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Simultaneous Polymerization and Schulz−Flory Oligomerization of Ethylene Made Possible by Activation with MAO of a C_1-Symmetric [2,6-Bis(arylimino)pyridyl]iron Dichloride Precursor

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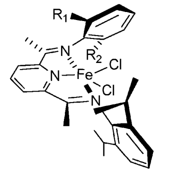
Summary: C_1-symmetric [2,6-bis(imino)pyridyl]iron dichloride complexes can form on activation by MAO highly active catalysts for the one-pot transformation of ethylene into mixtures of linear homopolymer and α-olefins with a Schulz−Flory distribution.

Upon treatment with methylaluminoxane (MAO) or other activators, [2,6-bis(arylimino)pyridyl]iron dihalide complexes can form very active catalysts for the conversion of ethylene into either high-density polyethylene (HDPE) or α-olefins with a Schulz−Flory distribution.[1,2] The number, nature, and position of the substituents on the aryl rings have been found to play a crucial role in driving the catalytic activity toward either polymerization or oligomerization. The simultaneous formation of both polyethylene and α-olefins with a Schulz−Flory distribution using a single catalyst precursor has never been reported. In this work, we show that the production of both PE and α-olefins in the same reaction is made possible by the use of C_1-symmetric [2,6-bis(arylimino)-pyridyl]iron dichloride precursors.

Following a known procedure,[3] we have synthesized the complexes **1**, **2**, and **3**, which differ from each other, inter alia, in molecular symmetry (Chart 1). Complexes **1** and **3** exhibit C_s symmetry, while **2** exhibits C_1 symmetry by virtue of hindered rotation of the tolyl group about the N−C bond.[1−3] Hindered rotation of the 2,6-diisopropylphenyl groups occurs in all complexes, whereas the unsubstituted phenyl ring in **1** rotates freely.

The Fe^{II} complexes **1**−**3** were all highly active catalysts on treatment with MAO for the conversion of ethylene, showing comparable turnover frequencies, in the range from 10^5 to 10^6 moles of C_2H_4 converted (mole of Fe × h)$^{-1}$. However, a different product composition was observed, depending on the molecular symmetry. Selected data are reported in Table 1.

Chart 1



1: (C_s) $R_1 = R_2 = H$
2: (C_1) $R_1 = Me$; $R_2 = H$
3: (C_s) $R_1 = R_2 = Me$

In ethylene oligomerization/polymerization by [2,6-bis(arylimino)pyridyl]iron^{II} catalysts, the chain-transfer rate is known to be disfavored by steric hindrance in the axial positions of the propagating Fe-alkyl species.[1−4] *Ortho* substituents on the arylimino rings have proved crucial to determine such steric hindrance. Consistent with this assumption, the C_s-symmetric complex **1**, with no substituents on the aryl ring, was found to oligomerize ethylene, yielding even olefins with a Schulz−Flory distribution with 93% selectivity in α-olefins (run 1), while the C_s-symmetric precursor **3**, with two *ortho* methyl substituents, produced exclusively PE (run 3). Surprisingly, the C_1-symmetric precursor **2** gave both even olefins and PE (run 2). The selectivity in even α-olefins was 95% with a Schulz−Flory parameter of 0.71. Significant amounts of even and odd alkanes and odd olefins were also produced by both precursors **1** and **2** (runs 1, 2), which is consistent with the occurrence of chain transfer to aluminum.[1a,2b,c]

To rule out the occurrence of fortuitous events leading to the generation of two different catalytic systems from precursor **2**, three different catalysis procedures were employed and the experimental conditions were varied as systematically as possible.[5] For example, the concentrations of catalysts and MAO were changed (runs

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Table 1. Ethylene Oligo/Polymerization with [2,6-Bis(imino)pyridyl]iron Dichloride Precursors[a]

run no.	catalysis procedure[b]	precatalyst	amount (μmol)	MAO (equiv)	pressure (bar)	T_{initial} (°C)	ΔT (°C)	even alkenes-alkanes TOF[c,d] ($\times 10^{-3}$)	α[c,e]	even alkanes[c] (%)	even α-olefin selectivity[c] (%)	odd alkenes-alkanes TOF[c,d] ($\times 10^{-3}$)	polymer TOF[d] ($\times 10^{-3}$)	M_w[f] (kg mol^{-1})	PDI[f]	T_m[g]/ΔH[g] (°C/J g^{-1})
1	A	**1**	12	300	5	22	44	144.9	0.79	1.3	93	2.9				
2	A	**2**	12	300	5	22	51	113.7	0.71	1.1	95	1.7	186.6	42.2	15.8	128/215
3	A	**3**	12	300	5	24	70						248.8	103.0	10.8	132/214
4	B	**1**	1.2	3000	5	23	30	625.8	0.78	1.8	94	18.0				
5	B	**2**	1.2	3000	5	23	33	435.1	0.73	1.5	98	10.2	919.2	25.4	10.6	126/213
6	B	**3**	1.2	3000	5	20	50						2357.1	130.0	10.0	134/207
7	A	**2**	12	300	5	−2	*h*	114.7	0.74	1.0	96	1.5	256.6	*h*	*h*	*h*
8	A	**2**	12	300	5	−20	*h*	85.3	0.76	1.1	98	1.1	194.6	33.0	11.0	127/210
9	B	**2**	1.2	3000	9	19	43	731.1	0.74	1.5	98	13.2	1145.0	*h*	*h*	*h*
10	B	**2**	1.2	3000	13	20	46	915.1	0.72	1.5	98	10.5	1340.9	70.0	26.0	*h*
11	C	**2**	12	300[i]	5	27	53	99.7	0.73	0.8	96	0.6	167.4	*h*	*h*	*h*
12	A	**4**	12	300	5	24	39	156.4	0.72	1.9	98	2.4				
13	A	**5**	12	300	5	23	46	132.0	0.81	1.8	97	2.7	108.1	73.3	23.7	126/217

[a] Reaction conditions: toluene 100 mL, 15 min. [b] See Supporting Information. [c] Determined by GC. [d] Moles of C_2H_4 converted (mole of Fe × h)$^{-1}$. [e] Schulz−Flory parameter, α = rate of propagation/(rate of propagation + rate of chain transfer) = moles C_{n+2}/moles C_n. [f] Determined by GPC. [g] Melting temperature determined by DSC (second heating run). [h] Not determined. [i] MAO treated with 125 equiv of 2,6-di-*tert*-butyl phenol for 1 h.

4−6) and the initial temperature of the reactions catalyzed by **2** was decreased to −2 (run 7) and −20 °C (run 8). Under the latter conditions, **2** gave a higher selectivity in even α-olefins (98%), but still mixtures of olefins and PE with traces of alkanes and odd olefins were obtained. Experiments in the C_2H_4 pressure range from 5 to 13 bar (runs 2, 9, 10) showed a linear dependence of activity with the pressure, while the Schulz−Flory α factor was independent of the pressure, indicating that the propagation and chain-transfer rates of the oligomerization reaction were first order in ethylene.[2a,b] A reaction with **2** was also performed with MAO previously treated with 2,6-di-*tert*-butyl phenol (run 11).[6] As a result, the production of alkanes and odd α-olefins decreased appreciably, while the catalytic activity of **2** did not significantly vary except for a slight decrease in the overall productivity, likely due to the diminished concentration of MAO.[6] GPC analysis of the solid materials obtained with both **2** and **3** showed very broad curves with bimodal character, characterized by two main different molecular weight populations. Samples obtained with **3** showed higher molecular weight values and lower polydispersity with respect to those obtained by using **2**. The melting points (132−134 °C) of the PE produced by **3** were slightly lower than those of typical HDPE (about 136 °C), which may be a consequence of the presence of several low molecular weight fractions. The lower molecular weight fractions were likely due to chain transfer to aluminum.[1b] In the case of samples obtained with **2**, the melting points (126−128 °C) were similar to those of low-density PE,[7] likely due to the presence of both low molecular weight PE fractions and the high molecular weight α-olefins with a Schulz−Flory distribution. Indeed, extraction of the latter with boiling acetone gave PE with melting points from 128 to 130 °C. All the samples showed a high crystallinity percentage and no branching was observed by ^{13}C NMR spectroscopy for the solid materials obtained with either **2** or **3**.

On the basis of all of these data as well as previous studies on the activation of metal halides by MAO and on the propagation and chain-transfer mechanisms of ethylene oligomerization/polymerization by [2,6-bis-(arylimino)pyridyl]iron precursors, we propose that the dual activity of the catalyst generated by **2** is just determined by the C_1 symmetry of this precursor. It is generally agreed that the propagation proceeds via Fe^{II}-alkyl species, which may be stabilized by *β*-agostic interactions (Scheme 1).[4] Due to the C_1 symmetry of the precursor **2** (a consequence of the hindered rotation of the tolyl group and the presence of four different donor atoms coordinated to iron),[8] two atropisomeric propagating alkyl species will form. Therefore, an incoming

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(5) The use of different catalysis procedures has allowed us to exclude any role, for either mass transfer or catalyst activation phenomena, in diversifying the activity of **2** (see Supporting Information).

(6) 2,6-Di-*tert*-butyl phenol reacts much faster with $AlMe_3$ than with MAO, and therefore it is used to minimize undesired effects caused by $AlMe_3$ contained in commercial MAO. See: Busico, V.; Cipullo, R.; Cutillo, F.; Friederichs, Nic.; Ronca, S.; Wang, B. *J. Am. Chem. Soc.* **2003**, *125*, 12402.

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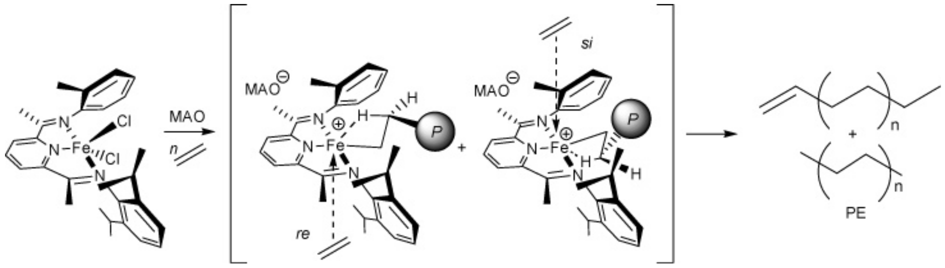
(8) Consistent with hindered rotation of the tolyl ring, the ^{1}H NMR spectrum of **2** shows four different signals for the *i*-Pr methyl groups (see Supporting Information).

Scheme 1



Scheme 2

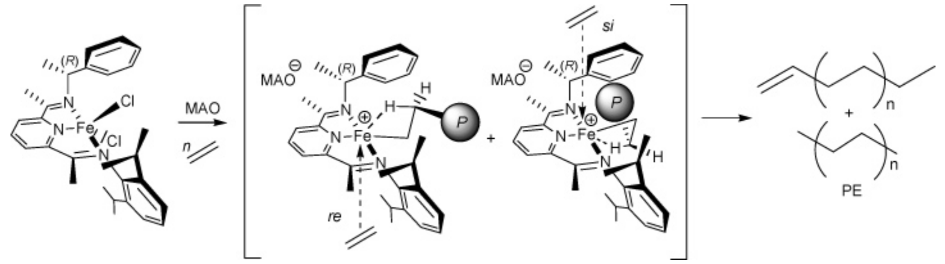
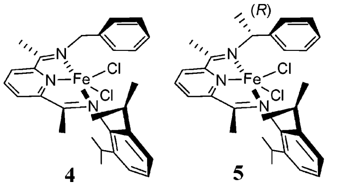


Chart 2



4 **5**

ethylene molecule will have two different faces (*re* and *si*) available at the metal for coordination and propagation (*back attack* at the Fe-alkyl).[4] The insertion through the *si* face is sterically comparable to that of [2,6-bis(arylimino)pyridyl]iron catalysts bearing two *ortho* substituents on each aryl ring,[1] for example **3**. Accordingly, the propagation rate would largely prevail over the chain-transfer rate, leading to PE production. In contrast, the insertion through the *re* face is sterically comparable to that of **1**, which gives only α-olefins, in fact.

In an attempt to provide further support to the symmetry-controlled mechanism proposed for **2**, the two $\mathrm{Fe^{II}}$ precursors **4** and **5** were synthesized (Chart 2). Complex **4** exhibits C_s symmetry by virtue of the freely rotating benzyl group, while complex **5** exhibits C_1 symmetry because of the presence of a stereogenic, stereohomogeneous carbon center.[3]

Under the same conditions of **1**−**3**, both **4** and **5** formed active catalysts for the conversion of ethylene. Again, the C_s-symmetric complex **4** gave exclusively α-olefins with a Schulz−Flory distribution (run 12), while the C_1-symmetric precursor **5** gave both α-olefins with a Schulz−Flory distribution and PE (run 13).[9] On activation of **5** by MAO, two diastereoisomeric propagating $\mathrm{Fe^{II}}$-alkyls are undoubtedly formed, which, as chemically distinct species, may have different kinetics of propagation and termination and therefore may give different products by reaction with the same substrate (Scheme 2).

In conclusion, we have shown for the first time that mixtures of high molecular weight α-olefins with a Schulz−Flory distribution and PE can be produced in one pot without making use of either reactor blending or multicomponent polymerization.[10] This finding may provide a new method for controlling the rheological and mechanical properties of polyolefins.

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Supporting Information Available: Text giving the synthesis and characterization of the ligands and of the $\mathrm{Fe^{II}}$ complexes **1**−**5** and text giving details of the oligomerization/polymerization procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] We have previously reported that **5** produces only oligomers with a TOF of 5.2×10^5 and an α value of 0.89.[3] Since we have no doubt that both PE and olefins with a Schulz−Flory distribution are obtained by applying the present experimental conditions, it may be concluded that the previous data are due to either different experimental conditions or, more likely, a wrong analytical procedure.

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