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# Effect of Cyclopentadienyl and Anionic Donor Ligands on Monomer Reactivities in Copolymerization of Ethylene with 2-Methyl-1-pentene by Nonbridged Half-Titanocenes−Cocatalyst Systems

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ABSTRACT: Copolymerization of ethylene (E) with 2-methyl-1-pentene (2M1P) took place with rather efficient 2M1P incorporation by using the $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**)−MAO catalyst system, whereas the 2M1P incorporations by the $Cp_2ZrCl_2$, $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$, $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp′ = Cp (**3**), Cp* (**4**)], and $Cp^*TiCl_3$−MAO catalyst systems were negligible under the same conditions. The effects of substituents in both the cyclopentadienyl and the aryloxide ligands toward the catalytic activities and the 2M1P incorporations were explored, and use of both Cp* and 2,6-diisopropylphenoxy ligands was found to be important to obtain poly(ethylene-*co*-2M1P)s with rather efficient and uniform 2M1P incorporations as well as with notable catalytic activities. No distinct differences in the 2M1P incorporations were seen in the copolymerization by **1** in the presence of various cocatalysts [methylaluminoxane (MAO), methylisobutylaluminoxanes (MMAOs), borates], and the nature of ligands directly affects the 2M1P incorporation. Copolymerizations of ethylene with 7-methyl-1,6-octadiene (MOD) by **1**,**3**,**4**−MAO catalyst systems proceeded at remarkable rates with efficient exclusive incorporation of monoolefins (without incorporating trisubstituted olefin), affording high molecular weight unsaturated poly(ethylene-*co*-MOD)s with high MOD contents. The MOD contents in the resultant copolymers in the ethylene/MOD copolymerization by **1**,**3**,**4**−MAO catalyst systems were thus closely related to those in the ethylene/1-octene copolymerizations under similar conditions.

## Introduction

Recent progress in transition-metal-catalyzed olefin coordination−insertion polymerization introduces new possibilities for evolution of new polymers possessing unique properties,[1−3] and the copolymerization is an important process that usually allows the alteration of the (physical, mechanical, and electronic) properties of a material through adjustment of the ratio of individual components. Copolymer consisting of ethylene and 2,2-disubstituted-1-olefins seems to be one of the promising targets because only a few examples for copolymerization of 2,2-disubstituted-1-olefins with other monoolefins had been known in transition-metal-catalyzed olefin coordination polymerization.[4]

Examples for ethylene/isobutene (IB) copolymerization by linked half-titanocenes (called constrained geometry catalyst, CGC)[5−9] and $[Et(indenyl)_2]ZrCl_2$[10]−cocatalyst systems were reported recently, and cyclopolymerization of 2-methyl-1,5-hexadiene was also known as a related example.[11] Moreover, ring-opening (or addition) (co)polymerization of *strained* methylenecycloalkanes such as methylenecyclobutane,[12] methylenecyclopropane, and the derivatives[12,13] (with ethylene) were also known. However, the copolymerization by the $[Et(indenyl)_2]ZrCl_2$−methylaluminoxane (MAO) catalyst system afforded the copolymer with low IB content (<2.8 mol %) even under large IB stoichiometric excess conditions (IB:ethylene = 4000:1).[10] The resultant copolymer in the ethylene/2-methyl-1-pentene (2M1P) copolymerization by the $[Me_2Si(MeC_5H_3)(N\text{-cyclododecyl})]TiMe_2$−$[PhN(H)Me_2][B(C_6F_5)_4]$ catalyst system (ethylene 6.2 bar, 2M1P 2.0 M) possessed broad molecular weight distributions with rather low $M_n$ value ($M_n$ = 10 780, $M_w/M_n$ = 5.9, 2M1P content 9.0 mol %),[5] although the ethylene/IB copolymerization using the $[Me_2Si(Me_4C_5)(N\text{-cyclododecyl})]TiMe_2$−MAO catalyst system afforded the copolymer with 45 mol % IB content under certain conditions (ethylene 0.34 bar, $M_n$ = 13 200, $M_w/M_n$ = 2.5).[5]

The notable improvement in the IB incorporation (30 times increases in the IB/ethylene reactivity ratio) could be achieved more recently by adopting a catalyst system consisting of binuclear constrained geometry type half-titanocenes in the presence of bifunctional borate cocatalyst,[7−9] and it has been proposed that the increased selectivity for highly encumbered comonomer enchainment presumably facilitated via cooperative comonomer capture/binding/delivery by the proximate cationic centers.[8,9] However, both the activity and the IB incorporation were sensitive to the cocatalyst, and the activity was slightly decreased upon increasing the catalyst/cocatalyst nuclearity; the resultant copolymer possessed a rather broad molecular weight distribution ($M_w/M_n$ = 3.67, IB 15.2 mol %). A similar trend was also observed in the copolymerization of ethylene with methylenecyclopentane, and the catalyst system consisted of a binuclear titanium complex−bifunctional borate exhibited better comonomer incorporation. In terms of the efficient synthesis of high molecular weight (co)polymers with unimodal molecular weight distributions, in particular, examples for copolymerization of ethylene with 2,2-disubstituted-1-olefin except IB have thus never been reported.

We recently communicated that copolymerization of ethylene with 2-methyl-1-pentene (2M1P) proceeded in the presence of *nonbridged* half-titanocenes of type $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [Cp′ = Cp* ($C_5Me_5$, **1**), ${}^tBuC_5H_4$ (**2**)]−MAO catalyst systems,[14] and the resultant polymers were poly(ethylene-*co*-2M1P)s with efficient 2M1P incorporation; the copolymer possessed high molecular weights with both unimodal molecular weight distributions and uniform 2M1P incorporation. $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp′ = Cp* (**3**), Cp (**4**)] showed negligible 2M1P incorporation under the same conditions, indicating that both

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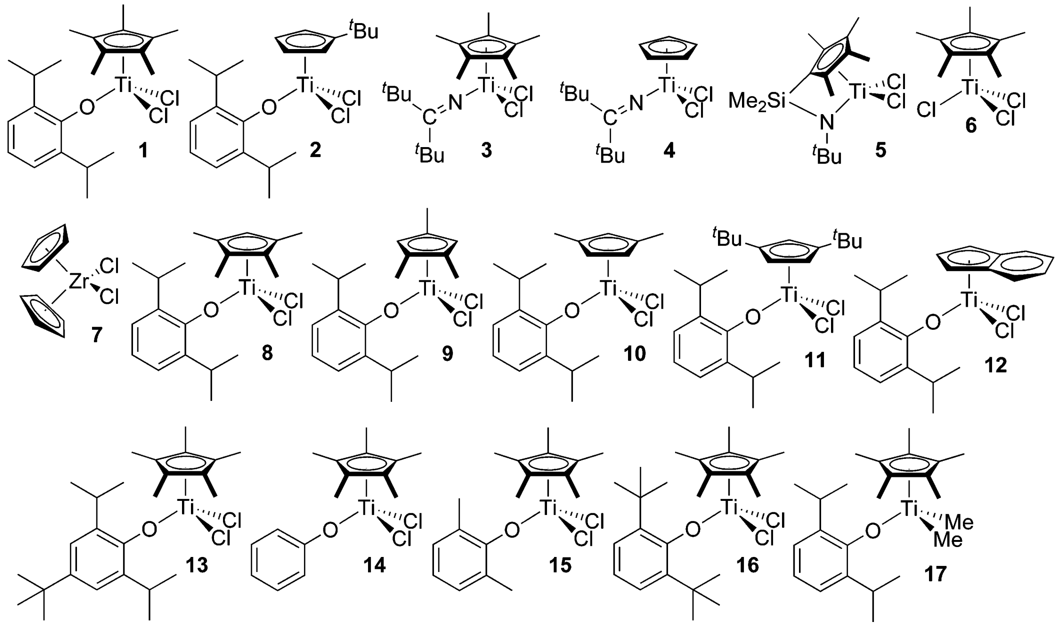
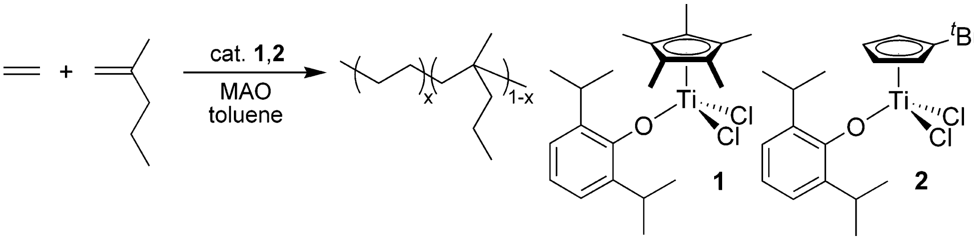
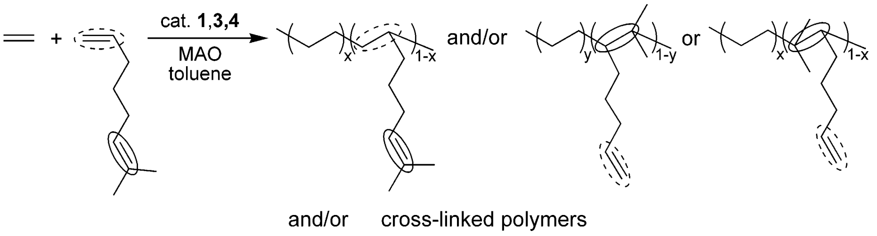
**Chart 1**



**Scheme 1. Copolymerization of Ethylene with 2-Methyl-1-pentene by $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [$Cp' = Cp^*$ (1, $Cp^* = C_5Me_5$), ${}^tBuC_5H_4$ (2)]−Methylaluminoxane (MAO) Catalyst Systems**



**Scheme 2. Copolymerization of Ethylene with 7-Methyl-1,6-octadiene by $Cp'TiCl_2(X)$ [$X = O\text{-}2,6\text{-}{}^iPr_2C_6H_3$ and $Cp' = Cp^*$ (1, $Cp^* = C_5Me_5$); $X = N{=}C{}^tBu_2$ and $Cp' = Cp^*$ (3), Cp (4)]−Methylaluminoxane (MAO) Catalyst Systems**



substituent on Cp′ and anionic donor ligand affect the 2M1P incorporation.[14] It has also been demonstrated that some *nonbridged* half-titanocenes containing anionic ancillary donor ligand (X) of the type $Cp'TiCl_2(X)$ (Cp′ = cyclopentadienyl group)−cocatalyst systems display unique characteristics especially in copolymerization of ethylene with α-olefins,[15−17] styrene,[18,19] cyclic olefins,[20−22] and vinylcylohexane (γ-disubstituted-α-olefin),[23] and the monomer reactivity can also be tuned by modification of both cyclopentadienyl and anionic donor ligands.[3,14−23] We thus decided to explore the detailed ligand effects toward both the monomer reactivity and the catalytic activity in the ethylene/2M1P copolymerization using various half-titanocenes−cocatalyst systems (Scheme 1).

Since remarkable difference in the reactivity should be observed between mono- and trisubstituted olefins, therefore, we explored the copolymerization of ethylene with 7-methyl-1,6-octadiene (MOD) using **1**,**3**,**4**−MAO catalyst systems to demonstrate whether the copolymer containing trisubstituted olefinic double bond in the side chain can be prepared exclusively in an efficient manner or not (Scheme 2).[24] We also compared the monomer reactivities between 1-octene (monoolefin) and MOD in the ethylene copolymerizations under the same conditions.

## Experimental Section

**General Procedure.** All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. Anhydrous grade toluene (Kanto Chemical Co., Inc.), 2-methyl-1-pentene (2M1P) of reagent grade (TCI Co., Ltd.), 7-methyl-1,6-octadiene (MOD) of reagent grade (Aldrich), and 1-octene (OC) of reagent grade (Wako Pure Chemical Ind., Ltd.) were stored in a drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16) after passing through an alumina short column under nitrogen. Ethylene of polymerization grade (Sumitomo Seika Chemicals, Ltd.) was used as received without further purification procedures.

Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were removed 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 drybox to give white solids. Other MMAO samples such as MMAO-3BH ($Me/^{i}Bu = 3.54$), MMAO-3AT ($Me/^{i}Bu = 2.33$), and MMAO-3AH ($Me/^{i}Bu = 2.67$) were supplied from Tosoh Finechem Co. and were used as white solids after removing solvent and $AlMe_3$, $Al(^{i}Bu)_3$ in vacuo according to the analogous procedure as that in PMAO-S, except that the resultant solid was redissolved in toluene (or in hexane) and then removed in vacuo to remove $Al(^{i}Bu)_3$ completely. Reagent grade $[Ph_3C][B(C_6F_5)_4]$, $[PhN(H)Me_2][B(C_6F_5)_4]$ (Asahi Glass Co., Ltd.), and $Al(^{i}Bu)_3$ (Kanto Chemical Co., Inc.) were stored in the drybox and were used as received.

(Aryloxo)(cyclopentadienyl)titanium(IV) complexes of the type $Cp'TiCl_2(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$ [$Cp' = Cp^*$ (**1**, $C_5Me_5$),[25] $^{t}BuC_5H_4$ (**2**),[25] $1,2,4\text{-}Me_3C_5H_2$ (**9**),[18] $1,3\text{-}Me_2C_5H_3$ (**10**),[25] $1,3\text{-}^{t}BuC_5H_3$ (**11**),[25] indenyl (**12**[20])], $Cp^*TiCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [R = H (**14**),[26] Me (**15**),[25] $^{t}Bu$ (**16**[27])], $Cp^*TiMe_2(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$ (**17**),[25] and $Cp^*TiCl_2(O\text{-}4\text{-}^{t}Bu\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$ (**13**)[27] were prepared according to the previous report. $(1,2,3,4\text{-}Me_4C_5H)TiCl_2(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$ (**8**) was prepared according to the analogous procedure for **1**, **2**, and **9**−**12** by reaction of $(1,2,3,4\text{-}Me_4C_5H)TiCl_3$ with $LiO\text{-}2,6\text{-}^{i}Pr_2C_6H_3$.[28] $Cp^*TiCl_2(N{=}C^{t}Bu_2)$ (**3**),[29] $CpTiCl_2(N{=}C^{t}Bu_2)$ (**4**),[29] and $[Me_2Si(C_5Me_4)(N^{t}Bu)]TiCl_2$ (**5**)[30] were prepared according to the published procedures. $Cp^*TiCl_3$ (**6**, Strem Chemicals, Inc.) and $Cp_2ZrCl_2$ (**7**, Wako Pure Chemical Ind., Ltd.) were used as received.

All $^{1}H$ and $^{13}C$ NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.78 MHz, $^{1}H$). 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 1,2,4-trichlorobenzene or *o*-dichlorobenzene-$d_4$. $^{13}C$ NMR spectra for polyethylene, poly(ethylene-*co*-2M1P)s, poly(ethylene-*co*-MOD)s, and poly(ethylene-*co*-1-octene)s were recorded on a JEOL JNM-LA400 spectrometer (100.53 MHz, $^{13}C$) with proton decoupling. The relaxation delay was 5.2 s, the acquisition time was 1.3 s, the pulse angle was 90°, and the number of transients accumulated was ca. 6000. The copolymer samples for analysis were prepared by dissolving the polymers in a mixed solution of 1,2,4-trichlorobenzene/benzene-$d_6$ (40/10 v/v) or *o*-dichlorobenzene-$d_4$.

Molecular weights and molecular weight distributions for the poly(ethylene-*co*-2M1P)s, poly(ethylene-*co*-MOD)s, and poly(ethylene-*co*-1-octene)s were measured by gel permeation chromatography (GPC, Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with polystyrene gel column (TSK gel $GMH_{HR}$-H HT × 2, 30 cm × 7.8 mm i.d.), ranging from $<10^2$ to $<2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05% w/v 2,6-di-*tert*-butyl-*p*-cresol as the solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

**Ethylene Homopolymerization, Copolymerizations of Ethylene with 2-Methyl-1-pentene (2M1P), 1-Octene (OC), and 7-Methyl-1,6-octadiene (MOD) in the Presence of MAO (MMAO) Cocatalyst.** The typical reaction procedure for ethylene homopolymerization (run 1, Table 1) is as follows. Toluene (29 mL) and MAO solid (174 mg, 3.0 mmol) were added into the autoclave (100 mL scale, stainless steel) in the drybox, and the reaction apparatus was then replaced and filled with ethylene (1 atm) at 25 °C. A toluene solution (1.0 mL) containing **1** (0.1 $\mu$mol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 3 atm (total ethylene pressure 4 atm). The mixture was magnetically stirred for 10 min, ethylene remained was purged after the reaction, and the mixture was then poured into MeOH (300 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, adequately washed with MeOH, and then dried in vacuo. The basic experimental procedure in the ethylene/2M1P copolymerization was the same as that in ethylene homopolymerization, except that various amounts of 2M1P (5 or 10 mL) were added in place of toluene partially (total 29 mL). Basic experimental procedures in the ethylene/OC copolymerization as well as ethylene/MOD copolymerization were the same as that in the ethylene homopolymerization, except that various amounts of OC or MOD (5 or 10 mL) were added in place of toluene partially (total 29 mL).

The 2M1P contents and the monomer sequence distributions in the resultant copolymers were estimated by the $^{13}C$ NMR spectra of the copolymers, and each resonance was assigned by the dept analysis and by comparison with the previous report concerning poly(ethylene-*co*-isobutene)s.[5,7] The 2M1P contents were estimated on the basis of the ratio of the total integration values of 2M1P vs ethylene at each resonances in the $^{13}C$ NMR spectra. Ethylene concentrations under the reaction conditions were estimated in the same manner as that reported previously by us,[14] i.e., estimated on the basis of the equation quoted by Kissin,[31] and the ethylene solubilities in the reaction mixture (1 atm) were used as those in toluene reported.[32] The 1-octene (OC) as well as 7-methyl-1,6-octadiene (MOD) contents and the monomer sequence distributions in the resultant copolymers were estimated by the $^{13}C$ NMR spectra of the copolymers, and the detailed procedures are shown in the Supporting Information.

**Ethylene/2-Methyl-1-pentene (2M1P) Copolymerization by $Cp^*TiMe_2(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$ (17) in the Presence of Borate Cocatalyst.** Typical procedures for copolymerization of ethylene with 2M1P by $Cp^*TiMe_2(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$ (**17**)−$[PhN(H)Me_2][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ catalyst systems are as follows. Toluene (18 mL), 2M1P (10 mL), and $Al(^{i}Bu)_3$ (0.50 mmol) were added into the autoclave in the drybox, and the reaction apparatus was then replaced and filled with ethylene (1 atm) at 25 °C. A toluene solution (1.0 mL) containing **17** (0.5 $\mu$mol) was then added in an independent Schlenk tube, followed by addition of a toluene solution (1.0 mL) containing $[PhN(H)Me_2][B(C_6F_5)_4]$ (0.5 $\mu$mol) or $[Ph_3C][B(C_6F_5)_4]$ (0.5 $\mu$mol). This mixture was stirred for ca. 10 min and then added into the autoclave. The reaction apparatus was then immediately pressurized to 5 atm (total ethylene pressure 6 atm), and the mixture was magnetically stirred for 10 min. After the reaction, ethylene remained was purged upon cooling in the ice bath, and the mixture was then poured into MeOH (300 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, was adequately washed with MeOH, and then dried in vacuo.

## Results and Discussion

**1. Copolymerization of Ethylene with 2-Methyl-1-pentene (2M1P).** Table 1 summarizes the results for copolymerization of ethylene with 2-methyl-1-pentene (2M1P) catalyzed by various half-titanocenes of the type $Cp'TiCl_2(L)$ [$L = O\text{-}2,6\text{-}^{i}Pr_2C_6H_3$; $Cp' = Cp^*$ (**1**), $^{t}BuC_5H_4$ (**2**), $L = N{=}C^{t}Bu_2$; $Cp' = Cp^*$ (**3**), Cp (**4**)]−MAO catalyst systems (in toluene at 25 °C). $[Me_2Si(C_5Me_4)(N^{t}Bu)]TiCl_2$ (**5**), $Cp^*TiCl_3$ (**6**), and $Cp_2ZrCl_2$ (**7**) were also chosen for comparison. 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.[25]

As communicated previously,[14] the copolymerizations by the **1**−MAO catalyst system took place with high catalytic activities, and the activity decreased upon increasing the 2M1P concentration and/or upon decreasing the ethylene pressure. The observed activities were also affected by the Al/Ti molar ratios, whereas no significant changes in the $M_n$ values (as well as with $M_w/M_n$ values) were observed by varying the Al/Ti molar ratios. The resultant polymers were poly(ethylene-*co*-2M1P)s confirmed by $^{13}C$ NMR spectra and DSC thermograms ($T_m$ values),[33] and the copolymers possessed high molecular weights with unimodal molecular weight distributions as well as with uniform 2M1P distributions. The 2M1P contents in the copolymers decreased upon increasing the ethylene pressure and/or upon decreasing the 2M1P concentration charged, and the $M_n$ values for the copolymers decreased upon increasing the 2M1P contents. A

**Table 1. Copolymerization of Ethylene with 2-Methyl-1-pentene (2M1P) by Various Half-Titanocenes, Cp′TiCl$_2$(X) [X = O-2,6-$^i$Pr$_2$C$_6$H$_3$, Cp′ = Cp* (1, Cp* = C$_5$Me$_5$), $^t$BuC$_5$H$_4$ (2); X = N=C$^t$Bu$_2$, Cp′ = Cp* (3), Cp (4); X = Cl, Cp′ = Cp* (6)], [Me$_2$Si(C$_5$Me$_4$)(N$^t$Bu)]TiCl$_2$ (5), Cp$_2$ZrCl$_2$ (7)−Methylaluminoxane (MAO) Catalyst Systems**[a]

| run | cat. (μmol) | MAO/mmol (Al/Ti)[b] | ethylene/ atm | 2M1P/ M | time/ min | yield/mg | activity[c] | $M_n$[d] × 10$^{-4}$ | $M_w/M_n$[d] | 2M1P[e]/ mol % |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **1** (0.1) | 3.0 (30000) | 4 | | 10 | 202 | 12100 | 40 | 3.7 | |
| 2 | **1** (0.5) | 1.5 (3000) | 6 | 1.35 | 10 | 412 | 4940 | 11 | 1.7 | |
| 3 | **1** (0.5) | 3.0 (6000) | 6 | 1.35 | 10 | 582 | 6980 | 13 | 1.7 | |
| 4 | **1** (0.5) | 4.5 (9000) | 6 | 1.35 | 10 | 672 | 8060 | 13 | 1.7 | 3.2 |
| 5 | **1** (0.5) | 6.0 (12000) | 6 | 1.35 | 10 | 656 | 7870 | 13 | 1.8 | |
| 6 | **1** (0.5) | 4.5 (9000) | 6 | 1.35 | 10 | 705 | 8460 | 12 | 2.1 | 3.3 |
| 7 | **1** (0.5) | 4.5 (9000) | 6 | 2.70 | 10 | 480 | 5760 | 10 | 1.8 | 5.7 |
| 8 | **1** (0.5) | 4.5 (9000) | 4 | 1.35 | 10 | 353 | 4240 | 6.5 | 2.0 | 5.0 |
| 9 | **1** (0.5) | 4.5 (9000) | 4 | 2.70 | 10 | 223 | 2680 | 4.9 | 1.6 | 9.4 |
| 10 | **2** (2.0) | 2.0 (1000) | 6 | 1.35 | 10 | 111 | 333 | 5.0 | 2.6 | |
| 11 | **2** (2.0) | 3.0 (1500) | 6 | 1.35 | 10 | 191 | 573 | 5.8 | 2.0 | |
| 12 | **2** (2.0) | 4.0 (2000) | 6 | 1.35 | 10 | 270 | 810 | 5.5 | 1.9 | 2.3 |
| 13 | **2** (2.0) | 5.0 (2500) | 6 | 1.35 | 10 | 264 | 792 | 6.3 | 1.8 | |
| 14 | **2** (2.0) | 4.0 (2000) | 6 | 2.70 | 10 | 226 | 678 | 4.3 | 2.0 | 3.2 |
| 15 | **2** (2.0) | 4.0 (2000) | 4 | 1.35 | 10 | 156 | 468 | 3.1 | 2.1 | 3.2 |
| 16 | **2** (2.0) | 4.0 (2000) | 4 | 2.70 | 10 | 108 | 324 | 1.8 | 2.3 | 5.1 |
| 17 | **3** (0.2) | 3.0 (15000) | 6 | 1.35 | 10 | 393 | 11800 | 68 | 2.0 | |
| 18 | **3** (0.2) | 3.0 (15000) | 6 | 2.70 | 10 | 259 | 7770 | 63 | 1.9 | 0.3 |
| 19 | **4** (0.2) | 3.0 (15000) | 6 | | 10 | 636 | 19100 | 53 | 2.1 | |
| 20 | **4** (0.2) | 3.0 (15000) | 6 | 1.35 | 10 | 336 | 10100 | 43 | 2.0 | |
| 21 | **4** (0.2) | 3.0 (15000) | 6 | 2.70 | 10 | 232 | 6960 | 34 | 1.8 | 0.3 |
| 22 | **5** (1.0) | 3.0 (3000) | 6 | 1.35 | 6 | 200 | 2000 | 13 | 2.4 | |
| 23 | **5** (1.0) | 3.0 (3000) | 6 | 2.70 | 6 | 184 | 1840 | 12 | 2.4 | 0.3 |
| 24 | **5** (1.0) | 3.0 (3000) | 4 | 1.35 | 6 | 142 | 1420 | 9.7 | 2.5 | |
| 25 | **5** (1.0) | 3.0 (3000) | 4 | 2.70 | 6 | 132 | 1320 | 7.4 | 2.4 | 0.4 |
| 26 | **6** (1.0) | 3.0 (3000) | 6 | 1.35 | 6 | 458 | 4580 | *f* | | |
| 27 | **6** (1.0) | 3.0 (3000) | 6 | 2.70 | 6 | 415 | 4150 | *f* | | |
| 28 | **7** (0.2) | 3.0 (15000) | 6 | 2.70 | 10 | 153 | 4590 | 148 | 2.7 | *g* |

[a] Conditions: 2M1P + toluene total 30 mL, methylaluminoxane (MAO, prepared by removing toluene and AlMe$_3$ from ordinary MAO), 25 °C, 6 or 10 min. [b] Al/Ti molar ratios. [c] Activity in kg of polymer/(mol of Ti h). [d] Gel permeation chromatography (GPC) data in *o*-dichlorobenzene vs polystyrene standards, $M_n$ = number-average molecular weight, $M_w$ = weight-average molecular weight. [e] 2M1P in copolymer (mol %) estimated by $^{13}$C NMR spectra. [f] Bimodal. [g] Trace.

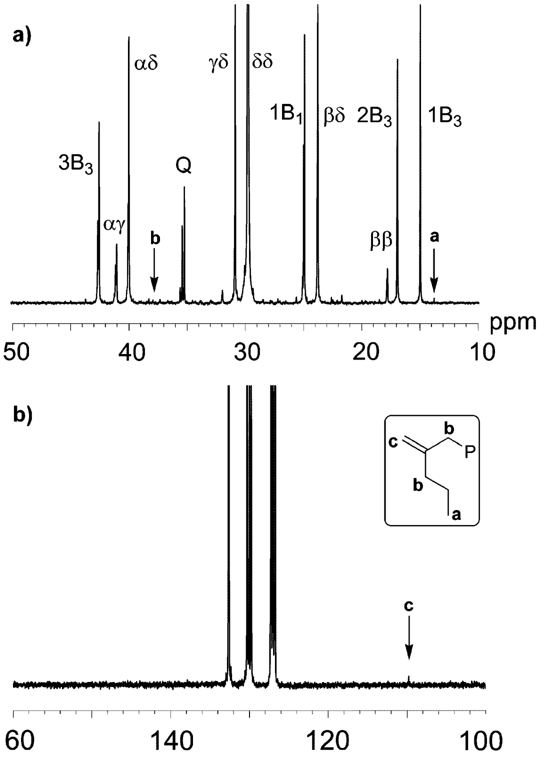


**Figure 1.** $^{13}$C NMR spectrum for poly(ethylene-*co*-2-methyl-1-pentene) prepared by Cp*TiCl$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$) (**1**, Cp* = C$_5$Me$_5$)−methylaluminoxane (MAO) catalyst system (in benzene-*d*$_6$/1,2,4-trichlorobenzene at 110 °C, Table 1, run 9).

linear relationship between $T_m$ values and the 2M1P contents was observed,[33] and these results thus strongly suggest that the copolymerization proceeded with single (uniform) catalytically active species.

**Scheme 3**

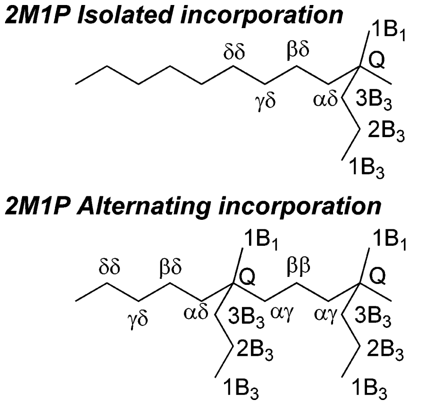
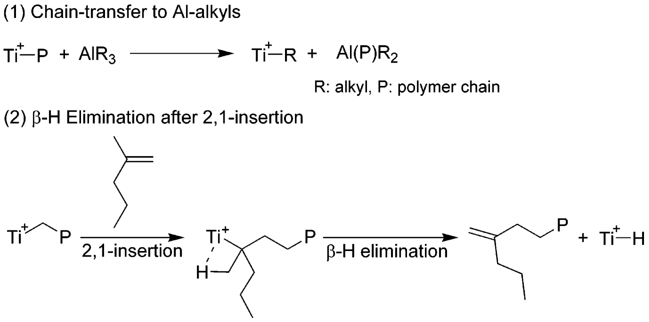


Figure 1 shows the $^{13}$C NMR spectrum for poly(ethylene-*co*-2M1P) (run 9, in benzene-*d*$_6$/1,2,4-trichlorobenzene at 110 °C),[33] and all resonances were identified by the dept analysis[14,33] as well as by comparison with poly(ethylene-*co*-isobutene)s reported previously.[7,8] The resultant copolymer possessed isolated 2M1P inserted unit among repeated ethylene insertions, and the alternating sequences (assigned as $\beta\beta$ and $\alpha\gamma$, Scheme 3) were also seen with low extents. No resonances ascribed to the repeated 2M1P incorporation were observed, and this fact would explain that the negligible or no catalytic activity was observed in an attempted 2M1P homopolymerization by the **1**−MAO catalyst system. The observed facts are an interesting contrast to those in ethylene/1-hexene copolymerization, whereas resonances ascribed to two (three) repeated 1-hexene incorporation(s) were observed, and the catalyst system showed high catalytic activities for 1-hexene homopolymerization. These would clearly explain why the 2M1P incorporation was not so efficient as the 1-hexene incorporation.

Two pathways (chain transfer to Al−alkyls and $\beta$-hydrogen elimination after 2,1-insertion of 2M1P, Scheme 4) would be

**Scheme 4**



considered as the main chain-transfer reaction in the copolymerization. As described above (Table 1, runs 2−5), the $M_n$ values were not dependent upon the Al/Ti molar ratios employed, suggesting that the degree of chain transfer to Al−alkyl is not the dominant chain-transfer step in the copolymerization. The assumption was also supported by the results described below that the $M_n$ values in the resultant copolymers were also independent upon the cocatalysts employed (MMAO, borate cocatalysts, Table 4). As shown in Figure 1b, a resonance ascribed to the olefinic double bond formed by the $\beta$-hydrogen elimination after 2,1-insertion of 2M1P (in addition to resonances ascribed to the chain end shown in Figure 1a) were observed in the copolymer with a rather high 2M1P content. Although we could not exclude the possibility of $\beta$-methyl elimination as the dominant (and/or accompanied) pathway, we assume that the dominant chain-transfer reaction in this copolymerization would be the $\beta$-H elimination after 2,1-insertion occurred to a certain degree.[34−37]

Although the ($^t$BuC$_5$H$_4$)TiCl$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$) (**2**)−MAO catalyst system incorporated 1-hexene more efficiently than the **1**−MAO catalyst system in ethylene/1-hexene copolymerization,[15,16] the 2M1P contents in poly(ethylene-*co*-2M1P)s prepared by **2** were lower than those by **1** under the same conditions. We thus speculated that the less 2M1P incorporation by **2** than **1** in the present copolymerization may be due to the steric hindrance of the *tert*-butyl group on Cp′ against the methyl group in inserted 2M1P. The optimized geometries for assumed catalytically active [cationic Ti(IV) alkyl] species,[19b] especially [Cp′Ti(OAr)(2-methyl-2-propylheptyl)(ethylene)]$^+$ [Cp′ = Cp* (**1′**), $^t$BuC$_5$H$_4$ (**2′**)], were calculated by molecular mechanics. It was revealed that the Cp* analogue (**1′**) was more stable than the *tert*-BuC$_5$H$_4$ analogue (**2′**), and the $\Delta E$ value (7.863 kcal/mol) was somewhat large, probably due to the steric bulk between the methyl group in the inserted 2M1P and *tert*-Bu group.[36]

Note that the 2M1P incorporations were affected by the anionic donor ligands (X) employed; both the ketimide analogues (**3**, **4**) and the Cp*TiCl$_3$ (**6**) showed negligible 2M1P incorporations under the same conditions. The molecular weight distributions in the resultant polymers by **6** were multimodal, suggesting the formation of several catalytically active species. These results clearly indicate that the anionic ancillary donor ligand (X) in Cp′TiCl$_2$(X) (X = O-2,6-$^i$Pr$_2$C$_6$H$_3$, N=C$^t$Bu$_2$, Cl) plays an essential role for the efficient 2M1P incorporation in the copolymerization.

Moreover, as shown in Table 1, 2M1P content in the resultant polymers prepared by the [Me$_2$Si(C$_5$Me$_4$)(N$^t$Bu)]TiCl$_2$ (**5**)−MAO catalyst system under the same conditions was extremely low (runs 22−25), although the $M_n$ values decreased upon increasing the 2M1P concentration.[5] The resultant polymer prepared by the Cp$_2$ZrCl$_2$ (**7**)−MAO catalyst system possessed high molecular weight with negligible 2M1P incorporation. These results thus clearly indicate that the observed fact (efficient 2M1P incorporation by **1**) should be one of the unique characteristics for using this type of catalyst precursor for olefin (co)polymerization.

**Effect of Cyclopentadienyl Fragment for 2M1P Incorporation in the Copolymerization.** It has been known that the structural features of the catalyst, in particular the steric bulk of ligand, bite angle, configuration, and conformation, do influence the coordination and/or insertion of monomers in transition-metal-catalyzed coordination polymerization reactions, and this is a distinct difference from conventional radical and ionic polymerization reactions.[38] We reported previously that the substituents on the cylopentadienyl ligand in Cp′TiCl$_2$(OAr) (Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$) directly affected the comonomer incorporation in the copolymerization of ethylene with α-olefin,[15,16] styrene,[18,19] norbornene,[20,21] and cyclohexene.[22] Since we observed significant difference in the 2M1P incorporation between the Cp* (**1**) and the $^t$BuC$_5$H$_4$ (**2**) analogues, we explored the more details by varying the substituents on Cp′. The results are summarized in Table 2.[39]

The catalytic activities in the ethylene/2M1P copolymerization with a series of Cp′TiCl$_2$(OAr)−MAO catalyst systems increased in the order Cp′ = Cp* (**1**) > 1,2,3,4-Me$_4$C$_5$H (**8**), 1,2,4-Me$_3$C$_5$H$_2$ (**9**) ≫ 1,3-Me$_2$C$_5$H$_3$ (**10**). The order seems somewhat analogous to that observed in the ethylene polymerization reported previously,[3,25] suggesting that the more electron-donating Cp* stabilizes the active species, leading to the higher activity. This fact may also suggests that the highest activity by **1** would be due to the unique bond angle in Ti−O−C(in Ar) (ca. 172°−175°) that are only observed by the combination of both Cp* and 2,6-diisopropylphenoxy ligands,[3,27] which would increase the stability of catalytically active species by more O → Ti $\pi$ donation. Although the reduction of the steric bulk on Cp′ was expected to improve the 2M1P incorporation, no significant differences in the 2M1P contents were observed in the copolymers prepared by the 1,2,3,4-Me$_4$C$_5$H (**8**), the 1,2,4-Me$_3$C$_5$H$_2$ (**9**) analogues, and the Cp* analogue−MAO catalyst systems. In addition, the molecular weight distributions by **8**−**10** became somewhat broad as seen in the poly(ethylene-*co*-1-hexene)s prepared by the 1,3-Me$_2$C$_5$H$_3$ analogue (**10**). Moreover, the 2M1P incorporation became inefficient if the 1,3-$^t$Bu$_2$C$_5$H$_3$ analogue (**11**) was employed instead of the $^t$BuC$_5$H$_4$ analogue (**2**) because of the increased steric bulk around the Cp′ as observed in the other ethylene copolymerizations.[15,16,20−22] The 2M1P incorporation by the indenyl analogue (**12**) was not so efficient as that by the Cp* analogue, although the remarkable norbornene incorporation was attained by **12**.[20] The resultant polymers prepared by the **12**−MAO catalyst system possessed broad molecular weight distributions, suggesting that the copolymerization did not proceed with a sole catalytically active species. The above assumption is also supported by the DSC thermograms in the resultant polymer (two melting temperatures, shown in the Supporting Information). Taking into account the above results, it is thus clear that the Cp* analogue (**1**) is the most suited as the catalyst precursor for the copolymerization in terms of both the activity and the 2M1P incorporation.

**Effect of Substituent in the Aryloxide Ligand.** The ethylene/2M1P copolymerizations using Cp*TiCl$_2$(OAr) [Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$ (**1**), 2,6-$^i$Pr$_2$-4-$^t$Bu-C$_6$H$_2$ (**13**), C$_6$H$_5$ (**14**), 2,6-Me$_2$C$_6$H$_3$ (**15**), 2,6-$^t$Bu$_2$C$_6$H$_3$ (**16**)] were conducted to explore the effect of substituent on the aryloxide ligand toward the catalytic activities, 2M1P contents, and molecular weight distributions in the resultant (co)polymers (Table 3).[39] This is because that the aryloxide ligand affected not only the catalytic activity in

**Table 2. Effect of Cyclopentadienyl Fragment in Copolymerization of Ethylene with 2-Methyl-1-pentene (2M1P) by Cp′$TiCl_2$(O-2,6-$^i$$Pr_2C_6H_3$) [Cp′ = Cp* (1, Cp* = $C_5Me_5$), $^t$$BuC_5H_4$ (2), 1,2,3,4-$Me_4C_5H$ (8), 1,2,4-$Me_3C_5H_2$ (9), 1,3-$Me_2C_5H_3$ (10), 1,3-$^t$$Bu_2C_5H_3$ (11), Indenyl (12)]−Methylaluminoxane (MAO) Catalyst Systems**[a]

| run | cat. (μmol) | MAO/mmol (Al/Ti)[b] | ethylene/ atm | 2M1P/ M | time/ min | yield/mg | activity[c] | $M_n$[d] × $10^{-4}$ | $M_w/M_n$[d] | 2M1P[e]/ mol % |
|---|---|---|---|---|---|---|---|---|---|---|
| 6 | **1** (0.5) | 4.5 (9000) | 6 | 1.35 | 10 | 705 | 8460 | 12 | 2.1 | 3.3 |
| 7 | **1** (0.5) | 4.5 (9000) | 6 | 2.70 | 10 | 480 | 5760 | 10 | 1.8 | 5.7 |
| 8 | **1** (0.5) | 4.5 (9000) | 4 | 1.35 | 10 | 353 | 4240 | 6.5 | 2.0 | 5.0 |
| 9 | **1** (0.5) | 4.5 (9000) | 4 | 2.70 | 10 | 223 | 2680 | 4.9 | 1.6 | 9.4 |
| 29 | **8** (1.0) | 3.0 (3000) | 6 | 1.35 | 6 | 255 | 2550 | 7.7 | 2.7 | 3.0 |
| 30 | **8** (1.0) | 3.0 (3000) | 6 | 2.70 | 6 | 183 | 1830 | 5.6 | 3.0 | 5.1 |
| 31 | **8** (1.0) | 3.0 (3000) | 4 | 1.35 | 6 | 137 | 1370 | 4.1 | 2.9 | 4.6 |
| 32 | **8** (1.0) | 3.0 (3000) | 4 | 2.70 | 6 | 101 | 1010 | 3.0 | 2.6 | 8.0 |
| 33 | **9** (1.0) | 3.0 (3000) | 6 | 1.35 | 6 | 208 | 2080 | 6.6 | 2.6 | 3.8 |
| 34 | **9** (1.0) | 3.0 (3000) | 6 | 2.70 | 6 | 192 | 1920 | 5.8 | 2.3 | 6.1 |
| 35 | **9** (1.0) | 3.0 (3000) | 4 | 1.35 | 6 | 139 | 1390 | 4.4 | 2.6 | 5.5 |
| 36 | **9** (1.0) | 3.0 (3000) | 4 | 2.70 | 6 | 92 | 920 | 2.5 | 2.6 | 9.5 |
| 37 | **10** (2.0) | 3.0 (1500) | 6 | 1.35 | 6 | 193 | 970 | 2.4 | 4.3[f] |  |
| 38 | **10** (2.0) | 3.0 (1500) | 6 | 2.70 | 6 | 188 | 940 | 1.9 | 4.1 |  |
| 39 | **10** (2.0) | 3.0 (1500) | 4 | 1.35 | 6 | 109 | 550 | 1.7 | 3.8 |  |
| 40 | **10** (2.0) | 3.0 (1500) | 4 | 2.70 | 6 | 81 | 410 | 1.2 | 3.4 |  |
| 41 | **11** (0.5) | 3.0 (6000) | 6 | 1.35 | 6 | 260 | 5200 | 25 | 2.6 | 0.7 |
| 42 | **11** (0.5) | 3.0 (6000) | 6 | 2.70 | 6 | 166 | 3320 | 17 | 2.4 | 1.3 |
| 12 | **2** (2.0) | 4.0 (2000) | 6 | 1.35 | 10 | 270 | 810 | 5.5 | 1.9 | 2.3 |
| 14 | **2** (2.0) | 4.0 (2000) | 6 | 2.70 | 10 | 226 | 678 | 4.3 | 2.0 | 3.2 |
| 43 | **12** (1.0) | 3.0 (3000) | 6 | 1.35 | 6 | 242 | 2420 | 5.3 | 5.2 |  |
| 44 | **12** (1.0) | 3.0 (3000) | 6 | 2.70 | 6 | 176 | 1760 | 3.7 | 5.6 | 3.2 |
| 45 | **12** (1.0) | 3.0 (3000) | 4 | 1.35 | 6 | 137 | 1370 | 3.8 | 5.3 |  |
| 46 | **12** (1.0) | 3.0 (3000) | 4 | 2.70 | 6 | 101 | 1010 | 2.2 | 6.2 |  |

[a] Conditions: 2M1P + toluene total 30 mL, methylaluminoxane (MAO, prepared by removing toluene and $AlMe_3$ from ordinary MAO),[39] 25 °C, 6 or 10 min. [b] Al/Ti molar ratios. [c] Activity in kg of polymer/(mol of Ti h). [d] Gel permeation chromatography (GPC) data in *o*-dichlorobenzene vs polystyrene standards, $M_n$ = number-average molecular weight, $M_w$ = weight-average molecular weight. [e] 2M1P in copolymer (mol %) estimated by $^{13}$C NMR spectra. [f] Observed low molecular weight shoulder.

**Table 3. Effect of the Aryloxide Ligand in Copolymerization of Ethylene with 2-Methyl-1-pentene (2M1P) by Cp*$TiCl_2$(OAr) [Cp* = $C_5Me_5$; Ar = 2,6-$^i$$Pr_2C_6H_3$ (1), 2,6-$^i$$Pr_2$-4-$^t$Bu−$C_6H_2$ (13), $C_6H_5$ (14), 2,6-$Me_2C_6H_3$ (15), 2,6-$^t$$Bu_2C_6H_3$ (16)]−Methylaluminoxane (MAO) Catalyst Systems**[a]

| run | cat. (μmol) | MAO/mmol (Al/Ti)[b] | ethylene/ atm | 2M1P/ M | time/ min | yield/ mg | activity[c] | $M_n$[d] × $10^{-4}$ | $M_w/M_n$[d] | 2M1P[e]/ mol % |
|---|---|---|---|---|---|---|---|---|---|---|
| 6 | **1** (0.5) | 4.5 (9000) | 6 | 1.35 | 10 | 705 | 8460 | 12 | 2.1 | 3.3 |
| 7 | **1** (0.5) | 4.5 (9000) | 6 | 2.70 | 10 | 480 | 5760 | 10 | 1.8 | 5.7 |
| 8 | **1** (0.5) | 4.5 (9000) | 4 | 1.35 | 10 | 353 | 4240 | 6.5 | 2.0 | 5.0 |
| 9 | **1** (0.5) | 4.5 (9000) | 4 | 2.70 | 10 | 223 | 2680 | 4.9 | 1.6 | 9.4 |
| 47 | **13** (0.2) | 3.0 (15000) | 6 | 1.35 | 6 | 188 | 9400 | 13 | 2.5 | 2.8 |
| 48 | **13** (0.2) | 3.0 (15000) | 6 | 2.70 | 6 | 132 | 6600 | 10 | 2.4 | 5.3 |
| 49 | **13** (0.5) | 3.0 (6000) | 4 | 1.35 | 6 | 220 | 4400 | 5.5 | 2.3 | 5.0 |
| 50 | **13** (0.5) | 3.0 (6000) | 4 | 2.70 | 6 | 161 | 3220 | 3.9 | 2.2 | 8.4 |
| 51 | **14** (0.5) | 3.0 (6000) | 6 | 1.35 | 6 | 280 | 5600 | 1.1 | 8.1[f] |  |
| 52 | **14** (0.5) | 3.0 (6000) | 6 | 2.70 | 6 | 200 | 4000 | 1.3 | 12.5[f] | trace[g] |
| 53 | **15** (1.0) | 3.0 (3000) | 6 | 1.35 | 6 | 347 | 3470 | 1.8 | 8.4 |  |
| 54 | **15** (1.0) | 3.0 (3000) | 6 | 2.70 | 6 | 246 | 2460 | 1.6 | 12.1 | 1.3[g] |
| 55 | **16** (5.0) | 3.0 (600) | 6 | 1.35 | 6 | 49 | 100 | 0.34 | 53.0 |  |
| 56 | **16** (5.0) | 3.0 (600) | 6 | 2.70 | 6 | 51 | 100 | 0.34 | 28.6 |  |

[a] Conditions: 2M1P + toluene total 30 mL, methylaluminoxane (MAO, prepared by removing toluene and $AlMe_3$ from ordinary MAO),[39] 25 °C, 6 or 10 min. [b] Al/Ti molar ratios. [c] Activity in kg of polymer/(mol of Ti h). [d] Gel permeation chromatography (GPC) data in *o*-dichlorobenzene vs polystyrene standards, $M_n$ = number-average molecular weight, $M_w$ = weight-average molecular weight. [e] 2M1P in copolymer (mol %) estimated by $^{13}$C NMR spectra. [f] Observed high molecular weight shoulder. [g] 2M1P contents in whole polymers estimated by $^{13}$C NMR spectra.

ethylene and 1-hexene polymerization[25,27] but also both the activity and the molecular weight distribution in the ethylene/1-hexene copolymerization.[16]

The catalytic activities in the ethylene/2M1P copolymerization with a series of Cp*$TiCl_2$(OAr)−MAO catalyst systems increased in the order Ar = 2,6-$^i$$Pr_2$-4-$^t$Bu-$C_6H_2$ (**13**) > 2,6-$^i$$Pr_2C_6H_3$ (**1**) > $C_6H_5$ (**14**), 2,6-$Me_2C_6H_3$ (**15**) ≫ 2,6-$^t$$Bu_2C_6H_3$ (**16**). The Cp*-2,6-diisopropylphenoxy analogues (**1**, **13**) showed the highest catalytic activities, and significant differences in the activities were not observed between **1** and **13**. As described in our recent report,[3,27] the results would suggest that the unique bond angles in Ti−O−C(Ar) for **1** and **13** (173.0° and 174.6°, respectively)[27] affect the high catalytic activity by more O → Ti π donation, which leads to better stabilization of the catalytically active species in the copolymerization.[40−42]

The molecular weight distributions in the resultant polymers were also affected by the substituent in the aryloxide ligand, and the distributions became unimodal if the aryloxide analogues containing two isopropyl groups in the 2,6-position were employed. Although the results seem somewhat analogous to those in the ethylene/1-hexene copolymerizations,[16] we believe that the facts are potentially important for designing the efficient catalyst with this series, in which the complexes containing both Cp* and 2,6-diisopropyl phenoxide analogues are prerequisites for the copolymerizations (ethylene with 1-hexene, 2M1P) to exhibit the high activities with single catalytically active species (affording the molecular weights with uniform distributions).[43]

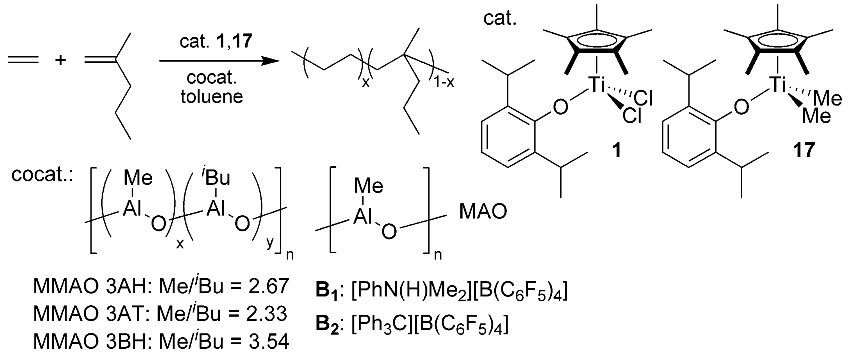
**Effect of Cocatalyst in the Ethylene/2M1P Copolymerization.** Table 4 summarizes the results for ethylene/2M1P copolymerization by **1** or Cp*$TiMe_2$(O-2,6-$^i$$Pr_2C_6H_3$) (**17**) in

**Table 4. Copolymerization of Ethylene with 2-Methyl-1-pentene (2M1P) by Cp*TiX$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$) [Cp* = C$_5$Me$_5$; X = Cl (1), Me (17)]−Cocatalyst Systems;[a] Effect of Cocatalyst**

| run | cat. ($\mu$mol) | cocatalyst | Al/mmol (Al/Ti)[b] | time/min | yield/mg | activity[c] | $M_n$[d] × $10^{-4}$ | $M_w/M_n$[d] | 2M1P[e]/mol % |
|---|---|---|---|---|---|---|---|---|---|
| 7 | **1** (0.5) | MAO | 4.5 (9000) | 10 | 480 | 5760 | 10 | 1.8 | 5.7 |
| 57 | **1** (0.5) | MMAO-3AH | 4.5 (9000) | 20 | 150 | 900 | 12 | 2.0 | 4.5 |
| 58 | **1** (0.5) | MMAO-3AT | 4.5 (9000) | 30 | 163 | 652 | 12 | 2.0 | 4.6 |
| 59 | **1** (0.5) | MMAO-3BH | 4.5 (9000) | 10 | 170 | 2040 | 11 | 2.1 | 4.7 |
| 60 | **17** (0.5) | Al($^i$Bu)$_3$/B$_1$[f] | 0.5 (1000) | 10 | 293 | 3520 | 14 | 2.1 | 4.1 |
| 61 | **17** (0.5) | Al($^i$Bu)$_3$/B$_2$[f] | 0.5 (1000) | 10 | 252 | 3020 | 16 | 2.1 | 4.0 |

[a] Conditions: 2M1P 2.70 M + toluene total 30 mL, methylaluminoxane (MAO) or modified methylaluminoxane (methylisobutylalumioxane) prepared by removing toluene and AlMe$_3$ [and/or Al($^i$Bu)$_3$] from ordinary MAO or MMAO, ethylene 6 atm, 25 °C. [b] Al/Ti molar ratios. [c] Activity in kg of polymer/(mol of Ti h)). [d] Gel permeation chromatography (GPC) data in *o*-dichlorobenzene vs polystyrene standards, $M_n$ = number-average molecular weight, $M_w$ = weight-average molecular weight. [e] 2M1P in copolymer (mol %) estimated by $^{13}$C NMR spectra. [f] [B]/[Ti] = 1.0, B$_1$ = [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$], B$_2$ = [Ph$_3$C][B(C$_6$F$_5$)$_4$]. MMAO-3BH (Me/$^i$Bu = 3.54), MMAO-3AT (Me/$^i$Bu = 2.33), MMAO-3AH (Me/$^i$Bu = 2.67).

**Scheme 5**



the presence of various cocatalysts (Scheme 5). The catalytic activities were affected by the cocatalyst employed, and the activity increased in the order **1**−MAO (5760 kg of polymer/(mol of Ti h)) ≫ **17**−Al$^i$Bu$_3$/[PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] (3520), **17**−Al$^i$Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] (3020) > **1** - MMAO-3BH (2040, ratio of Me/$^i$Bu = 3.54) ≫ **1**−MMAO-3AH (900, ratio of Me/$^i$Bu = 2.67) > **1**−MMAO-3AT (652, ratio of Me/$^i$Bu = 2.33). It might be interesting to note that the activity was highly affected the type of Al cocatalyst employed (probably electronic, anionic, nature of Al cocatalyst, might be explained as so-called catalyst/cocatalyst nuclearity effect[44]), whereas the activities were not highly influenced by the borate compounds (B$_1$, B$_2$) employed. The molecular weight distributions in the resultant copolymers were unimodal in all cases, suggesting that the copolymerization proceeded with a single catalytically active species.

Note that the no significant differences in both the 2M1P contents and microstructures were seen in the resultant copolymers, clearly suggesting that the copolymerization by **1** or **17**−cocatalyst systems took place with the similar catalytically active species; this also suggests that the cocatalyst only affects the catalytic activity. Although the observed facts are similar to those observed in ethylene/1-hexene copolymerization using Cp′TiCl$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$)−cocatalyst systems[16] as well as by ordinary metallocenes,[1] the facts should be an interesting contrast to those reported in the copolymerization of ethylene with isobutene or 1-octene using (mononuclear/dinuclear) constrained geometry (linked half-titanocene) complexes−cocatalyst systems, in which both the activities and the comonomer contents in the resultant copolymers were highly affected by the cocatalyst employed.[7] Moreover, the $M_n$ values in the copolymers were not affected by the cocatalyst employed. The fact thus clearly suggests that the dominant chain-transfer step in the copolymerization were not affected by the cocatalyst (nor chain transfer to Al), and as described above, $\beta$-hydrogen elimination after 2,1-insertion of 2M1P in a certain degree should be thus considered.

**2. Copolymerization of Ethylene with 1-Octene (OC) or 7-Methyl-1,6-octadiene (MOD) by Cp′TiCl$_2$(X) [X = O-2,6-$^i$Pr$_2$C$_6$H$_3$, Cp′ = Cp* (1); X = N=C$^t$Bu$_2$, Cp′ = Cp* (3), Cp (4)]−MAO Catalyst Systems.** As described above, we have shown that 2,2-disubstituted-1-olefin (2M1P) could be incorporated into polyethylene rather efficiently to afford high molecular weight poly(ethylene-*co*-2M1P)s with uniform molecular weight distributions/compositions. It also turned out that both the cyclopentadienyl fragment and nature of anionic ancillary donor ligand *directly affect* the catalytic activity and comonomer incorporation for the ethylene/2M1P copolymerization using Cp′TiCl$_2$(X)−MAO catalyst systems, as demonstrated in the metal-catalyzed ethylene/α-olefin copolymerization.[16,38] The next target in the copolymerization should be to explore a possibility for incorporation of trisubstituted olefins[11] and establishment for the relative monomer reactivities compared with mono- and disubstituted olefins in transition-metal-catalyzed coordination polymerization. Since it has been known in the radical polymerization that the steric bulk around the olefinic double bond strongly affects the monomer reactivity, we thus compared the reactivity between monoolefin and trisubstituted olefins under the same conditions. 7-Methyl-1,6-octadiene (MOD) was chosen for the purpose, and 1-octene (OC) was also chosen for comparison;[15] the results are summarized in Table 5.[45]

The catalytic activities by the **1**−MAO catalyst system for the ethylene/OC copolymerization was higher than the ethylene/MOD copolymerization under the optimized Al/Ti molar ratios [e.g., 154 000 kg of polymer/(mol of Ti h) (run 62, OC) vs 97 800 kg of polymer/(mol of Ti h) (run 65, MOD)]. The activities in the copolymerization of ethylene with between MOD and OC using the Cp*-ketimide analogue (**3**)−MAO catalyst system were similar, whereas the activities in the ethylene/MOD copolymerization by the Cp-ketimide analogue (**4**)−MAO catalyst system was lower than those in the ethylene/OC copolymerization. The reason for the significant decrease in the activity by **4**−MAO catalyst system in the ethylene/MOD

**Table 5. Copolymerization of Ethylene with 1-Octene (OC) or 7-Methyl-1,6-octadiene (MOD) by 1,3,4-Methylaluminoxane (MAO) Catalyst Systems**[a]

| run no. | cat. (mmol) | MAO/mmol (Al/Ti × $10^{-3}$)[b] | ethylene/atm | MOD or OC (conc/M) | yield/mg | activity[c] | $M_n$[d] × $10^{-4}$ | $M_w/M_n$[d] | comonomer[e]/mol % |
|---|---|---|---|---|---|---|---|---|---|
| 62 | **1** (0.02) | 3.0 (150) | 6 | OC (1.06) | 308 | 154000 | 13 | 2.1 | 27.9 |
| 63 | **1** (0.02) | 3.0 (150) | 4 | OC (1.06) | 158 | 79000 | 12 | 2.0 | 33.2 |
| 64 | **1** (0.05) | 1.5 (30.0) | 6 | MOD (1.01) | 400 | 80000 | 13 | 2.2 | |
| 65 | **1** (0.05) | 3.0 (60.0) | 6 | MOD (1.01) | 489 | 97800 | 12 | 2.2 | 24.7 |
| 66 | **1** (0.05) | 4.5 (90.0) | 6 | MOD (1.01) | 483 | 96600 | 10 | 2.2 | |
| 67 | **1** (0.05) | 3.0 (60.0) | 6 | MOD (1.01) | 486 | 97200 | 12 | 2.3 | 25.5 |
| 68 | **1** (0.05) | 3.0 (60.0) | 4 | MOD (1.01) | 231 | 46200 | 11 | 2.2 | 32.9 |
| 69 | **1** (0.05) | 3.0 (60.0) | 4 | MOD (2.02) | 194 | 38800 | 13 | 2.1 | 43.7 |
| 70 | **3** (0.2) | 3.0 (15.0) | 6 | OC (1.06) | 256 | 12800 | 25 | 3.4 | 19.4 |
| 71 | **3** (0.2) | 3.0 (15.0) | 4 | OC (1.06) | 118 | 5900 | 18 | 2.5 | 27.9 |
| 72 | **3** (0.2) | 3.0 (15.0) | 6 | MOD (1.01) | 253 | 12700 | 31 | 3.2 | 20.2 |
| 73 | **3** (0.2) | 3.0 (15.0) | 4 | MOD (1.01) | 151 | 7550 | 22 | 2.3 | 24.6 |
| 74 | **4** (0.02) | 3.0 (150) | 6 | OC (1.06) | 257 | 129000 | 49 | 3.6 | 22.6 |
| 75 | **4** (0.02) | 3.0 (150) | 4 | OC (1.06) | 188 | 94000 | 40 | 3.2 | 31.2 |
| 76 | **4** (0.05) | 4.5 (90.0) | 6 | MOD (1.01) | 220 | 44000 | 35 | 2.8 | 19.7 |
| 77 | **4** (0.05) | 4.5 (90.0) | 4 | MOD (1.01) | 117 | 23400 | 25 | 2.6 | 28.3 |

[a] Conditions: 1-octene (OC) or 7-methyl-1,6-octadiene (MOD) + toluene total 30 mL, methylaluminoxane (MAO, prepared by removing toluene and $AlMe_3$ from ordinary MAO), 25 °C, 6 min. [b] Al/Ti molar ratios. [c] Activity in kg of polymer/(mol of Ti h). [d] Gel permeation chromatography (GPC) data in *o*-dichlorobenzene vs polystyrene standards, $M_n$ = number-average molecular weight, $M_w$ = weight-average molecular weight. [e] OC or MOD in copolymer (mol %) estimated by $^{13}$C NMR spectra.

**Table 6. Triad Sequence Distributions in Poly(ethylene-*co*-1-octene)s Prepared by 1,3,4-Methylaluminoxane (MAO) Catalyst Systems**[a]

| | | | | triads[d] | | | | | | dyads[e] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| run | cat. | [OC]/[E][b] | OC cont[c]/mol % | EEE | EEO + OEE | OEO | EOE | OOE + EOO | OOO | EE | EO + OE | OO | $r_E$[f] | $r_O$[f] | $r_E r_O$[g] |
| 62 | **1** | 1.47 | 27.9 | 0.307 | 0.334 | 0.080 | 0.203 | 0.068 | 0.008 | 0.48 | 0.48 | 0.04 | 2.9 | 0.12 | 0.34 |
| 63 | **1** | 2.20 | 33.2 | 0.225 | 0.326 | 0.116 | 0.209 | 0.109 | 0.015 | 0.39 | 0.54 | 0.07 | 3.1 | 0.12 | 0.37 |
| 70 | **3** | 1.47 | 19.4 | 0.481 | 0.281 | 0.044 | 0.154 | 0.036 | 0.004 | 0.62 | 0.36 | 0.02 | 5.1 | 0.09 | 0.44 |
| 71 | **3** | 2.20 | 27.9 | 0.320 | 0.314 | 0.087 | 0.187 | 0.076 | 0.016 | 0.48 | 0.47 | 0.05 | 4.5 | 0.10 | 0.47 |
| 74 | **4** | 1.47 | 22.6 | 0.421 | 0.295 | 0.057 | 0.180 | 0.038 | 0.009 | 0.57 | 0.40 | 0.03 | 4.2 | 0.09 | 0.39 |
| 75 | **4** | 2.20 | 31.2 | 0.288 | 0.298 | 0.102 | 0.211 | 0.078 | 0.023 | 0.44 | 0.50 | 0.06 | 3.8 | 0.11 | 0.43 |

[a] For detailed polymerization conditions, see Table 5 (OC, O = 1-octene, E = ethylene). [b] Initial molar ratio of OC/ethylene in the reaction mixture. [c] 1-Octene content in mol % estimated by $^{13}$C NMR spectra. [d] Estimated by $^{13}$C NMR spectra. [e] [EE] = [EEE] + $^1/_2$[EEO + OEE], [EO + OE] = [OEO] + [EOE] + $^1/_2${[EEO + OEE] + [OOE + EOO]}, [OO] = [OOO] + $^1/_2$[OOE + EOO]. [f] $r_E = [O]_0/[E]_0 \times 2[EE]/[EO + OE]$, $r_O = [E]_0/[O]_0 \times 2[OO]/[EO + OE]$. [g] $r_E r_O = 4[EE][OO]/[EO + OE]^2$.

copolymerization was not clear at this moment. No significant differences in the $M_n$ values as well as the comonomer contents in the resultant copolymers were observed between OC and MOD.[41]

Figure 2 shows a typical $^{13}$C NMR spectrum for poly(ethylene-*co*-MOD)s prepared by the **1**−MAO catalyst system (run 69),[45] and the basic set of monomer sequences (isolated, alternating, repeated MOD insertion) are summarized in Scheme 6. On the basis of the dept analysis,[45] it was revealed that MOD was incorporated only with 1,2-insertion of monoolefins without incorporation of trisubstituted olefins. The trend in the resultant copolymers could be seen not only by the Cp*-aryloxo analogue (**1**) but also by the Cp*-ketimide analogue (**3**) and the Cp-ketimide analogue (**4**).[45] The fact indicates that the monoolefins are preferred to be incorporated than the trisubstituted olefins, probably due to the lower reactivity caused by the steric bulk. The synthesis of high molecular weight unsaturated polyolefins could be thus achieved.[46]

Triad sequence distributions, dyads, $r_E$, $r_O$, and $r_E$ $r_O$ (E = ethylene; O = OC, 1-octene) values estimated on the basis of $^{13}$C NMR spectra for poly(ethylene-*co*-OC)s prepared by **1**,**3**,**4**−MAO catalyst systems are summarized in Table 6.[45,47] The triad sequence distributions, dyads, the $r_E$, $r_M$, and $r_E$ $r_M$ values (M = MOD, 7-methyl-1,6-octadiene) estimated on the basis of $^{13}$C NMR spectra for poly(ethylene-*co*-MOD)s are also summarized in Table 7.[45] No significant differences in the triad sequence distributions in the resultant copolymers (ethylene/OC copolymers vs ethylene/MOD copolymers) were observed, although the ratios of the MOD three repeated incorporations (MMM sequence) were lower than those of the OC three repeated incorporations (OOO sequence).

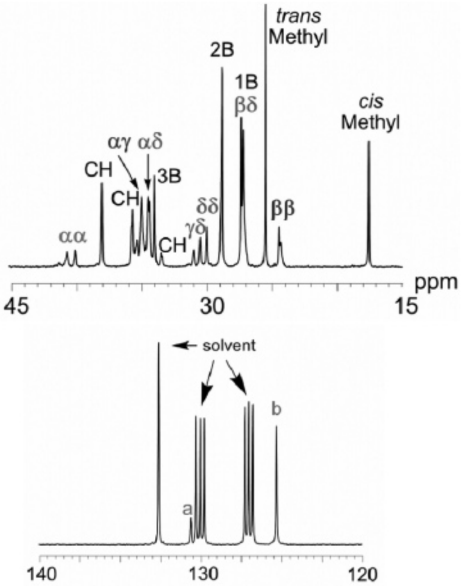


**Figure 2.** $^{13}$C NMR spectrum for poly(ethylene-*co*-7-methyl-1,6-octadiene) prepared by $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**, Cp* = $C_5Me_5$)−methylaluminoxane (MAO) catalyst system (in *o*-dichlorobenzene-$d_4$ at 110 °C, Table 5, run 69).

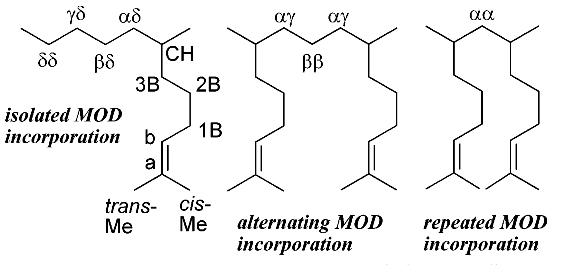
Note that the $r_E$ value by **1** in the ethylene/OC copolymerization was lower than the $r_E$ value in the ethylene/MOD copolymerization ($r_E$ = 2.9, 3.1 for ethylene/OC, $r_E$ = 3.8, 3.7

**Table 7. Triad Sequence Distributions in Poly(ethylene-*co*-MOD)s Prepared by 1,3,4-Methylaluminoxane (MAO) Catalyst Systems**[a]

| | | | | triads[d] | | | | | | dyads[e] | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| run | cat. | [MOD]/ [E][b] | MOD cont[c]/ mol % | EEE | EEM + MEE | MEM | EME | MM + EMM | MMM | EE | EM + ME | MM | $r_E$[f] | $r_M$[f] | $r_Er_M$[g] |
| 65 | **1** | 1.39 | 24.7 | 0.423 | 0.268 | 0.060 | 0.190 | 0.059 | trace | 0.56 | 0.41 | 0.03 | 3.8 | 0.10 | 0.36 |
| 67 | **1** | 1.39 | 25.5 | 0.433 | 0.244 | 0.066 | 0.195 | 0.062 | trace | 0.56 | 0.41 | 0.03 | 3.7 | 0.10 | 0.37 |
| 68 | **1** | 2.09 | 32.9 | 0.322 | 0.242 | 0.107 | 0.211 | 0.111 | 0.007 | 0.44 | 0.50 | 0.06 | 3.7 | 0.12 | 0.45 |
| 72 | **3** | 1.39 | 20.2 | 0.493 | 0.257 | 0.048 | 0.161 | 0.037 | 0.004 | 0.62 | 0.36 | 0.02 | 4.8 | 0.09 | 0.44 |
| 73 | **3** | 2.09 | 24.6 | 0.423 | 0.253 | 0.074 | 0.184 | 0.066 | trace | 0.55 | 0.42 | 0.03 | 5.5 | 0.06 | 0.35 |
| 76 | **4** | 1.39 | 19.7 | 0.500 | 0.255 | 0.048 | 0.161 | 0.036 | trace | 0.63 | 0.35 | 0.02 | 4.9 | 0.07 | 0.35 |
| 77 | **4** | 2.09 | 28.3 | 0.385 | 0.250 | 0.082 | 0.198 | 0.076 | 0.009 | 0.51 | 0.44 | 0.05 | 4.8 | 0.10 | 0.49 |

[a] For detailed polymerization conditions, see Table 5 (MOD, M = 7-methyl-1,6-octadiene, E = ethylene). [b] Initial molar ratio of MOD/ethylene in the reaction mixture. [c] MOD content in mol % estimated by $^{13}$C NMR spectra. [d] Estimated by $^{13}$C NMR spectra. [e] [EE] = [EEE] + $^1/_2$[EEM + MEE], [EM + ME] = [MEM] + [EME] + $^1/_2${[EEM + MEE] + [MME + EMM]}, [MM] = [MMM] + $^1/_2$[MME + EMM]. [f] $r_E = [M]_0/[E]_0 \times 2[EE]/[EM + ME]$, $r_M = [E]_0/[M]_0 \times 2[MM]/[EM + ME]$. [g] $r_Er_M = 4[EE][MM]/[EM + ME]^2$.

**Scheme 6**



MOD: 7-methyl-1,6-octadiene

for ethylene/MOD copolymerization, respectively), whereas the $r_E$ $r_O$ and the $r_E$ $r_M$ values were somewhat similar ($r_E$ $r_O$ = 0.34, 0.37 vs $r_E$ $r_M$ = 0.36, 0.37). The lower $r_E$ $r_O$ and $r_Er_M$ values indicate that these copolymerization by the **1**−MAO catalyst system did not take place in a random manner (comonomer incorporations were not proceeded in a random manner), and the facts were, we believe, one of the unique characteristics for using *nonbridged* half-titanocenes in the ethylene copolymerizations (especially with monoolefins).

The rather larger $r_E$ values in the ethylene/MOD copolymerization than those in the ethylene/OC copolymerization should reflect the degree in ethylene/comonomer incorporation after ethylene insertion ($r_E = k_{EE}/k_{EO}$ or $k_{EE}/k_{EM}$), which means that the MOD incorporation is more difficult than the OC incorporation after ethylene insertion. One probable reason for the observed difference is due to the steric bulk in the side chain between MOD and OC. It might also be assumed a possibility that once coordinated trisubstituted olefin would be dissociated, regenerating the former alkyl species after ethylene insertion or rapid replacement with ethylene without MOD incorporation. Although the latter assumption does not fully (directly) explain the larger $r_E$ values in the ethylene/MOD copolymerization than the ethylene/OC copolymerization in these catalyst systems, the assumption may suggest a possibility of coordination of trisubstituted olefins to the Ti. Therefore, the efficient incorporation of trisubstituted olefins in the copolymerization might be achieved by designing better catalysts. We believe that the next target on this project is thus to explore the possibility of designing the new catalysts for efficient incorporation of trisubstituted olefins for evolution of new polyolefins.

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**Supporting Information Available:** Additional (co)polymerization results catalyzed by Cp′TiCl$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$) [Cp′ = Cp* (**1**), $^t$BuC$_5$H$_4$ (**2**)], Cp*TiCl$_2$(OPh) (**14**), Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**15**) in the presence of MAO (reproducibility in the polymerization experiments); selected $^{13}$C NMR spectra for poly(ethylene-*co*-2M1P)s prepared by Cp′TiCl$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$) [Cp′ = Cp* (**1**, Cp* = C$_5$Me$_5$), 1,2,3,4-Me$_4$C$_5$H (**8**), 1,3,4-Me$_3$C$_5$H$_2$ (**9**)]−methylaluminoxane (MAO) catalyst systems; GPC traces and selected $^{13}$C NMR spectrum and DSC thermogram for resultant polymers prepared by (indenyl)TiCl$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$) (**12**)−MAO catalyst system; selected DSC thermograms and $^{13}$C NMR spectra for resultant polymers prepared by Cp*TiCl$_2$(OAr) [Ar = Ph (**14**), 2,6-Me$_2$C$_6$H$_3$ (**15**), 2,6-$^t$Bu$_2$C$_6$H$_3$ (**16**)]−MAO catalyst systems (shown in Table 3); selected $^{13}$C NMR spectra for poly(ethylene-*co*-MOD)s and poly(ethylene-*co*-1-octene)s prepared by **1**, Cp′TiCl$_2$(N=C$^t$Bu$_2$) [Cp′ = Cp* (**3**), Cp (**4**)]−MAO catalyst systems; and assumed basis set for microstructure analysis for copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) This assumption was also supported by the reported facts in the copolymerization of ethylene with methylenecyclopentane (MCP) using mononuclear/binuclear constrained geometry catalysts, in which the chain transfer (termination) becomes a competitive pathway due to the difficulty of insertion of the next monomer (due to the steric hindrance) if MCP insertion occurred in 2,1-insertion manner.[8]

(35) Although these resonances observed by $^{13}$C NMR strongly suggested the possibility that $\beta$-H elimination after 2,1-insertion of 2M1P should be the dominant chain-transfer step, these could not exclude the possibility that the $\beta$-H elimination after ethylene insertion accompanied as the probable chain-transfer step in the copolymerization, although the degree may be lower than that after 2,1-insertion of 2M1P because we could not observe the other resonances in the $^{13}$C NMR spectrum.

(36) Calculations for the optimized geometries were made as follows: equilibrium geometry at ground state with semiempirical PM3, geometry optimization, RHF/PM3D, Spartan Pro '04 for Windows (Wavefunction Inc.). Assumed structures for the optimized geometry for assumed catalytically active species (ethylene coordinated species after 2M1P insertion, 2-methyl-2-propylheptyl) in both the Cp*−aryloxo (**1**) and the *tert*-butyl−aryloxo (**2**) analogues and for the cationic species derived from **1** after 2M1P insertion were shown in the following article (symposium issue): Nomura, K.; Itagaki, K. *Stud. Surf. Sci. Catal.* **2006**, *161*, 179−184.

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(38) Fink, G.; Richter, W. J. In *Polymer Handbook*, 4th ed.; Briandrup, J., Immergut, E. H., Grulle, E. A., Eds.; John Wiley & Sons: New York, 1999; p II/329.

(39) High Al/Ti molar ratios are required if the observed catalytic activities were high because we have to reduce the amount of catalyst without reducing the amount of MAO. This is because a certain concentration of MAO should be necessary to exhibit the high catalytic activity (to remove impurities, shift equilibrium between dormant and the active species, for good reproducibility).

(40) A reviewer commented that the Ti−O $\pi$ bonding would be weak because poor correlation between the M−O−C(in Ar) angle and the M−O(in Ar) distance was observed. In fact, no significant differences in the Ti−O(in Ar) bond distances are observed in the series of Cp′TiCl$_2$(OAr).[25,27] Related reports for synthesis and structural characterization of a series of Cp′TiX$_2$(OAr): (a) Vilardo, J. S.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Chem. Commun.* **1998**, 2425−2426. (b) Vilardo, J. S.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Chem. Commun.* **1998**, 2427−2428. (c) Thorn, M. G.; Vilardo, J. S.; Lee, J. T.; Hanna, B.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2000**, *19*, 5636−5642. (d) Sturla, S. J.; Buchwald, S. L. *Organometallics* **2002**, *21*, 739−748. (e) Nomura, K.; Fudo, A. *Inorg. Chim. Acta* **2003**, *345*, 37−43. (f) Fenwick, A. E.; Phomphrai, K.; Thorn, M. G.; Vilardo, J. S.; Trefun, C. A.; Hanna, B.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2004**, *23*, 2146−2156.

(41) Descriptions concerning the correlation between the catalytic activity and substituents in the aryloxide ligands are summarized in our recent review article.[3]

(42) Recently, a correlation between activity [propagation constant in 1-hexene polymerization in the presence of B(C$_6$F$_5$)$_3$ cocatalyst] and the underlying catalyst structures in Cp′TiMe$_2$(OAr) [Cp′ = Cp or C$_5$Me$_5$] is developed using DFT-computed ligand cone angles and ion pair separation energies as structural and electronic descriptors. The correlation takes the form of an Arrhenius-like relationship where the preexponential factor is correlated to the ligand cone angles and the activation energy term is correlated to the ion pair separation energies, suggesting the idea that the ability of the monomer to access the metal center is a key factor affecting the reaction rate. Manz, T. A.; Phomphrai, K.; Medvedev, G.; Krishnamurthy, B. B.; Sharma, S.; Haq, J.; Novstrup, K. A.; Thomson, K. T.; Delgass, W. N.; Caruthers, J. M.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 3776. However, we believe, these results may not explain the reason why Cp*TiCl$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$) (**1**) showed exceptionally high catalytic activities (as well as efficient comonomer incorporations) copolymerization of ethylene not only with 1-hexene (1-octane)[16] but also with 2-methyl-1-pentene.

(43) The resultant polymer prepared by the **14**−MAO catalyst (run 52) did not contain 2M1P, and the polymer prepared by the **15**−MAO catalyst (run 54) contained 2M1P in a small amount (estimated by $^{13}$C NMR spectra). Although the resultant polymers prepared by **14** and **15** possessed broad molecular weight distributions, their DSC thermograms (single melting temperature) suggest that the resultant (co)polymers possessed uniform composition(s). In contrast, the resultant polymer prepared by the **16**−MAO catalyst (run 56) possessed two melting temperatures, suggesting the composition in the polymer was not uniform and the presence of several catalytically active species. One probable reason for the broad molecular weight distributions by **14**−**16** is the formation of several catalytically active species due to that the proposed catalytically active species, Cp′TiR-

(OAr)$^+$, may not be stable and would generate several catalytically active species such as Ti(III) (cationic, neutral) and aryloxo-dissociated cationic Ti(IV) species. On the basis of the above $^{13}$C NMR spectra and the DSC thermograms, it is clear that we have to explore and discuss more critically what kind of side reactions (decomposition pathways) occurred in the reaction mixture using **14**−**16** in the presence of MAO. Selected DSC thermograms and $^{13}$C NMR spectra for resultant polymers prepared by **14**−**16**−MAO catalysts are shown in the Supporting Information. A related recent article concerning the catalytically active species in syndiospecific styrene polymerization and ethylene/styrene copolymerization using $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$−MAO catalyst systems is: Zhang, H.; Nomura, K. *Dalton Trans.* **2007**, 1802−1806. It was also reported recently that some Ti(III) intermediates formed from $[\eta^3\text{-}PhC(NSiMe_3)_2]_2TiCl_2$ in the presence of MAO (characterized by ESR) were not active in the polymerization of ethylene and propylene but were cleanly oxidized upon exposure of propylene to Ti(IV) species, Volkis, V.; Lisovskii, A.; Tumanskii, B.; Shuster, M.; Eisen, M. S. *Organometallics* **2006**, *25*, 2656. The more detailed studies concerning the effect of anionic donor ligand are still under investigation. K.N. expresses his thanks to a reviewer for the critical comment.

(44) A reviewing article for ion pairing in transition metal organometallic chemistry: Macchioni, A. *Chem. Rev.* **2005**, *105*, 2039−2074.

(45) Selected $^{13}$C NMR spectra for poly(ethylene-*co*-MOD)s (MOD = 7-methyl-1,6-octadiene) including the dept spectrum and basic assumptions for estimation of MOD contents as well as monomer sequence distributions in the copolymers are shown in the Supporting Information. No resonances ascribed to cyclization or partial cross-linking which may be occurring by incorporating trisubstituted olefins were seen, and the fact also supports that the present copolymerization took place with exclusive incorporation of monoolefins in MOD.

(46) Synthesis of unsaturated polyolefins using metallocene catalysts, for example: Chung, T. C. *Functionalization of Polyolefins*; Academic Press: San Diego, CA, 2002.

(47) These calculations (for ethylene/1-octene copolymers) were made by the following paper using $^{13}$C NMR spectra of copolymers: Randall, J. C. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29*, 201−317. The estimations for poly(ethylene-*co*-MOD)s were made on the basis of the assumption described above, and the details are described in the Supporting Information.

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