Macromolecules **1998,** *31,* 8009−8015

Ethylene Homopolymerization and Ethylene/1-Butene Copolymerization Catalyzed by a $[1,8\text{-}C_{10}H_6(NR)_2]TiCl_2$−Cocatalyst System

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Received May 6, 1998; Revised Manuscript Received September 1, 1998

ABSTRACT: $[1,8\text{-}C_{10}H_6(NR)_2]TiCl_2$ [R = Si^iPr_3 (**3a**), Si^tBuMe_2 (**3b**), $SiMe_3$ (**3c**)] complexes have been prepared from dilithio salts $[1,8\text{-}C_{10}H_6(NR)_2]Li_2$ (**2**) and $TiCl_4$ in diethyl ether in moderate yields (60−63%). These complexes could be identified by ^1H and ^{13}C NMR, mass spectroscopy, and elemental analysis. It turned out that these complexes exhibited high catalytic activities for ethylene homopolymerization and for ethylene/1-hexene copolymerization in the presence of methylaluminoxane (MAO), methyl isobutyl aluminoxane (MMAO), or Al^iBu_3− or $AlEt_3$−$Ph_3CB(C_6F_5)_4$ as a cocatalyst. The effect of cocatalyst as well as solvent is very important for high activity, and it turned out that the catalytic activities performed in heptane (cocat. MMAO) were higher than those carried out in toluene (cocat. MAO). The catalytic ethylene/1-butene copolymerizations by the **3b**−MMAO, $(TBP)TiCl_2$−MAO [TBP = 2,2′-thiobis(4-methyl-6-*tert*-butylphenolato)], or $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$−$Al^iBu_3/Ph_3CB(C_6F_5)_4$ catalyst system were also explored under the various conditions, and it was found that the 1-butene contents and the triad sequence distributions of the resultant copolymer were highly dependent upon the catalyst used.

Introduction

Group 4 metal complexes that contain bidentate bis(amide) ligand are promising systems for application in olefin polymerization catalysis because of their relationship to the well-studied metallocene analogues,[1] hybrid “half-metallocene” complexes such as $(C_5R_4SiR_2NR)MX_2$,[2] bis(amide) complexes of the type $(R_2N)_2MX_2$,[3] or chelate bis(amide) complexes,[4,5] and others.[6,7] Several reports concerning catalytic alkene polymerization using Ti and Zr complexes containing various amide ligands were known; however low catalytic activities were observed in most catalyst systems.[8]

One of our ongoing projects is to prepare various 14e and 12e titanium and zirconium complexes containing chelate bis(amide) ligands, not only because the preparations of these complexes are relatively easy and efficient but also because of their potential possibility as olefin polymerization catalysts.[1−7] We believe that these studies should be very important for designing a highly efficient catalyst complex with/without a cyclopentadienyl group[9] and for understanding the scope and the limitation of these types of catalyst system for olefin polymerization.

We have recently reported as a preliminary communication that $[1,8\text{-}C_{10}H_6(NR)_2]TiCl_2$ complexes [R = Si^iPr_3 (**3a**), Si^tBuMe_2 (**3b**), $SiMe_3$ (**3c**)] showed remarkable catalytic activities for ethylene polymerization and for ethylene/1-hexene polymerization in the presence of cocatalysts such as methylaluminoxane (MAO), methylisobutylaluminoxane (MMAO), and Al^iBu_3− or $AlEt_3$−$Ph_3CB(C_6F_5)_4$.[10] The effect of cocatalyst as well as solvent was found to be important for high activity in these catalyst systems. In this paper, we would like to present more detailed results for olefin polymerization catalyzed by the $[1,8\text{-}C_{10}H_6(NR)_2]TiCl_2$−cocatalyst system, including the results explored for ethylene/1-butene copolymerization under various conditions. We would also like to present the detailed synthetic procedure for titanium(IV) complexes that contain bis(silylamide) ligand of the type $[1,8\text{-}C_{10}H_6(NR)_2]^{2-}$, including identification by various methods. Furthermore, we would also like to present the detailed results for the catalytic copolymerizations of ethylene with 1-butene by **3b**, by the five-coordinated $(TBP)TiCl_2$ [**4**, TBP = 2,2′-thiobis(4-methyl-6-*tert*-butyl-phenolato)],[6a,c] or by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$[2b] (**5**) as catalysts presented by treatment with cocatalysts.

Results and Discussion

1. Synthesis of $[1,8\text{-}C_{10}H_6(NR)_2]TiX_2$ Complexes.

$1,8\text{-}C_{10}H_6(NHR)_2$ (**1a**−**c**) could be synthesized by the sequence of steps shown in Scheme 1.[10] This is an improved method for preparing *N,N*′-bis(silylamino)-*o*-diaminobenzene reported by Aoyagi et al.,[4b] and THF was chosen as an effective solvent to complete the reaction of chlorosilane with dilithium amide, which was prepared by the treatment of 1,8-naphthalenediamine with *n*-butyllithium. The desired products (**1a**−**c**) could be isolated by recrystallization in hexane at −25 °C. The corresponding dilithio salts $[1,8\text{-}C_{10}H_6(NR)_2]Li_2$ (**2a**−**c**) could also be prepared by the reaction of **1a**−**c** with ^nBuLi in high yields, and isolated as a white−pale yellow solid from chilled hexane solution due to their extremely low solubility. The reaction of **2a**−**c** with $TiCl_4$ in diethyl ether (−25 °C) gave the titled bis(silylamide) complexes, $[1,8\text{-}C_{10}H_6(NR)_2]TiCl_2$ (**3a**−**c**), in relatively high yields (60−63%) as deep brown−purple microcrystals after the purification procedures.

It was revealed that ^1H and ^{13}C NMR spectra of these complexes were very similar to those for both **1a**−**c** and **2a**−**c** and were thus analogous to the titled complexes, strongly supporting the formation of $[1,8\text{-}C_{10}H_6(NR)_2]TiCl_2$ as a sole isolated product. In addition, **3b** and **3c**

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10.1021/ma9807163 CCC: \$15.00

Scheme 1

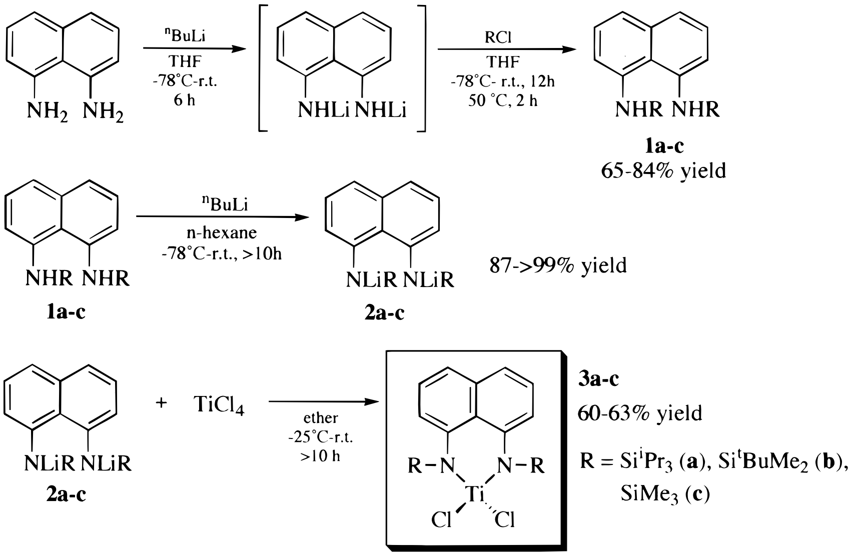


Table 1. Polymerization of Ethylene with the $[1,8\text{-}C_{10}H_6(NR)_2]TiCl_2$−MMAO Catalyst System[a]

run	cat. (amt, μmol)	cocat.	polymer yield (g)	activity[b]	$10^{-4}M_w$[c]	M_w/M_n[c]
1	**3a** (17.0)	MMAO	0.71	41.8	28.3	5.6[d]
2	**3b** (17.5)	MMAO	12.4	709	21.4	5.4[e]
3	**3c** (9.1)	MMAO	1.50	165	36.5	19.3[e]

[a] Reaction conditions: heptane 300 mL, ethylene 4 kg/cm^2, 60 °C, 1 h, MMAO (methyl isobutyl aluminoxane, 5.8 wt % (Al) in hexane), Al/Ti (molar ratio) = 1000. [b] Polymerization activity: kg of polymer/(mol of Ti·h). [c] GPC data in *o*-dichlorobenzene vs polystyrene standard. [d] Three M_w peaks were observed on the GPC trace. [e] A bimodal peak was observed on the GPC trace.

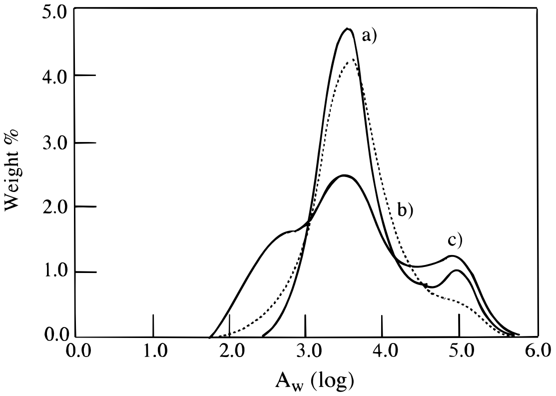


Figure 1. GPC traces of polyethylene prepared by the **3a**−**c**−MMAO catalyst (runs 1−3 in Table 1): (a) R = Si^iPr_3 (**3a**); (b) R = Si^tBuMe_2 (**3b**); (c) R = $SiMe_3$ (**3c**).

could be determined by mass spectroscopy as the M$^-$ fragment, and the results for elemental analysis of **3a** and **3b** were also satisfactory. The reaction chemistry derived from these complexes is under study.

2. Catalytic Ethylene Polymerization with $[1,8\text{-}C_{10}H_6(NR)_2]TiCl_2$ in the Presence of Cocatalyst. **3a**−**c** showed high catalytic activities for ethylene polymerization in the presence of cocatalysts such as MAO (methylaluminoxane), MMAO (methylisobutylaluminoxane), or $AlEt_3$− or Al^iBu_3−$Ph_3CB(C_6F_5)_4$, and the catalytic activities performed in heptane (cocatalyst: MMAO) were higher than those performed in toluene (cocatalyst: MAO).[10] The observed catalytic activity among the dichloride complexes increased in the order (cocatalyst MMAO): **3b** > **3c** > **3a** (Table 1), and the catalytic activity of 709 kg of PE/(mol of Ti·h) (2.53 × 10^4 turnovers/h) could be achieved (run 2, C_2' 4 kg/cm^2, 60 °C). Polymerization in the presence of 1-hexene (10 mL) under the same conditions of run 2 gave ethylene/1-hexene copolymer (600 kg of polymer/(mol of Ti·h), SCB (side chain branching) 32.4/1000 carbons, T_m 121.4 °C, $M_n = 7.35 \times 10^4$, $M_w/M_n = 4.8$).

As shown in Figure 1, three M_w peaks were observed on the GPC trace for the polymer prepared by **3c** (cocatalyst MMAO, run 3), whereas bimodal peaks were observed for those prepared by both **3a** and **3b** (cocatalyst MMAO, run 1 and 2, respectively). In addition, the weight fraction ratio of lower/higher M_w peaks was dependent upon the catalyst used. It seems likely that the activity order (**3b** > **3a** > **3c**) is due to the stability of the active species, especially the stability of the *N*-trialkylsilyl bond, in the solution under these reaction conditions.

The effects of both cocatalyst and solvent are an important factor in order for this reaction to proceed at significant rates, because the polymerization activity by **3b** performed with MMAO in heptane was higher than that performed with MMAO or MAO in toluene (Table 2). The reason is, however, not clear at this moment, probably due to the cocatalyst or due to the coordination of toluene to the catalytically active species, as was previously speculated by $[NAr(CH_2)_3NAr]TiCl_2$ (Ar = 2,6-$^iPr_2C_6H_3$) catalyst system.[4k]

It was revealed that the molecular weight distributions (M_w/M_n) of the resultant polymers were relatively broad (M_w/M_n = 3.0−19.3, Tables 1 and 2). These results were very similar to those reported for the previous catalysts[11] such as $[\{Me_3SiN(CH_2CH_2NSiMe_3)_2\}ZrCH_2Ph]^+[PhCH_2B(C_6F_5)_3]^-$ (M_n 52 200, $M_w/M_n = 4.4$),[5a] $[\{(Me_3Si)_2N\}Zr(CH_2SiMe_2NSiMe_3)]^+\{B(C_6F_5)_4\}^-$ complex (M_n 414 000, $M_w/M_n = 8.4$),[3d] or another catalyst using N−O type group 4 metal complexes containing quinolinolato or pyridine−alkoxide ligands[7a−c] or the bis(alkylamidinate) ligand.[7e] The reason for the broad M_w/M_n values in the present catalytic reactions might be due to the fact that titanium−nitrogen bonds were broken during the reaction or due to the formation of several catalytically active species. In fact, a narrow

Table 2. Polymerization of Ethylene with the 3b−Cocatalyst System[a]

run	cat. (amt, μmol)	cocat.	Al/Ti[b]	solvent	polymer yield (g)	activity[c]	$10^{-4}M_w$[d]	M_w/M_n[d]
2	**3b** (17.5)	MMAO	1000	heptane	12.4	709	21.4	5.4[e]
4	**3b** (17.5)	MMAO	1000	heptane	1.68	2880	12.1	1.8
5	**3b** (21.4)	MMAO	1000	toluene	4.10	192	38.6	3.0
6	**3b** (21.8)	MAO[f]	1000	toluene	1.62	74.3	39.8	4.8[e]
7	**3b** (9.9)	$Al(^iBu)_3$/B[g]	500	toluene	0.75	75.8		

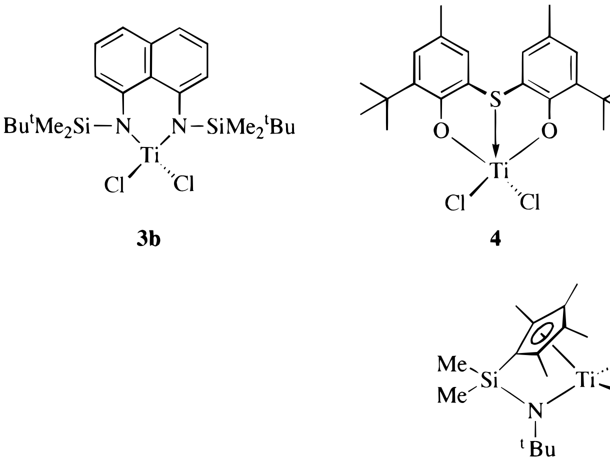
[a] Reaction conditions: toluene or heptane 300 mL, ethylene 4 kg/cm^2, 60 °C, 1 h. [b] Molar ratio of Al/Ti. [c] Polymerization activity: kg of polymer/(mol of Ti·h). [d] GPC data in *o*-dichlorobenzene vs polystyrene standard. [e] Bimodal peak was observed on GPC trace. [f] MAO: methylaluminoxane (9.5 wt % (Al) in toluene). [g] B = $Ph_3CB(C_6F_5)_4$, $Ph_3CB(C_6F_5)_4$/Ti = 1.0.

Table 3. Copolymerization of Ethylene with 1-Butene with the $[1,8\text{-}C_{10}H_6(NSi^tBuMe_2)_2]TiCl_2$−MMAO System[a]

run no.	cat. (amt, μmol)	cocat.	solvent	ethylene pressure (kg/cm^2)	amt of 1-butene (g)	polymer yield (g)	activity[b]	1-butene[c] (mol concn %)	$10^{-4}M_n$[d]	M_w/M_n[d]
8	**3b** (10.9)	MMAO[e]	heptane	6	50	11.4	1050	18.6	3.3	5.7
9	**3b** (11.1)	MMAO[e]	heptane	6	20	10.0	900	12.1	2.7	6.4
10	**3b** (10.7)	MMAO[e]	heptane	2	50	3.3	310	41.1	0.7	4.6
11	**3b** (7.7)	MMAO[e]	heptane	2	20	2.4	310	21.1	1.7	4.0
12	**4** (0.42)	MAO[e]	toluene	6	50	3.6	8560	6.7	32.2	4.0
13	**4** (2.7)	MAO[e]	toluene	2	50	8.0	2960	9.0	4.1	2.2
14	**5** (1.4)	Al^iBu_3/B[f]	toluene	6	10	17.4	12400	31.3	7.0	2.2

[a] Reaction conditions: toluene or heptane 200 mL, 70 °C, 1 h. **3b**: $[1,8\text{-}C_{10}H_6(NSi^tBuMe_2)]TiCl_2$. **4**: $(TBP)TiCl_2$, TBP = 2,2′-thiobis(4-methyl-6-*tert*-butylphenolato), **5**: $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$. [b] Polymerization activity: kg of polymer/(mol of Ti·h). [c] 1-Butene in copolymer (mol %). [d] GPC data in *o*-dichlorobenzene vs polystyrene standard. [e] Al/Ti (molar ratio) = 1000. [f] B = $Ph_3CB(C_6F_5)_4$, molar ratio of $Ph_3CB(C_6F_5)_4/Al^iBu_3$/Ti = 1.0/500/1.0.

Chart 1



3b **4** **5**

M_w/M_n value (1.8) was observed, if the polymerization by **3b** (under the same conditions as run 2) was terminated at 2 min (run 4, Table 2). We thus believe at this moment that the broad M_w/M_n value would be due to the scission of the titanium−nitrogen bond by cocatalyst, which gives another catalytically active species under these reaction conditions.[12]

3. Catalytic Copolymerization of Ethylene and 1-Butene with $[1,8\text{-}C_{10}H_6(NSi^tBuMe_2)_2]TiCl_2$−MMAO System. Copolymerization of ethylene and 1-butene with **3b** was conducted at 70 °C under the same conditions of which **3b** showed higher activity for ethylene polymerization (MMAO in heptane). The copolymerizations were also explored with $(TBP)TiCl_2$ [**4**, TBP = 2,2′-thiobis(4-methyl-6-*tert*-butyl-phenolato)]−MAO[6a,c] or with the $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**5**)[2b]−$Al^iBu_3/Ph_3CB(C_6F_5)_4$ catalyst system (Chart 1) in toluene for references. The contents of 1-butene in the copolymer prepared by these catalyst systems were determined by ^{13}C NMR spectra,[13] and these results are summarized in Table 3.

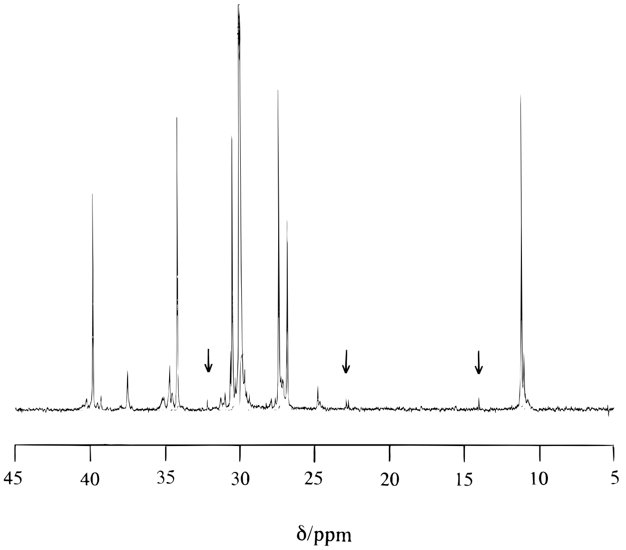


Figure 2. ^{13}C NMR spectrum of poly(ethylene-*co*-1-butene) prepared by the **3b**−MMAO catalyst (run 9, Table 3). Peaks which are ascribed to the chain end are indicated with ↓.

The ^{13}C NMR spectrum of poly(ethylene-*co*-1-butene) prepared by **3b** (run 9) is shown in Figure 2. If the insertion of 1-butene proceeds in a regioselective manner (1,2-insertion or 2,1-insertion), $S_{\beta\beta}$ and $S_{\alpha\gamma}$ (S = secondary carbon) in the BEB sequence and $S_{\alpha\delta}$, $S_{\beta\delta}$, and $S_{\gamma\gamma}$ in the BEEB sequence (B = 1-butene, E = ethylene) between the two ethyl side chains can be composed as shown in Chart 2a. On the other hand, $S_{\alpha\beta}$, $S_{\alpha\delta}$, and $S_{\beta\gamma}$ can be formed as shown in Chart 2b, if one of the 1-butene in the BEB sequence is inserted in a different manner (1,2-insertion and 2,1-insertion). These chemical shifts for the carbon species can be calculated from the Lindeman and Adams relationship[14] and are summarized in Table 4. It is to be noted that calculated chemical shifts of the carbons derived from regioselective insertion of 1-butene (Chart 2a) are in good agreement with those observed. In addition, the resonances from $S_{\alpha\beta}$, $S_{\alpha\delta}$, and $S_{\beta\gamma}$ could not be detected

Chart 2

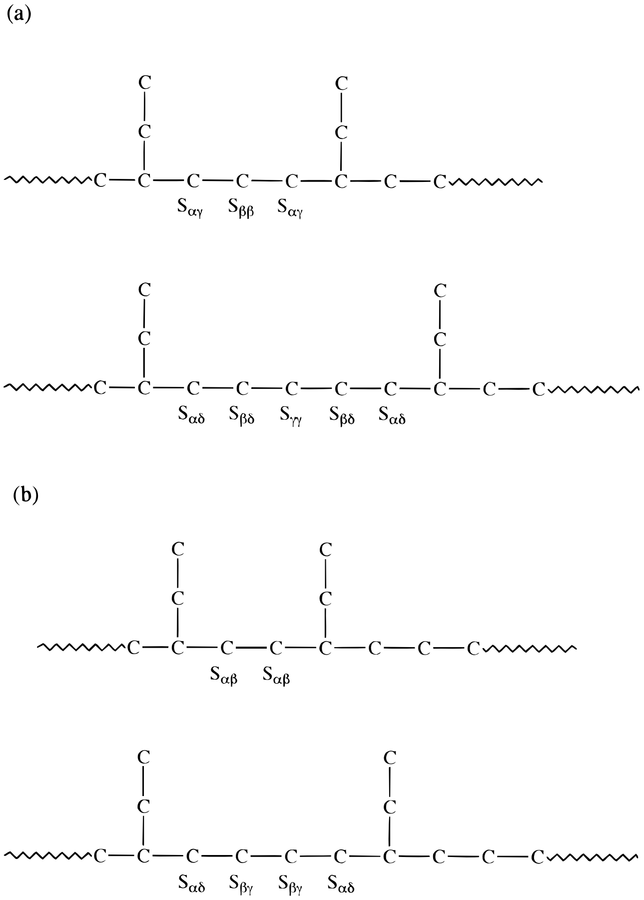


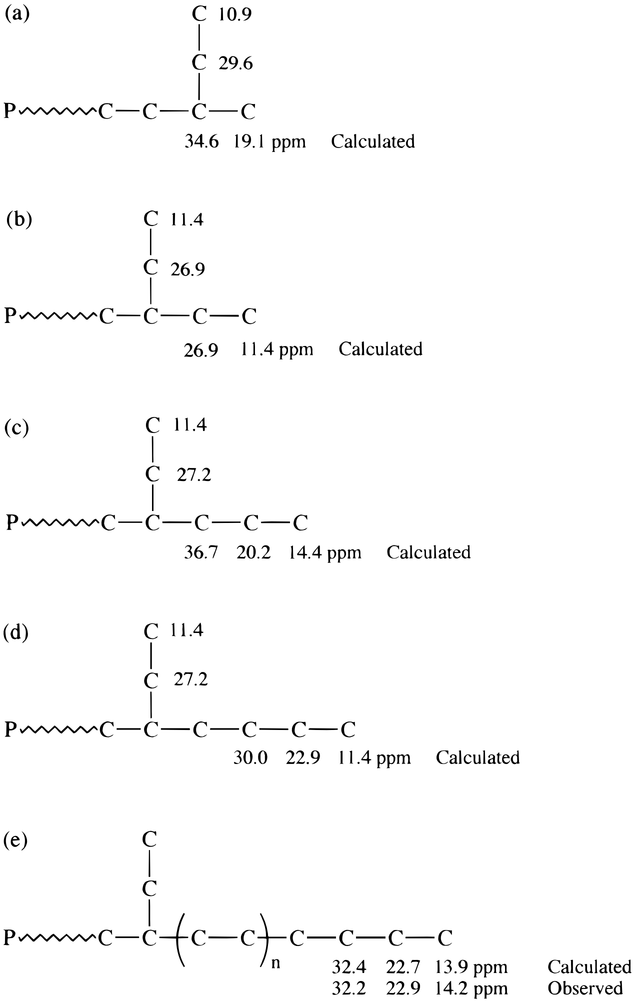
Table 4. ^{13}C NMR Assignments of Methylene Carbons in Ethylene/1-Butene Copolymer

carbon species[a]	calcd δ (ppm)	obsd δ (ppm)
(a) $S_{\beta\beta}$	25.08	24.71
$S_{\alpha\gamma}$	34.47	34.16−34.66
$S_{\alpha\delta}$	34.22	
$S_{\beta\delta}$	27.52	27.36
$S_{\gamma\gamma}$	30.46	30.92
(b) $S_{\alpha\beta}$	31.78	
$S_{\alpha\delta}$	34.22	
$S_{\beta\gamma}$	27.77	

[a] Shown in Chart 2.

in the ^{13}C NMR of poly(ethylene-*co*-1-butene) by **3b** (Figure 2). It is thus clear that the 1-butene insertion in the ethylene/1-butene polymerization with **3b** proceeds with the same regioselectivity.

Chart 3



The resonances (at 14.1, 22.7, 22.9, and 32.2 ppm) assignable to chain end structures are found in Figure 2. Five types of chain end structures with isolated 1-butene can be assumed, as shown in Chart 3.[13,14] Parts a and c of Chart 3 show the chain end structures of B−E− insertion and E−B− insertion with 2,1-inserted 1-butene, respectively, whereas parts b and d of Chart 3 show the chain end structures of E−B− insertion and E−E-B− or B−B− insertion with 1,2-inserted 1-butene, respectively. The resonances corresponding to the chain end structures shown in Chart 3a,b could not be found, and this result suggests that 1,2-insertion of 1-butene proceeds predominantly in this catalysis (**3b**−MMAO). Two kinds of methylene carbons at 22.7 and 22.9 ppm (next to the chain end methyl carbons) were observed, and the chain end structure shown in Chart 3d,e can thus be considered. The chain end structure of Chart 3d can also be explained by B−B− insertion or E−E−B− insertion at the initial propagation step.

Table 5 summarizes the monomer sequence distributions of obtained poly(ethylene-*co*-1-butene) determined by ^{13}C NMR spectroscopy.[13] The degree of the incorporation of 1-butene decreased in the following order: **5** > **3b** > **4** (ethylene of 6.0 kg/cm^2, Tables 3 and 5). 1-Butene contents for the resultant copolymers by **3b** were between 12.1 and 41.4 mol % and turned out that the n_E, n_B, and $r_E{\cdot}r_B$ values by **3b** were almost the same as that by **5**, which showed the highest activity among these catalysts. The values of $r_E{\cdot}r_B$ (r_E and r_B are monomer reactive ratios of ethylene and 1-butene, respectively) by **3b** are almost 1, and these results indicate that the copolymerization proceeds in a random manner. It also turned out that the **4**−MAO system showed higher activities than the **3b**−MMAO system under the same conditions, and the activity by the **4**−MAO system is highly dependent upon ethylene pressure. It seems difficult to prepare the copolymer containing high 1-butene content due to the especially high reactivity of **4** to ethylene.[15]

The difference observed here is probably due to the structure or due to the electronic nature of the catalytically active species. This information is, we believe, very important to understand or to design the better catalyst complex for obtaining the desired copolymer. The next step of our project is to observe a precised

Table 5. Monomer Sequence Distribution of Ethylene/1-Butene Copolymers Prepared by the [1,8-$C_{10}H_6(NSi^tBuMe_2)_2$]$TiCl_2$−MMAO Catalyst System[a]

		triad sequence distributions[b](%)						1-butene			
run no.	cat.	EEE	EEB + BEE	BEB	EBE	BBE + EBB	BBB	concn[b] (mol %)	n_E[c]	n_B[d]	$r_E{\cdot}r_B$[e]
8	**3b**	61.8	16.0	3.6	13.0	4.2	1.4	18.6	7.0	1.2	1.37
9	**3b**	73.0	13.0	1.9	9.7	2.4		12.1	10.5	1.1	1.02
10	**3b**	31.3	18.4	8.9	22.2	10.5	8.7	41.4	3.2	1.5	1.09
11	**3b**	57.6	17.1	4.2	13.1	4.9	3.2	21.1	6.2	1.4	1.85
12	**4**	84.2	8.8		6.7			6.7	21.2	1.0	
13	**4**	77.0	13.2	0.8	8.3	0.7		9.0	12.3	1.0	
14	**5**	36.7	26.2	5.8	16.8	11.9	2.6	31.3	3.6	1.4	0.98

[a] Detailed reaction conditions, see Table 3. [b] Calculated based on ^{13}C NMR spectra.[13] [c] Average sequence length n_E = [EEE + (EEB + BEE) + BEB]/[BEB + (EEB + BEE)/2]. [d] Average sequence length n_B = [BBB + (EBB + BBE) + EBE]/[EBE + (EBB + BBE)/2]. [e] $r_E{\cdot}r_B$ = 4[EE][BB]/[EB]^2, [EE] = [EEE] + [EEB + BEE]/2, [EB] = [EEB + BEE]/2 + [BEB] + [EBE] + [BBE + EBB]/2, [BB] = [BBB] + [BBE + EBB]/2.

relationship between the structure and the microanalysis datas including the effect of substituents in various ligands, cocatalysts, reaction temperature, and others.

Experimental Section

General Procedure. All experiments were carried out under a 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. Tetrahydrofuran, diethyl ether, hexane, and dichloromethane were purchased from Kanto Chemical Co., Ltd. as anhydrous grade and stored in the presence of molecular sieves. Toluene for synthesis of various complexes was purchased as the same grade and stored over sodium/potassium alloy. All deuterated NMR solvents were stored over molecular sieves in a drybox. (TBP)$TiCl_2$ (**4**, TBP = 2,2′-thiobis(4-methyl-6-*tert*-butylphenolato)) was prepared by the published method,[6c] and [$Me_2Si(C_5Me_4)(N^tBu)$]$TiCl_2$ (**5**) was purchased from Kanto Chemical Co., Ltd.

All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 spectrometer (270.2 MHz, ^{1}H). All chemical shifts are given in ppm and are referenced to tetramethylsilane. Obvious multiplicities and routine coupling constants are usually not listed. All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. All ^{13}C NMR spectra for the ethylene/1-butene copolymer were performed by using a Bruker AM-400 spectrometer (100.614 MHz, ^{13}C: invgate method, *o*-dichlorobenzene-d_4) or a Bruker AC 250 spectrometer at 135 °C.

All the mass spectra (negative) were recorded by using a JEOL JMS-700 double focusing mass spectrometer equipped with a frit−CI interface. The sample solutions in dehydrated toluene were introduced into the ion source of the mass spectrometer at the rate of 2−5 μL/min. Microanalyses (C, H, N) were performed on a Perkin-Elmer PE2400 microanalyzer.

1,8-$C_{10}H_6(NHSi^iPr_3)_2$ (1a). A solution of 1,8-naphthalenediamine (1,8-$C_{10}H_6(NH_2)_2$, 5.00 g, 31.6 mmol) in tetrahydrofuran (100 mL) was cooled to −78 °C, and ^{n}BuLi (39.7 mL, 1.6 M solution in hexane, 63.5 mmol) was then added in several portions over 30 min. The stirred reaction mixture was warmed slowly to room temperature and was stirred for 6 h. The reaction mixture was then cooled to −78 °C, and $^iPr_3SiCl$ (12.49 g, 64.8 mmol) was added slowly in several portions by using a hypodermic syringe over 30 min. The mixture was warmed slowly to room temperature and was stirred for 12 h. The solution was then warmed to 50 °C and stirred for an additional 2 h to complete the reaction. After the above procedures, the reaction mixture was taken to dryness under vacuum, and the resultant solid was extracted with hexane (200 mL). The hexane extract was concentrated to ca. 60 mL and was dissolved completely by heating. The chilled (−25 °C) hexane solution gave white−purple microcrystals of the titled compound (12.56 g), which were washed quickly with chilled hexane and dried in vacuo. Yield: 84%. ^{1}H NMR (C_6D_6): δ 1.16 (d, J = 7 Hz, 36H, $SiCH(CH_3)_2$), 1.32−1.43 (m, 6H, $SiCHMe_2$), 5.08 (s, 2H, NH), 6.88 (dd, J = 1 and 7 Hz, 2H, $C_{10}H_6$), 7.23 (t, J = 8 Hz, 2H, $C_{10}H_6$), 7.33 (dd, J = 1 and 8 Hz, 2H, $C_{10}H_6$). ^{13}C NMR (C_6D_6): δ 13.4, 18.8, 113.9, 120.5, 125.9, 138.2, 145.1.

1,8-$C_{10}H_6(NLiSi^iPr_3)_2$ (2a). To a cold (−78 °C) solution of 1,8-$C_{10}H_6(NHSi^iPr_3)_2$ (**1a**, 9.95 g, 21.13 mmol) in hexane (100 mL) was added ^{n}BuLi (27.1 mL, 1.6 M solution in hexane, 43.32 mmol) slowly in several portions over 30 min. The reaction mixture was warmed slowly to room temperature and was stirred overnight (>10 h). The reaction mixture was concentrated to 50 mL and was then cooled to −25 °C. White−pale yellow solids were collected from the chilled solution, which were washed quickly with cold hexane, and dried in vacuo. Yield: 10.2 g (>99%). ^{1}H NMR (THF-d_8): δ 1.17 (d, J = 7 Hz, 36H, $SiCH(CH_3)_2$), 1.3−1.4 (m, 6H, $SiCHMe_2$), 6.51 (dd, J = 1 and 8 Hz, 2H, $C_{10}H_6$), 6.66 (dd, J = 1 and 8 Hz, 2H, $C_{10}H_6$), 6.81 (t, J = 8 Hz, 2H, $C_{10}H_6$).

[1,8-$C_{10}H_6(NSi^iPr_3)_2$]$TiCl_2$ (3a). $TiCl_4$ (2.0 g, 10.54 mmol) was added dropwise to a chilled diethyl ether (−25 °C, 60 mL) solution over 30 min. To the cold ether solution (−25 °C) containing a yellow suspension of $TiCl_4(ether)_n$, 1,8-$C_{10}H_6(NLiSi^iPr_3)_2$ (**2a**, 5.09 g, 10.54 mmol) was added in several portions over 30 min. The stirred reaction mixture was warmed slowly to room temperature and was stirred overnight (>10 h). The reaction mixture was then dried in vacuo, and the resultant solid was extracted with toluene (ca. 80 mL). The toluene extract was concentrated to ca. 50 mL and then placed in the freezer (−25 °C) for several days. Deep brown microcrystals were collected, which were washed quickly with cold toluene and dried in vacuo. First crop: 3.42 g. The concentrated (to ca. 20 mL) mother liquor placed in the freezer (−25 °C) gave another crop (460 mg). Total yield: 3.88 g (63%). ^{1}H NMR (C_6D_6): δ 1.08 (d, J = 8 Hz, 36H, $SiCH(CH_3)_2$), 1.66 (m, 6H, $SiCHMe_2$), 6.93 (dd, J = 1 and 8 Hz, 2H, $C_{10}H_6$), 7.13 (t, J = 8 Hz, 2H, $C_{10}H_6$), 7.29 (dd, J = 1 and 8 Hz, 2H, $C_{10}H_6$). ^{13}C NMR (C_6D_6): δ 14.8, 19.1, 118.5, 125.2, 126.3, 135.9, 147.2. Anal. Calcd for $C_{28}H_{48}N_2Cl_2Si_2Ti$: C, 57.23; H, 8.23; N, 4.77. Found (1): C, 57.02; H, 8.50; N, 4.70. Found (2): C, 57.54; H, 8.68; N, 4.76.

1,8-$C_{10}H_6(NHSi^tBuMe_2)_2$ (1b), 1,8-$C_{10}H_6(NLiSi^tBuMe_2)_2$ (2b). Synthesis of **1b** was the same as that for **1a** except that 1,8-naphthalenediamine (1,8-$C_{10}H_6(NH_2)_2$, 4.00 g, 25.3 mmol), THF (60 mL), ^{n}BuLi (31.7 mL, 1.6 M solution in hexane, 50.7 mmol), and $^tBuMe_2SiCl$ (7.66 g, 50.8 mmol) in place of $^iPr_3SiCl$ were used. The mixture after adding $^tBuMe_2SiCl$ was stirred at room temperature for 12 h and was then stirred at 50 °C for additional 3 h. After the above procedures, the reaction mixture was taken to dryness under vacuum, and the resultant solid was then extracted with hexane (200 mL). The hexane extract was concentrated to ca. 30 mL and was dissolved completely upon heating. The chilled (−25 °C) hexane solution gave white−pale purple microcrystals containing the titled compound. The above solids were dissolved in hot hexane (30 mL) and then placed in the freezer. The chilled solution gave white−pale purple microcrystals, which were pure by ^{1}H NMR (6.40 g), which were then washed quickly with chilled hexane and dried in vacuo. Yield: 65%. ^{1}H NMR (C_6D_6): δ 0.23 (s, 12H, $\mathrm{Si(C}H_3)_2{}^t\mathrm{Bu}$), 0.99 (s, 18H, $\mathrm{SiMe_2C(C}H_3)_3$), 5.27 (s, 2H, NH), 6.88 (dd, $J = 1$ and 8 Hz, 2H, $\mathrm{C_{10}}H_6$), 7.22 (t, $J = 8$ Hz, 2H, $\mathrm{C_{10}}H_6$), 7.35 (dd, $J = 1$ and 8 Hz, 2H, $\mathrm{C_{10}}H_6$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ −3.0, 19.5, 38.0, 116.4, 122.1, 122.2, 125.7, 138.0, 144.8.

To a cold (−78 °C) solution of 1,8-$\mathrm{C_{10}H_6(NHSi^tBuMe_2)_2}$ (**1b**, 10.00 g, 25.79 mmol) in hexane (100 mL) was added ^{n}BuLi (32.3 mL, 1.6 M solution in hexane, 51.70 mmol) slowly in several portions over 30 min. The reaction mixture was warmed slowly to room temperature and was stirred overnight (>10 h). The reaction mixture was concentrated to 50 mL and was then cooled to −25 °C. White−pale yellow solids were collected from the chilled solution, washed quickly with cold hexane, and dried in vacuo. Yield: 96%. ^{1}H NMR (THF-d_8): δ 0.20 (s, 12H, $\mathrm{Si^tBu(C}H_3)_2$), 1.04 (s, 18H, $\mathrm{Si}^t\mathit{Bu}\mathrm{(CH_3)_2}$), 6.45 (dd, $J = 1$ and 8 Hz, 2H, $\mathrm{C_{10}}H_6$), 6.63 (d, $J = 7$ Hz, 2H, $\mathrm{C_{10}}H_6$), 6.81 (t, $J = 8$ Hz, 2H, $\mathrm{C_{10}}H_6$).

[1,8-$\mathbf{C_{10}H_6(NSi^tBuMe_2)_2}$]$\mathbf{TiCl_2}$ (3b). $\mathrm{TiCl_4}$ (1.11 g, 5.80 mmol) was added dropwise to a chilled ether (−25 °C, 50 mL) solution over 30 min. To the cold ether solution (−25 °C) containing yellow suspension of $\mathrm{TiCl_4(ether)}_n$, 1,8-$\mathrm{C_{10}H_6}$-$\mathrm{(NLiSi^tBuMe_2)_2}$ (**2b**, 2.36 g, 5.92 mmol) was added in several portions over 30 min. The stirred reaction mixture was warmed slowly to room temperature and was stirred overnight (>10 h). The reaction mixture was then filtered through a Celite pad, which was washed with additional ether (ca. 20 mL). The combined filtrate and wash were dried in vacuo, and the resultant deep brown solids were dissolved in a minimum amount of ether, and then the solution was placed in the freezer (−25 °C) for several days. Deep brown needles were collected, which were washed quickly with cold hexane and dried in vacuo. First crop: 1.82 g (yield 61%). It is also possible to obtain **3b** by the same isolation/purification procedure in **3a**. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.37 (s, 12H, $\mathrm{Si^tBu(C}H_3)_2$), 0.97 (s, 18H, $\mathrm{Si}^t\mathit{Bu}\mathrm{(CH_3)_2}$), 6.80 (dd, $J = 1$ and 8 Hz, 2H, $\mathrm{C_{10}}H_6$), 7.13 (t, $J = 8$ Hz, 2H, $\mathrm{C_{10}}H_6$), 7.26 (dd, $J = 1$ and 8 Hz, 2H, $\mathrm{C_{10}}H_6$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ −0.5, 21, 29, 117.6, 125.6, 125.9, 136.4, 147.7. MS: calcd for $\mathrm{C_{22}H_{36}Cl_2N_2Si_2Ti}$, 503.5; found ($\mathrm{M^-}$), 502.0. Anal. Calcd: C, 52.48; H, 7.21; N, 5.57. Found: C, 52.40; H, 7.54; N, 5.41.

1,8-$\mathbf{C_{10}H_6(NHSiMe_3)_2}$ (1c), **1,8-$\mathbf{C_{10}H_6(NLiSiMe_3)_2}$ (2c).** Synthesis of **1c** was the same as that in **1a** except that 1,8-naphthalenediamine (1,8-$\mathrm{C_{10}H_6(NH_2)_2}$, 4.00 g, 25.3 mmol), ^{n}BuLi (31.7 mL, 50.7 mmol), and $\mathrm{Me_3SiCl}$ (5.52 g, 50.8 mmol) in place of $\mathrm{^iPr_3SiCl}$ were used. After the reaction procedures, the mixture was taken to dryness under vacuum and was extracted with hexane (100 mL). The extract was taken under reduced pressure to remove hexane, and then the flask was placed in the freezer (−25 °C) for ca. 1 week. The resultant solid was almost pure by ^{1}H NMR and enough for preparing the lithium salt. Yield: 6.12 g (80%). ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.19 (s, 18H, $\mathrm{Si(C}H_3)_3$), 5.39 (br s, 2H, N-H), 6.72 (dd, $J = 1$, 7 Hz, 2H, $\mathrm{C_{10}}H_6$), 7.20 (t, $J = 8$ Hz, 2H, $\mathrm{C_{10}}H_6$), 7.34 (dd, $J = 1$, 8 Hz, 2H, $\mathrm{C_{10}}H_6$).

To a cold (−78 °C) solution of 1,8-$\mathrm{C_{10}H_6(NHSiMe_3)_2}$ (**1c**, 2.20 g, 7.28 mmol) in hexane (100 mL) was added ^{n}BuLi (9.12 mL, 1.6 M solution in hexane, 14.59 mmol) slowly in several portions over 30 min. The stirred reaction mixture was warmed slowly to room temperature and was stirred overnight (>10 h). The reaction mixture was concentrated to 50 mL and then cooled to −25 °C. White−pale yellow solids were collected from the chilled solution, which were washed quickly with cold hexane and dried in vacuo. Yield: 2.0 g (87%). ^{1}H NMR (THF-d_8): δ 0.17 (s, 18H, $\mathrm{Si}Me_3$), 6.34 (dd, $J = 1$ and 7 Hz, 2H, $\mathrm{C_{10}}H_6$), 6.47 (dd, $J = 1$ and 8 Hz, 2H, $\mathrm{C_{10}}H_6$), 6.69 (t, $J = 8$ Hz, 2H, $\mathrm{C_{10}}H_6$).

[1,8-$\mathbf{C_{10}H_6(NSiMe_3)_2}$]$\mathbf{TiCl_2}$ (3c). The titled compound, **3c**, was prepared by a procedure similar to that for **3b**. $\mathrm{TiCl_4}$ (600 mg, 3.16 mmol) was added dropwise to chilled diethyl ether (−25 °C, 30 mL) over 30 min. To the cold ether solution (−25 °C) containing a yellow suspension of $\mathrm{TiCl_4(ether)}_n$, 1,8-$\mathrm{C_{10}H_6}$-$\mathrm{(NLiSiMe_3)_2}$ (**2c**, 994 mg, 3.16 mmol) was added in several portions over 10 min. The stirred reaction mixture was warmed slowly to room temperature and was stirred overnight (>10 h). The reaction mixture was then filtered through Celite pad, which was washed with addtional ether (ca. 20 mL). To the resultant ether solution was added dichloromethane, and the mixture was dried in vacuo. The resultant deep brown solids were dissolved in a minimum amount of ether and then placed in the freezer (−25 °C) for several days. Deep brown needles were collected which were washed quickly with cold hexane and dried in vacuo. First crop: 798 mg. Yield: 60%. ^{1}H NMR ($\mathrm{C_6D_6}$): δ 0.60 (s, 18H, $\mathrm{Si}Me_3$), 6.66 (dd, $J = 1$ and 8 Hz, 2H, $\mathrm{C_{10}}H_6$), 7.15 (t, $J = 8$ Hz, 2H, $\mathrm{C_{10}}H_6$), 7.37 (dd, $J = 1$ and 8 Hz, 2H, $\mathrm{C_{10}}H_6$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ 1.9, 110.9, 125.4, 126.8, 137.7, 148.5. MS: calcd for $\mathrm{C_{16}H_{24}Cl_2N_2Si_2Ti}$, 419.3; found ($\mathrm{M^-}$), 417.8.

Polymerization of Ethylene. The catalytic polymerizations of ethylene were performed by using a 1 L scale autoclave. A typical reaction procedure (Table 1, run 10) is as follows: Heptane (300 mL) was added into the autoclave filled with nitrogen, and to the reaction apparatus was then introduced ethylene to 4 kg/cm^2. The premixed toluene solution of [1,8-$\mathrm{C_{10}H_6(NSi^tBuMe_2)_2}$]$\mathrm{TiCl_2}$ (**3b**) (17.5 μmol) with MMAO (5.8 wt % (Al) in hexene, 17.5 mmol) was introduced into the autoclave under pressurized conditions. In the case of the polymerization with $\mathrm{Ph_3CB(C_6F_5)_4}$, the borate in toluene solution was added soon after the addition of complex. The reaction mixture was stirred for 1 h at 4 kg/cm^2 (60 °C), and the polymerization was terminated with the addition of ethanol (15 mL). The solution was then poured into ethanol (200 mL), and the resultant white precipitate was adequately washed with ethanol and then dried in vacuo for several hours. Molecular weights and the molecular weight distributions of the resultant polymers were measured at 145 °C by means of gel-permeation chromatography (Waters 150 CV) using *o*-dichlorobenzene as solvent and the calibration with standard polystyrene samples.

Copolymerization of Ethylene with 1-Butene and Ethylene with 1-Hexene. The catalytic copolymerization of ethylene/1-hexene was carried out in the same manner as that of ethylene polymerization except that 1-hexene was added before introducing ethylene. The catalytic copolymerization of ethylene/1-butene was carried out in the same manner as that of ethylene except that a 400 mL scale autoclave was used in place of the 1 L scale autoclave and 1-butene was introduced before introducing ethylene (reaction temperature 70 °C).

Acknowledgment. K.N. would like to express his heartfelt thanks to Mr. S. Kiuchi for experimental assistance and Mr. A. Kondo (Sumitomo Chemical Co., Ltd.) for mass spectroscopy. K.N. and N.N. would also like to express their thanks to Prof. T. Shiono (Research Laboratory of Resources Utilization, Tokyo Institute of Technology) for his helpful comments.

Supporting Information Available: ^{13}C NMR spectra of ethylene/1-butene copolymers (Tables 3 and 5, runs 8−14, total 7 pages). See any current masthead page for ordering and Internet access assistance.

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(9) We have recently reported that nonbridged cyclopentadienyl(aryloxy)titanium(IV) complexes showed remarkable activities for ethylene polymerization and copolymerization of ethylene with 1-butene: Nomura, K.; Naga, N.; Miki, M.; Yanagi, K.; Imai, A. *Organometallics* **1998**, *17*, 2152.

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(11) The catalytic activity by $[\mathrm{ArN(CH_2)_3NAr}]\mathrm{TiCl_2}$ (Ar = 2,6-$^i\mathrm{Pr_2C_6H_3}$)[4j,k] under the same conditions as run 6 (complex 25.6 μmol, PMAO cocatalyst) was 16.4 kg of PE/(mol of Ti·h) (polymer yield 0.42 g), and the polydispersity value was very broad ($M_w = 11.1 \times 10^4$, $M_w/M_n = 107$). The activity was almost the same when the polymerization was carried out at 40 °C (complex 14.7 μmol, polymer yield 0.20 g, activity 13.6 kg of PE/(mol of Ti·h). Although the polymerization acitivity for ethylene under the same conditions as in run 2 (complex 26.0 μmol, MMAO cocatalyst in heptane) was low (7.8 kg of PE/(mol of Ti·h), polymer yield 0.20 g), this complex showed a remarkable activity for 1-hexene polymerization (1121 kg of poly(1-hexene)/(mol of Ti·h), complex 14.7 μmol in toluene 1 mL, MMAO (Al/Ti = 500), 1-hexene 15 mL, room temperature, 1 h). It is interesting to note that the polymerization activity for ethylene with the $[^t\mathrm{BuN(CH_2)_3N}^t\mathrm{Bu}]\mathrm{TiCl_2}$−MMAO catalyst system was higher (1113 kg of polymer/(mol of Ti·h), catalyst 14.2 μmol, same conditions as in run 2) than that with the $[\mathrm{ArN(CH_2)_3NAr}]\mathrm{TiCl_2}$−MMAO catalyst system under the same conditions, although the polymerization activity for 1-hexene was low, K. Nomura et al. unpublished results. We have also recently found that the polymerization activity by $[\mathrm{ArN(CH_2)_3NAr}]\mathrm{TiCl_2}$ changed with use of several independent MMAO lots.

(12) A similar fact was also observed for ethylene polymerization by the $[^t\mathrm{BuN(CH_2)_3N}^t\mathrm{Bu}]\mathrm{TiCl_2}$−MMAO catalyst system (in heptane): K. Nomura et al., unpublished results. In this case, the M_w/M_n value changed during the polymerization [M_w/M_n = 2.7 (after 5 min) and 7.5 (after 30 min), 1 L flask scale experiment, ethylene 1 atm, 30 °C, MMAO cocatalyst (Al/Ti = 1000)]. We assume from these results, including the case by $[\mathrm{ArN(CH_2)_3NAr}]\mathrm{TiCl_2}$,[11] that the broad M_w/M_n value would be due to the scission of the titanium−nitrogen bond and then generating other active species during the reaction.

(13) These calculations were made by the following paper using ^{13}C NMR spectra of copolymers: (a) Randall, J. C. *J. Polym., Sci., Polym. Phys. Ed.* **1973**, *11*, 275. (b) Randall, J. C. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29&30*, 201.

(14) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.

(15) In addition, the polymerization with **4** proceeded at a remarkable rate at the initial stage but decreased significantly within 10 min. We belive that this is due to the deactivation of the catalyst species during the reaction. The degree of deactivation during the polymerization is also dependent upon the substitutent on the phenoxy group (e.g., ^{i}Pr in place of ^{t}Bu) used: K. Nomura and K. Takaoki, unpublished results.

MA9807163