Ethylene Polymerization Catalyzed by Ruthenium and Iron Complexes Containing 2,6-Bis(2-oxazolin-2-yl)pyridine (Pybox) Ligand-Cocatalyst System

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RuX_2(ethylene)(pybox) [X = Cl (**1**), I (**2**), and CF_3SO_3 (**3**); pybox = 2,6-bis[(4*S*)-4-isopropyl-2-oxazolin-2-yl]-pyridine] complexes have exhibited moderate catalytic activity for ethylene homopolymerization and ethylene/1-hexene copolymerization in the presence of MAO. The incorporation of 1-hexene (27.2 mol%) in the resultant copolymer was confirmed by ^{13}C NMR spectrum. The resonances corresponding to the triad sequence of HHH were negligible. A small $r_E \cdot r_H$ value of 0.32, where r_E and r_H are the monomer reactivity ratios of ethylene and 1-hexene, respectively, was thus obtained, indicating a significantly alternating tendency. $FeCl_2$(pybox) (**4**) has also exhibited the activity for ethylene polymerization in the presence of MAO. The attempted copolymerization of ethylene with 1-hexene by **4** gave linear polyethylene without incorporating 1-hexene.

Olefin polymerization by homogeneous catalysis has been one of the most attractive subjects in the fields of both organometallic chemistry and catalysis. There are thus many reports concerning this topic using group 4B transition metal complexes such as metallocene analogues,[1] hybrid 'half-metallocene' analogues,[2] nonbridged 'half-metallocene' analogues,[3] and others.[4—7] In addition, since efficient nickel,[8] palladium-,[8] cobalt-,[9,10] and iron-based[10] catalysts have been reported recently, the topic with late transition metal complexes has thus attracted particular attention.

A large number of useful reactions have been developed recently using both stoichiometric and catalytic amounts of ruthenium complexes. The reason for this can be understood as follows: Ruthenium complexes have a variety of useful characteristics including high electron transfer ability, high Lewis acidity, low redox potentials, and stabilities of reactive metallic species such as oxometals, metallacycles, and metal carbene complexes, as was recently reviewed by Murahashi et al.[11] We also reported that ruthenium catalyze chemoselective reduction of aromatic nitro compounds under CO/H_2O conditions.[12]

From such a research background, our ongoing project recently is thus to find an efficient ruthenium catalyst for precise olefin polymerization. We have already introduced in our preliminary communication that $RuCl_2$(ethylene)(pybox) (pybox = 2,6-bis[(4*S*)-4-isopropyl-2-oxazolin-2-yl]pyridine) exhibited moderate catalytic activity for ethylene polymerization as well as for ethylene/1-hexene copolymerization.[13] In this paper, we wish to introduce more details concerning this catalysis. In addition, since incorporation of 1-hexene could be confirmed in the ethylene/1-hexene copolymerization which should be an interesting contrast to the previous result by iron catalyst containing 2,6-bis(imino)pyridine ligand,[10] we thus prepared the iron analogue, $FeCl_2$(pybox), and explored the polymerization in the presence of cocatalyst to clarify the reasons for this difference.

Experimental

General Procedure. All experiments were carried out under nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were reagent grade and were purified by the standard purification procedures. Toluene, hexane and heptane for polymerization were distilled in the presence of Na and benzophenone under nitrogen atmosphere, and were stored in a Schlenk tube under N_2.

$RuCl_2$(ethylene)(pybox) (**1**), which can be prepared by the treatment of $[RuCl_2(p\text{-cymene})]_2$ complex[14] with 2,6-bis[(4*S*)-4-isopropyl-2-oxazolin-2-yl]pyridine (pybox) in CH_2Cl_2 under ethylene atmosphere, was prepared according to the previous report by Nishiyama et al.[15] Pybox was purchased from Aldrich, and was used as received.

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^1H). All deuterated NMR solvents were stored over molecular sieves under nitrogen atmosphere. All chemical shifts are given in ppm and are referenced to Me_4Si. All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. ^{13}C NMR spectra for polyethylene and poly(ethylene-*co*-1-hexene) were recorded on JEOL JNM-LA400 spectrometer (100.40 MHz, ^{13}C) with proton decoupling at 130 °C (polyethylene) or 50 °C [poly(ethylene-*co*-1-hexene)]. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was 10000. The polymer solutions were prepared by dissolving polymers in *o*-dichlorobenzene-d_4.

Molecular weight and molecular weight distribution of the resul-

tant polymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with polystyrene gel column (TSK gel GMHHR-H(20)HT×3) at 145 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*t*-butyl-*p*-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

Synthesis of RuI_2(ethylene)(pybox) (2), and $Ru(CF_3SO_3)_2$ (ethylene)(pybox) (3). Into a cold CH_2Cl_2 solution (30 mL) containing $[RuI_2(p\text{-cymene})]_2$ (624 mg, 0.638 mmol) complex[14] under ethylene atmosphere (1 atm), 2,6-bis[(4*S*)-4-isopropyl-2-oxazolin-2-yl]pyridine (384 mg, 1.274 mmol) in CH_2Cl_2 (10 mL) was added slowly at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, and then was warmed slowly to room temperature. The resultant deep purple solution was further stirred for 2 h at r.t., and was then filtered through a Celite pad in a drybox. The filtrate was concentrated in vacuo to 15 mL, and hexane (ca. 30 mL) was then added to the resultant solution. The flask containing mixed CH_2Cl_2–hexane solution was placed in the freezer (−30 °C). Deep purple microcrystals were collected, washed quickly with chilled ether/hexane (1/1 vol%) and then dried in vacuo. Yield 758 mg (90.5%). ^{1}H NMR ($CDCl_3$) δ = 0.88 (d, J = 6.6 Hz, 6H), 1.02 (d, J = 7.1 Hz, 6H), 2.53 (m, 2H), 4.36 (m, 2H), 4.78 (t, J = 9.1 Hz, 2H), 4.90 (m, 2H), 5.13 (m, 2H, ethylene), 5.55 (m, 2H, ethylene), 7.89 (s, 3H). ^{13}C NMR ($CDCl_3$) δ = 15.2, 19.4, 29.3, 66.1, 71.1, 72.2, 123.4, 133.5, 145.9, 163.7.

$Ru(CF_3SO_3)_2$(ethylene)(pybox) (**3**) could also be prepared by a similar procedure from $[Ru(CF_3SO_3)_2(p\text{-cymene})]_2$ that was prepared from $[RuCl_2(p\text{-cymene})]_2$ by the treatment of CF_3SO_3Ag in CH_2Cl_2. Yield 75.0% (932 mg). ^{1}H NMR ($CDCl_3$) δ = 0.66 (d, J = 6.6 Hz, 6H), 1.06 (d, J = 7.1 Hz, 6H), 2.21 (m, 2H), 4.63 (m, 2H), 5.00 (m, 2H), 5.45 (m, 2H, ethylene), 5.53 (m, 2H, ethylene), 8.11 (m, 3H). ^{13}C NMR ($CDCl_3$) δ = 13.8, 19.2, 29.9, 70.8, 72.3, 72.9, 116.2 (q, CF_3, $^1J_{C-F}$ = 318 Hz), 124.7, 137.4, 149.0, 166.9.

Synthesis of $FeCl_2$(pybox) (4). Into a cold CH_2Cl_2 solution (20 mL) containing anhydrous $FeCl_2$ (50 mg, 0.394 mmol) under nitrogen atmosphere (1 atm), 2,6-bis[(4*S*)-4-isopropyl-2-oxazolin-2-yl]pyridine (120 mg, 0.398 mmol) in CH_2Cl_2 (5 mL) was added slowly at 0 °C. The reaction mixture was warmed slowly to room temperature, and then stirred overnight. The resultant deep purple solution was then filtered through a Celite pad in the drybox. The filtrate was concentrated, and Et_2O was then added into the solution. The flask containing mixed CH_2Cl_2–Et_2O solution (1/2 vol%) was placed in the freezer (−30 °C). Purple microcrystals were collected, washed quickly with chilled ether/hexane (1/1 vol%) and then dried in vacuo. Yield 130 mg (76.5%). ^{1}H NMR ($CDCl_3$) δ = −4.93 ($\Delta_{1/2}$ = 64 Hz), −2.74 ($\Delta_{1/2}$ = 29 Hz), −1.57 ($\Delta_{1/2}$ = 32 Hz), 0.88 (br.s), 1.26 (br.s), 9.37 ($\Delta_{1/2}$ = 27 Hz), 11.05 ($\Delta_{1/2}$ = 56 Hz), 12.95 ($\Delta_{1/2}$ = 96 Hz). Anal. Calcd for $C_{17}H_{25}Cl_2FeN_3O_2$: C, 47.46; H, 5.86; N, 9.77%. Found (1): C, 47.65; H, 5.30; N, 9.77%. Found (2): C, 47.21; H, 5.31; N, 9.60%.

Polymerization Procedures. Ethylene polymerizations were conducted in a 100 mL scale stainless steel autoclave. The typical reaction procedure (Run 3, Table 1) is as follows. **1** (50 μmol) and MAO solid (1450 mg, prepared from ordinary MAO (Tosoh Akzo Co. PMAO-S) by removing toluene and $AlMe_3$) were added into the autoclave in the drybox, and the reaction apparatus was then filled with ethylene (1 atm) at room temperature. Hexane (30 mL) was then added into the autoclave, and the apparatus was then placed into an oil bath preheated at 50 °C. The autoclave was immediately pressurized to 6 atm, and the reaction mixture was magnetically stirred for 1 h. After the above procedure, the autoclave was placed in an ice bath (0 °C), and any ethylene which remained was removed. The reaction mixture was then poured into EtOH (50 mL) containing HCl (5 mL). The resultant polymer (white precipitate) was carefully collected on a filter paper by filtration, and was adequately washed with EtOH and water, then dried in vacuo for several hours. Copolymerization of ethylene with 1-hexene was performed in the same manner of that for ethylene polymerization except that 1-hexene (3 mL) was added into the autoclave in advance.

Table 1. Ethylene Polymerization by $RuCl_2$(ethylene)(pybox) (**1**)-Cocatalyst System[a]—Effect of Solvent and Cocatalyst—

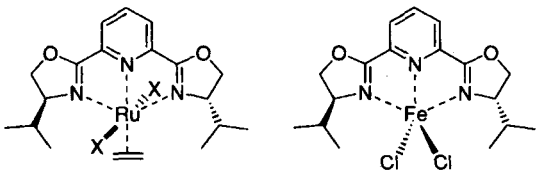
Run No.	Cocatalyst (Al/Ru)[b]	Solvent	Activity kg-PE/mol-Ru·h
1	MAO[c] (500)	Toluene	Trace
2	MAO[d] (250)	Hexane	0.30
3	MAO[d] (500)	Hexane	0.70
4	MAO[d] (500)	Toluene	0.36
5	MAO[d] (500)	Heptane	0.94
6	$AlEt_3/Ph_3B(C_6F_5)_4$[e] (500)	Hexane	0.16
7	$Al^iBu_3/Ph_3B(C_6F_5)_4$[e] (500)	Hexane	0.16
8	MMAO[f] (500)	Hexane	0.42

a) Reaction conditions: complex 50 μmol, solvent 30 mL, ethylene 6 atm, 50 °C, 1 h, 100 mL autoclave; b) Molar ratio of Al/Ru; c) MAO 9.5 wt% (Al) toluene solution; d) MAO white solid (prepared by removing toluene and $AlMe_3$); e) Ru/Borate = 1/3, molar ratio; f) MMAO 5.8 wt% (Al) hexane solution.

Results and Discussion

Synthesis of Ruthenium and Iron Complexes Containing Pybox Ligand. Synthesis of $RuCl_2$(ethylene)(pybox) (**1**) was according to the previous report,[15] and the deep violet microcrystals were isolated from the chilled CH_2Cl_2–hexane solution (−30 °C). The corresponding iodo (**2**) and trifluromethanesulfonato (**3**) analogues could also be prepared from $[RuI_2(p\text{-cymene})]_2$ and $[Ru(CF_3SO_3)_2(p\text{-cymene})]_2$ in the same manner (Chart 1). ^{1}H and ^{13}C NMR spectra of **2** and **3** were very similar to those for **1**, and a typical CF_3 pattern (q, 116.2 ppm, $^1J_{C-F}$ = 318 Hz) was observed on ^{13}C NMR spectrum for **3**. These results suggest the formation of these complexes.

It turned out that $FeCl_2$(pybox) (**4**) could also be isolated in high yield from $FeCl_2$ by treating with pybox under nitrogen atmosphere. The same reaction under ethylene atmosphere in place of nitrogen gave the same complex. ^{1}H NMR spectrum of **4** showed broad resonances at 12.95 ($\Delta_{1/2}$ = 96 Hz), 11.05 ($\Delta_{1/2}$ = 56 Hz), 9.37 ($\Delta_{1/2}$ = 27 Hz), 1.26, 0.88,



X = Cl (**1**), I (**2**), CF_3SO_3 (**3**) **4**

Chart 1.

−1.57 ($\Delta_{1/2}$ = 32 Hz), −2.74 ($\Delta_{1/2}$ = 29 Hz), and −4.93 ppm ($\Delta_{1/2}$ = 64 Hz). The ^{1}H NMR spectrum pattern did not change if the measurements were performed at lower temperatures, even at −30 °C. This result would suggest the formation of paramagnetic, penta-coordinate Fe(II) species; the compound could be identified as **4** by repeated elemental analyses.

Ethylene Homopolymerization and Ethylene/1-Hexene Copolymerization Catalyzed by RuX_2(ethylene)(pybox) [X = Cl (1), I (2), CF_3SO_3 (3)]-Cocatalyst System. It turned out that **1** exhibited the moderate catalytic activity in the presence of MAO (methylaluminoxane) solid, which was prepared from the commercially-available MAO (PMAO-S, Tosoh Akzo Co.) by removing toluene and $AlMe_3$ in vacuo (Table 1, Runs 3 and 5). The use of this MAO is important in order for this catalysis to proceed at a relatively significant rate. The effect of cocatalyst is thus important for the activity, and the catalytic activities in the presence of MMAO (isobutyl methyl aluminoxane, Run 8), $AlEt_3/Ph_3CB(C_6F_5)_4$ (Run 6), or $Al^iBu_3/Ph_3CB(C_6F_5)_4$ (Run 7) in place of MAO solid were low, as shown in Table 1. One possible reason for the lower activity with ordinary MAO and MMAO than with the MAO solid would be the deactivation of the catalytically-active species by $AlMe_3$ and Al^iBu_3 contained in these aluminoxanes. In addition, the catalytic activity was also affected by solvent, and the use of hexane or heptane was preferred. The choices of both cocatalyst and solvent are thus important factors for exhibiting high activity.

As shown in Table 2, the pybox ligand plays an important role, and no polymerization took place without Ru complex or the ligand (Table 2, Runs 3, 5, and 11, 12). **1** seems the most suited among the series of these complexes (**1**—**3**).

These polymerization results are reproducible as depicted in Table 2, and the polymer yields increased at higher ethylene pressure. The observed catalytic activities increased if the reaction was performed at higher temperatures (activity: 14, 25, and 67 kg-PE/mol-Ru·h at 25, 40 and 50 °C, respectively, Table 2, Runs 13—17), but the rate decreased at 60 °C (activity 67, and 56 kg-PE/mol-Ru·h at 50 and 60 °C, respectively). It was also revealed that the rate decreased over the time courses probably due to the gradual deactivation of catalytically-active species (Table 2, Runs 16, 22, and 23).

The resultant polyethylene gave high molecular weight ($M_w = 208.8\times10^4$, Table 3, Run 4), and the molecular weight distribution was relatively narrow (M_w/M_n = 2.93). This result is an interesting contrast with that reported by iron based catalyst containing tridentate 2,6-bis(imino)pyridine ligand,[10a,10b] and we assume at this stage that the difference of M_w value is probably due to the cocatalyst (MMAO containing $AlMe_3$ and Al^iBu_3, and MAO solid containing trace amount of $AlMe_3$) that reduces the extent of chain-transfer reaction by removing $AlMe_3$ in this catalysis. Only one peak [δ = 29.4 (^{13}C) and 1.45 (^{1}H), respectively, in *o*-dichlorobenzene-d_4 at 130 °C], which is ascribed to the typical

Table 2. Ethylene Polymerization by RuX_2(ethylene)(pybox)-Cocatalyst System [X = Cl (**1**), I (**2**), and CF_3SO_3 (**3**)][a)]

Run	Complex	Solvent	Ethylene	Temp	Time	Polymer	Activity
No.	(μmol)		atm	°C	h	yield/mg	kg-PE/mol-Ru·h
3	**1**	Hexane	6	50	1	35	0.70
5	**1**	Heptane	6	50	1	47	0.94
9	**2**	Heptane	6	50	1	15	0.30
10	**3**	Hexane	6	50	1	16	0.32
11	Ru[b)]	Heptane	6	50	1	—	—
12	None[c)]	Hexane	6	50	1	—	—
13	**1**	Hexane	8	25	1	14	0.28
14	**1**	Hexane	8	40	1	25	0.50
15	**1**	Hexane	8	40	1	29	0.58
16	**1**	Hexane	8	50	1	67	1.34
17	**1**	Hexane	8	50	1	71	1.42
18	**1**	Hexane	8	60	1	56	1.12
19	**1**	Hexane	8	60	1	55	1.10
3	**1**	Hexane	6	50	1	35	0.70
16	**1**	Hexane	8	50	1	67	1.34
20	**1**	Hexane	12	50	1	105	2.10
21	**1**	Hexane	12	50	1	107	2.14
22	**1**	Hexane	8	50	0.5	51	2.04
16	**1**	Hexane	8	50	1	67	1.34
23	**1**	Hexane	8	50	2	83	0.83

a) Reaction conditions: complex 50 μmol, solvent 30 mL, 100 mL autoclave, MAO white solid; b) $[RuCl_2(p\text{-cymene})]_2$ was used in place of **1**; c) The reaction was attempted under the same conditions as Run 3 without **1**.

Table 3. Copolymerization of Ethylene with 1-Hexene by **1**-MAO Catalyst System[a)]

Run No.	1-Hexene mL	Temp °C	Polymer yield/ mg	Activity[b)]	M_w[c)] $\times 10^{-4}$	M_w/M_n[c)]
4	—	50	67	1.34	208.8	2.93
24	3	50	73	1.46		
25	3	60	86	1.72	29.4	1.89

a) Reaction conditions: **1** 50 μmol, hexane 30 mL, MAO white solid 1450 mg (Al/Ru = 500), ethylene 8 atm, 1 h; b) Polymerization activity (kg-polymer/mol-Ru·h); c) GPC data in *o*-dichlorobenzene vs. polystyrene standard.

methylene proton or carbon ($\delta^+\delta^+$), was observed on ^{1}H and ^{13}C NMR spectra of these polymers, indicating that the resultant polyethylene is linear and does not have any carbon branches.

1 also exhibits moderate catalytic activity for copolymerization of ethylene with 1-hexene. The attempt for 1-hexene polymerization with **1**-MAO catalyst (1-hexene 10 mL, 150 μmol, Al/Ru = 500, r.t. 1 d) gave only a trace amount of poly(1-hexene) or oligomer. Note that incorporation of 1-hexene was confirmed by the ^{13}C NMR spectrum of poly(ethylene-*co*-1-hexene) in *o*-dichlorobenzene-d_4 (Fig. 1).[16] The molecular weight distribution (M_w/M_n) of the resul-

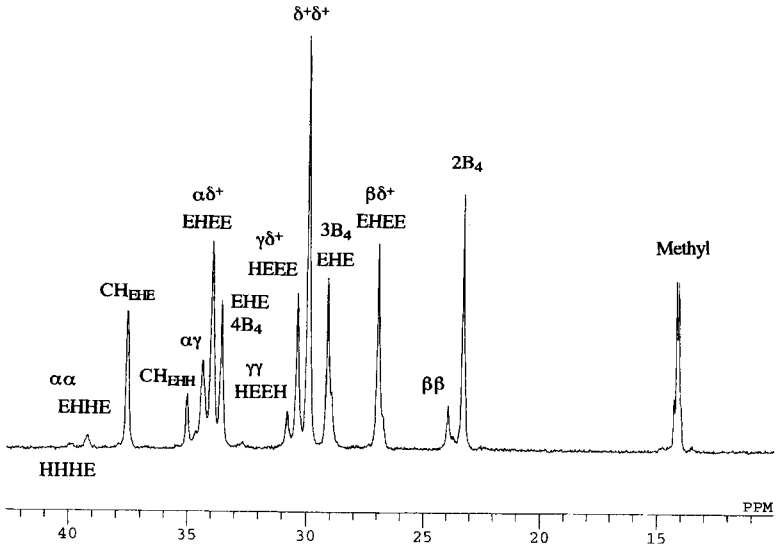
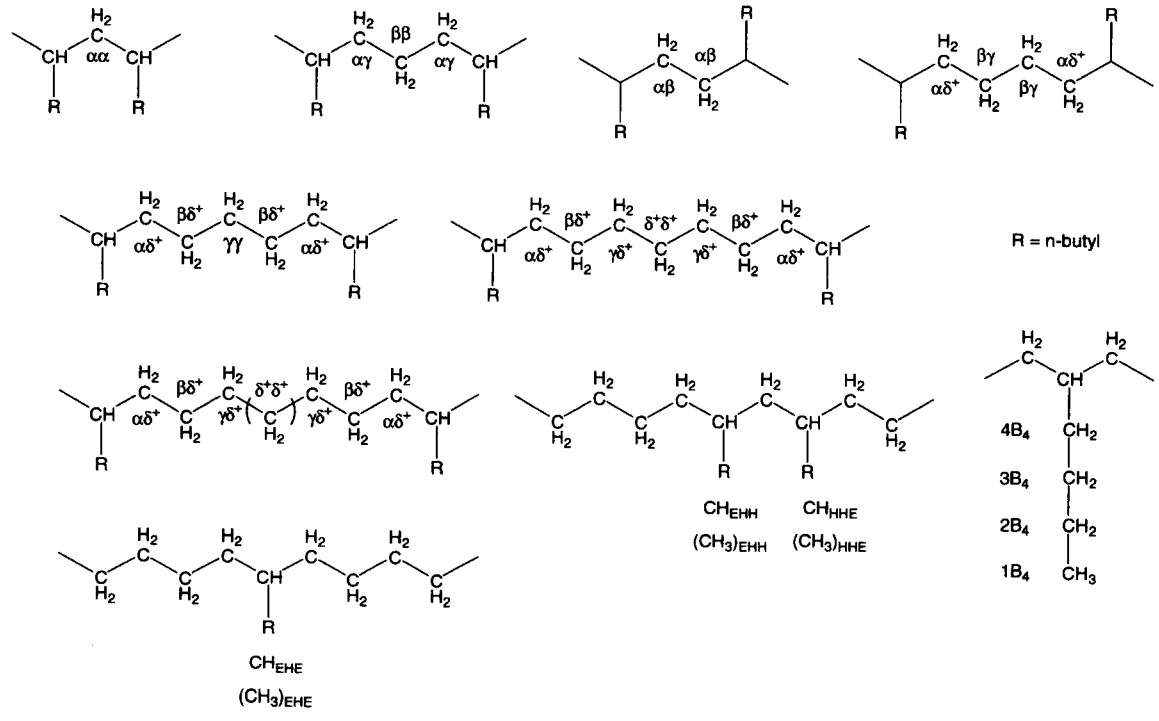


Fig. 1. ^{13}C NMR spectrum of poly(ethylene-*co*-1-hexene) prepared by **1**-MAO catalyst (Run 25, Tables 3 and 4, in *o*-dichlorobenzene-d_4 at 130 °C).



Scheme 1.

tant copolymer was 1.89, and the M_w value decreased compared with the homopolymer (Table 3). All resonances on ^{13}C NMR spectrum of the copolymer were assigned (Fig. 1, Scheme 1) and no peaks corresponding to 2,1-insertion of 1-hexene were observed. In addition, resonances which corresponded to HHHE ($\alpha\alpha$), and CH_{HHH} were negligible; this might be due to the extremely low activity for 1-hexene polymerization under the same conditions. Triad sequence distribution of the resultant poly(ethylene-*co*-1-hexene) is summarized in Table 4. A small $r_E \cdot r_H$ value (r_E and r_H are monomer reactivity ratios of ethylene and 1-hexene) was thus obtained, indicating a significantly alternating tendency.

As described above, we have shown that **1** exhibits the moderate catalytic activity not only for ethylene polymerization but also for ethylene/1-hexene copolymerization. In addition, as is evident from the ^{13}C NMR spectrum of the poly(ethylene-*co*-1-hexene), the insertion of 1-hexene took place in 1,2-fashion and the copolymerization does not proceeded in a random manner. This is an interesting contrast with that by the iron-based catalyst system, in which incorporation of α-olefin seemed very difficult.[10c] In this context, we assumed previously that the difference presented here might be due to the original nature of the ligand or due to the nature of the centered metal (iron or ruthenium). On the other hand, we also assumed that pybox ligand would have a more open space around the active metal center than the 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine ligand,[10] which might facilitate the coordination of 1-hexene. In order to clarify the reason of this difference, we prepared the iron analogue and explored the copolymerization behavior.

Olefin Polymerization Catalyzed by $FeCl_2$(pybox) (4)-Cocatalyst System. It turned out $FeCl_2$(pybox) (**4**) also exhibited moderate catalytic activities for ethylene polymerization in the presence of MAO solid (Tables 5 and 6). The effects of cocatalyst and solvent for the activity were somewhat different from those in ruthenium catalyst, and the use of $AlEt_3$- or Al^iBu_3–$Ph_3CB(C_6F_5)_4$ cocatalyst was also found to be effective (Table 5, Runs 33 and 34). The polymerization took place even at low temperature of −20 °C (Table 6, Runs 38 and 39), and the activity did not increase significantly at higher temperature (Table 6, Runs 38—43). The temperature dependence observed here was different from that in the case of ruthenium (Table 2, Runs 13—19), but we can not explain the reason clearly at this moment. The polymer yield increased at higher ethylene pressures (Table 6, runs 44—47). These polymerization results shown in Tables 5 and 6 are also reproducible.

The resultant polyethylene gave relatively high molecular weight ($M_w = 90.5\times10^4$, Table 7, Run 40), and the molecular weight distribution was relatively narrow ($M_w/M_n = 2.4$). In addition, the M_w value increased at higher ethylene pressure ($M_w = 90.5\times10^4 \longrightarrow 366\times10^4$). These results are interesting contrasts with those reported for iron-based catalyst containing tridentate 2,6-bis(imino)pyridine ligand.[6a,6b] We assume that the difference observed here is also due to the cocata-

Table 5. Ethylene Polymerization by $FeCl_2$(pybox) (**4**)-Cocatalyst System[a]—Effect of Solvent and Cocatalyst—

Run No.	Cocatalyst (Al/Fe)[b]	Solvent	Activity kg-PE/mol-Fe·h
26	MAO[c] (250)	Hexane	0.38
27	MAO[c] (500)	Hexane	0.72
28	MAO[c] (500)	Hexane	0.70
29	MAO[c] (500)	Toluene	0.60
30	MAO[c] (500)	Toluene	0.64
31	$Al^iBu_3/Ph_3CB(C_6F_5)_4$[d] (500)	Hexane	0.48
32	$Al^iBu_3/Ph_3CB(C_6F_5)_4$[d] (200)	Hexane	0.22
33	$Al^iBu_3/Ph_3CB(C_6F_5)_4$[d] (500)	Hexane	0.74
34	$AlEt_3/Ph_3CB(C_6F_5)_4$[d] (500)	Hexane	0.84
35	MMAO[e] (500)	Toluene	0.34
36	MMAO[e] (200)	Hexane	0.14
37	MMAO[e] (500)	Hexane	0.38

a) Reaction conditions: complex 50 μmol, solvent 30 mL, ethylene 8 atm, 50 °C, 1 h, 100 mL autoclave; b) Molar ratio of Al/Fe; c) MAO white solid (prepared by removing toluene and $AlMe_3$); d) Fe/Borate = 1/1.5 (Runs 31 and 32), and 1/3 (Runs 33 and 34), respectively (molar ratio); e) MMAO 5.8 wt% (Al) hexane solution.

Table 6. Ethylene Polymerization by **4**-MAO Catalyst System[a]

Run No.	Solvent	Ethylene atm	Temp °C	Time h	Polymer yield/ mg	Activity kg-PE/mol-Fe·h
38	Hexane	8	−20	1	33	0.66
39	Hexane	8	−20	1	27	0.54
40	Hexane	8	40	1	32	0.64
41	Hexane	8	40	1	38	0.76
27	Hexane	8	50	1	36	0.72
28	Hexane	8	50	1	35	0.70
42	Hexane	8	60	1	42	0.84
43	Hexane	8	60	1	43	0.86
44	Hexane	4	50	1	15	0.30
45	Hexane	6	50	1	30	0.60
27	Hexane	8	50	1	36	0.72
46	Hexane	10	50	1	43	0.86
47	Hexane	12	50	1	54	1.08

a) Reaction conditions: complex 50 μmol, solvent 30 mL, 100 mL autoclave, MAO white solid (prepared by removing toluene and $AlMe_3$), Al/Fe = 500 (molar ratio).

Table 4. Monomer Sequence Distribution of Ethylene/1-Hexene Copolymer Prepared by **1**-MAO Catalyst System[a]

Run No.	[1-Hexene][b] mol%	Triad sequence distribution[b] (%) EEE	HEE+EEH	HEH	EHE	EHH+HHE	HHH	Diads [EE]	[EH]	[HH]	$r_E \cdot r_H$[c]
25	27.16	34.16	31.46	7.22	20.30	6.78	0.08	49.89	46.64	3.47	0.32

a) Detailed polymerization conditions, see Table 3; b) Determined by ^{13}C NMR spectra; c) $r_E \cdot r_H = 4[EE][HH]/[EH]^2$.

Table 7. Ethylene Polymerization by **4**-MAO Catalyst System in the Presence of 1-Hexene[a)]

Run No.	1-Hexene mL	Ethylene atm	Temp °C	Polymer yield/ mg	Activity[b)]	M_w [c)] $\times 10^{-4}$	M_w/M_n [c)]
45	—	6	50	30	0.60		
40	—	8	40	32	0.64	90.5	2.4
41	—	8	40	38	0.76	76.6	2.5
27	—	8	50	36	0.72		
47	—	12	50	54	1.08	366	5.4
48	3	6	50	41	0.82		
49	3	8	50	45	0.90		
50	3	8	50	47	0.94		
51	6	8	50	35	0.70		

a) Reaction conditions: complex (**4**) 50 μmol, hexane 30 mL, MAO white solid 1450 mg (Al/Fe = 500), 1 h; b) Polymerization activity (kg-polymer/mol-Fe·h); c) GPC data in *o*-dichlorobenzene vs. polystyrene standard.

lyst (MMAO containing $AlMe_3$ and Al^iBu_3, and MAO solid containing trace amount of $AlMe_3$) which would reduce the extent of chain-transfer reaction by removing $AlMe_3$ in this catalysis. Only one peak was observed on ^1H and ^{13}C NMR spectra of these polymers (δ = 29.4 (^{13}C) and 1.45 (^1H), respectively, in *o*-dichlorobenzene-d_4 at 130 °C), indicating that the resultant polyethylene is linear and does not have any carbon branches.

It turned out that **4** exhibited the moderate catalytic activities for ethylene polymerization in the presence of 1-hexene. The observed activity slightly increased upon the copresence of 1-hexene [ex. 0.60 (Run 45) → 0.82 (Run 48), 0.72 (Run 27) → 0.94 kg-polymer/mol-Fe·h (Run 50), Table 7], but we do not have an exact reason at this moment. The activity decreased with the increase in the initial 1-hexene concentration [activity: 0.94 (Run 50) → 0.70 (Run 51), Table 7].

In addition, importantly, the ^{13}C NMR spectrum for the resultant polymer (Fig. 2) reveals that no incorporation of 1-hexene took place under these reaction conditions. This is an interesting contrast with that obtained by the ruthenium catalyst (Fig. 1), and these results strongly indicate that the difference observed here is due to the nature of the centered metal (ruthenium or iron). We believe that this information should be potentially important for the design of catalyst especially for precise olefin copolymerization.

It has been reported by Brookhart et al. that polymerization of propylene by iron complex containing 2,6-bis[1-(2, 6-diisopropylphenylimino)ethyl]pyridine ligand proceeded with 2,1-insertion mode and that the activity decreased at higher reaction temperature.[10d] The difference (Figs. 1 and 2) observed here might be thus due to the difference of insertion mode between ruthenium (1,2-) and iron (2,1-) catalysts; 2,1-insertion of 1-hexene might be sterically hindered compared to the 1,2-insertion. Although this can be a plausible explanation for the difference, we do not now exclude the possibility of a substituent effect on the ligand. We're now

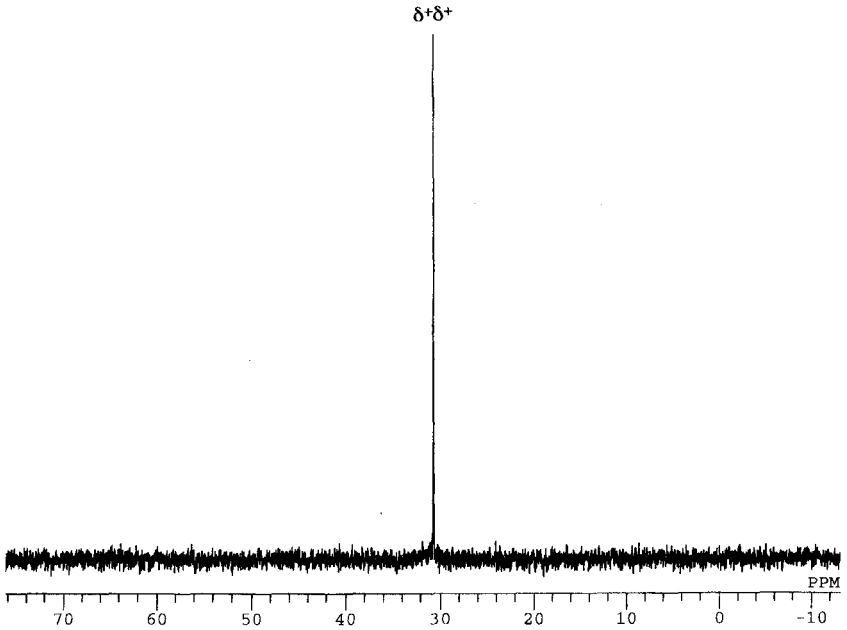


Fig. 2. ^{13}C NMR spectrum of the polymer prepared by **4**-MAO catalyst under the conditions of Run 50 (ethylene 8 atm, 1-hexene 3 mL, in *o*-dichlorobenzene-d_4 at 130 °C).

exploring in more details, including the effect of substituents on the ligand in both ruthenium and iron-based catalyst; our results will be introduced in the near future.

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