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Novel Catalytic System for Ethylene Oligomerization: An Iron(III) Complex with an Anionic N,N,N Ligand

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Supporting Information

ABSTRACT: We report a novel iron(III)-based catalytic system formed by the addition of an anionic N,N,N ligand to an iron(III) precursor. The complex has been characterized by FT-IR, mass spectrometry, and X-ray diffraction. This precatalyst proved to form a stable, active species for the selective oligomerization of ethylene. Up to 66 wt % of butenes was obtained with a selectivity of 98% in 1-butene.



inear α -olefins (LAOs) are of considerable importance in the Lchemical and petrochemical industries. They represent an expanding market with a total demand of 4.2 million tons in 2006. The demand for LAO is growing faster in the C_4-C_{10} range than in the C_{12} + range. Light LAOs (C_4 - C_8) are mainly used as comonomers in the copolymerization of ethylene to produce high-density polyethylene and linear low-density polyethylene. Whereas several processes lead from short $(C_4 - C_8)$ to full range (C_6-C_{30}) distributions in LAOs,¹ such as the Shell Higher Olefin Process (SHOP), the Gulftene process (Chevron-Phillips), the Ethyl process (Ineos), and the Idemitsu process, some processes are highly selective for 1-butene (Alphabutol²) or 1-hexene formation (Alphahexol^{1c} and Phillips³ processes). Although good iron catalysts for ethylene polymerization are known,⁴ the initial discoveries of Brookhart⁵ and Gibson⁶ triggered considerable interest in iron(II) complexes with neutral tridentate N,N,N ligands as precursors to highly active and selective catalysts for ethylene oligomerization.⁷ The exact mechanism of olefin polymerization/oligomerization and the determination of whether the active species formed by treatment of the catalyst precursor with methylaluminoxane (MAO) is an iron(II) or an iron(III) species remain under discussion.⁸ The few catalytic systems reported so far using iron(III) precursors led to good activities but modest selectivities for light $C_4 - C_{12}$ LAO (Schulz-Flory constant ca. 0.6).⁹ Mostly neutral tridentate N,N,N ligand-based systems have been reported, but a larger diversity of ligands is crucial if one wishes to optimize an ironbased oligomerization process. Anionic ligands associated with iron(II)^{85,10} or iron(III)¹¹ precursors have rarely been reported, and they afforded inactive or poorly active systems, suggesting that an electron-rich central donor group might be detrimental to catalytic activity.8b We disclose here a novel, well-defined

Scheme 1. Synthesis of the Iron(III) Complex 1



iron(III)-based catalytic system obtained by treatment of an anionic ligand with an iron(III) precursor. This remarkably stable catalyst precursor affords interesting selectivity in the oligomerization of ethylene to short-chain linear α -olefins.

Synthesis and Characterization of an Iron Complex Bearing 2-Methyl-2,4-bis(pyridin-2-yl)-1,2-dihydro-1,10-phenanthroline. Ligand L, previously reported by our group,¹² was unexpectedly obtained by the condensation of 2 equiv of 2-acetylpyridine with 1 equiv of 8-aminoquinoline. Ligand L was deprotonated with *n*-BuLi, and an in situ reaction with an equimolar THF solution of FeCl₃ afforded the iron(III) complex 1 in excellent yield (>95%) (Scheme 1).

This complex shows good stability in the solid state and in solution, and crystals suitable for X-ray diffraction were grown by diffusion of pentane into a chlorobenzene solution under an inert atmosphere at room temperature (Figure 1). The shift of the $\nu_{C=N}$ absorption band of the imino group to lower wavenumbers in the FT-IR spectrum, which becomes weaker in comparison with that of the free ligand (1630 to 1603 cm⁻¹, see the

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Figure 1. ORTEP of the iron(III) complex 1 in $1 \cdot C_6H_5Cl$ (H omitted for clarity). Selected bond lengths (Å) and angles (deg): Fe(1)-N(1) = 2.167(3), Fe(1)-Cl(1) = 2.2588(9), Fe(1)-N(2) = 1.950(2), Fe(1)-Cl(2) = 2.2399(8), Fe(1)-N(3) = 2.158(3); N(1)-Fe(1)-N(3) = 148.56(9), N(1)-Fe(1)-Cl(1) = 93.55(7), N(1)-Fe(1)-N(2) = 77.42(10), N(3)-Fe(1)-Cl(1) = 97.25(7), N(1)-Fe(1)-Cl(2) = 104.75(7), N(2)-Fe(1)-Cl(1) = 141.27(8), N(3)-Fe(1)-Cl(2) = 99.95(7), Cl(2)-Fe(1)-Cl(1) = 107.60(3), N(2)-Fe(1)-Cl(2) = 111.12(8).

Supporting Information),^{7d,9a} confirms the effective coordination of the anionic ligand on the iron center. The disappearance of the N–H band of the free ligand at 3386 cm⁻¹ after deprotonation and complexation to the iron(III) precursor support the anionic character of the ligand. In 1, the metal is pentacoordinated with a pseudo-square-pyramidal coordination geometry (Figure 1). The methyl (C13) and the uncoordinated pyridyl groups are almost perpendicular to the plane defined by the iron atom and the three coordinated nitrogen atoms (N1, N2, and N3). The metrical parameters confirm the +III oxidation state of the metal, the short Fe–N2 bond distance of 1.950(2) Å being indicative of a covalent bond.^{8b,13} The molecular formula is confirmed by ESI-FT/MS with the exact mass measurement of the M^{•+} ion (mass accuracy 0.04 ppm; see the Supporting Information).

Ethylene Oligomerization by Iron(III) Catalyst. The optimized procedure for conducting the ethylene oligomerization experiments is to add the MAO as activator at room temperature under ethylene to the reactor containing the complex solution. No exotherm was observed at a precatalyst concentration of 0.4 mM. Then the temperature was increased to 80 °C with an adjustment to the desired pressure (30 bar; see the Supporting Information). The precatalyst 1 shows a good and stable activity in the presence of MAO at the molar ratio Al/Fe = 200 (Table 1, entry 1). Ethylene consumption was steady over 2 h with an activity of 2.16×10^5 g of products (mol of Fe)⁻¹ h⁻¹. Shortchain oligomers were obtained, up to 63 wt % of butenes with a selectivity in 1-butene of >97 wt % (Table 1, entry 1). Increasing the MAO concentration to reach the ratio AI/Fe = 500 led to a similar activity and a slight increase in polymer formation (14 wt %, Table 1, entry 2). With the alkylating agent trimethylaluminum (TMA) and diethylaluminum chloride (DEAC), tested at the ratio Al/Fe = 200, no consumption of ethylene was observed. Thus, MAO is crucial for activating the precatalyst. When additional TMA was used with MAO in the molar ratio MAO/ TMA/Fe = 200/20/1, the activity slightly decreased and up to 66 wt % of butenes was produced with a fraction of 1-butene of >98 wt %.

Table 1. Iron-Catalyzed Oligomerization of Ethylene^a

				oligomer distribn ^{c,d}			
	entry	cocatalyst (amt, equiv)	$activity^b$	$C_4 (1-C_4)^e$	$C_6 (1-C_6)^e$	C ₈₊ ^f	PE
	1	MAO (200)	2.16	63 (>97)	18 (>90)	7	12
	2	MAO (500)	2.13	61 (>95)	19 (>87)	6	14
	3	MAO/TMA (200/20)	1.34	66 (>98)	16 (>93)	7	12
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^{*a*} Reaction conditions: toluene (50 mL), Fe (20 μ mol), ethylene pressure 30 bar, 80 °C, reaction time 2 h. ^{*b*} In units of 10⁵ g of products (mol of Fe)⁻¹ h⁻¹ estimated over the steady period of ethylene consumption. ^{*c*} Determined by GC. ^{*d*} In units of wt % among all the products formed. ^{*e*} In units of wt % in the C_n fraction. ^{*f*} Fraction C₈ and higher oligomers.

Scheme 2. Iron Complexes Tested in Ethylene Oligomerization



For comparison, other iron(II) or iron(III) complexes bearing the dihydro-1,10-phenanthroline ligand (in 2 and 3), or its deprotonated form (in 4), have been evaluated (Scheme 2), but none of them displayed activity toward ethylene oligomerization. These results reveal that for the ligand family studied both the anionic character of the ligand (complexes 2 and 3 vs complex 1) and the +III oxidation state of the metal center (complexes 2 and 4 vs complex 1) are key parameters for obtaining an active catalyst.

In the course of our investigations on the synthesis of 1, we obtained some dark violet crystals by slow diffusion of Et₂O into a MeCN solution of the reaction mixture. An X-ray diffraction analysis revealed for $5 \cdot \text{Et}_2 O$ the unexpected structure shown in Figure 2. Two oxo bridges connect two dinuclear units which result from a C–C coupling reaction between two phenanthroline moieties at the para position of their central ring. Each Fe(III) metal center carries a terminal chloride ligand and is pentacoordinated. A symmetry axis passing through the oxygen atoms relates the halves of the molecule (for details, see the Supporting Information). Although the quantity of crystals obtained was too low to perform the usual analyses and the experimental conditions required to obtain this complex are not yet clearly identified, we believe that its structure deserves attention and conveys an important caveat about the importance of carefully establishing the nature and structure of complexes used as precatalysts.

In conclusion, we have presented here the first catalytic system with a fully characterized iron(III) precursor bearing an anionic nitrogen donor ligand for the highly selective oligomerization of ethylene to short-chain oligomers (C_4-C_6). The catalyst exhibits high activity (up to 2.16×10^5 g (mol of Fe)⁻¹ h⁻¹) and high stability with time, and it requires only a modest amount of MAO (Al/Fe = 200). Up to 66 wt % of butenes was obtained with a selectivity of >98 wt % in 1-butene. The synergistic influence of



Figure 2. View of the structure of complex 5 in $5 \cdot \text{Et}_2\text{O}$ (H omitted for clarity). Selected bond distances (Å) and angles (deg): Fe(1)-O(1) = 1.780(3), Fe(2)-O(1) = 1.787(3), Fe(1)-N(2) = 1.978(3), Fe(2)-N(5) = 1.968(3), Fe(1)-N(1) = 2.178(3), Fe(2)-N(4) = 2.187(4), Fe(1)-N(3) = 2.180(3), Fe(2)-N(6) = 2.194(3), Fe(1)-Cl(1) = 2.2496(14), Fe(2)-Cl(2) = 2.2489(14); Fe(1)-O(1)-Fe(2) = 139.27(16).

the anionic character of the ligand and the +III oxidation state of the iron precursor on the catalytic activity have been established. We are currently optimizing such systems and investigating the potential of other iron(III) complexes bearing anionic ligands for the catalytic oligomerization of ethylene.

ASSOCIATED CONTENT

Supporting Information. Text, figures, and tables giving general considerations, complex syntheses, IR spectra of the iron(III) complexes 1-5, mass spectra analyses, the ethylene oligomerization procedure, and details concerning 5 and CIF files giving the crystal structures of 1 and 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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