

# Synthesis of Half-Titanocenes Containing Aryloxy Ligands Attached to the ROMP Polymer Chain End: Unique Catalyst Precursors for Ethylene (Co)polymerization

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Half-titanocenes containing aryloxy ligands immobilized on the chain end of ring-opened poly-(norbornene)s,  $(C_5Me_5)TiMe_2[O-2,6-R_2C_6H_2-4-CH\{CH-(1,3-cyclo-C_5H_8)-CH\}_nCHCMe_2Ph]$  [R = H (**1**), Me (**2**), <sup>i</sup>Pr (**3**)], prepared by living ring-opening metathesis polymerization (ROMP) by  $Mo(N-2,6-^iPr_2C_6H_3)(CHCMe_2Ph)(O^iBu)_2$ , have been prepared and identified by <sup>1</sup>H and <sup>13</sup>C NMR spectra, elemental analysis, and X-ray photoelectron spectroscopy. These complexes showed high catalytic activities for ethylene polymerization in the presence of methylaluminoxane (MAO) cocatalyst, and the effect of the substituent on the aryloxy on both the activity and molecular weight of the resultant polymer was the same as that using nonsupported  $(C_5Me_5)TiCl_2(O-2,6-R_2C_6H_3)$  (R = H, Me, <sup>i</sup>Pr). Complex **3** showed both notable catalytic activities and efficient 1-hexene incorporation with the same monomer reactivity ratio as nonsupported  $(C_5Me_5)TiCl_2(O-2,6-^iPr_2C_6H_3)$  (**3'**) for ethylene/1-hexene copolymerization in the presence of MAO.

## Introduction

The preparation of supported transition metal complex catalysts that maintain unique characteristics in the homogeneous analogues (so-called “single-site” heterogeneous catalysts) is one of the most attractive subjects in the fields of organometallic chemistry, catalysis, and synthetic organic chemistry.<sup>1</sup> As an attempt to combine the advantages and to minimize the disadvantages associated with homogeneous and heterogeneous catalysts, the use of soluble polymer-supported ligands (instead of insoluble polymer resins such as divinylbenzene and cross-linked polystyrene<sup>2</sup>) has attracted considerable attention.<sup>3</sup> While particular attention has been devoted to studies concerning polymer<sup>3</sup>- or dendrimer<sup>4</sup>-supported catalysts, there have been few examples of the use of ligands attached to the polymer chain end prepared by a controlled living polymerization technique. The exclusive end-functionalization of ring-opened poly(norbornene) can be achieved by the living ring-opening metathesis polymerization (ROMP) using molybdenum-alkylidene initiators,  $Mo(N-2,6-^iPr_2C_6H_3)(CHCMe_2Ph)(O^iBu)_2$ ,<sup>5–7</sup> and the

resultant ROMP polymers are rather linear compared to ordinary vinyl polymers such as poly(acrylamide)s.<sup>8</sup> The rather linear nature of the ROMP polymer suggests that the functionality at the polymer chain end may not be strongly affected by the polymer main chain, which would contribute to maintaining the nature of homogeneous catalysis.<sup>9,10</sup> In this paper, we present an interesting example in which remarkable catalytic activities, monomer reactivities ( $r_E$  and  $r_{E/H}$  values in ethylene/1-hexene copolymerization), and the observed ligand effect are maintained upon the immobilization of half-titanocenes<sup>11,12</sup> containing an aryloxy ligand at the ROMP polymer chain end.<sup>13–15</sup>

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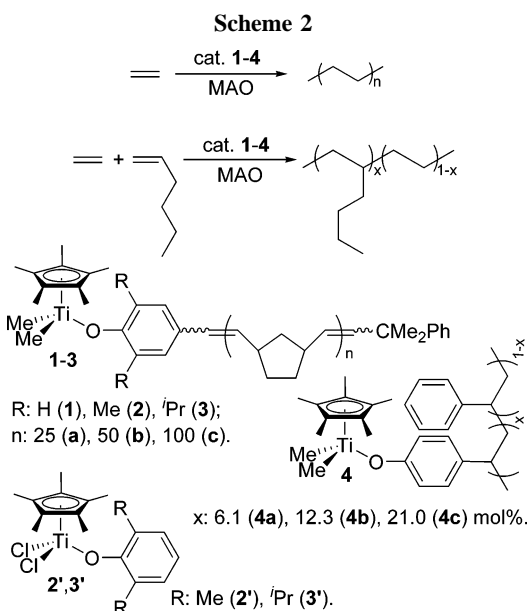
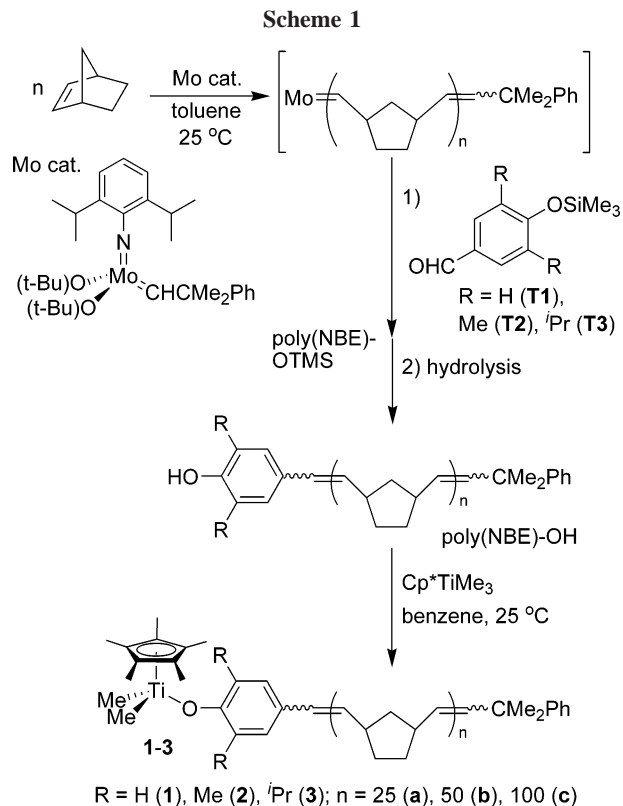
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## Results and Discussion

**1. Synthesis and Characterization of Half-Titanocenes Containing Aryloxy Ligands Attached to a ROMP Polymer Chain End.** The living ring-opening metathesis polymerization technique using a molybdenum-alkylidene catalyst was chosen, because the introduction of a functionality exclusively into the polymer chain end can be easily achieved.<sup>7,10</sup> These characteristics enable us to prepare poly(macromonomer)s by repetitive ROMP,<sup>7a,c</sup> as well as to efficiently prepare various amphiphilic block copolymers by grafting poly(ethylene glycol) to end-functionalized block ROMP copolymers.<sup>7b</sup>

ROMP of norbornene (NBE) using Mo(CHCMe<sub>2</sub>Ph)(N-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>(O<sup>t</sup>Bu)<sub>2</sub>) was performed in toluene at 25 °C, and 4-Me<sub>3</sub>-SiO-C<sub>6</sub>H<sub>4</sub>CHO (**T1**), 2,6-Me<sub>2</sub>-4-Me<sub>3</sub>SiO-C<sub>6</sub>H<sub>2</sub>CHO (**T2**), or 2,6-<sup>i</sup>Pr<sub>2</sub>-4-Me<sub>3</sub>SiO-C<sub>6</sub>H<sub>2</sub>CHO (**T3**) was added in excess amounts after the consumption of NBE not only to terminate the polymerization but also to quantitatively introduce an aryloxy moiety into the chain end of a ring-opened polymer (Scheme 1).<sup>16</sup> Selected results are summarized in Table 1.<sup>16</sup> The procedure is analogous to that established previously,<sup>7</sup> and the aryloxy moiety could be introduced by cleaving the polymer-metal bond via a Wittig-like reaction with the aldehyde. The yields were higher than 98% in all cases, and the SiMe<sub>3</sub> (TMS) group in the resultant polymer could be removed by treatment with acidified THF. The resultant ROMP polymers were isolated as white precipitates by pouring the mixture into a cold MeOH solution<sup>7,16</sup> and were identified by <sup>1</sup>H and <sup>13</sup>C NMR spectra as a mixture of *cis*- and *trans*-olefinic double bonds. The *M<sub>n</sub>* and low *M<sub>w</sub>/M<sub>n</sub>* values (*M<sub>w</sub>/M<sub>n</sub>* = 1.07–1.20) suggest that polymerization proceeded in a living manner, which implies that every poly(NBE) consisted of a very similar number of NBE repeating units. Moreover, the *M<sub>n</sub>* values estimated from <sup>1</sup>H NMR spectra were consistent with the calculated values based on NBE/Mo molar ratios, indicating that efficient quantitative initiation was achieved in the present ROMP technique (Table 1). Neither *M<sub>n</sub>* nor *M<sub>w</sub>/M<sub>n</sub>* by GPC changed after unmasking the TMS group, indicating that no side reactions occurred in this procedure.<sup>16</sup>

Various half-titanocenes (**1–3**) containing aryloxy ligands attached to the ring-opened poly(NBE) chain end could be prepared by reacting Cp\*TiMe<sub>3</sub> (Cp\* = C<sub>5</sub>Me<sub>5</sub>) with corresponding phenols in benzene at 25 °C. This is a modification of a procedure reported previously for the synthesis of Cp\*TiMe<sub>2</sub>-



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(13) Synthesis of dendrimer-supported half-titanocenes, for example: Arévalo, S.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R. *Organometallics* **2001**, *20*, 2583.

(14) Synthesis of half-titanocenes supported on polystyrene: (a) Kasi, R. M.; Coughlin, E. B. *Macromolecules* **2003**, *36*, 6300. (b) Kitiyanan, B.; Nomura, K. *Stud. Surf. Sci. Catal.* **2006**, *161*, 213.

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(16) Detailed experimental procedures including preparation/identifications of catalysts and additional polymerization results are shown in the Supporting Information.

(O-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>),<sup>17</sup> and the prepared complexes could be identified by NMR, X-ray photoelectron spectroscopy (XPS), and elemental analysis.<sup>16</sup> Resonances ascribed to Ti-CH<sub>3</sub> in the <sup>13</sup>C NMR spectra were shifted from 61.2 (Cp\*TiMe<sub>3</sub>)<sup>18</sup> to 54.2 ppm (catalysts **1–3**), which are almost identical to Cp\*TiMe<sub>2</sub>(O-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (Ti-CH<sub>3</sub>, δ 54.2 ppm),<sup>17</sup> and other resonances assigned to the ring-opened poly(NBE), the end groups, and Cp\* were also seen in both the <sup>1</sup>H and <sup>13</sup>C NMR spectra.<sup>16</sup> The results of XPS also confirmed the existence of Ti in the catalysts, and the electron binding energy (BE) of the catalysts was 455.9 eV, which was relatively close to that in

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**Table 1. Selected Results of Ring-Opening Metathesis Polymerization of Norbornene (NBE) with Mo(CHCMe<sub>2</sub>Ph)(N-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(O*i*Bu)<sub>2</sub> with Various Terminating Reagents<sup>a</sup>**

run	NBE/Mo <sup>b</sup>	term.	poly(NBE)-OTMS				poly(NBE)-OH		
			$M_n(\text{calc})^c \times 10^{-4}$	$M_n(\text{NMR})^d \times 10^{-4}$	$M_w/M_n^e$	yield <sup>f</sup> /%	$M_n(\text{NMR})^g \times 10^{-4}$	$M_w/M_n^d$	yield <sup>h</sup> (%)
1	50	<b>T3</b>	0.51	0.65	1.17	>98	0.68	1.17	>98
2	25	<b>T2</b>	0.27	0.34	1.16	98	0.33	1.20	>98
3	50	<b>T2</b>	0.51	0.60	1.10	>98	0.62	1.13	>98
4	100	<b>T2</b>	0.98	1.13	1.07	>99	1.16	1.11	>98
5	50	<b>T1</b>	0.50	0.63	1.12	>98	1.15	1.15	>98

<sup>a</sup> Conditions: toluene (5.0 g) at 25 °C, 30 min.<sup>16</sup> <sup>b</sup>Molar ratio of NBE/Mo. <sup>c</sup>Calculated on the basis of NBE/Mo initial molar ratio. <sup>d</sup>Estimated by <sup>1</sup>H NMR spectra (using integration ratio vs SiMe<sub>3</sub>). <sup>e</sup>GPC data in THF vs polystyrene standards. <sup>f</sup>Isolated yield. <sup>g</sup> $M_n$  estimated by <sup>1</sup>H NMR spectra [using integration ratio vs di-CH(CH<sub>3</sub>)<sub>2</sub> (**T3**) and di-CH<sub>3</sub> (**T2**)]. <sup>h</sup>Isolated yield after removal of TMS protecting group.

**Table 2. Ethylene Polymerization by (1–4)–MAO Catalysts<sup>a</sup>**

run	cat. (μmol)	yield <sup>b</sup> /mg	activity <sup>c</sup>	$M_w^d \times 10^{-4}$	$M_w/M_n^d$
6	<b>3'</b> (0.1)	221	13 300	212	2.3
7	<b>2'</b> (0.1)	294	17 600	7.2	2.1
8	<b>3b</b> (0.1)	122	7350	328	2.3
9	<b>2a</b> (0.2)	289	8680	7.9	2.4
10	<b>2b</b> (0.2)	319	9570	6.0	2.2
11	<b>2c</b> (0.2)	182	5460	6.6	2.1
12	<b>1b</b> (0.2)	134	4020	6.5	2.1
13	<b>4a</b> (0.5) <sup>e</sup>	420	5040	5.0	2.1
14	<b>4b</b> (0.5) <sup>e</sup>	303	3640	5.7	2.3
15	<b>4c</b> (0.5) <sup>e</sup>	139	1670	3.4	3.5

<sup>a</sup> Conditions: ethylene 6 atm, toluene 30 mL, 25 °C, 10 min, MAO (prepared by removing AlMe<sub>3</sub> and toluene from ordinary PMAO) 3.0 mmol, 100 mL scale autoclave.<sup>16</sup> <sup>b</sup>Polymer yield based on PE. <sup>c</sup>Activity in kg-polymer/mol-Ti·h. <sup>d</sup>GPC data in *o*-dichlorobenzene vs polystyrene standards. <sup>e</sup>Cited from ref 14b.

Cp\*<sub>2</sub>TiCl<sub>2</sub> (BE 456.26 eV).<sup>16,19</sup> Moreover, the carbon and hydrogen contents based on the results of the elemental analysis were in good agreement with the calculated values.

**2. Ethylene Polymerization and Ethylene/1-Hexene Copolymerization.** Ethylene polymerizations by catalysts **1–3** were conducted in the presence of methylaluminoxane (MAO) as a cocatalyst. Half-titanocenes supported in polystyrene (**4a–c**)<sup>14b</sup> and nonsupported Cp\*TiCl<sub>2</sub>(OAr) (**2'**, **3'**)<sup>17,20</sup> were also chosen for comparison (Scheme 2). The polymerization results are summarized in Table 2.

ROMP polymer-supported half-titanocenes (**1–3**) exhibited notable catalytic activities to give linear polyethylenes (PEs) with unimodal molecular weight distributions (runs 8–12). The observed trend in the activities (effect of the aryloxy substituent in the *ortho*-position) was somewhat similar to that observed in the polymerization by nonsupported Cp\*TiCl<sub>2</sub>(OAr)–MAO catalysts (ethylene 4 atm at 60 °C),<sup>17</sup> although the observed activities with **1–3** were somewhat lower than those with **2'** and **3'** (runs 8–11 vs runs 6, 7). The  $M_w$  values for the resultant PEs were strongly affected by the substituents on the aryloxy ligand used, and complexes containing diisopropyl phenoxy moieties (**3b** and **3'**) gave high-molecular-weight PEs with unimodal distributions. The  $M_w/M_n$  values were close to 2, and the results might suggest that these polymerizations proceeded with only catalytically active species.

Ethylene polymerization with (**2a–c**)–MAO [with different NBE repeating units (chain length),  $n = 25$  (**2a**), 50 (**2b**), 100 (**2c**)] and (**4a–c**)–MAO [with different Ti loadings, molar ratio,  $x = 6.1$  (**4a**), 12.3 (**4b**), 21.0 (**4c**) mol %]<sup>14b</sup> catalysts was performed to explore the effect of Ti loadings on catalytic activities. No significant differences in the observed activities

by **2a** ( $n = 25$ ) and by **2b** ( $n = 50$ ) were seen, although the activity with **2c** ( $n = 100$ ) seemed slightly lower than those with **2a, b**. In contrast, the activity with **4** strongly depended on the Ti loading (molar ratio of styrene and substituted styrene), and **4c** showed the lowest activity under the same conditions. Moreover, no significant differences in the  $M_w$  values were seen for PEs prepared with **2a–c**, whereas the  $M_w$  values prepared by polystyrene-supported half-titanocenes (**4a–c**) were strongly affected by the amount of Ti loading (runs 9–11 vs runs 13–15). The  $M_w$  value with **4c**–MAO catalyst showed a rather broad distribution, suggesting the presence of several active species. These findings are interesting, since the amount of Ti in the ROMP polymer-attached complex (**1–3**) can be tuned without a significant decrease in the activity by adopting this approach.

To evaluate the catalyst performance of the prepared ROMP polymer-attached half-titanocenes (**1–3**), ethylene/1-hexene copolymerization catalyzed by **1–3** was conducted in the presence of MAO (Scheme 2).<sup>21,22</sup> The copolymerizations were terminated at the initial stage (10 min) to obtain copolymers with uniform compositions, and the results are summarized in Table 3.<sup>22</sup>

Note that the diisopropylphenoxy analogue (**3b**) showed exceptionally high catalytic activities with efficient 1-hexene incorporation, to give relatively high-molecular-weight poly(ethylene-*co*-1-hexene)s with high 1-hexene content as well as with unimodal distributions (by both GPC and <sup>13</sup>C NMR spectra, Table 3).<sup>22</sup> Moreover, the observed activities with **3b** in the copolymerization were much higher than that in the ethylene homopolymerization; the observed trend is the same as that seen in the copolymerization with the **3'**–MAO catalyst system.<sup>21</sup> The 1-hexene content, the  $M_n$  values, and the microstructure in the copolymer with **3b** were the same as those with **3'**.<sup>21,22</sup> The activity increased with an increase in the ethylene pressure, and 1-hexene content in the copolymer increased upon increasing the 1-hexene concentration or lowering the ethylene pressure, as seen in the copolymerization with **3'**.<sup>21b</sup>

In contrast, the activities with both the dimethylphenoxy analogue (**2b**) and the phenoxy analogue (**1b**) in the copolymerizations were lower than those in the ethylene polymerizations, and the resultant polymers possessed bimodal molecular weight distributions. The observed activities by **1b, 2b** in the copolymerization were much lower than those by **3b** under the same conditions (runs 20–22 vs runs 17, 18). The trends observed in the copolymerization using these supported half-titanocenes (**1b–3b**) are similar to those observed with the

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(22) Additional polymerization results and typical <sup>13</sup>C NMR spectra for the (co)polymers for estimation of the monomer sequences are shown in the Supporting Information.



**Table 3. Copolymerization of Ethylene with 1-Hexene by (1–4)–MAO Catalysts<sup>a</sup>**

run	cat. ( $\mu\text{mol}$ )	ethylene/atm	1-hexene/mL	yield/mg	activity <sup>b</sup>	$M_w^c \times 10^{-4}$	$M_w/M_n^c$	1-hexene <sup>d</sup> /mol %	$r_E^e$	$r_H^e$	$r_E r_H^e$
16	<b>3b</b> (0.02)	4	5.0	125	37500	26.3	2.0	41.2	2.55	0.13	0.34
17	<b>3b</b> (0.02)	6	5.0	178	53400	30.2	2.0	33.7	2.64	0.14	0.36
18	<b>3b</b> (0.02)	6	10.0	176	52800	31.1	2.0	44.4	2.84	0.12	0.33
19	<b>3b</b> (0.02)	8	5.0	233	69900	35.0	2.0	27.3	2.87	0.12	0.35
20	<b>2b</b> (0.5)	6	5.0	281	3380	bimodal					
21	<b>2b</b> (0.5)	6	10.0	261	3140	bimodal					
22	<b>1b</b> (2.0)	6	10.0	65	194	bimodal					
23	<b>4b</b> (2.5)	6	5.0	146	350	0.9	5.4				

<sup>a</sup> Conditions: toluene + 1-hexene total 30 mL, 25 °C, 10 min, MAO 3.0 mmol. <sup>b</sup> Activity in kg-polymer/mol-Ti·h. <sup>c</sup> GPC data in *o*-dichlorobenzene vs polystyrene standards. <sup>d</sup> Estimated by <sup>13</sup>C NMR spectra.<sup>22</sup> <sup>e</sup> Estimated by <sup>13</sup>C NMR spectra and initial monomer concentration,  $r_E = k_{EE}/k_{EH} = [H]_0/[E]_0 \times 2[EE]/[EH + HE]$ ;  $[H]_0$  and  $[E]_0$  are the initial concentration. Details are shown in the SI.<sup>22</sup>

original half-titanocenes reported previously.<sup>21b</sup> The copolymerization with polystyrene-supported half-titanocenes (**4b**) showed low catalytic activity under the same conditions, to give low-molecular-weight polymer (oligomer) with a broad distribution (run 23).

The monomer reactivity ratios [ $r_E$ ,  $r_H$  ( $r_E = k_{EE}/k_{EH}$ ,  $r_H = k_{HH}/k_{HE}$ )] and  $r_E r_H$  values were estimated on the basis of the <sup>13</sup>C NMR spectra in the resultant copolymers and the monomer concentrations.<sup>22,23</sup> Note that both the  $r_E$  and  $r_H$  values with **3b** ( $r_E = 2.55$ – $2.87$ ,  $r_H = 0.12$ – $0.14$ ) are almost identical to those with Cp\*TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**3'**,  $r_E = 2.29$ – $2.70$ ,  $r_H = 0.11$ – $0.13$ ) reported previously.<sup>21b</sup> The  $r_E r_H$  values with **3b** are 0.33–0.36, indicating that the copolymerization (1-hexene incorporation) did not proceed in a random manner, as seen in copolymerization using some metallocenes and linked half-titanocenes ( $r_E r_H = \text{ca. } 1$ ).<sup>21b,23</sup> The trend is also the same as that observed in the copolymerization with **3'**–MAO catalyst.<sup>21</sup> These facts clearly indicate that the nature of the catalyst performance, which is a factor in the design of an immobilized catalyst, can be maintained by tethering the half-titanocenes at the chain end of ring-opened poly(NBE)s through the aryloxide moieties.

We have shown that not only remarkable catalytic activities but also monomer reactivities and the observed ligand effect can be retained by the immobilization of half-titanocenes containing an aryloxide ligand at the ROMP polymer chain end. The present approach may become a method for the immobilization of homogeneous transition metal complex catalysts. We are currently exploring the catalyst performance in other organic reactions (including cyclization)<sup>24</sup> in addition to olefin polymerization and are also exploring the possibility of preparing other unique ROMP–polymer-supported catalysts (ball/star shape, grafted, etc.) by adopting this approach.

## Experimental Section

**General Procedure.** All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were of reagent grade and were purified by standard purification procedures. Anhydrous-grade toluene (Kanto Kagaku Co. Ltd) was transferred to a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox and was used without further purification. 1-Hexene (Kanto Kagaku Co. Ltd) was stored in the drybox in the presence of molecular sieves after being passed through a short alumina column under a nitrogen atmosphere. Toluene and AlMe<sub>3</sub> in commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C

to remove toluene and AlMe<sub>3</sub> and then heated at >100 °C for 1 h for completion) in the drybox to give white solids. Cp\*TiCl<sub>2</sub>(O-2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**2'**)<sup>20</sup> and Cp\*TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**3'**)<sup>17</sup> were prepared according to the previous reports.

All <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, <sup>1</sup>H; 100.40 MHz, <sup>13</sup>C), and all chemical shifts are given in ppm. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. All deuterated NMR solvents were stored over molecular sieves, and all chemical shifts are given in ppm. <sup>13</sup>C NMR spectra for poly(ethylene-*co*-1-hexene)s were recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, <sup>13</sup>C) with proton decoupling. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was ca. 6000. The copolymer samples for analysis were prepared by dissolving the polymers in a mixed solution of 1,2,4-trichlorobenzene/benzene-*d*<sub>6</sub> (90/10 wt), and the spectra were measured at 110 °C.

GPC analyses were performed at 40 °C on a Shimadzu SCL-10A using an RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt % 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm  $\phi$ ) were calibrated versus polystyrene standard samples. HPLC-grade THF was used for GPC and was degassed prior to use. The molecular weights and molecular weight distributions of polyethylene and poly(ethylene-*co*-1-hexene)s were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GMH<sub>HR</sub>-H HT × 2, 30 cm × 7.8 mm  $\phi$  i.d.), ranging from <10<sup>2</sup> to <2.8 × 10<sup>8</sup> MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v % 2,6-di-*tert*-butyl-*p*-cresol as the solvent. The molecular weight was obtained by a standard procedure based on calibration with standard polystyrene samples.

X-ray photoelectron spectra were obtained on a X-ray photoelectron spectroscope (XPS, Kratos AXIS 165) using Al radiation (1486.6 eV). The spectra were taken at room temperature in low-resolution mode within a binding energy range of 0–1000 eV and in high-resolution mode for the C 1s, O 1s, and Ti 2p regions. Samples were first dissolved in benzene and then dropped on a clean, flat silicon substrate. Samples were then mounted on a copper holder with adhesive carbon tape and placed under vacuum to remove the solvent. Samples were prepared in a glovebox and then transferred to an introduction chamber, which was then evacuated to 10 mbar by a turbo-molecular pump. Prior to the analysis, the sample surface was etched with Ar<sup>+</sup> ion to remove any contamination on the surface. The acceleration voltage ( $E_0$ ) and beam current ( $I_e$ ) of the Ar<sup>+</sup> ion beam were 1.5 kV and 10 mA, respectively. The spot size of the beam was 5 × 5 mm, and the etching time was 40 s. Surface atomic ratios were estimated on the basis of integrated areas and calculated atomic sensitivities factors, which were empirically derived for the electron energy analyzer. Elemental analyses were performed by using a PE2400II Series (Perkin-Elmer Co.).

(23) For example: Suhm, J.; Schneider, M. J.; Mühlaupt, R. *J. Mol. Catal. A* **1998**, *128*, 215.

(24) Sturla, S. J.; Buchwald, S. L. *Organometallics* **2002**, *21*, 739.

4-Hydroxy-3,5-diisopropylbenzaldehyde was prepared according to the published procedure,<sup>25</sup> and 3,5-*i*-Pr<sub>2</sub>-4-Me<sub>3</sub>SiO-C<sub>6</sub>H<sub>2</sub>CHO (**T3**), 3,5-Me<sub>2</sub>-4-Me<sub>3</sub>SiC<sub>6</sub>H<sub>2</sub>CHO (**T2**), and 4-Me<sub>3</sub>SiOC<sub>6</sub>H<sub>4</sub>CHO (**T1**) were prepared from 4-hydroxy-3,5-diisopropylbenzaldehyde, 4-hydroxy-3,5-dimethylbenzaldehyde, and 4-hydroxybenzaldehyde, respectively, according to the published procedure (for the synthesis of **T1**).<sup>7a</sup> The detailed synthetic procedures are shown in the Supporting Information.

**Synthesis of Ring-Opened Poly(norbornene) [poly(NBE)-OTMS].** Ring-opened poly(norbornene)s with an OTMS-protecting terminus (**T1**, **T2**, **T3**) were synthesized according to the reported procedure,<sup>7</sup> and the detailed procedures are shown in the Supporting Information. The yields were higher than 98% in all cases. <sup>1</sup>H NMR (CDCl<sub>3</sub>) for the poly(norbornene) main chain: δ 5.22 and 5.35 (br m, 2H olefinic), 2.80 and 2.37 (br s, 2H), 1.85 and 1.08 (m, 2H), 1.81 and 1.36 (m, 4H); and for the TMS-protected group (**T3**): 3.19 (m, (CH<sub>3</sub>)<sub>2</sub>CH-), 1.28 (12H, (CH<sub>3</sub>)<sub>2</sub>CH-), and 0.26 (-Si(CH<sub>3</sub>)<sub>3</sub>); (**T2**): 2.16 (-CH<sub>3</sub>) and 0.26 (-Si(CH<sub>3</sub>)<sub>3</sub>), (**T1**): 0.26 (-Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 134.0, 133.9, 133.8, 133.7, and 133.1, 133.0, and 132.8 (olefinic), 128.0, 126.9, 126.1, 125.5, and 120.1 (aromatic carbon), 68.0, 50.8, 43.4, 43.2, 42.7, 42.1, 41.3, 38.6, 38.4, 33.1, 32.9, 32.3, 32.2, and (**T3**): 27.3, 22.7, and 0.2 [Si(CH<sub>3</sub>)<sub>3</sub>]; (**T2**): 17.8 and 0.2 [Si(CH<sub>3</sub>)<sub>3</sub>]; (**T1**): 0.2 [Si(CH<sub>3</sub>)<sub>3</sub>].

**Removal of a TMS Protecting Group from the Poly(norbornene) Terminus.** A SiMe<sub>3</sub> protecting group was removed from the chain end of poly(NBE)-OTMS by a procedure similar to that reported previously.<sup>7</sup> HCl (0.5 M) aqueous solution was added dropwise to a rapidly stirred solution of poly(NBE)-OTMS dissolved in THF (1 drop of 0.5 M HCl(aq) per 10 mg of polymer), and the mixture was stirred for 1 h at room temperature (25 °C). The solution was then poured dropwise into cold methanol to give a hydroxyl group-terminated ROMP polymer, [poly(NBE)-OH], as a white precipitate, which was collected by filtration and dried in vacuo. Yield > 98%.

**Synthesis of a Half-Titanocene Containing an Aryloxide Ligand Supported on the Chain End of Ring-Opened Poly(norbornene).** The reaction of Cp\*TiMe<sub>3</sub> with the hydroxyl group at the chain end of ring-opened poly(norbornene) is analogous to the synthesis of Cp\*TiMe<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sup>17</sup> from Cp\*TiMe<sub>3</sub><sup>18</sup> by treating it with HO-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>. For example, **3b** was synthesized by reacting poly(NBE)<sub>50</sub>-OH (poly(NBE)-OH with *n* = 50) with Cp\*TiMe<sub>3</sub> as follows. In the drybox, poly(NBE)-OH (1.174 g) was dissolved in benzene (20 mL) and added dropwise to a stirred benzene (1.0 mL) solution containing Cp\*TiMe<sub>3</sub> (0.053 g, 1 equiv). After the reaction mixture was stirred for 24 h with protection from light, benzene was then removed in vacuo, resulting in the catalyst-supported polymer solid. The resultant polymer-supported complex was adequately washed with cold *n*-hexane. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): for

the poly(norbornene) main chain: δ 5.32 and 5.46 (br m, 2H olefinic), 2.85 and 2.48 (br s, 2H), 1.97 and 1.19 (br m, 2H), 1.81 and 1.36 (br m, 4H), and from the attached half-titanocenes, δ 1.75 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 0.71 (Ti-CH<sub>3</sub>), and from the *ortho* position of aryloxo analogue, δ 3.22 (m, (CH<sub>3</sub>)<sub>2</sub>CH-) (**3b**) and 2.2 (d, -(CH<sub>3</sub>)) (**2b**). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 149.5, 138.7, 134.2, 134.1, 133.5, 133.4, 133.3, 132.7, 132.5 (olefinic), 128.5, 128.3, 126.4, 126.0, 121.3 (aromatic carbon), 44.0, 43.6, 43.2, 42.5, 41.8, 39.1, 38.8, 33.4, 33.3, 32.7, 32.6, 29.2, and from the attached half-titanocenes, 122.3 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), 54.2 (Ti-CH<sub>3</sub>), 11.6 (C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), and from *ortho* position of aryloxo analogue, 27.0 ((CH<sub>3</sub>)<sub>2</sub>CH-), 24.0 ((CH<sub>3</sub>)<sub>2</sub>CH-) (**3b**) and 17.8 (CH<sub>3</sub>) (**2b**). Anal. Calcd for cat. **3b**: C, 88.21; H, 10.57. Found: C, 87.77; H, 10.65. Calcd for cat. **2a**: C, 87.35; H, 10.39. Found: C, 85.89; H, 10.20. Calcd for cat. **2b**: C, 88.23; H, 10.53. Found: C, 88.25; H, 10.60. Calcd for cat. **2c**: C, 88.74; H, 10.62. Found: C, 88.87; H, 10.82. Calcd for cat. **1b**: C, 88.25; H, 10.51. Found: C, 86.44; H, 10.54. The rather lower C values for catalysts **3b**, **2a**, and **1b** are due to incomplete combustion by the partial formation of TiC.

**Ethylene/1-Hexene Copolymerization.** A typical reaction procedure for the copolymerization (run 17, Table 3) is as follows. Toluene (24 mL), 1-hexene (5.0 mL), and solid d-MAO (174 mg, 3.0 mmol) were added to an autoclave (100 mL scale stainless steel) in the drybox, and the reaction apparatus was then filled with ethylene (1 atm) at room temperature (25 °C). A toluene solution (1.0 mL) containing **3b** (0.02 μmol) was then added to the autoclave, and the reaction system was immediately pressurized to the gauged pressure of 5 atm (absolute ethylene pressure 6 atm). The mixture was magnetically stirred for 10 min. The ethylene supply was stopped, and any remaining ethylene was purged from the autoclave after the reaction. The mixture was then poured into EtOH (50 mL) containing concentrated HCl (5 mL). The resultant polymer was adequately washed with EtOH, then collected by filtration and subsequently dried in vacuo at 60 °C for 8 h.

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**Supporting Information Available:** Additional detailed procedures including the preparation/identification of catalyst precursors including the preparation of hydroxyl-terminated ring-opened poly(norbornene)s, additional polymerization results, and typical <sup>13</sup>C NMR spectra for the (co)polymers. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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