> = Me (**1**), Et (**2**), *i*Pr (**3**), Cl (**4**), Br (**5**); 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>2</sub>-4-R<sup>2</sup>, R<sup>2</sup> = Me (**6**), Br (**7**)]. The molecular structures of Fe1, Fe3, and Fe5 were determined by the single-crystal X-ray diffraction. Complexes Fe1 and Fe3 both display distorted trigonal-bipyramidal geometries, whereas complex Fe5 is a distorted square

pyramid. Upon activation with modified methylaluminoxane, all iron complexes showed moderate to good activities [up to ca. 10<sup>6</sup> g(product) × (mol Fe)<sup>−1</sup> h<sup>−1</sup> bar<sup>−1</sup>] for the oligomerization and polymerization of ethylene, with high selectivity for vinyl-terminated oligomers or polyethylene waxes.

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### Introduction

The discovery of 2,6-diiminopyridyliron(II) complexes as highly active catalysts by the groups of Bennett,<sup>[1a]</sup> Brookhart,<sup>[1b]</sup> and Gibson<sup>[2]</sup> was a milestone in the development of ethylene polymerization and oligomerization catalysts. Most research has involved modifications in the substituent pattern of the 2,6-diiminopyridine skeleton or variation of the reaction conditions.<sup>[3–9]</sup> Bianchini et al.<sup>[10]</sup> described complexes with unsymmetrical ligands in which one of the arylimino groups was replaced by an alkyl or aryl substituent. Several modified Fe<sup>II</sup> complexes are very active and present high activity in ethylene polymerization as well as oligomerization, although in most cases ligand modification did not lead to competitive catalytic activities.<sup>[11]</sup> These results have been summarized in review articles.<sup>[12]</sup>

We recently reported several alternative iron complexes as catalysts for ethylene oligomerization and polymerization.<sup>[13]</sup> Iron complexes bearing 2-ester-6-iminopyridines showed moderate activities,<sup>[14]</sup> whereas complexes ligated by 2-imino-1,10-phenanthrolines (Figure 1, **A**),<sup>[15]</sup> 2-benzimidazolyl-6-iminopyridines (**B**),<sup>[16]</sup> 2-benzimidazolyl-1,10-phenanthroline (**C**),<sup>[17]</sup> 2-quinoxaliny-6-iminopyridines (**D**),<sup>[18]</sup> *N*-[(pyridin-2-yl)methylene]quinolin-8-amines (**E**),<sup>[19]</sup> and 2-oxazoline/benzoxazole-1,10-phenanthrolines<sup>[20]</sup> (**F**) as

well as bimetallic complexes<sup>[21]</sup> were found to have good to high activities towards ethylene oligomerization and polymerization. However, N,N,N-tridentate ligands for iron complexes do not necessarily lead to good activities; for example, bis(imino)bipyridine<sup>[22]</sup> (Figure 1, complex **G**) or bis(imino)phenanthroline complexes<sup>[23]</sup> (complex **H**) showed only low to moderate activity for ethylene polymerization. Part of the reason for this is thought to be the free imino group, which is likely to compete with ethylene for a coordination site in the active species.

For practical applications, iron catalyst show two advantageous features: high selectivity in forming vinyl-terminated products and good activity for linear  $\alpha$ -olefins from C<sub>4</sub> to C<sub>28</sub>. Highly active catalytic systems are of great interest for the preparation of  $\alpha$ -olefins,<sup>[24]</sup> and this is the basis of a joint venture between PetroChina and DuPont in the iron-catalyzed oligomerization of ethylene.<sup>[25]</sup> Finding oligomerization catalysts with improved efficiency continues therefore to be of great importance.

One approach to ligand design has been to replace the imino groups by heterocycles. For example, Nomura made complexes of 2,6-bis(2-oxazoliny)pyridines that showed moderate polymerization activity.<sup>[26]</sup> Iron complexes of 2,6-bis(2-benzimidazolyl)pyridines gave no improvement; however, their chromium(III) analogues showed good activity towards ethylene oligomerization and polymerization.<sup>[27]</sup> Replacing one of the imino groups in 2,6-diiminopyridine<sup>[1,2]</sup> resulted in 2-(benzimidazolyl)-6-iminopyridines **B**, which formed iron(II) complexes with high ethylene oligomerization activities.<sup>[16]</sup> 2-(2-Benzoxazolyl)-6-[1-(arylimino)ethyl]pyridines, which have previously been shown to give nickel complexes with high ethylene oligomerization activities,<sup>[28]</sup> could also be of interest in iron catalysts. We describe here the synthesis and characterization of new

[a] Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China  
Fax: +86-10-62618239  
E-mail: whsun@iccas.ac.cn

[b] School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich, NR4 7TJ, United Kingdom

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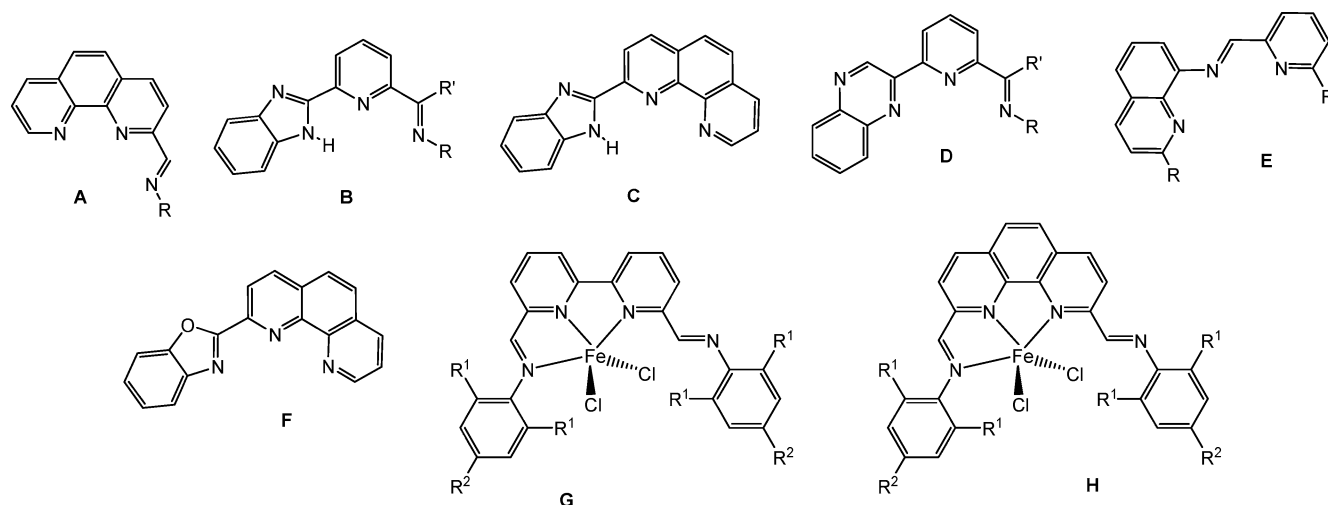


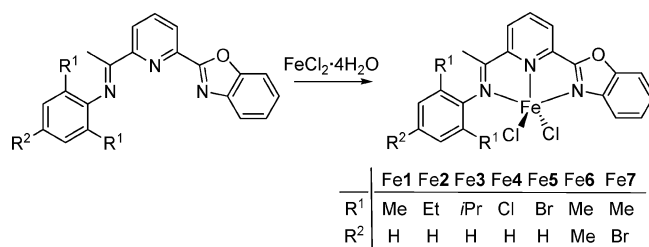
Figure 1. Ligands and complexes as models for iron catalysts.

iron(II) complexes with ligands bearing one heterocyclic substituent, as well as their behavior in ethylene oligomerization and polymerization.

## Results and Discussion

### Syntheses and Characterization of the Iron Complexes

The 2-(2-benzoxazolyl)-6-[1-(arylimino)ethyl]pyridines used as ligands were prepared according to our reported procedure.<sup>[28]</sup> On treating these ligands with ferrous dichloride in ethanol at room temperature for 10 h the product complexes precipitated as blue powders in high yield (Scheme 1). The complexes are air stable in the solid state. The FTIR spectra show C=N stretching vibrations in the range of 1613–1618 cm<sup>-1</sup> compared to 1644–1651 cm<sup>-1</sup> for the free ligands. The reduced intensity of this band compared to the free ligand is indicative of a coordinated C=N group. This was confirmed by the molecular structures of complexes Fe1, Fe3, and Fe5.



Scheme 1. Synthesis of ferrous complexes.

Single crystals of complexes Fe1, Fe3, and Fe5 suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into methanol solutions under a nitrogen atmosphere. Complexes Fe1 and Fe3 both show distorted trigonal-bipyramidal geometries, whereas complex Fe5 is a distorted square pyramid. Selected bond lengths and angles are collected in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for complexes Fe1, Fe3, and Fe5.

|             | Fe1        | Fe3        | Fe5        |
|-------------|------------|------------|------------|
| Fe1–N1      | 2.133(3)   | 2.142(4)   | 2.128(4)   |
| Fe1–N2      | 2.223(3)   | 2.258(4)   | 2.209(3)   |
| Fe1–N3      | 2.215(3)   | 2.285(4)   | 2.228(4)   |
| Fe1–Cl1     | 2.2524(12) | 2.3072(14) | 2.3547(14) |
| Fe1–Cl2     | 2.3243(12) | 2.2709(14) | 2.2634(14) |
| N2–C6       | 1.297(4)   | 1.298(6)   | 1.291(5)   |
| O1–C6       | 1.357(4)   | 1.356(5)   | 1.360(5)   |
| N3–C12      | 1.283(4)   | 1.280(5)   | 1.295(6)   |
| N1–Fe1–N2   | 73.64(11)  | 73.91(14)  | 74.17(13)  |
| N2–Fe1–N3   | 144.56(11) | 146.23(13) | 143.46(13) |
| N1–Fe1–N3   | 72.63(11)  | 72.56(13)  | 72.48(13)  |
| N1–Fe1–Cl1  | 140.95(8)  | 113.30(10) | 94.28(10)  |
| N2–Fe1–Cl1  | 97.13(8)   | 96.01(10)  | 91.34(10)  |
| N3–Fe1–Cl1  | 102.15(8)  | 100.69(10) | 105.57(10) |
| N1–Fe1–Cl2  | 100.45(8)  | 134.04(10) | 153.27(10) |
| N2–Fe1–Cl2  | 91.36(8)   | 94.53(11)  | 102.92(10) |
| N3–Fe1–Cl2  | 105.11(8)  | 105.86(10) | 100.13(10) |
| Cl1–Fe1–Cl2 | 117.90(5)  | 112.06(5)  | 112.42(5)  |

In the structure of complex Fe1 (Figure 2), the pyridine nitrogen atom (N1) and two chlorine atoms lie approximately in the equatorial plane. The iron atom deviates by 0.0382 Å from the equatorial plane; the equatorial angles range from 140.95(8) to 100.45(8)°. The equatorial plane and the *trans* nitrogen atoms N2 and N3 form angles of 87.1 and 86.0°, respectively. The 2,6-dimethylphenyl substituent is oriented almost orthogonally (92.5°) to the N3–N1–N2 plane. The two Fe–Cl bond lengths are significantly different, with the Fe1–Cl1 bond being 0.072 Å shorter than the Fe1–Cl2 bond. This is usually seen in apically elongated square-pyramidal (N,N,N)FeCl<sub>2</sub> complexes<sup>[9b]</sup> and might be ascribed to a distortion towards such a structure. The molecular structure of Fe3 is given in the Supporting Information.

The structure of complex Fe5 (Figure 3) is best described as distorted square-pyramidal, with the basal plane composed of N1, N2, N3, and Cl2. The iron atom deviates from

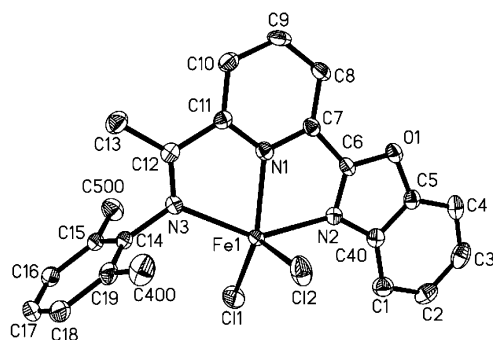


Figure 2. Molecular structure of Fe1. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

this plane by 0.1293 Å, whereas Cl2 deviates by 0.0392 Å to the opposite side. The two fused rings of Fe1–N2–C6–C7–N1–Fe1 and Fe1–N1–C11–C12–N3–Fe1 formed through coordination are coplanar and nearly perpendicular to the aryl ring linked to the imino group (88.0°). The Fe–N bond lengths are in the order Fe1–N3 > Fe1–N2 > Fe1–N1. The two Fe–Cl bond lengths are significantly different, similar to the structures of Fe1, Fe3, and its 2-(benzimidazolyl)-6-[1-(arylimino)ethyl]pyridyliron(II) analogue.<sup>[16]</sup> The N2–C6 bond length is 1.291(5) Å, which is shorter than the C6–O1 bond length of 1.360(5) Å, displaying clear C=N character.

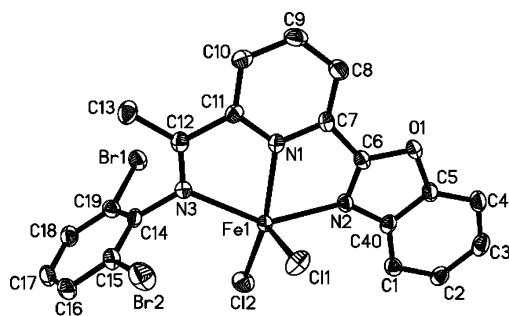


Figure 3. Molecular structure of Fe5. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms are omitted for clarity.

The Cl1–Fe1–Cl2 angle in Fe1 [117.90(5)°] is much wider than that in Fe3 [112.06(5)°] and Fe5 [112.42(5)°]. Thus, the molecular structure of Fe1 is more open, something that would favor ethylene coordination, in line with the observation that the catalytic activity of Fe1 is about an order of magnitude higher than that of Fe3 and Fe5.

Although the complexes are paramagnetic, <sup>1</sup>H NMR spectroscopy can be informative. Complexes Fe1–Fe3 and Fe6, which have better solubility in CDCl<sub>3</sub>, were characterized by <sup>1</sup>H NMR spectroscopy. Figure 4 shows the <sup>1</sup>H NMR spectra of Fe2 and Fe3. All protons resonate at chemical shifts significantly different from the corresponding protons in the free ligands. In the spectrum of Fe2, five peaks can be assigned clearly, on the basis of integration and proximity to the paramagnetic center, to pyridyl protons (A = H<sub>m</sub>, B = H<sub>m</sub>, C = H<sub>p</sub>), ketimine protons (D = NCMe), and methyl protons on the aromatic rings (E =

Me). In Fe3, seven peaks can be assigned to pyridyl protons (A = H<sub>m</sub>, B = H<sub>m</sub>, C = H<sub>p</sub>), ketimine protons (D = NCMe), and isopropyl protons (E = CHMe<sub>2</sub>, F = CHMe<sub>2</sub>). Two relatively narrow signals for the *i*Pr groups confirm the hindered rotation of the aryl group. Similar phenomena have been observed in symmetric 2,6-bis(imino)pyridyliron<sup>[6]</sup> complexes and asymmetric (*N*-{(*E*)-1-[6-(cyclohexylethanimidoyl)-2-pyridinyl]ethylidene}-2,6-diisopropylaniline)iron dichloride.<sup>[10a]</sup> The only differences between complexes Fe1–Fe3 and Fe6 are indicated with the chemical shifts of the protons of the aryl substituents, which are caused by the different distance between the aryl substituents and the paramagnetic iron centre on the NMR timescale.

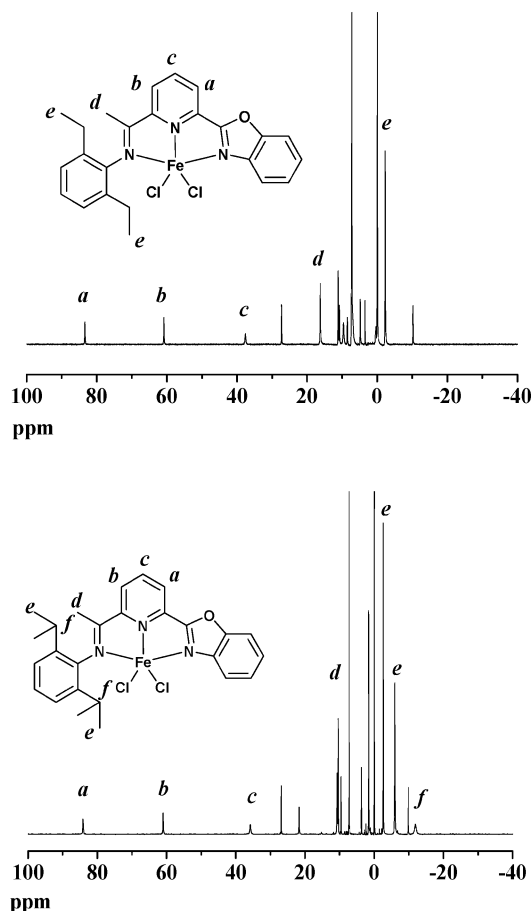


Figure 4. <sup>1</sup>H NMR spectra of Fe2 and Fe3 in CDCl<sub>3</sub> at 298 K.

## Reactions with Ethylene

Precatalyst Fe1 was studied in ethylene oligomerization and polymerization by using different activators [methylaluminoxane (MAO), modified methylaluminoxane (MMAO), Et<sub>2</sub>AlCl, and Et<sub>3</sub>Al]. Because the activity at ambient ethylene pressure is low, the influence of the activator was assessed at 10 atm C<sub>2</sub>H<sub>4</sub> (Table 2). Mixtures of Fe1 with AlEt<sub>3</sub> or AlClEt<sub>2</sub> were inactive. However, with modified MMAO the activity for ethylene polymerization and oligomerization was much higher than that of its 2-(benzimidazolyl)-6-[1-

(arylimino)ethyl]pyridyliron(II) analogue,<sup>[16]</sup> with high selectivity for  $\alpha$ -olefins. The oligomers showed a Schulz–Flory distribution (Table 3). The probability of chain propagation is given by  $K$ , where  $K = (\text{rate of propagation})/[(\text{rate of propagation}) + (\text{rate of chain transfer})] = (\text{mol of } C_{n+2})/(\text{mol of } C_n)$ ; the  $K$  values were determined by the molar ratio of the  $C_{12}$  and  $C_{14}$  fractions.<sup>[29]</sup>

Table 2. Ethylene oligomerization activity of Fe1 as a function of the catalyst activator.<sup>[a]</sup>

| Entry | Activator            | Al/Fe | Oligomer activity <sup>[b]</sup> | Oligomer distribution <sup>[c]</sup> | Polymer activity <sup>[d]</sup> |
|-------|----------------------|-------|----------------------------------|--------------------------------------|---------------------------------|
| 1     | MAO                  | 1000  | 2.41                             | C <sub>4</sub> –C <sub>28</sub>      | trace                           |
| 2     | MMAO                 | 1000  | 6.81                             | C <sub>4</sub> –C <sub>28</sub>      | 9.70                            |
| 3     | Et <sub>2</sub> AlCl | 200   | –                                | –                                    | –                               |
| 4     | Et <sub>3</sub> Al   | 200   | –                                | –                                    | –                               |

[a] Reaction conditions: Fe1 (5  $\mu\text{mol}$ ), ethylene (10 atm), 30 min, 30 °C, toluene (100 mL). [b] In units of  $10^5 \text{ g}(\text{mol Fe})^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ . [c] Determined by GC. [d] Polymerization activity:  $10^4 \text{ g PE}(\text{mol Fe})^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ .

The substituents of the imino N-aryl rings strongly influenced the catalytic performance (Table 3). The effects are rather subtle, and both steric and electronic factors are important, with the former dominating. Of the 2,6-dialkyl-substituted complexes Fe1–Fe3 (Table 3, Entries 1–3), complex Fe2, with ethyl groups in the *ortho* positions, gave the highest catalytic activity, whereas methyl substituents gave lower oligomerization activities but a higher  $K$  value, as well as larger amounts of low-molecular-weight wax (Table 3, Entry 1). Changing R<sup>1</sup> to isopropyl resulted in decreased catalytic activity. Furthermore, the bulkier the R<sup>1</sup> group, the smaller the  $K$  value and the lower the amount of polyethylene produced. The same trend was observed in the 2-(benzimidazolyl)-6-[1-(arylimino)ethyl]pyridyliron(II) system.<sup>[16]</sup> Compared with complexes Fe1–Fe3, which contain electron-donating 2,6-substituents, complexes Fe4 and Fe5, bearing halogen groups, exhibited comparable activity and relatively lower selectivity for  $\alpha$ -olefins (Table 3, Entries 4 and 5). As to the distribution of oligomers, the bulkier the R<sup>1</sup> substituents, the higher the content of C<sub>4</sub>, and the distribution of oligomers obtained did not strictly follow Schulz–Flory rules (Table 3).

The substituents at the 4-position of the aryl ring also influence the catalytic activity and the  $K$  value. For example, 2,4,6-trimethyl-substituted complex Fe6 exhibited higher catalytic activity in ethylene oligomerization and polymerization and a larger  $K$  value than catalyst Fe7, which bears a 4-bromo-2,6-dimethyl group.

The influence of reaction parameters on ethylene oligomerization and polymerization activities was investigated in detail for complex Fe2 (Table 4). When the Al/Fe molar ratio was increased from 500 to 1000, both oligomerization and polymerization activities increased sharply (Table 4, Entries 1–3), but a further increase in the molar ratio to 1500 resulted in decreased polymerization activity and a slightly increased oligomerization activity. Increasing the ratio to 2000 decreased both polymerization and oligomerization. In contrast, the Al/Fe molar ratio had little influence on the oligomer distribution and  $K$  values.

Raising the reaction temperature from 30 to 50 °C resulted in an obvious decrease in productivity and selectivity for  $\alpha$ -olefins (Table 4, Entries 3, 7, and 8), suggesting that active centers are thermally unstable under these conditions.

In the Fe2/MMAO system, the oligomerization rate was fairly constant, whereas the polymerization rate was quite low over the first 20 min (Table 4, Entries 9–11) but then increased dramatically in the second 20 min period (Table 4, Entries 3 and 12). With prolonged reaction times, both oligomerization and polymerization activity decreased (Table 4, Entry 13).

Compared with the iron(II) complexes bearing 2-benzimidazole-6-(1-aryliminoethyl)pyridines<sup>[16]</sup> and 2,6-bis(2-oxazolin-2-yl)pyridine,<sup>[26]</sup> the benzoxazolyl(aryliminoethyl)pyridine complexes described here present much higher catalytic activities. These results also follow conclusions drawn from computational studies on the relationship of the catalytic activity with the net charge of late-transition-metal complexes in that the stronger the electron-donating ability of the ligand the lower the net charge on the metal and the lower the catalytic activity.<sup>[12a,30]</sup>

In most cases, some polyethylene waxes accompanied the formation of oligomers. According to their FTIR spectra, the waxes are mainly linear  $\alpha$ -olefins. <sup>1</sup>H and <sup>13</sup>C NMR spectra (Figure 5) of the waxes produced by complex Fe1

Table 3. Polymerization and oligomerization of ethylene with Fe1–Fe7/MMAO.<sup>[a]</sup>

| Entry | Catalyst | R <sup>1</sup> | K    | $\alpha$ -O <sup>[b]</sup><br>[%] | Activity                |                    | Oligomer distribution [%] <sup>[c]</sup> |                    |                    |                       |
|-------|----------|----------------|------|-----------------------------------|-------------------------|--------------------|------------------------------------------|--------------------|--------------------|-----------------------|
|       |          |                |      |                                   | Oligomer <sup>[d]</sup> | Wax <sup>[d]</sup> | C <sub>4</sub> /ΣC                       | C <sub>6</sub> /ΣC | C <sub>8</sub> /ΣC | ΣC <sub>≥10</sub> /ΣC |
| 1     | Fe1      | Me             | 0.75 | 97.0                              | 6.81                    | 9.70               | 21.1                                     | 19.7               | 14.6               | 44.6                  |
| 2     | Fe2      | Et             | 0.71 | 96.8                              | 10.20                   | 0.73               | 30.3                                     | 22.4               | 15.1               | 32.2                  |
| 3     | Fe3      | <i>i</i> Pr    | 0.55 | 99.0                              | 6.05                    | 0.14               | 44.2                                     | 26.3               | 13.9               | 15.6                  |
| 4     | Fe4      | Cl             | 0.65 | 96.6                              | 7.40                    | 1.54               | 27.8                                     | 23.6               | 16.0               | 32.6                  |
| 5     | Fe5      | Br             | 0.64 | 92.4                              | 7.72                    | 0.70               | 49.7                                     | 24.2               | 10.2               | 15.9                  |
| 6     | Fe6      | Me             | 0.78 | 99.0                              | 8.37                    | 10.44              | 20.3                                     | 17.8               | 14.7               | 47.2                  |
| 7     | Fe7      | Me             | 0.77 | 94.9                              | 1.85                    | 6.68               | 20.2                                     | 17.1               | 14.6               | 48.1                  |

[a] Reaction conditions: catalyst (5  $\mu\text{mol}$ ), MMAO (1000 equiv.), ethylene (10 atm), 30 °C, 30 min, toluene (100 mL). [b] Percent  $\alpha$ -olefin content determined by GC. [c] Oligomerization activity:  $10^3 \text{ g}(\text{mol Fe})^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ . [d] Polymerization activity:  $10^4 \text{ g}(\text{mol Fe})^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ . [e] Determined by GC; ΣC denotes the total amount of oligomers.

Table 4. Polymerization and oligomerization of ethylene with Fe2/MMAO.<sup>[a]</sup>

| Entry | Al/Fe | <i>t</i><br>[min] | <i>T</i><br>[°C] | <i>K</i> | $\alpha$ -O <sup>[b]</sup><br>[%] | Activity                |                    | Oligomer distribution [%] <sup>[c]</sup> |                    |                    |                       |
|-------|-------|-------------------|------------------|----------|-----------------------------------|-------------------------|--------------------|------------------------------------------|--------------------|--------------------|-----------------------|
|       |       |                   |                  |          |                                   | Oligomer <sup>[c]</sup> | Wax <sup>[d]</sup> | C <sub>4</sub> /ΣC                       | C <sub>6</sub> /ΣC | C <sub>8</sub> /ΣC | ΣC <sub>≥10</sub> /ΣC |
| 1     | 500   | 30                | 30               | 0.69     | 96.9                              | 9.36                    | 0.16               | 29.6                                     | 22.4               | 14.5               | 33.5                  |
| 2     | 800   | 30                | 30               | 0.71     | 96.8                              | 9.60                    | 0.54               | 29.9                                     | 22.6               | 14.8               | 32.7                  |
| 3     | 1000  | 30                | 30               | 0.71     | 96.8                              | 10.20                   | 0.73               | 30.3                                     | 22.4               | 15.1               | 32.2                  |
| 4     | 1200  | 30                | 30               | 0.70     | 96.6                              | 10.56                   | 0.71               | 35.4                                     | 24.4               | 14.5               | 25.7                  |
| 5     | 1500  | 30                | 30               | 0.68     | 96.8                              | 10.80                   | 0.69               | 36.5                                     | 25.5               | 13.3               | 24.7                  |
| 6     | 2000  | 30                | 30               | 0.53     | 96.7                              | 9.86                    | 0.53               | 42.4                                     | 22.1               | 11.7               | 23.8                  |
| 7     | 1000  | 30                | 40               | 0.64     | 96.6                              | 7.09                    | trace              | 29.1                                     | 23.6               | 16.6               | 30.7                  |
| 8     | 1000  | 30                | 50               | —        | 72.2                              | 0.07                    | —                  | 100                                      | —                  | —                  | —                     |
| 9     | 1000  | 5                 | 30               | 0.73     | 98.0                              | 13.00                   | trace              | 33.5                                     | 19.4               | 13.5               | 33.6                  |
| 10    | 1000  | 10                | 30               | 0.71     | 98.3                              | 11.70                   | 0.08               | 33.0                                     | 23.3               | 15.2               | 28.5                  |
| 11    | 1000  | 20                | 30               | 0.71     | 97.5                              | 11.28                   | 0.25               | 29.0                                     | 22.2               | 16.0               | 32.8                  |
| 12    | 1000  | 40                | 30               | 0.67     | 98.0                              | 8.10                    | 0.69               | 37.5                                     | 24.8               | 15.1               | 22.6                  |
| 13    | 1000  | 60                | 30               | 0.70     | 98.3                              | 5.74                    | 0.54               | 27.4                                     | 21.5               | 16.0               | 35.1                  |

[a] Reaction conditions: Fe2 (5 μmol), ethylene (10 atm), 30 min, toluene (100 mL). [b] Percent  $\alpha$ -olefin content determined by GC. [c] Oligomerization activity: 10<sup>5</sup> g(mol Fe)<sup>−1</sup> h<sup>−1</sup> bar<sup>−1</sup>. [d] Polymerization activity: 10<sup>4</sup> g(mol Fe)<sup>−1</sup> h<sup>−1</sup> bar<sup>−1</sup>. [e] Determined by GC.

further confirmed that the wax consisted mainly of linear  $\alpha$ -olefins with vinyl chain ends with a carbon number of about 34.

## Conclusions

Iron complexes of 2-(benzoxazolyl)-6-[1-(arylimino)-ethyl]pyridines form a new type of readily accessible oligomerization catalysts. Whereas AlEt<sub>3</sub> and AlClEt<sub>2</sub> proved ineffective as catalyst activators, activation with MMAO gave activities of up to 10<sup>5</sup> g(mol Fe)<sup>−1</sup> h<sup>−1</sup> bar<sup>−1</sup> for ethylene polymerization and 1.3 × 10<sup>6</sup> g(mol Fe)<sup>−1</sup> h<sup>−1</sup> bar<sup>−1</sup> for oligomerization.  $\alpha$ -Olefins were in the range of C<sub>4</sub>–C<sub>28</sub>, with high selectivity for terminal unsaturation. The catalytic activity, oligomer distribution, and selectivity depend on both the steric and the electronic properties of the substituents on the N-aryl rings, with moderately large alkyl groups (i.e., ethyl) showing superior properties than methyl or isopropyl. Raising the reaction temperature resulted in an obvious decrease in productivity and in the selectivity for  $\alpha$ -olefins.

## Experimental Section

**General Considerations:** All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere by using standard Schlenk techniques. Toluene was heated at reflux over sodium–benzophenone and distilled under argon prior to use. MAO (1.46 M in toluene) and modified MMAO (1.93 M in heptane) were purchased from Akzo Nobel Corp. Diethylaluminum chloride (Et<sub>2</sub>AlCl, 1.7 M in toluene) was purchased from Acros Chemicals. Other reagents were purchased from Aldrich or Acros Chemicals. FTIR spectra were recorded with a Perkin–Elmer System 2000 FTIR spectrometer. Elemental analyses were carried out by using a Flash EA 1112 microanalyzer. GC analyses were performed with a Varian CP-3800 gas chromatograph equipped with a flame ionization detector and a 30 m (0.2 mm i.d., 0.25 μm film thickness) CP-Sil 5 CB column. The yield of oligomers was determined by GC calculated by referencing to the mass of the solvent assuming that the mass of each fraction was approximately proportional to its integrated areas in the GC trace. Selectivity for the linear  $\alpha$ -olefin was defined as (amount of linear  $\alpha$ -olefin of all fractions)/(total amount of oligomer products) in percent. <sup>1</sup>H NMR spectra of the iron complexes were recorded with a Bruker DMX 600 MHz instrument at 25 °C with the use of TMS as the internal standard.

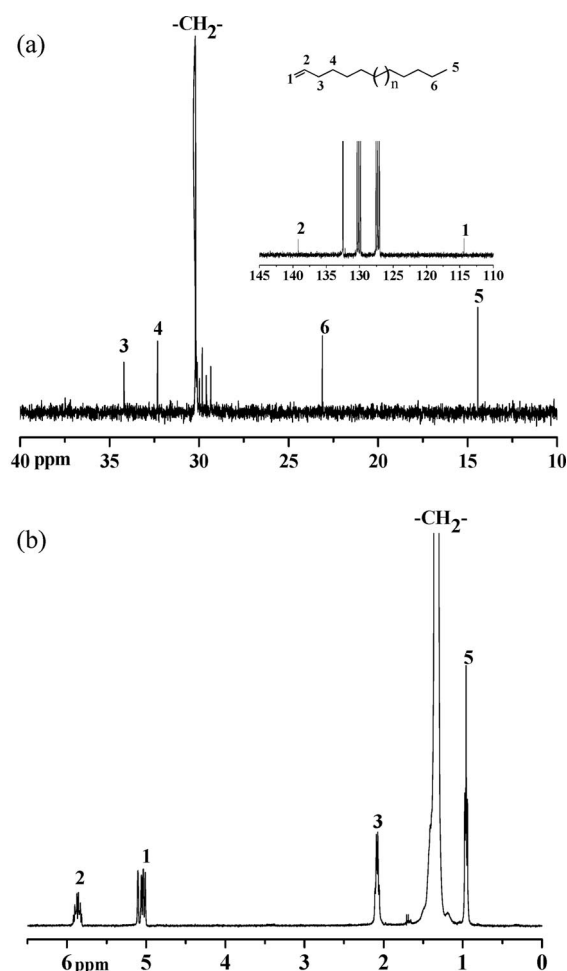


Figure 5. (a) <sup>13</sup>C NMR and (b) <sup>1</sup>H NMR spectra of the polyethylene waxes obtained by Fe1 (cf. Table 3, Entry 1).

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the PE samples were recorded with a Bruker DMX 400 MHz instrument at 25 °C in 1,2-[D<sub>4</sub>]dichlorobenzene with the use of tetramethylsilane as the internal standard.

***N*-(1*E*)-1-[6-(1,3-Benzoxazol-2-yl)pyridin-2-yl]ethylidene]-*N*-(2,6-dimethylphenyl)amine FeCl<sub>2</sub> (Fe1):** Schlenk tube was charged with solid *N*-(1*E*)-1-[6-(1,3-Benzoxazol-2-yl)pyridin-2-yl]ethylidene]-*N*-(2,6-dimethylphenyl)amine (0.20 g, 0.6 mmol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (0.12 g, 0.6 mmol) and purged three times with argon, followed by the addition of ethanol (10 mL). The reaction mixture was stirred at room temperature for 10 h. The resulting precipitate was filtered off, washed twice with diethyl ether, and dried in vacuo to furnish the pure product as a blue powder. Yield: 0.258 g, 92.0%.  $^1\text{H}$  NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 83.12 (s, 1 H, Py,  $H_m$ ), 60.91 (s, 1 H, Py,  $H_m$ ), 37.56 (s, 1 H, Py,  $H_p$ ), 27.33 (s, 1 H, Ar  $H$ ), 18.55 (s, 3 H, N=CCH<sub>3</sub>), 11.35 (s, 2 H, Ar  $H$ ), 10.63 (s, 6 H, CH<sub>3</sub> × 2), 6.59 (s, 2 H, Ar  $H$ ), 3.48 (s, 1 H, Ar), -10.28 (s, 1 H, Ar  $H$ ) ppm. FTIR (KBr disk):  $\tilde{\nu}$  = 2919 (w), 1615 ( $\nu_{\text{C=N}}$ ) (s), 1594 (w), 1548 (w), 1468 (m), 1450 (s), 1375 (s), 1278 (s), 1212 (m), 1172 (w), 1096 (w), 1018 (w), 812 (w), 789 (m) cm<sup>-1</sup>. C<sub>22</sub>H<sub>19</sub>Cl<sub>2</sub>FeN<sub>3</sub>O (468.16): calcd. C 56.44, H 4.09, N 8.98; found C 56.32, H 4.04, N 8.77.

***N*-(1*E*)-1-[6-(1,3-Benzoxazol-2-yl)pyridin-2-yl]ethylidene]-*N*-(2,6-diethylphenyl)amine FeCl<sub>2</sub> (Fe2):** Prepared according to the procedure outlined for Fe1. Yield: 0.27 g, 89.3%.  $^1\text{H}$  NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 83.41 (s, 1 H, Py,  $H_m$ ), 60.81 (s, 1 H, Py,  $H_m$ ), 37.67 (s, 1 H, Py,  $H_p$ ), 27.27 (s, 1 H, Ar  $H$ ), 16.24 (s, 3 H, N=CCH<sub>3</sub>), 11.12 (s, 2 H, Ar  $H$ ), 10.76 (s, 1 H, Ar  $H$ ), 9.61 (s, 2 H, CH<sub>2</sub>), 8.55 (s, 1 H, Ar  $H$ ), 4.86 (1 H, CH), 3.47 (s, 1 H, Ar  $H$ ), -2.27 (s, 6 H, CH<sub>3</sub> × 2), -10.20 (s, 1 H, Ar  $H$ ) ppm. FTIR (KBr disk):  $\tilde{\nu}$  = 2967 (m), 1614 ( $\nu_{\text{C=N}}$ ) (s), 1593 (m), 1546 (m), 1449 (s), 1374 (s), 1276 (s), 1208 (w), 1194 (w), 1173 (w), 1102 (w), 1020 (w), 855 (w), 813

(w), 788 (s) cm<sup>-1</sup>. C<sub>24</sub>H<sub>23</sub>Cl<sub>2</sub>FeN<sub>3</sub>O (496.21): calcd. C 58.09, H 4.67, N 8.47; found C 57.85, H 4.61, N 8.38.

***N*-(1*E*)-1-[6-(1,3-Benzoxazol-2-yl)pyridin-2-yl]ethylidene]-*N*-(2,6-diisopropylphenyl)amine FeCl<sub>2</sub> (Fe3):** Prepared according to the procedure outlined for Fe1. Yield: 0.29 g, 91.4%.  $^1\text{H}$  NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 84.14 (s, 1 H, Py,  $H_m$ ), 60.94 (s, 1 H, Py,  $H_m$ ), 35.76 (s, 1 H, Py,  $H_p$ ), 26.82 (s, 1 H, Ar  $H$ ), 21.69 (s, 1 H, Ar  $H$ ), 10.66 (s, 3 H, N=CCH<sub>3</sub>), 10.37 (s, 2 H, Ar  $H$ ), 9.56 (s, 1 H, Ar  $H$ ), 3.71 (s, 1 H, Ar  $H$ ), -2.62 (s, 6 H, CH<sub>3</sub> × 2), -5.98 (s, 6 H, CH<sub>3</sub> × 2), -9.83 (s, 1 H, Ar  $H$ ), -11.86 (br. s, 2 H, CH × 2) ppm. FTIR (KBr disk):  $\tilde{\nu}$  = 2962 (s), 1613 ( $\nu_{\text{C=N}}$ ) (m), 1593 (m), 1548 (m), 1448 (s), 1373 (vs), 1278 (s), 1192 (w), 1103 (w), 817 (w), 789 (m) cm<sup>-1</sup>. C<sub>26</sub>H<sub>27</sub>Cl<sub>2</sub>FeN<sub>3</sub>O (524.26): calcd. C 59.57, H 5.19, N 8.02; found C 59.18, H 5.15, N 8.00.

***N*-(1*E*)-1-[6-(1,3-Benzoxazol-2-yl)pyridin-2-yl]ethylidene]-*N*-(2,6-dichlorophenyl)amine FeCl<sub>2</sub> (Fe4):** Prepared according to the procedure outlined for Fe1. Yield: 0.27 g, 87.6%. FTIR (KBr disk):  $\tilde{\nu}$  = 3058 (w), 1615 ( $\nu_{\text{C=N}}$ ) (m), 1592 (w), 1562 (m), 1438 (s), 1375 (s), 1278 (s), 1230 (m), 1174 (w), 813 (m), 784 (vs) cm<sup>-1</sup>. C<sub>20</sub>H<sub>13</sub>Cl<sub>4</sub>FeN<sub>3</sub>O·0.5H<sub>2</sub>O (518.00): calcd. C 46.37, H 2.72, N 8.11; found C 46.41, H 2.84, N 7.90.

***N*-(1*E*)-1-[6-(1,3-Benzoxazol-2-yl)pyridin-2-yl]ethylidene]-*N*-(2,6-dibromophenyl)amine FeCl<sub>2</sub> (Fe5):** Prepared according to the procedure outlined for Fe1. Yield: 0.33 g, 91.0%. FTIR (KBr disk):  $\tilde{\nu}$  = 3051 (w), 1616 ( $\nu_{\text{C=N}}$ ) (m), 1594 (w), 1548 (m), 1449 (m), 1430 (s), 1373 (s), 1277 (s), 1228 (m), 1175 (m), 1102 (w), 1021 (w), 852 (w), 769 (s) cm<sup>-1</sup>. C<sub>20</sub>H<sub>13</sub>Br<sub>2</sub>Cl<sub>2</sub>FeN<sub>3</sub>O (597.90): calcd. C 40.18, H 2.19, N 7.03; found C 39.89, H 2.30, N 6.91.

***N*-(1*E*)-1-[6-(1,3-Benzoxazol-2-yl)pyridin-2-yl]ethylidene]-*N*-mesitylamine FeCl<sub>2</sub> (Fe6):** Prepared according to the procedure out-

Table 5. Crystal data and structure refinement for Fe1, Fe3, and Fe5.

|                                                             | Fe1                                                                | Fe3                                                                | Fe5·CH <sub>3</sub> OH                                                                          |
|-------------------------------------------------------------|--------------------------------------------------------------------|--------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
| Empirical formula                                           | C <sub>22</sub> H <sub>19</sub> Cl <sub>2</sub> FeN <sub>3</sub> O | C <sub>26</sub> H <sub>27</sub> Cl <sub>2</sub> FeN <sub>3</sub> O | C <sub>21</sub> H <sub>17</sub> Br <sub>2</sub> Cl <sub>2</sub> FeN <sub>3</sub> O <sub>2</sub> |
| Formula weight                                              | 468.15                                                             | 524.26                                                             | 629.95                                                                                          |
| Crystal color                                               | blue                                                               | blue                                                               | blue                                                                                            |
| Temperature [K]                                             | 173(2)                                                             | 173(2)                                                             | 173(2)                                                                                          |
| Wavelength [Å]                                              | 0.71073                                                            | 0.71073                                                            | 0.71073                                                                                         |
| Crystal system                                              | triclinic                                                          | monoclinic                                                         | monoclinic                                                                                      |
| Space group                                                 | <i>P</i> $\bar{1}$                                                 | <i>P</i> 2 <sub>1</sub>                                            | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                                              |
| <i>a</i> [Å]                                                | 9.3605(19)                                                         | 8.7478(17)                                                         | 10.781(2)                                                                                       |
| <i>b</i> [Å]                                                | 9.6060(19)                                                         | 15.527(3)                                                          | 15.446(3)                                                                                       |
| <i>c</i> [Å]                                                | 11.636(2)                                                          | 9.865(2)                                                           | 13.822(3)                                                                                       |
| $\alpha$ [°]                                                | 93.03(3)                                                           | 90                                                                 | 90                                                                                              |
| $\beta$ [°]                                                 | 99.54(3)                                                           | 101.23(3)                                                          | 100.58(3)                                                                                       |
| $\gamma$ [°]                                                | 95.34(3)                                                           | 90                                                                 | 90                                                                                              |
| <i>V</i> [Å <sup>3</sup> ]                                  | 1024.8(3)                                                          | 1314.3(5)                                                          | 2262.7(8)                                                                                       |
| <i>Z</i> , <i>D</i> <sub>calcd.</sub> [g cm <sup>-3</sup> ] | 2, 1.517                                                           | 2, 1.325                                                           | 4, 1.849                                                                                        |
| $\mu$ [mm <sup>-1</sup> ]                                   | 1.015                                                              | 0.799                                                              | 4.459                                                                                           |
| <i>F</i> (000)                                              | 480                                                                | 544                                                                | 1240                                                                                            |
| Crystal size [mm]                                           | 0.29 × 0.18 × 0.13                                                 | 0.37 × 0.26 × 0.07                                                 | 0.34 × 0.25 × 0.18                                                                              |
| $\theta$ range [°]                                          | 2.13–25.00                                                         | 2.48–25.00                                                         | 2.00–25.00                                                                                      |
| Limiting indices                                            | –11 ≤ <i>h</i> ≤ 11<br>–11 ≤ <i>k</i> ≤ 11<br>–13 ≤ <i>l</i> ≤ 13  | –10 ≤ <i>h</i> ≤ 10<br>–18 ≤ <i>k</i> ≤ 18<br>–11 ≤ <i>l</i> ≤ 11  | –12 ≤ <i>h</i> ≤ 12<br>–18 ≤ <i>k</i> ≤ 18<br>–16 ≤ <i>l</i> ≤ 16                               |
| No. of collected/unique reflections                         | 6631/3608                                                          | 4623/4623                                                          | 7763/3987                                                                                       |
| No. of parameters                                           | 262                                                                | 298                                                                | 285                                                                                             |
| Completeness to $\theta$ [%]                                | 99.9                                                               | 99.9                                                               | 99.8                                                                                            |
| Abs. corr.                                                  | multiscan                                                          | multiscan                                                          | multiscan                                                                                       |
| Goodness of fit on <i>F</i> <sup>2</sup>                    | 1.204                                                              | 0.923                                                              | 1.110                                                                                           |
| Final <i>R</i> indices [ <i>I</i> > 2σ ( <i>I</i> )]        | <i>R</i> <sub>1</sub> = 0.0529, <i>wR</i> <sub>2</sub> = 0.1099    | <i>R</i> <sub>1</sub> = 0.0456, <i>wR</i> <sub>2</sub> = 0.0925    | <i>R</i> <sub>1</sub> = 0.0450, <i>wR</i> <sub>2</sub> = 0.0773                                 |
| <i>R</i> indices (all data)                                 | <i>R</i> <sub>1</sub> = 0.0667, <i>wR</i> <sub>2</sub> = 0.1147    | <i>R</i> <sub>1</sub> = 0.0586, <i>wR</i> <sub>2</sub> = 0.0956    | <i>R</i> <sub>1</sub> = 0.0660, <i>wR</i> <sub>2</sub> = 0.0825                                 |
| Largest diff peak and hole [e Å <sup>-3</sup> ]             | 0.525 and –0.482                                                   | 0.385 and –0.288                                                   | 0.633 and –0.601                                                                                |

lined for Fe1. Yield: 0.25 g, 86.0%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 83.29 (s, 1 H, Py,  $H_m$ ), 60.84 (s, 1 H, Py,  $H_m$ ), 38.88 (s, 1 H, Py,  $H_p$ ), 27.26 (s, 1 H, Ar  $H$ ), 19.48 (s, 3 H,  $\text{N}=\text{CCH}_3$ ), 16.54 (s, 3 H,  $\text{CH}_3$ ), 11.30 (s, 1 H, Ar  $H$ ), 10.80 (s, 3 H,  $\text{CH}_3$ ), 10.69 (s, 5 H,  $\text{CH}_3$  and Ar  $H$ ), 4.11 (s, 1 H, CH), 3.48 (s, 1 H, Ar  $H$ ) ppm. FTIR (KBr disk):  $\tilde{\nu}$  = 2912 (w), 1614 ( $\nu_{\text{C}=\text{N}}$ ) (m), 1591 (w), 1541 (m), 1478 (m), 1448 (m), 1371 (m), 1276 (s), 1217 (s), 1171 (m), 1104 (w), 863 (m), 813 (m), 771 (s)  $\text{cm}^{-1}$ .  $\text{C}_{23}\text{H}_{21}\text{Cl}_2\text{FeN}_3\text{O}$  (482.18): calcd. C 57.29, H 4.39, N 8.71; found C 56.82, H 4.40, N 8.66.

***N*-(1*E*)-1-[6-(1,3-Benzoxazol-2-yl)pyridin-2-yl]ethylidene]-*N*-(4-bromo-2,6-dimethylphenyl)amine FeCl<sub>2</sub> (Fe7):** Prepared according to the procedure outlined for Fe1. Yield: 0.30 g, 90.0%. FTIR (KBr disk):  $\tilde{\nu}$  = 2911 (w), 1618 ( $\nu_{\text{C}=\text{N}}$ ) (m), 1594 (w), 1549 (m), 1450 (m), 1374 (s), 1276 (s), 1210 (s), 1103 (w), 1019 (w), 865 (w), 772 (m)  $\text{cm}^{-1}$ .  $\text{C}_{22}\text{H}_{18}\text{BrCl}_2\text{FeN}_3\text{O}$  (547.05): calcd. C 48.30, H 3.32, N 7.68; found C 47.91, H 3.39, N 7.56.

**General Procedure for Ethylene Reactions:** Ethylene oligomerization and polymerization were performed in a 500-mL stainless-steel autoclave equipped with a mechanical stirrer and a temperature controller. Toluene, the desired amount of modified MMAO, and a toluene solution of the catalyst precursor was added to the reactor in this order under an ethylene atmosphere; the total volume was 100 mL. When the desired reaction temperature was reached, ethylene (10 atm) was introduced to start the reaction, and the ethylene pressure was maintained by a constant feed of ethylene. After 30 min, the pressure was released and a small amount of the reaction solution was collected, which was then analyzed by gas chromatography (GC) to determine the composition and mass distribution of oligomers obtained. Because the acid concentration of the HCl-acidified ethanol (5%) was low and because we tested the sample as quickly as possible, acid-catalyzed C=C bond isomerization was considered negligible. Then, the remaining reaction mixture was quenched with HCl-acidified ethanol (5%), and the precipitated polyethylene was filtered, washed with ethanol, and dried under vacuum at 60 °C to constant weight.

**X-ray Crystallography:** Single-crystals of Fe1, Fe3, and Fe5 suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into their methanol solutions. Data were collected with a Rigaku RAXIS Rapid IP diffractometer with graphite monochromated Mo- $K_\alpha$  radiation ( $\lambda$  = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on  $F^2$ . All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.<sup>[31]</sup> Crystal data and processing parameters for Fe1, Fe3, and Fe5 are summarized in Table S. CCDC-716205 (for Fe1) -716206 (for Fe3), and -716207 (for Fe5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Supporting Information** (see footnote on the first page of this article): The molecular structure of Fe3 along with the plots of Fe1, Fe3, and Fe5.

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