Effect of Cyclopentadienyl Fragment in Copolymerization of Ethylene with Cyclic Olefins Catalyzed by *Non-Bridged* (Aryloxo)(cyclopentadienyl)titanium(IV) Complexes

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Dedicated in honor to Prof. Richard R. Schrock on the occasion of his 60th birthday.

Abstract: The effect of the cyclopentadienyl fragment in the copolymerization of ethylene with norbornene (NBE) by various *non-bridged* (aryloxo)(cyclopentadienyl)titanium(IV) complexes of the type, Cp′TiCl$_2$(OAr) [Cp′ = indenyl (**1**), C$_5$Me$_5$ (Cp*, **2**), *t*-BuC$_5$H$_4$ (**3**), 1,2,4-Me$_3$C$_5$H$_2$ (**4**); OAr = O-2,6-*i*-Pr$_2$C$_6$H$_3$], −MAO catalyst systems has been explored. The catalytic activity and the NBE incorporation were highly dependent upon substituent on Cp′ employed, and **1** exhibited both a remarkable catalytic activity and an efficient NBE incorporation, affording high molecular weight polymers with unimodal molecular weight distributions. NBE repeat units were observed in the resultant poly(ethylene-*co*-NBE)s prepared by **1**, **3**, and **4**, and the degree of NBE dyads as well as alternating sequences was strongly influenced by the Cp′ employed. These complexes (**1**,**3**,**4**) also exhibited high catalytic activities for ethylene/cyclopentene (CPE) copolymerization, but the CPE incorporation by **1** was less efficient than the NBE incorporation under the same conditions. The *ab initio* density functional (DF) molecular orbital (MO) methods were utilized to explore the effect of substituents on Cp′ toward the catalytic activity, the NBE incorporation and the monomer sequence distribution. Good correlations between the $\Delta E_{coord}{}^{Et}$ (coordination energy of ethylene) after NBE insertion and the activity, and between $\Delta E_{coord}{}^{NBE}$ (coordination energy of NBE) after ethylene (or NBE insertion) and NBE content were observed, strongly suggesting that the capability producing NBE repeat units was dependent upon $\Delta E_{coord}{}^{NBE}$ after NBE insertion.

Keywords: coordination energy; DFT calculation; ethylene; norbornene; polymerization; titanium

Introduction

The design and synthesis of efficient transition metal complex catalysts have been the key for the evolution of new polyolefin materials possessing unique properties by controlled olefin polymerization.[1] Poly(ethylene-*co*-norbornene)s prepared by so-called single-site catalysts have been known as amorphous materials with a promising combination of a high glass transition temperature (T_g), transparency in the UV-VIS region as well as humidity- and heat-resistance.[2,3] It has also been reported that bridged (*ansa*)-zirconocenes like [Me$_2$Si(Ind)$_2$]ZrCl$_2$ and linked half-titanocene complexes like [Me$_2$Si(C$_5$Me$_4$)(N-*t*-Bu)]TiCl$_2$ showed high catalytic activity with efficient norbornene (NBE) incorporation for ethylene/NBE copolymerization.[4–8] However, the microstructures possess few NBE repeat units and contain alternating ethylene-NBE sequences in addition to isolated NBE units.[5–8]

Non-bridged half-metallocene-type titanium(IV) complexes containing anionic ancillary donor ligand of type, Cp′M(L)X$_2$ [M = Ti, Zr, Hf; Cp′ = cyclopentadienyl; L = anionic donor ligand such as aryloxo, amide, anilide, ketimide, phosphinide, amidinate, etc.] have attracted considerable attention,[9–23] because these complexes display unique characteristics that are different from ordinary metallocene-type or linked half-metallocene-type complexes used as the catalyst precursors, especially for copolymerization of ethylene with α-olefins[9,14,23] or styrene.[10a, b] It has been demonstrated

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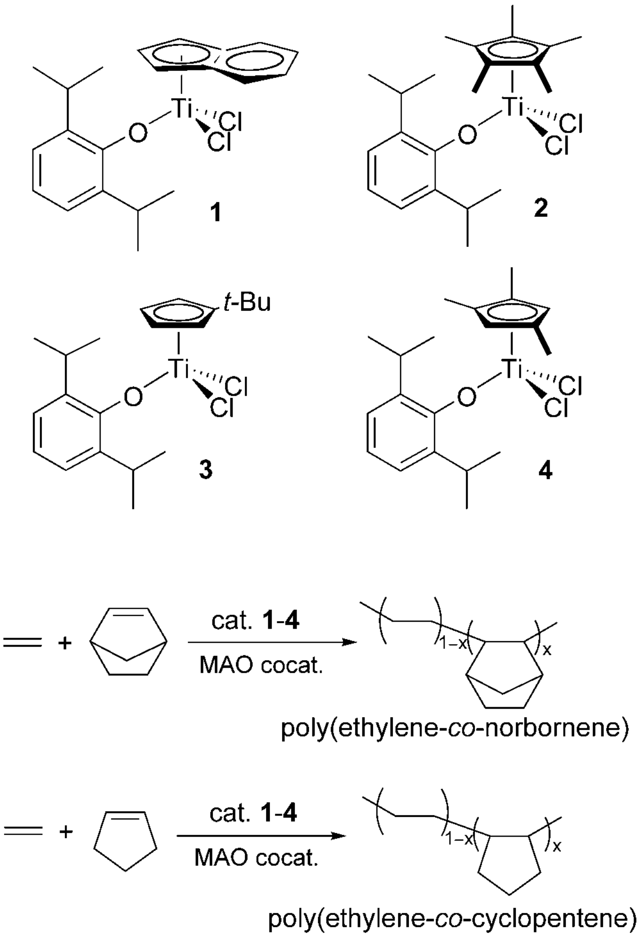


Scheme 1.

that both the monomer reactivities and the monomer sequence distributions could be tuned by a simple modification of the cyclopentadienyl fragment.[9b,10b,14] Moreover, an efficient catalyst for syndiospecific styrene polymerization can be modified to an efficient catalyst for ethylene polymerization by replacing the substituent on Cp′ of the half-titanocenes containing aryloxo,[10a, c] anilide[13] and amide ligands.[14]

We have recently reported in a preliminary communication that (indenyl)$TiCl_2[O-2,6-(i-Pr)_2C_6H_3]$ (**1**) is an effective catalyst precursor for ethylene/NBE copolymerization, affording poly(ethylene-*co*-NBE)s with uniform NBE incorporation.[11] Since it was assumed that the effect of the substituent on Cp′ plays an important role for both the monomer reactivity and the microstructure, in this paper, we present our detailed results concerning effect of the cyclopentadienyl fragment in this copolymerization using a series of (aryloxo)(cyclopentadienyl)titanium(IV) complexes of type, $Cp'TiCl_2(OAr)$ [Cp′ = indenyl (**1**), Cp* ($Cp^* = C_5Me_5$, **2**), t-BuC_5H_4 (**3**), 1,2,4-$Me_3C_5H_2$ (**4**); OAr = O-2,6-$(i\text{-}Pr)_2C_6H_3$, Scheme 1], under optimized polymerization conditions in the presence of methylaluminoxane (MAO) cocatalyst (Scheme 1).[24] Moreover, as also shown in Scheme 1, we introduce our results for the copolymerization of ethylene with cyclopentene and cyclohexene using $Cp'TiCl_2(OAr)$-MAO catalyst systems.

As described above, ligand modification plays an essential role for designing superior catalysts in controlled olefin polymerization. On the other hand, quantum chemical analysis has become a very powerful tool for predicting structures of catalytically-active species and properties of molecules prior to actual proof by experiment.[25] Since recent computational investigations suggest that the rate-determining step in ethylene polymerization is not the insertion but the coordination of a monomer to a cationic metal center,[26] we therefore focused on the coordination energy (ΔE_{coord}) of ethylene and NBE to Ti(IV) cationic species after prior insertion of the monomer. In this paper, the coordination energies were thus calculated for cationic states of $Cp'Ti^+$-R(OAr) (Cp′ = indenyl, Cp*, t-BuC_5H_4, 1,3-t-$Bu_2C_5H_3$) with the use of the density functional theory (DFT), and the correlation between ΔE_{coord} and experimental results has been considered.

Results and Discussion

Effect of Cyclopentadienyl Fragment in Copolymerization of Ethylene with Norbornene with (Aryloxo)(cyclopentadienyl)titanium(IV) Complex-MAO Catalyst Systems

In Table 1 are summarized the results of the copolymerization of ethylene with NBE by the (indenyl)$TiCl_2$(OAr) (**1**)-MAO catalyst system under various conditions.[27] MAO was prepared as a white solid by removing toluene and $AlMe_3$ from commercially available MAO (PMAO, Tosoh Finechem Co.) and was chosen as the cocatalyst because it was effective in the preparation of high molecular weight ethylene/α-olefin copolymers with unimodal molecular weight distributions when the Cp* analogue (**2**) was used as the catalyst precursor.[9a]

It was revealed that **1** exhibited both remarkable catalytic activity and efficient NBE incorporation, and the activity for the copolymerization was found to be higher than that for ethylene homopolymerization (runs 1–4), and an extremely low activity was observed (activity <1 kg polymer/mol Ti·h) when the polymerization was performed in the absence of ethylene.[11] The resultant copolymers possessed relatively high molecular weights with narrow, unimodal molecular weight distributions ($M_n = 14.2-14.6 \times 10^4$, $M_w/M_n = 1.48-1.61$).[28] The activity was somewhat dependent upon the Al/Ti molar ratio (runs 2–4), but both the molecular weights and the NBE contents for the resultant poly(ethylene-*co*-NBE)s were independent of the Al/Ti molar ratio, suggesting that the dominant chain-transfer pathway is

Table 1. Copolymerization of ethylene with norbornene (NBE) by the (indenyl)$TiCl_2[O\text{-}2,6\text{-}(i\text{-}Pr)_2C_6H_3]$ (**1**)-MAO catalyst system.[a]

Run	Cat. **1** [μmol]	Al/Ti[b]	NBE conc.[c] × 10^2	Polymer Yield [mg]	Activity[d]	NBE content[e] [mol %]	M_n[f] × 10^{-4}	M_w/M_n[f]
1	**1** (0.2)	15000	–	232.0	6960	–	22.5	1.88
2	**1** (0.2)	10000	20	345.0	10400	13.7	14.2	1.48
3	**1** (0.2)	15000	20	349.6	10500	14.0	14.6	1.56
4	**1** (0.2)	25000	20	444.0	13300		14.6	1.61
5[g]	**1** (0.2)	15000	20	362.0	10900	20.1	4.84	1.47
1	**1** (0.2)	15000	–	232.0	6960	–	22.5	1.88
6	**1** (0.2)	15000	5.0	245.9	7380	4.9	19.2	2.14
7	**1** (0.2)	15000	5.0	236.0	7080		17.9	2.15
8	**1** (0.1)	30000	5.0	202.2	12100	4.6	21.4	2.03
3	**1** (0.2)	15000	20	349.6	10500	14.0	14.6	1.56
9	**1** (0.2)	15000	30	297.4	8920	18.9	14.6	1.55
10	**1** (0.2)	15000	30	278.7	8360		14.5	1.59
11	**1** (0.2)	15000	40	300.7	9020	22.9	9.46	1.78
12	**1** (0.2)	15000	50	240.8	7220	25.6	9.15	1.72
13	**1** (0.2)	15000	100	68.4	2050		6.51	1.69
14	**1** (0.5)	6000	100	192.0	2300	35.2	5.87	1.82

[a] Conditions: toluene 50 mL, d-MAO (prepared by removing $AlMe_3$ and toluene from PMAO) 3.0 mmol, ethylene 4 atm, 25 °C, 10 min.
[b] Molar ratio of Al/Ti.
[c] Norbornene (NBE) concentration charged (mol/L).
[d] Activity in kg polymer/mol Ti·h.
[e] NBE content (mol %) estimated from ^{13}C NMR spectra.
[f] GPC data in *o*-dichlorobenzene *vs.* polystyrene standards.
[g] Polymerization at 40 °C.

not the chain-transfer to aluminum alkyls but seems to be the β-hydrogen elimination in the copolymerization under these conditions. The molecular weight decreased when the copolymerization was conducted at the higher temperature of 40 °C, although the apparent activity calculated based on the polymer yield remained unchanged (or the activity slightly decreased based on monomer reacted) under these conditions (run 3 *vs.* run 5). This result also supports the above suggestion that the dominant chain-transfer would be the β-hydrogen elimination from propagating metal-alkyl species.

The observed catalytic activities increased upon increasing the NBE concentration, but the activity decreased gradually at higher NBE concentration conditions (runs 6–14). The NBE content increased at higher NBE concentrations, and the M_n values for the resultant copolymers decreased upon increasing the NBE content whereas the M_w/M_n values were unchanged in all cases ($M_w/M_n = 1.55–2.15$), which suggests that resultant copolymer possessed uniform NBE incorporation in all cases.[29]

In Table 2 are summarized the polymerization results with various $Cp'TiCl_2[O\text{-}2,6\text{-}(i\text{-}Pr)_2C_6H_3]$ [Cp′ = indenyl (**1**), Cp* (**2**), $t\text{-}BuC_5H_4$ (**3**), 1,2,4-$Me_3C_5H_2$ (**4**)]-MAO catalyst systems. High catalytic activities were observed when the Cp* analogue **2** was chosen as the catalyst precursor, but the activity decreased upon increasing the initial NBE concentration. The resultant polymers prepared by **2** were poly(ethylene-*co*-NBE)s with high molecular weights ($M_n = 29.6–65.1 \times 10^4$) as well as with narrow molecular weight distributions ($M_w/M_n = 1.46–1.67$), but showed less NBE incorporation than with **1** under the same conditions. Since we assumed that this might be due to the steric bulk of Cp* (**2**) compared to indenyl (**1**), the polymerizations by $Cp^*TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**2a**)-MAO were thus examined. However, the resultant copolymers possessed bimodal molecular weight distributions (runs 28–30, Table 2),[30] although the observed trend for the activity was similar to that observed in the polymerization by **2**. The results with **2a** were somewhat similar to those obtained in ethylene/1-hexene copolymerization,[9b] and thus the copolymerization did not proceed in a single-site nature.

The *t*-BuCp analogue **3** showed better NBE incorporation than **2**, and the efficiency is at the same level as that by **1**, although the observed catalytic activities were lower than those by **1** and **2**. In addition, the activity under high NBE concentration was lower than that by **1** (run 12 *vs.* run 24, NBE 0.5 mol/L). The Me_3Cp analogue **4** showed both high catalytic activity and relatively efficient NBE incorporation, and the activity was higher than that for the homopolymerization (runs 25 and 26). The NBE incorporation by **4** was more efficient than that by **2** (run 17 *vs.* run 26, run 19 *vs.* run 27 by **2** and **4**, respectively), suggesting that the steric bulk on

Table 2. Copolymerization of ethylene with norbornene (NBE) by Cp′TiCl$_2$(OAr) [Cp′=indenyl (**1**), Cp* (**2**), t-BuC$_5$H$_4$ (**3**), 1,2,4-Me$_3$C$_5$H$_2$ (**4**); OAr=O-2,6-(i-Pr)$_2$C$_6$H$_3$]-MAO catalyst systems.[a]

Run	Cat. [μmol]	Al/Ti[b]	NBE conc.[c] × 10^2	Polymer yield [mg]	Activity[d]	NBE content[e] [mol %]	M_n[f] × 10^{-4}	M_w/M_n[f]
1	**1** (0.2)	15000	–	232.0	6960	–	22.5	1.88
6	**1** (0.2)	15000	5.0	245.9	7380	4.9	19.2	2.14
3	**1** (0.2)	15000	20	349.6	10500	14.0	14.6	1.56
12	**1** (0.2)	15000	50	240.8	7220	25.6	9.15	1.72
14	**1** (0.5)	6000	100	192.0	2300	35.2	5.87	1.82
15	**2** (0.2)	15000	–	280.0	8400	–	65.2	1.90
16	**2** (0.2)	15000	10	263.1	7890	4.6	65.1	1.67
17	**2** (0.2)	15000	20	218.1	6540	8.2	57.9	1.61
18	**2** (0.2)	15000	50	124.2	3730	14.9	34.0	1.57
19	**2** (0.2)	15000	100	87.9	2640	21.7	29.6	1.46
20	**3** (0.3)	10000	–	83.0	1660	–	11.5	1.97
21	**3** (0.3)	10000	5.0	211.3	4230		24.8	1.84
22	**3** (0.3)	10000	10	252.6	5050	8.2	18.5	1.75
23	**3** (0.3)	10000	20	119.5	2390	13.4	10.9	1.69
24	**3** (0.3)	10000	50	58.8	1180	24.2	7.40	1.65
25	**4** (0.2)	15000	–	151.0	4530	–	32.2	1.54
26	**4** (0.2)	15000	20	472.0	14200	14.3	29.3	1.75
27	**4** (0.2)	15000	100	65.0	1950	36.6	9.56	1.51
28	**2a**[g] (0.1)	30000	10	172.3	10300		bimodal	
29	**2a**[g] (0.1)	30000	30	121.7	7300		bimodal	
30	**2a**[g] (0.1)	30000	100	50.7	3040		12.3	2.58[h]

[a] Conditions: toluene 50 mL, d-MAO (prepared by removing AlMe$_3$ and toluene from PMAO), ethylene 4 atm, 25 °C, 10 min.
[b] Molar ratio of Al/Ti.
[c] Norbornene (NBE) concentration charged (mol/L).
[d] Activity in kg polymer/mol Ti·h.
[e] NBE content (mol%) estimated from ^{13}C NMR spectra.
[f] GPC data in o-dichlorobenzene *vs.* polystyrene standards.
[g] Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**2a**) was used in stead of Cp*TiCl$_2$[O-2,6-(i-Pr)$_2$C$_6$H$_3$] (**2**).
[h] Bimodal molecular weight distributions.

Cp′ plays a role. The activity drastically decreased at high NBE concentration (run 27). Based on these results, **1** seemed more suited as catalyst precursor exhibiting both high catalytic activity and efficient NBE incorporation.

Figure 1 shows ^{13}C NMR spectra for the resultant poly(ethylene-*co*-NBE)s prepared by **1**–**4**-MAO catalyst systems (NBE content *ca.* 14 mol %), and possible monomer sequences in the copolymer (up to the dyads level) are summarized in Scheme 2. Figure 2 depicts expanded ^{13}C NMR spectra around the C7 regions (*ca.* 33–34 ppm) in the poly(ethylene-*co*-NBE)s prepared by **1**–**4**, and Table 3 summarizes results for the microstructure analyses (NBE contents 8.2–25.6 mol %) estimated based on the ^{13}C NMR spectra to clarify the effect of the cyclopentadienyl group toward the monomer sequences.

The microstructure from **2** possesses few NBE repeat units and contains both *meso* and *racemo* alternating ethylene-NBE sequences (EN) as well as isolated NBE units (33.0–33.5 ppm, Figure 1 **a**, Figure 2 **a**), and the NBE dyads (NN) were also observed as a tiny trace in the spectrum for the copolymer with higher NBE content (Figure 2 **b**, run 19 in Table 3, NBE content 21.7 mol %). In contrast, resonances ascribed to NBE dyads were observed (shown as * in Figure 1 **b**–**d**, corresponding to C5, C6 and C7 carbons) in the spectra for the copolymer by **1**, **3**, and **4**.[31] The microstructure by **1**, **3** estimated by ^{13}C NMR spectra thus possessed a mixture of NBE repeat units (including dyads) in addition to alternating and isolated NBE sequences (Figure 2 **c**–**d**, **g**–**i**). The observed results may be suited as an appropriate explanation for the observed difference in the NBE incorporation between **2** and **1**, **3**. In contrast, the microstructure by **4** possessed a mixture of NBE repeat units and the isolated sequences (Figure 2 **e**, **f**), and the amount of alternating sequences was significantly lower than those by **1**–**3**, especially for the copolymer at high NBE content (Figure 2 **f**, NBE 36.6 mol %). Moreover, as summarized in Table 3, the ratios of isolated/alternative/dyad sequences were highly dependent upon the cyclopentadienyl fragment employed, because the percentage of alternative sequences by **3** was higher than that by **1** under the same NBE content (Table 3, run 23

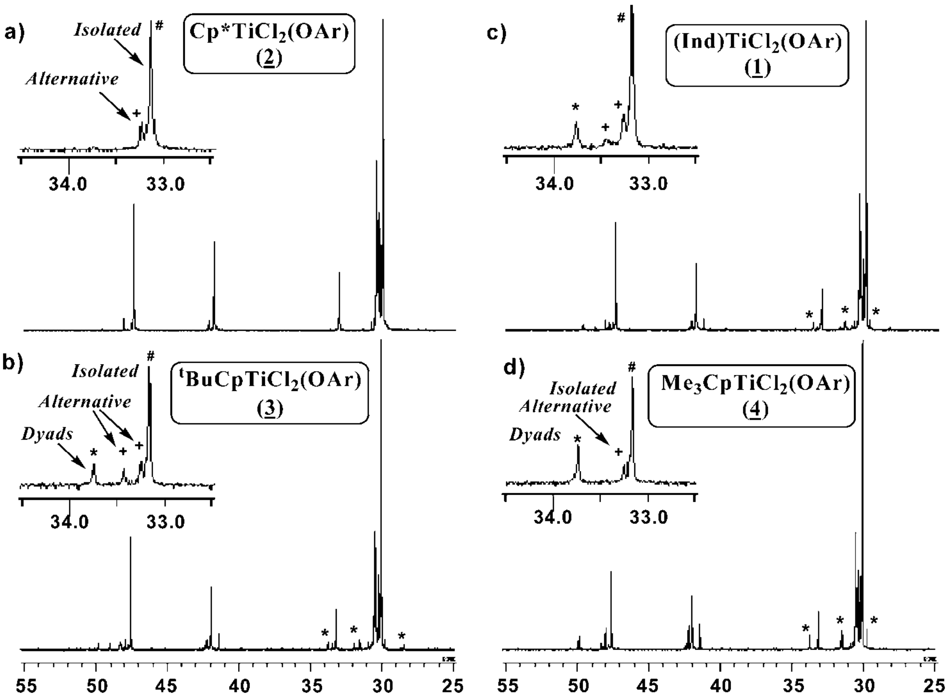


Figure 1. ^{13}C NMR spectra for poly(ethylene-*co*-norbornene)s (in benzene-d_6/1,2,4-trichlorobenzene at 110 °C) prepared by **1** – **4**-MAO catalyst systems, **a**) by **2** (run 18, NBE 14.9 mol %); **b**) by **3** (run 23, NBE 13.4 mol %); **c**) by **1** (run 2, NBE 13.7 mol %); **d**) by **4** (run 26, NBE 14.3 mol%).

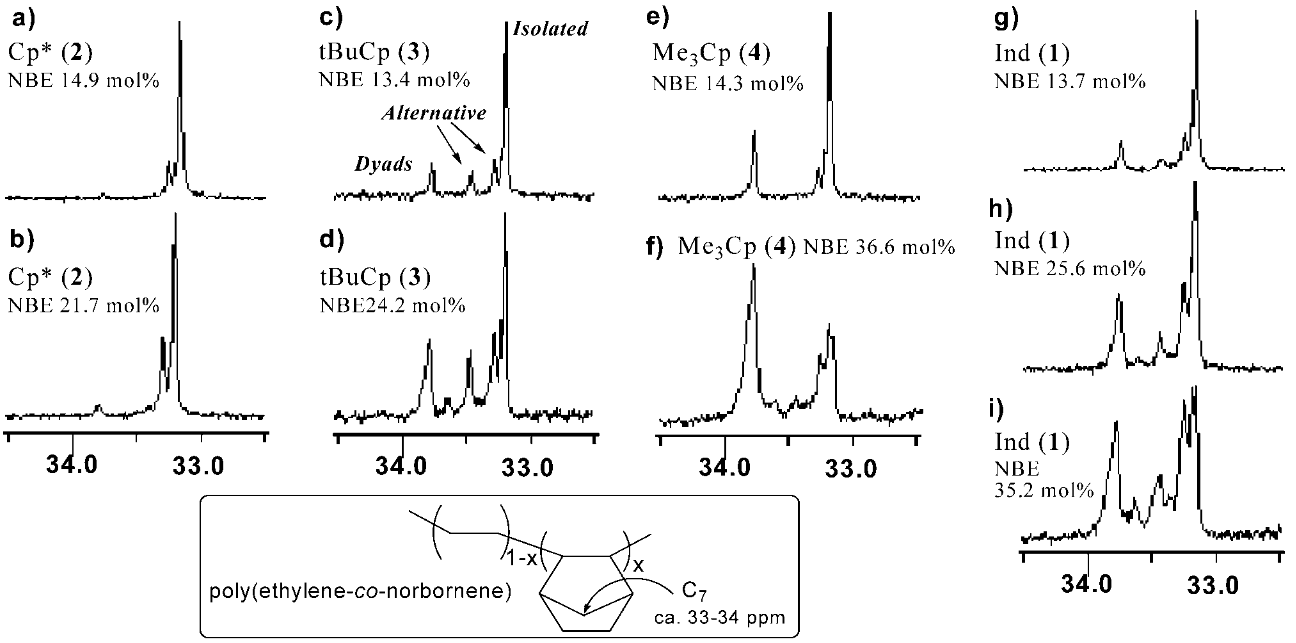
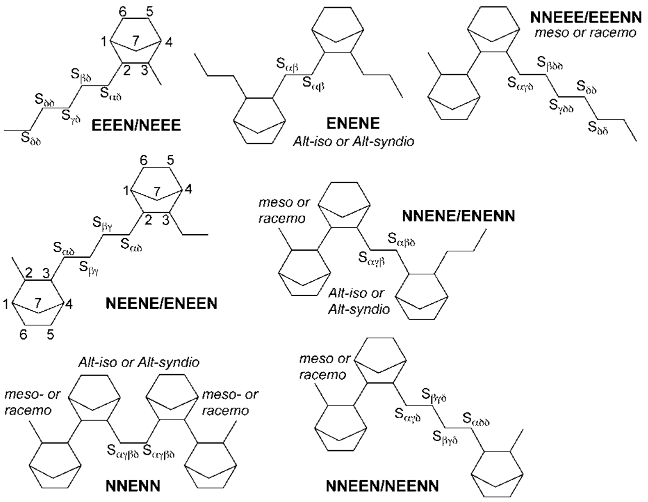


Figure 2. Expanded charts (32.5–34.5 ppm, C7 region, in benzene-d_6/1,2,4-trichlorobenzene at 110 °C) for poly(ethylene-*co*-norbornene)s prepared by Cp′TiCl$_2$[O-2,6-(i-Pr)$_2$C$_6$H$_3$] (**1** – **4**)-MAO catalyst systems. Conditions: **a**, **b**) Cp′ = Cp* (**2**), runs 18, 19, respectively; **c**, **d**) Cp′ = t-BuC$_5$H$_4$ (**3**), runs 23, 24, respectively; **e**, **f**) Cp′ = 1,2,4-Me$_3$C$_5$H$_2$ (**4**), runs 26, 27, respectively; **g**, **h**, **i**) Cp′ = indenyl (**1**), runs 2, 12, 14, respectively. Detailed polymerization results are summarized in Tables 1 and 2.

vs. run 2, run 24 *vs.* runs 11, 12), and the ratio of alternative sequences by **4** was lower than those by **1**, **3**, as also exemplified in Figure 2 **f** (*vs.* Figure 2 **i**). These results thus clearly indicate that the substituent on Cp′ *directly affects* both monomer reactivities and monomer sequence distributions in the copolymerization. Since res-



Scheme 2.

onances ascribed to NBE triads (NNN) as well as NBE dyads (NN) were observed in the ^{13}C NMR spectra for the copolymers prepared by **1** (and by **4**) with higher NBE content, also since **1** exhibited high catalytic activities with efficient NBE incorporation affording a relatively high molecular weight copolymer with uniform NBE incorporation in a random manner, **1** should be the most suited catalyst precursor among **1**–**4** for this copolymerization.

Copolymerization of Ethylene and Cyclopentene with 1–4-MAO Catalyst Systems

In Table 4 are summarized the results of the copolymerization of ethylene with cyclopentene (CPE) using **1**–**4**-MAO catalyst systems.[32,33] The catalytic activities by **1**, **3**, **4** increased with the presence of CPE (runs 32, 35, 36, 38), but decreased upon increasing the CPE concentration. The observed trend was similar to that observed in the ethylene/NBE copolymerization. In contrast, M_n values for the copolymer by **1** significantly decreased with the presence of CPE, and the copolymer prepared by **3** under high CPE concentration possessed bimodal molecular weight distributions.

In Figure 3 are summarized the ^{13}C NMR spectra for poly(ethylene-*co*-CPE)s prepared by the **1-**, **3-**, **4-**MAO catalyst systems. It is clear that CPE was incorporated with the 1,2-insertion mode, and that no or a negligible amount of 1,3-inserted units – as are observed in the copolymer using ordinary zirconocene catalysts – were seen.[33a–d] The fact clearly suggests that CPE incorporation took place in a regioselective manner as seen with some titanium complex catalysts,[33e, f] and this exclusive selectivity may be attributed to a lower tendency to undergo β-hydrogen elimination than those using zirconocene complex catalysts as proposed previously.[33f] These microstructures possessed both isolated and alternative CPE sequences, and the degree of alternative sequences seemed to be dependent upon the cyclopentadienyl fragment employed. Although the M_n values for the resultant copolymer were low, the polymer from **1** possessed a relatively high degree of CPE alternative sequences; the copolymer from **4** possessed a low degree of the CPE alternative sequences. Taking into account these results, **3** may be best suited as the catalyst precursor for this copolymerization in terms of exhibiting a high catalytic activity with efficient CPE incorporation, but a more suitable complex catalyst will be designed by a modification of the cyclopentadienyl fragment. Copolymerization of ethylene with cyclohexene by **1** was attempted under the same conditions (run 31, Table 4), and a slight increase in the catalytic activity and the de-

Table 3. Microstructure analysis in poly(ethylene-*co*-norbornene)s prepared by Cp′TiCl$_2$(OAr) [Cp′ = indenyl (**1**), Cp* (**2**), *t*-BuC$_5$H$_4$ (**3**), 1,2,4-Me$_3$C$_5$H$_2$ (**4**); OAr = O-2,6-(*i*-Pr)$_2$C$_6$H$_3$]-MAO catalyst systems (NBE incorporation mode, estimated by C7 region in ^{13}C NMR spectra).[a]

Run	Cat. Cp′	NBE content[b]	NBE incorporation[c] [%]		
			isolated	alternative	dyads
17	Cp* (**2**)	8.2	92	8	–
18	Cp* (**2**)	14.9	84	16	Trace
19	Cp* (**2**)	21.7	69	27	4
22	*t*-BuC$_5$H$_4$ (**3**)	8.2	80	13	7
23	*t*-BuC$_5$H$_4$ (**3**)	13.4	65	23	12
24	*t*-BuC$_5$H$_4$ (**3**)	24.2	38	35	27
2	indenyl (**1**)	13.7	71	18	11
11	indenyl (**1**)	22.9	48	28	24
12	indenyl (**1**)	25.6	46	28	26
26	1,2,4-Me$_3$C$_5$H$_2$ (**4**)	14.3	59	12	28

[a] Detailed conditions, see Table 2.
[b] NBE content in mol %.
[c] Estimated from ^{13}C NMR spectra in the C7 region (shown in Figure 2, selected spectra).

Table 4. Copolymerization of ethylene with cyclopentene (CPE) by $Cp'TiCl_2(OAr)$ [Cp′ = indenyl (**1**), Cp* (**2**), t-BuC_5H_4 (**3**), 1,2,4-$Me_3C_5H_2$ (**4**); OAr = O-2,6-(i-Pr)$_2C_6H_3$]-MAO catalyst systems[a] and attempted copolymerization of ethylene with cyclohexene (CHE).

Run	Cat. [μmol]	Al/Ti[b]	CPE conc.[c] × 10^2	Polymer yield[mg]	Activity[d]	CPE content[e] [mol %]	M_n[f] × 10^{-4}	M_w/M_n[f]
1	**1** (0.2)	15000	–	232.0	6960	–	22.5	1.88
31	**1** (0.2)	15000	20[g]	268.0	8040	none[g]	18.0	2.19
32	**1** (0.2)	15000	20	429.0	12900	9.0	0.85	2.08[h]
33	**1** (0.2)	15000	100	166.0	4980	12.1	0.56	1.88[h]
15	**2** (0.2)	15000	–	280.0	8400	–	65.2	1.90
34	**2** (0.2)	15000	20	237.0	7110	3.0	59.3	2.09
20	**3** (0.3)	10000	–	83.0	1660	–	11.5	1.97
35	**3** (0.3)	10000	20	124.0	2480	11.5	2.52	1.93[h]
36	**3** (0.3)	10000	40	289.0	5980	17.2	2.10	1.93[h]
37	**3** (0.3)	10000	100	50.0	1080		31.8	2.27
							0.94	1.66
25	**4** (0.2)	15000	–	151.0	4530	–	32.2	1.54
38	**4** (0.2)	15000	20	216.0	6480	10.5	12.20	1.55

[a] Conditions: toluene + cyclopentene (CPE) total 50 mL, d-MAO (prepared by removing $AlMe_3$ and toluene from PMAO), ethylene 4 atm, 25 ^{0}C, 10 min.

[b] Molar ratio of Al/Ti.

[c] CPE concentration charged [mol/L).

[d] Activity in kg polymer/mol Ti·h.

[e] CPE content [mol %] estimated from ^{13}C NMR spectra.

[f] GPC data in o-dichlorobenzene *vs.* polystyrene standards.

[g] Cyclohexene (CHE) was used in place of cyclopentene (CPE).

[h] High molecular weight shoulder was also observed on GPC trace.

crease in the M_n value was obtained in the presence of cyclohexene. However, the resultant polymer possessed no or a negligible amount of cyclohexene incorporation as suggested by the previous report.[33f]

DFT Investigation Concerning the Role of the Cyclopentadienyl Fragment in Ethylene/NBE Copolymerization Catalyzed by Half-Titanocenes Containing an Aryloxo Ligand

Quantum chemical analysis has become a very powerful tool for predicting the structures of catalytically active species prior to the actual experimental proof.[25] Coordination energies (ΔE_{coord}) of ethylene and NBE monomers to Ti(IV) cationic complexes after prior insertion of monomers were calculated, because a recent computational investigation suggested that the rate-determining step in ethylene polymerization is not the insertion of a monomer but the coordination of a monomer to a cationic metal center.[26] Density functional theory (DFT) was chosen to calculate the coordination energies for cationic states of $Cp'Ti^+R(OAr)$ [Cp′ = indenyl (**1′**), Cp* (**2′**), t-BuC_5H_4 (**3′**), 1,3-(t-Bu)$_2C_5H_3$ (**5′**); R = alkyl], and the correlations between ΔE_{coord} and the experimental results were explored. The 1,3-t-Bu_2Cp analogue (**5′**) was chosen for comparison, because this complex was quite ineffective for ethylene/NBE copolymerization[11] whereas relatively high catalytic activity and efficient 1-hexene incorporation were observed in the ethylene/1-hexene copolymerization.[9b]

Coordination after Ethylene Insertion

A cationic Ti-pentyl complex shown in Figure 4 (exemplified as the indenyl analogue) was used as the model after ethylene (Et) insertion whereby the agostic interaction between β-H and the Ti metal center (in dashed line) can be seen. Two types of NBE coordination leading to 2,3-*exo-cis*-addition through 2,3- and 3,2-insertion, which are defined as 2,3- and 3,2-coordination (Figure 5), were also considered.[2a]

ΔE_{coord} values after ethylene insertion are presented in Table 5, and optimized structure of the indenyl analogue is depicted in Figure 6. These coordination energies (ΔE_{coord}) of ethylene (ΔE_{coord}^{Et}), NBE (ΔE_{coord}^{NBE}) are larger than 7.0 kcal/mol in all cases (the indenyl, Cp*, t-Bu-, and t-Bu_2Cp analogues), indicating that all of the π-complexes formed after ethylene insertions are stable. In addition, ΔE_{coord}^{NBE} values were larger than ΔE_{coord}^{Et} in all cases, indicating that the π-complex of NBE is more stable than that of ethylene. This probably originates from the strong orbital interaction between the highest occupied molecular orbital (HOMO) of NBE and the lowest unoccupied molecular orbital (LUMO) of these complexes. The HOMO energies of NBE and ethylene were thus calculated to be −0.23136

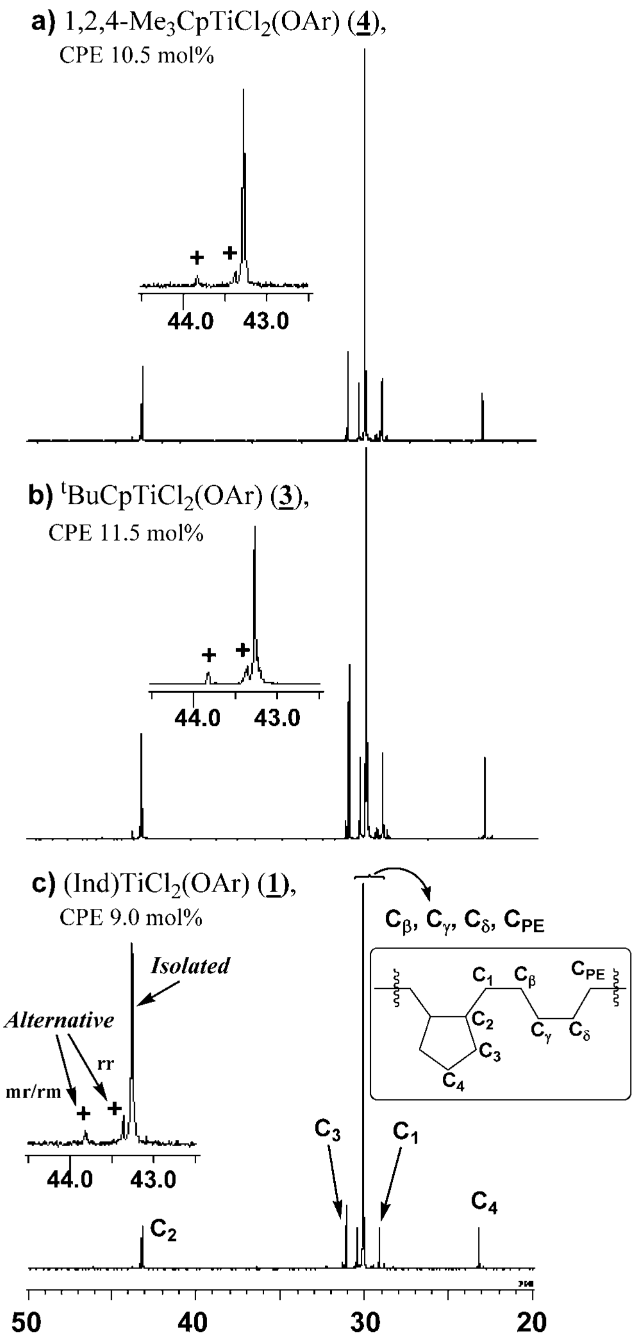


Figure 3. ^{13}C NMR spectra for poly(ethylene-*co*-cyclopentene)s (in benzene-d_6/1,2,4-trichlorobenzene at 110 °C) prepared with **1**-, **3**- ,**4**-MAO catalyst systems.

and – 0.26734 hartree, respectively, whereas the LUMO energies of these complexes were from – 0.22849 to – 0.23874 hartree. In the case of NBE coordination, strong orbital interaction is thus expected on account of the small HOMO-LUMO level separation between reactants, and the higher energy level of the π orbital of NBE than that of ethylene is attributed to the strained structure of NBE itself. For instance, the calculated C2–C3–C4 angle of NBE was 107.5°, which is very different from ideal value of 120.0°. This strain leads to unnatural sp^2 or sp^3 hybridization, resulting in a weakening of the π-bonding between the C2 and C3 atoms.

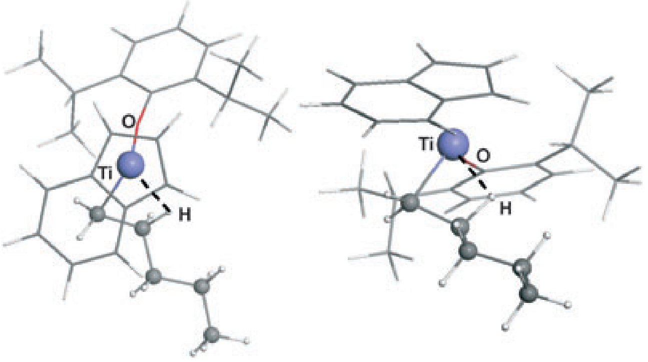


Figure 4. Optimized structure of (indenyl)Ti(pentyl)[O-2,6-(*i*-Pr)$_2$C$_6$H$_3$] complex.

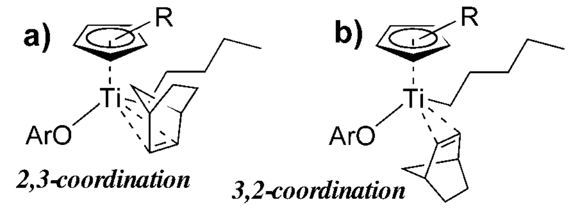


Figure 5. Supposed two NBE coordination modes on to the Ti metal center.

ΔE_{coord}^{Et} and ΔE_{coord}^{NBE} values for **3′** were larger than those for the other complexes, probably due to its sterically-open structure. Note that ΔE_{coord}^{NBE} for **1′** is the same as that for **3′**, and the bond length between Ti and C2 of NBE (2.56 Å for 2,3-coordination; 2.55 Å for 3,2-coordination) in **1′** is much shorter than those in other complexes (2.58–2.70 Å), suggesting that NBE would coordinate to Ti with the strong orbital interaction.

It should be noted that $\Delta E_{coord}^{NBE}(3,2)$ is about 2 kcal/mol larger than $\Delta E_{coord}^{NBE}(2,3)$ for **1′**, whereas $\Delta E_{coord}^{NBE}(3,2)$ and $\Delta E_{coord}^{NBE}(2,3)$ values for **2′**, **3′** and **5′**are nearly equal. Therefore, NBE insertion by **1′** should proceed in a stereospecific manner with a favored 3,2-coordination mode, and this would be due to the steric repulsion between methylene groups including C7 of NBE and the indenyl group in 2,3-coordination which leads to smaller $\Delta E_{coord}^{NBE}(2,3)$ values than $\Delta E_{coord}^{NBE}(3,2)$ values.

Since no correlation between the catalytic activities in ethylene/NBE copolymerization and ΔE_{coord}^{Et}, ΔE_{coord}^{NBE}, and $\Delta E_{coord}^{NBE} - \Delta E_{coord}^{Et}$ values were observed, the activities are unpredictable in terms of stability of the π-complexes generated after ethylene insertion. In contrast and importantly, the catalytic activities for ethylene polymerization by these complexes were found to increase with decreasing ΔE_{coord}^{Et} value (Figure 7). Taking into account that the energy barrier of

Table 5. Calculated results for ΔE_{coord}^{Et}, ΔE_{coord}^{NBE}, and $\Delta E_{coord}^{NBE} - \Delta E_{coord}^{Et}$ after ethylene (Et) insertion, and the catalytic activities and the NBE contents from the experiments.

Complex	Calculated Results				Exp. 1[a]	Exp. 2[b]		Exp. 3[c]	
Cp′	ΔE_{coord}^{Et} [kcal/mol]	$\Delta E_{coord}^{NBE}(2,3)$ [kcal/mol]	$\Delta E_{coord}^{NBE}(3,2)$ [kcal/mol]	$\Delta E_{coord}^{NBE} - \Delta E_{coord}^{Et}$ [kcal/mol]	Activity[d] [TOF × 10^{-3}][f]	Activity[d] [TOF × 10^{-3}][f]	NBE[e] [mol %]	Activity[d] [TOF × 10^{-3}][f]	NBE[e] [mol %]
indenyl (**1′**)	7.78	10.64	12.50	4.73	6960 (248)	10500 (278)	14.6	7220 (154)	28.3
Cp* (**2′**)	7.09	8.57	8.48	1.48	8400 (299)	6540 (194)	8.6	3730 (97.4)	15.5
t-BuCp (**3′**)	9.33	12.55	11.97	3.22	1660 (59.2)	2390 (63.0)	15.0	1180 (25.7)	27.1
t-Bu$_2$Cp (**5′**)	7.55	8.29	8.33	0.78	–	45[g] (1.6)[g]	–	–	–

[a] Ethylene homopolymerization results (ethylene 4 atm) shown in Table 2.
[b] Conditions: ethylene 4 atm, initial NBE conc. 0.20 mol/L (ex. run 3 by **1**).
[c] Conditions: ethylene 4 atm, initial NBE conc. 0.50 mol/L (ex. run 12 by **1**).
[d] Activity in kg polymer/mol Ti·h.
[e] NBE content in mol % estimated from ^{13}C NMR spectra.
[f] TOF (turnover frequency) = (molar amount of ethylene and NBE reacted)/mol Ti·h.
[g] Cited from ref.[11] and the TOF value was estimated based on polyethylene due to the inefficient NBE incorporation as well as the low activity.

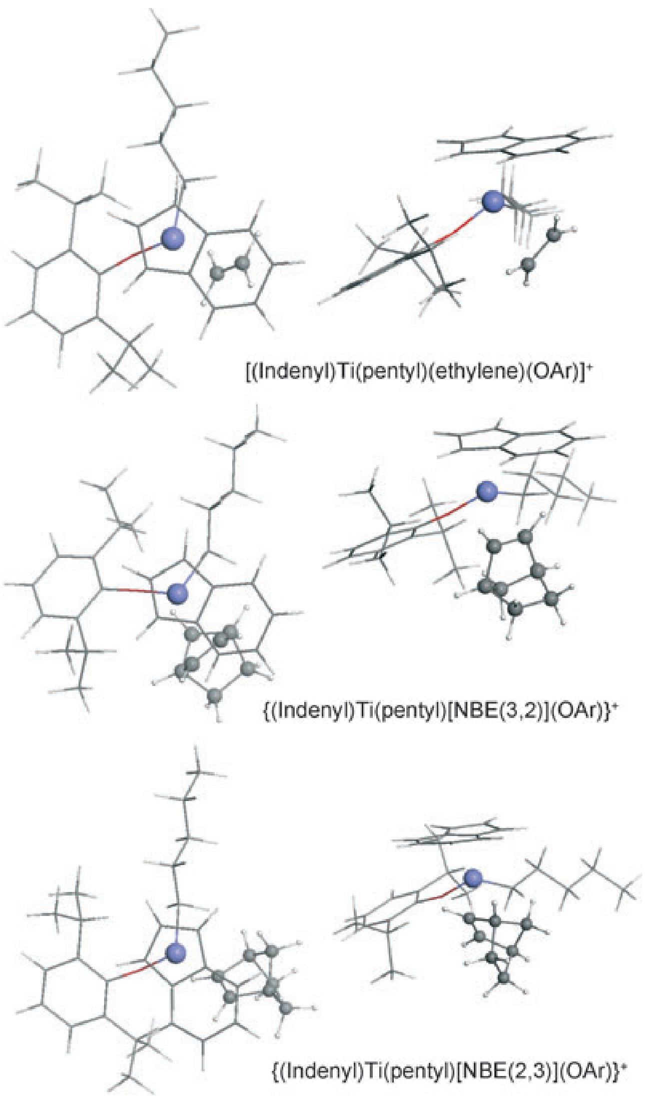


Figure 6. Optimized structures of ethylene, and NBE coordinated complexes.

monomer insertion tends to increase upon increasing the stability of the π-complex, the catalytic activities should depend on the rate of insertion of monomer rather than on the rate of coordination of monomer in this case. The trend seen here is somewhat different from that proposed by the calculation study for ethylene polymerization, from which ethylene coordination should be the rate-determining step.[26] The observed difference here may indicate that the rate-determining process in this catalysis is the insertion of the monomer or that the rates of ethylene coordination are nearly the same among these half-titanocene species, and the rate of other processes like insertion of monomer thus influences the catalytic activities.

As shown in Figure 8, relatively good relationships between ΔE_{coord}^{NBE}, $\Delta E_{coordm}^{NBE} - \Delta E_{coord}^{Et}$ values (based on DFT calculation) and the NBE contents (experimental values, Table 2) were observed, and these suggest

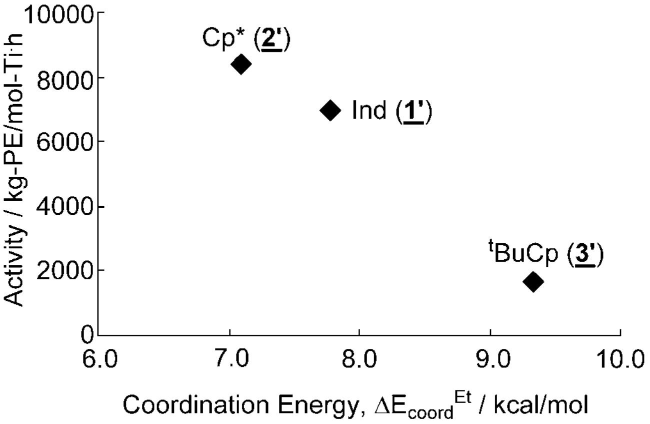


Figure 7. Plots of catalytic activity (in ethylene polymerization, Table 2) *vs.* coordination energy, ΔE_{coord}^{Et} calculated by DFT.

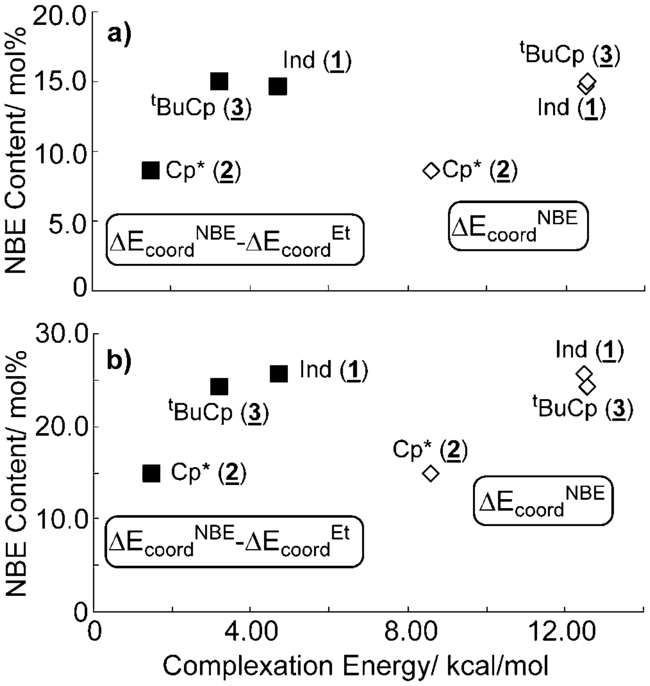


Figure 8. Plots of NBE contents (experimental results in Table 2) *vs.* complexation energies, $\Delta E_{coord}^{NBE} - \Delta E_{coord}^{Et}$ and ΔE_{coord}^{NBE} calculated by DFT. Experimental conditions for copolymerization of ethylene with NBE: **a**) ethylene 4 atm, initial NBE 0.20 mol/L (ex. run 3 by **1**); **b**) ethylene 4 atm, initial NBE 0.50 mol/L (ex. run 12 by **1**).

that the NBE incorporation is thus affected by the energetic preference of coordination between NBE and ethylene into the alkyl-cationic species.

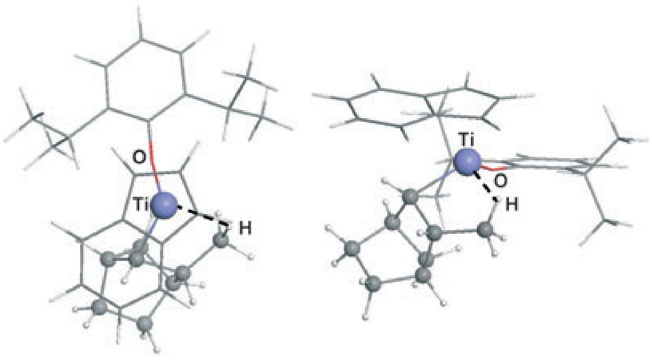


Figure 9. Optimized structure of (indenyl)Ti[(3-methyl)-2-bicyclo[2.2.1]heptyl][O-2,6-(*i*-Pr)$_2$C$_6$H$_3$] complex.

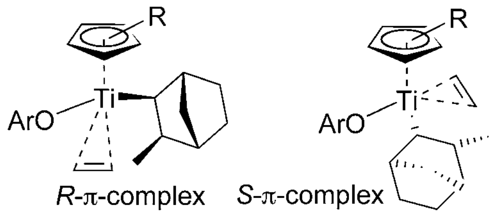


Figure 10. Proposed two coordination types of NBE into titanium complexes after NBE insertion (3,2-coordination mode).

Coordination after NBE Insertion

A cationic (3-methyl)-2-bicyclo[2.2.1]heptyl complex shown in Figure 9 (exemplified as the indenyl analogue) was used as the model after NBE insertion whereby the agostic interaction between γ-H and the Ti can be seen. The Ti atom of the complexes becomes a stereogenic center with different coordination sites in this case, leading to the formation of *R* and *S* π-complexes as shown in Figure 10.[34] Only 3,2-coordination was considered for NBE, because the energy of 3,2-coordination after ethylene insertion by **1′** was larger than that of 2,3-coordination and no significant differences were observed between 2,3- and 3,2-coordination by the other complexes.

In Table 6 are summarized the values of the coordination energy, ΔE_{coord}, after NBE insertion. The ΔE_{coord} values after NBE insertion are smaller than the ΔE_{coord} values after ethylene insertion in all cases. This would be due to that the resultant cationic complex after NBE insertion possesses a narrower coordination space than that arising after ethylene insertion because of the increased steric bulk of NBE, and subsequent monomer coordination should hardly occur smoothly without reconstructing the structure of the cationic species for coordination of the next monomer to the Ti. For instance, as shown Figure 11, the cationic complex is transformed from a γ-H agostic to an α-H agostic structure by olefin insertion. Since the reconstruction should require additional energy, the π-complex formed after NBE insertion should be less stable than that formed after ethylene insertion.

It was found that the ΔE_{coord}^{Et} value is larger than ΔE_{coord}^{NBE} in all cases, suggesting that the π-complex of

Table 6. Calculated results for $\Delta E_{coord}{}^{Et}(R)$, $\Delta E_{coord}{}^{Et}(S)$, $\Delta E_{coord}{}^{NBE}(R)$, $\Delta E_{coord}{}^{NBE}(S)$, and $\Delta E_{coord}{}^{NBE} - \Delta E_{coord}{}^{Et}$ after NBE insertion.

Complex Cp′	$\Delta E_{coord}{}^{Et}(R)$ [kcal/mol]	$\Delta E_{coord}{}^{Et}(S)$ [kcal/mol]	$\Delta E_{coord}{}^{NBE}(R)$ [kcal/mol]	$\Delta E_{coord}{}^{NBE}(S)$ [kcal/mol]	$\Delta E_{coord}{}^{NBE} - \Delta E_{coord}{}^{Et}$ [kcal/mol]
indenyl (**1**′)	3.58	5.30	1.88	0.82	–3.42
Cp* (**2**′)	0.39	1.23	–5.18	–5.49	–6.41
t-BuCp (**3**′)	4.81	4.96	0.12	3.03	–1.93
t-Bu$_2$Cp (**5**′)	–2.63	–1.01	–4.80	–2.86	–1.85

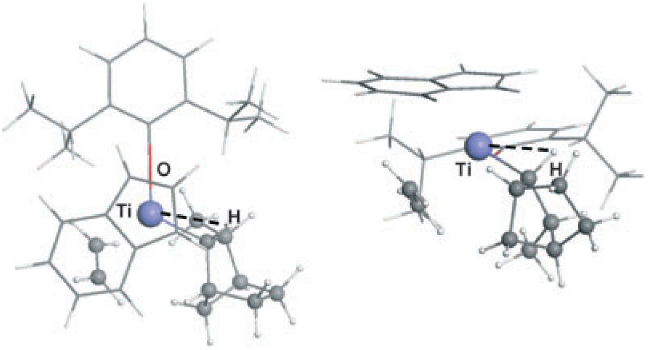


Figure 11. Optimized structure of (indenyl)Ti[(3-methyl)-2-bicyclo[2.2.1]heptyl][O-2,6-(i-Pr)$_2$C$_6$H$_3$](ethylene) complex.

NBE is less stable than that of ethylene, also suggesting that this trend is opposite to that after ethylene insertion. As mentioned above, since monomer coordination after NBE insertion should require the reconstruction of a cationic complex due to the increased steric bulk of NBE, NBE coordination should thus require more energy than the ethylene coordination, causing the π-complex of NBE to be less stable than that of ethylene. Although, as shown above, the high energy level of the π orbital of an NBE molecule makes the π-complex of NBE more stable than that of ethylene, the former effect should be more significant than the latter effect, which results in the tendency that $\Delta E_{coord}{}^{Et}$ is larger than $\Delta E_{coord}{}^{NBE}$.

Both $\Delta E_{coord}{}^{Et}$ and $\Delta E_{coord}{}^{NBE}$ values (after NBE insertion) for **1**′ and **3**′are positive, suggesting that the monomer coordination leads to the stabilization. This may be attributed to the open space for monomer coordination for these cationic complexes, and both NBE and ethylene coordination should occur after NBE insertion, supporting our experimental observation that the resultant copolymers form **1** and **3** possessed NBE repeat units. In contrast, the $\Delta E_{coord}{}^{NBE}$ values for **2**′ are negative, indicating that the NBE coordination to the Ti atom after NBE insertion seems difficult. This result also supports our experimental observation that resultant copolymer prepared with **2** possessed only few NBE repeat units. Moreover, both $\Delta E_{coord}{}^{Et}$ and $\Delta E_{coord}{}^{NBE}$ values for **5**′ are negative, and this suggests that coordination of ethylene or NBE seemed to be very difficult, leading to a low catalytic activity as well as an inefficient NBE incorporation.

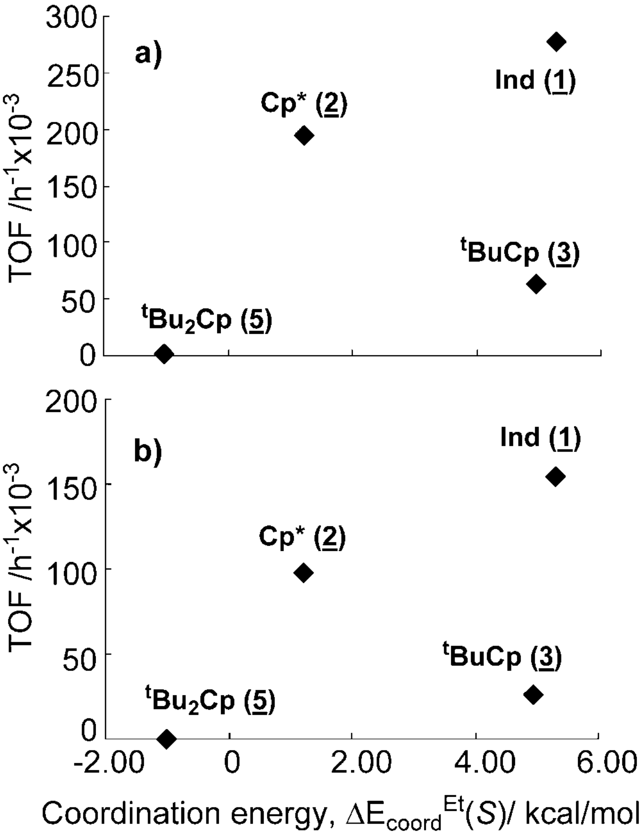


Figure 12. Plots of TOF (experimental results, Tables 6) *vs.* coordination energy, $\Delta E_{coord}{}^{Et}(S)$ calculated by DFT. Experimental conditions for copolymerization of ethylene with NBE: **a**) ethylene 4 atm, initial NBE 0.20 mol/L (ex. run 3 by **1**); **b**) ethylene 4 atm, initial NBE 0.50 mol/L (ex. run 12 by **1**).

As shown in Figure 12, a good correlation was found between the catalytic activities (TOF) in the ethylene/NBE copolymerization and the coordination energy of ethylene after NBE insertion, $\Delta E_{coord}{}^{Et}(S)$, with preferred coordination mode. Although **3** deviated from this trend as a sole exception,[35] the observed trend suggests that the stability of the π-complex formed after NBE insertion affects the catalytic activity.[36] In addition to the observed relationship between NBE contents and

ΔE_{coord}^{NBE} or $\Delta E_{coord}^{NBE} - \Delta E_{coord}^{Et}$ after ethylene insertion (Figure 8), which suggests that the NBE incorporation is affected by the energetic preference of coordination between NBE and ethylene into the alkyl-cationic species, the NBE incorporation in this catalysis may be strongly affected by the stability of the π-complex of NBE after NBE and ethylene insertion.

Conclusion

We have shown that (aryloxo)(cyclopentadienyl)titanium complexes exhibit remarkable catalytic activities for the copolymerization of ethylene with norbornene in the presence of MAO cocatalyst. We have also demonstrated that the catalytic activity and monomer reactivity as well as the monomer sequence distributions can be tuned by modification of the cyclopentadienyl fragment. These are one of the unique characteristics of using *non-bridged* half-titanocenes as the catalyst precursor for precise olefin polymerization, as we demonstrated previously in the copolymerization of ethylene with α-olefins as well as styrene. The indenyl analogue **1** exhibit both high catalytic activity and efficient NBE incorporation in a random manner, affording high molecular weight polymers with unimodal molecular weight distributions. High catalytic activities were also observed for the copolymerization of ethylene with cyclopentene (CPE) by these catalysts, but the CPE incorporations by **1** and **3** were less efficient than the NBE incorporations under the same conditions. Since the attempted copolymerization of ethylene with cyclohexene afforded polyethylene, therefore, the more suited complex catalyst for these copolymerizations will be designed by a modification of cyclopentadienyl fragment.

We have calculated the coordination energies ΔE_{coord}^{Et} and ΔE_{coord}^{NBE} after ethylene and NBE insertion into the alkyl cationic titanium(IV) species, and explored the correlation between the coordination energies and the experimental results (catalytic activity, NBE content, monomer sequence). We have found that the catalytic activities increased upon increasing the ΔE_{coord}^{Et} after NBE insertion, suggesting that the stability of the π-complex generated after NBE insertion affects the catalytic activity. The relatively high stability of the π-complex formed after NBE insertion is considered as being necessary for repeated NBE units to be incorporated into the polymer chain. Moreover, it has been shown that the NBE contents increased upon increasing ΔE_{coord}^{NBE} and $\Delta E_{coord}^{NBE} - \Delta E_{coord}^{Et}$ values after ethylene and NBE insertion. These facts clearly demonstrate that a superior molecular catalyst, which exhibits notable catalytic activity and controls NBE content as well as the NBE sequence in the copolymer, should be predicted by calculating coordination energies in this catalysis.

Experimental Section

General Procedure

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres dry-box or by using standard Schlenk techniques unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Toluene for polymerization was distilled in the presence of sodium and benzophenone under a nitrogen atmosphere, and was stored in a Schlenk tube in the dry-box in the presence of molecular sieves. Ethylene was of polymerization grade (purity > 99.9%, Sumitomo Seika Co. Ltd) and was used as received. Norbornene and/or cyclopentene of reagent grade (Aldrich) were stored in a bottle in the dry-box. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were taken to dryness under reduced pressure (at *ca.* 50 °C for removing toluene, $AlMe_3$, and then heated at > 100 °C for 1 h for completion) in the dry-box to give white solids. (Aryloxo)(cyclopentadienyl)titanium(IV) complexes of the type, $Cp'TiCl_2(OAr)$ [$Cp' = C_5Me_5$ (**2**), t-BuC_5H_4 (**3**), 1,2,3-$Me_3C_5H_2$ (**4**); OAr = O-2,6-i-$Pr_2C_6H_3$] or Cp^*TiCl_2(O-2,6-$Me_2C_6H_3$) (**2a**), were prepared according to our previous report.[9a]

Molecular weights and molecular weight distributions for polyethylene and poly(ethylene-*co*-norbornene)s were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GMH_{HR}-H HT × 2, 30 cm × 7.8 mm ϕ ID), ranging from $< 10^2$ to $< 2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v % 2,6-di-*tert*-butyl-*p*-cresol as eluent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

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 a nitrogen atmosphere, and 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 poly(ethylene-*co*-norbornene)s were recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, ^{13}C) with proton decoupling. The pulse interval was 5.2 sec, the acquisition time was 0.8 sec, the pulse angle was 90°, and the number of transients accumulated was *ca.* 8000. The analysis samples were prepared by dissolving polymers in a mixed solution of 1,2,4-trichlorobenzene/benzene-d_6 (90/10 wt), and these spectra were measured at 110 °C.

Synthesis of (Indenyl)$TiCl_2$[O-2,6-(i-Pr)$_2C_6H_3$] (1)

LiO-2,6-(i-Pr)$_2C_6H_3$ (684 mg, 3.71 mmol) was added in one portion to an Et_2O solution (30 mL) containing (indenyl)$TiCl_3$ (1000 mg, 3.71 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature, and stirred for 10 h. The mixture was then filtered through Celite, and the filter cake washed with Et_2O. The combined filtrate and the washings were taken to dryness under reduced pressure to give a deep red solid. The solid was then dissolved in a minimum amount of CH_2Cl_2 layered by a small amount of *n*-hexane. The chilled (−30 °C) solution gave purple microcrystals (1st crop), and the chilled concentrated mother liquor gave a second crop. Yield: 1.19 g (78%). ^{1}H NMR (C_6D_6): $\delta = 1.26$ [d, 12H, ($\underline{CH_3}$)$_2$CH-], 3.38 (m, 2H, Me$_2$C$\underline{H}$-), 6.18 (t, 1H, $\underline{\text{Ind}}$), 6.46 (d, 2H, $\underline{\text{Ind}}$), 6.87–7.18 (m, 5H), 7.37 (m, 2H); ^{13}C NMR (C_6D_6): $\delta = 23.8$, 27.1, 112.6, 121.4, 123.5, 124.9, 125.6, 129.3,139.1; anal. calcd.: C 61.34, H 5.88; found: C 61.67, H 6.03.

Copolymerization of Ethylene with Norbornene, Cyclopentene

A typical procedure was performed as follows: the prescribed amounts of toluene, norbornene and MAO were added into the autoclave (100 mL, stainless steel) in the dry-box, and the apparatus was then purged with ethylene. The reaction mixture was then pressurized to the prescribed ethylene pressure soon after the addition of a toluene solution containing titanium complex. The polymerization was terminated with the addition of EtOH, and the resultant polymer was adequately washed with EtOH containing HCl and then dried under vacuum for several hours. The copolymerization of ethylene with cycylopentene was also conducted in the same manner except that cyclopentene was used in place of norbornene, and the polymerization of ethylene was also performed in the same manner in the absence of norbornene.

Computational Details

All the density function theory (DFT) calculations were performed using the Jaguar 4.2 program,[37] on the Alpha GS/160 supercomputer. Geometry optimization and energy evaluation of the complexes were performed at the B3LYP (Becke's three-parameter DFT using the Lee-Yang-Parr correlation function)/6–31G** level of theory.[38] B3LYP is a hybrid functional including electron correlation. The LACVP basis set, which is an effective core potential basis set developed at Los Alamos National Laboratory,[39] was adopted for Ti. ΔE_{coord} values were calculated as the difference in energy between the optimized π-complex on the one hand and the cationic complex and the monomer on the other hand, namely $\Delta E_{coord} = E_{cation} + E_{monomer} - E_{\pi\text{-complex}}$.

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[27] In order to control NBE conversion to less than 10%, we terminated the reaction at the initial stage. The observed catalytic activities under the present optimized conditions were higher than those in our preliminary communication,[11] although the observed trends (efficient NBE incorporation, NBE content in the copolymer, properties for resultant copolymers etc.) here were the same as those in the preliminary communication.[11]

[28] NBE contents (mol %) in the resultant poly(ethylene-*co*-norbornene)s were estimated from ^{13}C NMR spectra as established previously by Tritto et al.[7]

[29] As reported in the preliminary communication,[11] DSC thermograms for the copolymer also showed sole glass transition temperatures (T_g), and the T_g values increased at higher NBE content (detailed results were shown in the Supporting Information in our preliminary communication[11]). Both GPC and DSC results thus indicate that the resultant copolymer possesses uniform NBE incorporation. The copolymers with relatively high NBE contents with both relatively high molecular weights and unimodal polydispersities were obtained when the polymerization was performed under higher NBE concentration conditions.

[30] The fact that poly(ethylene-*co*-norbornene)s prepared by Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**2a**)-MAO catalyst system possessed bimodal molecular weight distribution was the same as that observed in the copolymerization of ethylene with 1-hexene,[9b] although we have no appropriate explanation why only complexes containing the O-2,6-(*i*-Pr)$_2$C$_6$H$_3$ ligand afforded copolymers with unimodal molecular weight distributions.

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