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Iron Complexes for Oligomerization of Hexene

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ABSTRACT

Chelating ligands: $RHN(CH_2)_3NHR$ (R = 2, 6-$^iPr_2C_6H_3$) and $RHN(CH_3)C{=}C(CH_3)C{=}NR$ (R = 2, 6-$^iPr_2C_6H_3$), were prepared and reacted with $FeCl_3$ to give the iron complexes. The ligands and iron complexes were characterized by FTIR, NMR and elemental analysis. When activated by either methylalumoxane (MAO) or triisobutylaluminum (TIBA) in combination with perfluorophenylborate $Ph_3CB(C_6F_5)_4$, the iron complexes exhibit activity for oligomerization of hexene, producing oligomers with a Mw of 1,358-2,323, a Mn of 1334-2293 and a narrow molecular weight distribution (Mw/Mn of 1.01). The activities using MAO are higher than boron cocatalyst.

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INTRODUCTION

The use of olefin oligomers as intermediates for specialty chemicals drives the interest in the catalytic oligomerization. Low-carbon linear α-olefins are used primarily as comonomers for the production of linear low-density polyethylene, plasticizers and synthetic lubricants. Currently, much effort is devoted towards the development of more efficient oligomerization of alkenes by early and late transition metal catalysts (Wang, *et al.* 2000; and Mingxing, *et al.* 2000). A new family of catalysts based on iron and cobalt complexes containing pyridine bisimine ligands has been found to be very active towards ethylene polymerization (Britovsek, *et al.* 1999). Ethylene oligomers are well established and nickel chelate complexes used in the SHELL-higher-olefin process (SHOP) feature prominently in their manufacturing (Britovsek, *et al.* 1998; and Koppl, *et al.* 2000). A series of zirconocenes was used for the oligomerization of 1-hexene and used combination methods to elucidate chain-termination mechanism (Janiak, *et al.* 2002). The chain termination reaction gives oligomers with most double-bond end groups, with which a functionalization reaction is possible leading to organic specialities with possible applications as blend compatibilizers, additives for fuels or in the paper industry.

EXPERIMENTAL

Materials

All reactions were carried out by using standard Schlenk techniques under an atmosphere of nitrogen. Toluene was dried and deoxygenated by distillation under nitrogen. The other chemicals were purchased commercially and used without further purification. Fe(II)(salen) (salen = N,N'-ethylene bis(salicylidene-aminato) was prepared from ferrous ammonium sulfate according to the literature (Marvel, *et al.* 1956).

Analytical methods

Fourier transformed infrared spectra were recorded on the Nicolet FT-IR Impact 410 FT-IR Spectrometer. NMR spectra were obtained in a $CDCl_3$ solution on a 200 MHz Bruker ACF 200. Broad-band decoupling was used to remove the ^{13}C-^{1}H coupling. Chemical shifts are given in ppm. Melting points were measured using electrothermal apparatus. Elemental analyses were carried out on a Perkin Elmer Elemental Analyser 2400 CHN analyzer. Matrix-assisted laser desorption ionization–time of flight mass spectrometry (MALDI-TOF MS), Biflex, Bruker, was used to determine molecular weight and molecular weight distribution of the oligomers. The matrix was dithranol, the cationizing agent silver trifluoroacetate. The ratio of polymer:matrix:cation = 1:2:1.

Synthesis of ligands

Ligand A: 1,3-Di(2,6-diisopropylphenyl) aminopropane, $RHN(CH_2)_3NHR$ ($R=2,6\text{-}^{i}Pr_2C_6H_3$).

n-BuLi (15% in hexane, 35 mL, 57 mmol) was added dropwise to a stirring solution of 2,6-diisopropylaniline (9.5 mL, 50 mmol) in THF (40 mL) at –78°C. The solution was warmed to room temperature and stirred for 30 minutes. Then it was cooled to 0°C and tetramethylethylenediamine (tmeda) (7.5 mL, 50 mmol) was added dropwise followed by 1,3-dibromopropane (2.5 mL, 25 mmol). After being stirred overnight at room temperature, the solution was poured into water (30 mL) and extracted with dichloromethane. The organic layer was dried (Na_2SO_4) and solvent was removed, the obtained orange oil was purified by column chromatography, eluting with dichloromethane:hexane (7:3) to give ligand **A** (8.69 g, 88 %). **^{1}H-NMR (C_6D_6):** δ 7.12 (m, 6H), 3.37 (sept, 4H), 3.02 (t, 4H), 2.67 (t, 2H), 1.77 (t, 2H), 1.26 (d, 24H). **^{13}C{H}-NMR ($CDCl_3$):** δ 143.5, 142.4, 123.6, 50.3, 32.4, 27.8, 24.4. **FTIR (NaCl):** 3371, 3050, 2950, 2865, 1621, 1451, 1362, 1254, 1103, 798, 753 cm^{-1}.

Ligand B: 1-{(2,6-Diisopropylphenyl)amino}-4-{(2,6-diisopropyl phenyl)imino}-2-pentene ; $RHN(CH_3)C{=}C(CH_3)C{=}NR$ (R = 2,6-$^iPr_2C_6H_3$).

Concentrated hydrochloric acid (0.04 mL, 4.8 mmol) was added to a solution of 2,4-pentanedione (0.50 mL, 4.9 mmol) and 2,6-diisopropylaniline (2.1 mL, 11 mmol) in ethanol (20 mL). The reaction mixture was heated at reflux for 3 days and concentrated. The crude brown product was extracted with dichloro-methane. After stirring with saturated solution of K_2CO_3 (20 mL), the organic layer was separated. Evaporation of solvent and recrystallization from methanol afforded the ligand **B** as a white crystalline solid (0.95 g, 46 %). **^{1}H-NMR ($CDCl_3$): δ** 12.09 (br, 1H), 7.10 (m, 6H), 4.84 (s, 1H), 3.09 (m, 4H), 1.69 (s, 6H), 1.20 (d, 12H), 1.12 (d, 12H). **FTIR (KBr):** 3381, 2959, 2880, 1625, 1550, 1442, 1376, 1277, 753 cm^{-1}; **mp** = 140-141°C.

Synthesis of iron complexes

Cat 1A: $[RHN(CH_2)_3NHR]FeCl_3$ (R = 2,6-$^iPrC_6H_3$).

A solution of ligand **A** (3.60 g, 14.2 mmol) in 25 mL of acetonitrile was added to anhydrous $FeCl_3$ (2.23 g, 13.7 mmol). The mixture was refluxed for 4 hours. The red powder was separated by filtration. The dark red filtrate was pumped off the solvent and added to diethyl ether to precipitate the dark red solids, **Cat 1A** (2.7454 g, 36 %). **FTIR (KBr):** 3409, 2968, 1574, 1461, 1367, 1051, 805 cm^{-1}. **Anal:** Calc for **$C_{27}H_{42}N_2FeCl_3$;** C, 58.23; H, 7.60; N, 5.03; Fe, 10.04. Found: C, 58.19; H, 8.26; N, 5.06; Fe, 9.70.

Cat 2B: $[RHN(CH_3)C{=}C(CH_3)C{=}NR]FeCl_3$ (R = 2,6-$^iPrC_6H_3$).

$FeCl_3$ 0.12 g (0.73 mmol) was added to a solution of ligand **B** (0.28 g, 0.66 mmol) in 20 mL of dichloromethane. The mixture was refluxed for 4 hours and stirred at room temperature overnight. The crude red solid was obtained after pumping off solvent. Chloroform (10 mL) was added to dissolve the solid. After filtration, yellow filtrate was evaporated off the solvent to obtain an orange solid, **Cat 2B** (0.0985 g, 26 %). **FTIR (KBr):** 3428, 2970, 2809, 1503, 1428, 1296, 1103, 1037, 798 cm^{-1}. **Anal:** Calc for $C_{29}H_{42}N_2FeCl_3.CH_2Cl_2$ C, 54.11; H, 6.61; N, 4.21; Fe, 8.39. Found: C, 54.27; H, 6.37; N, 4.40; Fe, 8.70.

Oligomerization of Hexene

In a Schlenk flask, iron complex solution (in toluene) was mixed with methylaluminoxane (MAO) and stirred for 1 hour. At the desired temperature, hexene monomer (5 mL, 40 mmol) was injected. The reaction was terminated by adding 5% aqueous hydrochloric acid. The organic layer was separated, dried (Na_2SO_4) and evacuated to remove solvent and unreacted hexene.

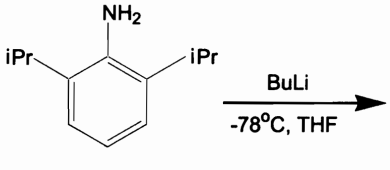
The above reaction of hexene was performed but replacing MAO cocatalyst with $Al^iBu_3/[Ph_3C][B(C_6F_5)_4]$, first various equivalents of triisobutyl-aluminum (Al^iBu_3) which acts as an alkylating agent was premixed with an iron complex solution in toluene and stirred at room temperature for 1 hour. Then one equivalent of boron compound, $[Ph_3C][B(C_6F_5)_4]$ in toluene solution was added and stirred for another hour at the desired temperature. The reaction was terminated as above.

In both cases, the experiment was repeated to ensure the reproducibility and the average of two runs were taken. The residues after solvent evaporation were analyzed by NMR, FTIR and MALDI-TOF MS. ^{13}C NMR: δ 42, 35, 34, 29, 23 and 14 ppm, FTIR: 2959, 2921, 2856, 1461, 1376, 1263, 1098, 1028, 800 and 725 cm^{-1}, MALDI-TOF MS: For the reaction using MAO cocatalyst, Mw 2323 Mn 2293 Mw/Mn 1.01, m/z 1800-3900; for the reaction using $[Ph_3C][B(C_6F_5)_4]$ cocatalyst, Mw 1358 Mn 1334 Mw/Mn 1.02, m/z 1100-2000.

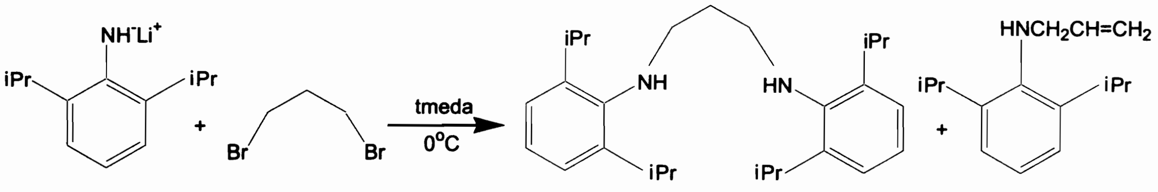
RESULTS AND DISCUSSION

Synthesis of ligands and iron complexes

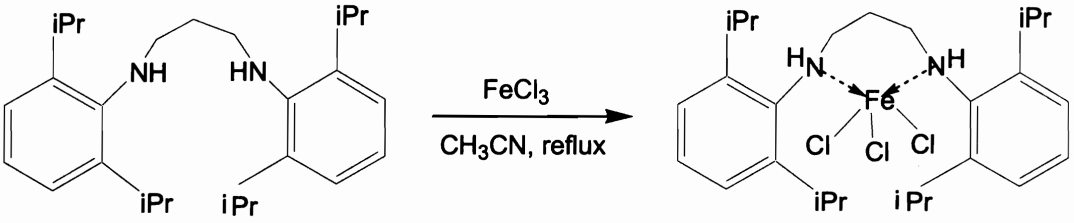
Ligand **A** was synthesized with a method modified from that in the literature Scollard, *et al.* (1998) syntheses of this ligand and titanium complex). 2,6-diisopropylaniline was lithiated with BuLi at –78°C to afford LiNHR. Then two equivalents of LiNHR were reacted with 1,3-dibromopropane. The elimination product $RHNCH_2CH=CH_2$ also occurred therefore tetramethylethylenediamine (tmeda) was needed to suppress this reaction. Ligand A was characterized spectroscopically, the results agree with those in the literature. The reaction of ligand **A** with $FeCl_3$ in refluxing acetonitrile afforded **Cat 1A** as dark red solids. The FTIR spectrum showed a peak of N-H stretching at 3409 cm.$^{-1}$, which revealed the presence of hydrogen at the amine groups. C=C Stretching appears at 1574 cm^{-1}, and C-N stretching at 1051 cm^{-1}. The elemental analysis result also confirmed the proposed structure below.



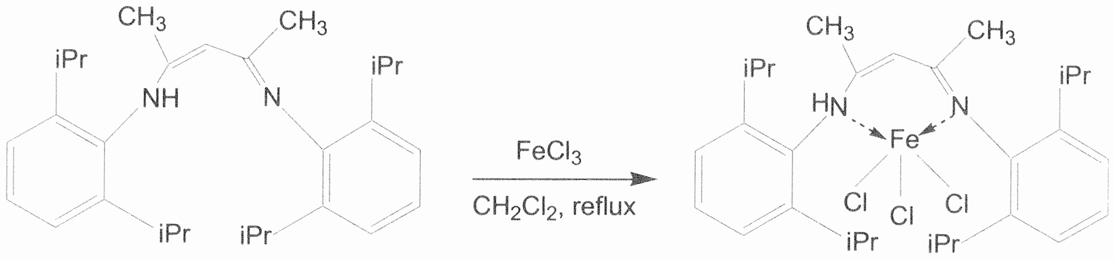
2,6-didisopropylaniline



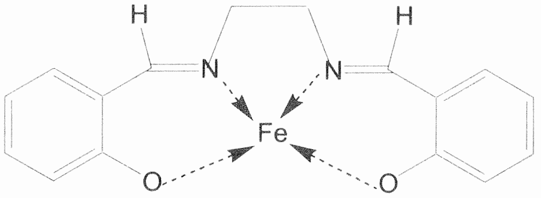
1,3-dibromopropane



Ligand **B** was prepared from the condensation of two equivalents of 2,6-diisopropylaniline with one equivalent of acetylacetone. Hydrochloric acid was added as a catalyst in the reaction. The treatment of one equivalent of $FeCl_3$ with one equivalent of ligand **B** in refluxing dichloromethane afforded **Cat 2B**. The structure of this complex was proposed according to FTIR and elemental analysis results. FTIR shows C=C stretching at 1503 and C-N stretching at 1296 cm^{-1}.



The structure of Fe(salen) was shown below.



Oligomerization of Hexene

The activities of three different complexes: **Cat 1A**, **Cat 2B** and Fe(salen) in the oligomerization of hexene were investigated using either MAO or $Al^iBu_3/[Ph_3C][B(C_6F_5)_4]$ as a cocatalyst. The results were summarized in Table 1 and Table 2.

Table 1 Oligomerization of hexene catalyzed by iron complexes/MAO.

Entry	Complex	Al/Fe mole ratio	T_p (°C)	Activity (kg polymer/mol Fe)
1	**Cat 1A**	1000	0	0
2	**Cat 1A**	500	30	2
3	**Cat 1A**	1000	30	14
4	**Cat 1A**	2000	30	15
5	**Cat 1A**	1000	50	23
6	**Cat 2B**	1000	50	22
7	Fe(salen)	1000	50	0

Reaction conditions: catalyst 10×10^{-6} mmol, 1-hexene 40 mmol, t 10 h.

From the results in Table 1, much excess amount (1000 times) of MAO is required since it helps to stabilize the cation active species and also acts as an impurity scavenger (Frauenrath, *et al.*1999). It was found that a higher temperature increases the activity as the reaction rate is increased.

In this catalytic system using MAO as a cocatalyst, **Cat 1A** and **Cat 2B** were shown to be active for oligomerization of hexene, while Fe(salen) was inactive.

Table 2 Oligomerization of 1-hexene catalyzed by iron complexes/Al^iBu_3/$[Ph_3C][B(C_6F_5)_4]$.

Entry	Complex	Al/Fe mole ratio	T_p (^oC)	Activity (kg polymer/ mol Fe)
1	**Cat 1A**	100	-20	0
2	**Cat 1A**	200	-20	11
3	**Cat 1A**	200	0	13
4	**Cat 1A**	400	0	15
5	**Cat 1A**	200	30	8
6	**Cat 2B**	200	30	4
7	Fe(salen)	200	30	0

Reaction conditions: catalyst $10x10^{-6}$ mmol, 1-hexene 40 mmol, t 10 h.

For the catalytic system using a boron cocatalyst, after alkylating the complex with Al^iBu_3 and activation with $[Ph_3C][B(C_6F_5)_4]$, **Cat 1A** and **Cat 2B** were found to be active in hexene oligomerization, Fe(salen) was inactive.

In order to enhance the activity, the effects of Al/Fe ratio and temperature on hexene oligomerization reaction was investigated. The catalytic activity was enhanced as the ratio of Al/Fe was increased from 100 to 400. Al^iBu_3 functions as an alkylating agent as well as a scavenger. Generally, a threshold amount of this aluminum compound was needed to effectively activate the precatalyst. For the boron cocatalyst, it was found that the reaction at lower temperature gave higher activity, this is consistent with the results from metallocene catalysts (Chien, *et al.* 1993). A difference between the oligomerization behaviors of the iron catalyst system using MAO and boron cocatalysts is that the activity of the former increases with the increase of temperature while the latter has the opposite dependence.

Cat 1A and **Cat 2B** not only possess a different ligand environment from Fe(salen), but the latter is also based on Fe(II) and without chloride, while the two former complexes are Fe(III) with three ancillary chlorides. The polymerization tests reveal different activities, this might indicate that the structure and chelating system may be related to the catalytic activity. However, it should be noted that some Fe(II) complexes and Fe(salen) in combination with ethylaluminoxane were reported to catalyze ethylene oligomerization (Mingxing, *et al.* 2000). This result shows the first time of using iron (III) complex with this diamide ligand to catalyze the oligomerization of hexene.

Characterization of the oligomeric product

Cat 1A and **Cat 2B** catalyze the oligomerization of hexene under mild conditions. The viscous liquid products obtained were characterized by FTIR, NMR and MALDI-TOF MS. The ^{13}C NMR spectrum (Figure 1) showed that the structure of the hexene oligomer matched with the atactic form (Warren, *et al.* 1998).

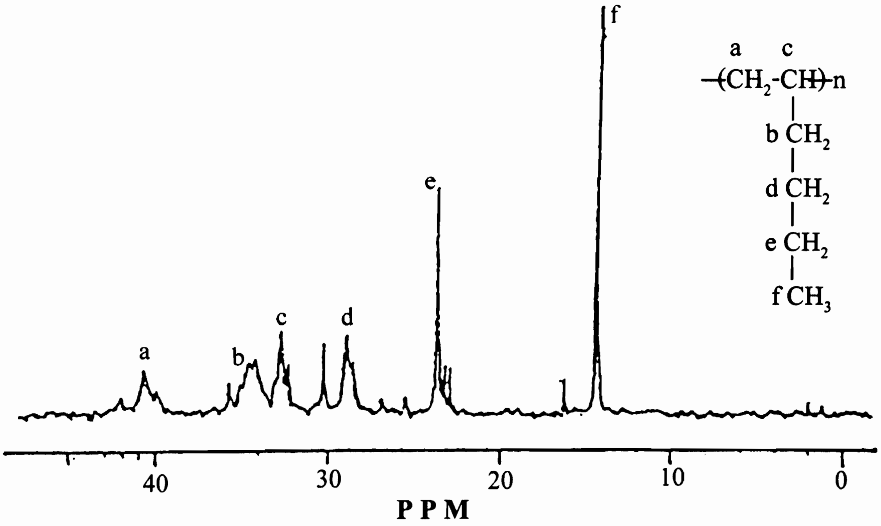


Figure 1 ^{13}C NMR spectrum of atactic hexene oligomer.

In FTIR spectra, there are two kinds of C=C stretching vibrations, a relatively strong vibration at 1461 cm^{-1} corresponding to vinylidene end groups and a strong one at 1376 cm^{-1} corresponding to internal double bonds. These results correspond to end groups resulting from β-H elimination following hexene insertions.

The MALDI-TOF MS offers the possibility to determine the molecular weight and molecular weight distribution of the oligomers. Polyolefins are in principle not susceptible to this technique, the reason that the oligomers promised a potential for analysis was because of their double bond end-group functionality. The results from MALDI-TOF MS reveal a low molecular weight oligomer of hexene. For the MAO system, Mw, Mn and molecular weight distribution of the oligomer obtained from **Cat 1A** (entry 5, Table 1) are of 2323, 2293 and 1.01, respectively; whereas those from **Cat 2B** (entry 6, Table 1) are of 2240, 2108 and 1.06, respectively. For the $Al^iBu_3/[Ph_3C][B(C_6F_5)_4]$ system, they are 1358, 1334 and 1.02, respectively, from **Cat 1A** (entry 4, Table 2); 1098, 1045 and 1.05, respectively, from **Cat 2B** (entry 6, Table 2). The monomer units in the oligomers can be calculated to be around 13-28. For comparison, the molecular weight, Mn of oligohexene using size exclusion chromatography (SEC) obtained with zirconocene/MAO is 350 with a molecular weight distribution of 1.5 (condition: 50 C, Al/Zr = 1000, t = 1 h, catalyst concentration 7.1×10^{-5} M) (Janiak, *et al.* 2002)

CONCLUSIONS

The iron (III) complexes reported herein, **Cat 1A** and **Cat 2B**, when activated with either the MAO or $Al^iBu_3/[Ph_3C][B(C_6F_5)_4]$ system displayed activity in the oligomerization of hexene. The catalytic activities depended on reaction temperature and Al/Fe ratios. The activity of **Cat 1A** is higher than that of **Cat 2B**, while the iron (II) complex, Fe(salen) is inactive. The different structures of the complexes seem to have influence on their catalytic activity, for example, the chelating system. From spectroscopic data, the chain termination reaction gives oligomers with mostly double-bond end groups, predominantly of the vinylidene type. Even though the activity obtained from this work is not high, but the potential for using iron, which has a low cost and is readily available is attractive.

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