Investigation of insertion reaction of 10-undecen-1-ol protected with alkylaluminum in En(Ind)$_2$ZrCl$_2$/MAO catalyst system

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Abstract

In this study, insertion reaction of 10-undecen-1-ol (Un-OH) into the metallocene active center was investigated in the absence of olefin monomers. 10-Undecen-1-ol protected with trialkylaluminum (Un-O-AlR$_2$; R = Me, Et, *n*-Bu, *i*-Bu) was treated with an En(Ind)$_2$ZrCl$_2$/MAO catalyst system. The reactant, after quenched with HCl, was analyzed to identify the resulting alcohol compounds by gas chromatography with the comparison of authentic samples and NMR methods. As a result, undecanol (saturated Un-OH) and other alcohol compounds, in which alkyl groups derived from trialkylaluminum were incorporated into Un-OH, were found mainly in the resulting compounds, supporting that Un-O-AlR$_2$ was inserted into the metallocene active center in the absence of olefin monomers. The mechanism of the insertion reaction of Un-O-AlR$_2$ was also discussed.
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1. Introduction

The investigation of elementary reactions in olefin polymerization, such as monomer insertion, chain propagation and termination, has become one of the most important subjects for the synthesis of the precisely controlled polymers [1–4]. Since the discovery of the metallocene catalyst system, a great amount of research on olefin polymerization with metallocene has contributed significantly to the knowledge of these reactions [5–14].

In previous papers, it was shown that metallocene catalyst systems were active in the copolymerization of olefin monomers with polar monomers protected with alkylaluminum [15–24]. Furthermore, recent studies found that alkylaluminum compounds were used in regioselective copolymerization of olefins with polar monomers, such as allyl alcohol and allyl amine, via chain transfer reactions [17,18,20]. In those papers, it was suggested that the kinds of alkylaluminum, which were used for the protection of functional groups of polar monomers, influence the chain transfer reaction. However, those reactions have been studied only by analysis of the chain structures of the resulting copolymers. Furthermore, the mechanism of the insertion reaction of polar monomers into the metallocene active center has never been clarified. This has led to interest in investigating the reaction of an activated metallocene and polar monomers in the absence of olefin monomers.

The purpose of this study is to investigate the insertion reaction of 10-undecen-1-ol (Un-OH) protected with several kinds of trialkylaluminum (trimethylaluminum, triethylaluminum, tri-*n*-butylaluminum and triisobutylaluminum) into the metallocene active center of the En(Ind)$_2$ZrCl$_2$/MAO catalyst system in the absence of olefin monomers for the first time. Also, we would like to refer to the effects of the different kinds of alkylaluminum for the insertion reaction of Un-O-AlR$_2$.

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2. Experimental

2.1. Materials

rac-Ethylenebis(indenyl)zirconiumdichloride (En(Ind)$_2$ZrCl$_2$) was purchased from Sigma–Aldrich Co. and used as received. Methylaluminoxane (MAO) purchased from Albemarle Co. was dried under vacuum and diluted in toluene. 10-Undecen-1-ol (Un-OH) was purchased from Tokyo Kasei Kogyo Co. Ltd. and purified by distillation. Alkylaluminum compounds, which were trimethylaluminum (TMAL), triethylaluminum (TEAL), tri-*n*-butylaluminum (TNBAL) and triisobutylaluminum (TIBAL), were purchased from Tosoh Finechem Co. and used as received. Toluene purchased from Wako Pure Chemical Industries Ltd. was dried over sodium metal and distilled before use. Ethylene monomer (Mitsui Chemicals) was used without any further purification. Organometallic compounds were treated under the nitrogen atmosphere. 1-Undecanol, 1-dodecanol, 1-tridecanol, 1-pentadecanol and 1-octadecanol were purchased from Kanto Kagaku. 11-Dodecen-1-ol was purchased from Sigma–Aldrich Co. Those reagents were used as received for gas chromatographic (GC) analysis.

2.2. Polymerization procedure of ethylene with Un-O-AlR$_2$

Polymerization experiments were carried out in 500 mL glass flasks each equipped with a mechanical stirrer, a thermocouple and a monomer inlet tube. Toluene (450 mL) was introduced into the reactor. Un-OH (2.0 mmol) pretreated with aluminum compounds (TMAL, TEAL and TIBAL; 2.2 mmol) for 15 min was added to the reactor, and then, En(Ind)$_2$ZrCl$_2$ (0.10 mmol) activated by MAO (10 mmol [Al]) for 30 min was added to the reactor. The reaction mixture was stirred for 10 min in the reactor. Then, the polymerization was started by introduction of an ethylene monomer into the reactor at 25 °C. This temperature was kept during the polymerization under the constant feed, 0.3 N L/h, of monomer gas. After 60 min, 50 mL of methanol was added to the reactor in order to terminate the polymerization. The reaction mixture was poured into 1 L of methanol. Polymers were collected by filtration and washed with 500 mL of methanol, then dried under the reduced pressure at 80 °C for 10 h.

2.3. Reaction of En(Ind)$_2$ZrCl$_2$/MAO and Un-O-AlR$_2$

Un-OH (10 mmol) was treated with trialkylaluminum (20 mmol) in decane (20 ml) at room temperature for 15 min to prepare alkylaluminum-protected Un-OH (Un-O-AlR$_2$) before the reaction. In a 30 mL Schlenk flask was placed 41.9 mg of En(Ind)$_2$ZrCl$_2$ (0.10 mmol) and toluene solution of MAO (6.52 mL; 10 mmol as [Al]) to activate metallocene in toluene. Un-O-AlR$_2$ (1.0 mmol) and excess trialkylaluminum in decane was added to the flask at room temperature. Each sample solution was poured into 10 mL of HCl aq (1N) solution. Then, the organic phase was separated and subjected to GC analysis.

2.4. Analysis

2.4.1. Analysis of polymers

Molecular weights and molecular weight distributions were determined by gel-permeation chromatography (GPC; Waters, Alliance GPC 2000) using *o*-dichlorobenzene as solvent at 140 °C. ^{1}H NMR spectra were recorded on a JEOL JNM GX-400 series spectrometer operated at 400 MHz in the pulse Fourier transform mode. Instrumental conditions were as follows: pulse angle, 45°; pulse repetition, 5.0 s; spectral width, 18,050 Hz; temperature, 110 °C; data points, 20,000. Polymer solutions used for NMR were prepared by dissolving 50 mg of polymer in 0.5 mL of 1,2-dichlorobenzene-d$_4$ (ODCB) as solvent.

2.4.2. Analysis of reaction samples

GC chart was recorded on a Shimadzu GC-1700 chromatograph with a capillary column DB-17 (0.25 mm × 30 m, carrier gas; helium, flow rate; 76.7 mL/min, split ratio; 1:30), J&W Scientific Inc. Measurement conditions were as follows: initial temperature; 150 °C for 15 min, rate; 10 °C/min, final temperature; 250 °C for 20 min, injection column temperature; 250 °C. Acetone was used as solvent for measurement. The resulting organic phase was diluted by acetone, and that solution was used for GC analysis.

Products were identified by comparison with authentic samples. 1-Undecanol, Rt = 10.40 min. 10-Undecen-1-ol, Rt = 10.82 min. 1-Dodecanol, Rt = 15.56 min. 11-Dodecen-1-ol, Rt = 16.22 min. 1-Tridecanol, Rt = 19.08 min. 1-Pentadecanol, Rt = 23.66 min. 1-Octadecanol, Rt = 26.68 min.

Gas chromatography–mass spectrometric (GC–MS) analysis was conducted on a Hewlett-Packard HP6890/HP5973 with using a capillary column DB-17 (0.25 mm × 30 m, carrier gas; helium, flow rate; 1.0 mL/min, split ratio; 1:10), J&W Scientific Inc. Measurement conditions were as follows: initial temperature; 50 °C, rate; 10 °C/min, final temperature; 250 °C for 40 min, injection column temperature; 250 °C. The organic phase was diluted by acetone, and the solution was used for GC analysis.

^{13}C NMR spectra were recorded on a JEOL ECP-500 spectrometer operated at 125 MHz in the pulse Fourier transform mode. For ^{13}C NMR instrumental conditions were as follows: pulse angle, 45°; pulse repetition, 8.0 s; spectral width, 32,000 Hz; temperature, 27 °C. For distortionless enhancement by polarization transfer (DEPT), the DEPT135 spectrum was measured. Used sample solutions for NMR was prepared by dissolving 50 mg of sample in 0.5 mL of chloroform-d$_3$ (CDCl$_3$) as solvent.

Table 1
Results of copolymerization of ethylene with Un-OH capped with AlR_3[a]

Entry	AlR_3	Yield (g)	M_w[b] ($\times 10^{-3}$)	M_w/M_n[b]	Un-OH cont.[c] (mol%)
1	TMAL	0.321	18.5	2.22	0.79
2	TEAL	0.355	5.2	1.97	0.65
3	TIBAL	0.368	7.7	1.93	0.40

[a] Polymerization condition; $En(Ind)_2ZrCl_2$ (0.1 mmol), MAO (10 mmol), AlR_3 (0.22 mmol), Un-OH (0.2 mmol), ethylene (0.3N L/h), 25 °C, 0.1 MPa. in toluene (400 mL) for 1 h.

[b] GPC data, PE standard.
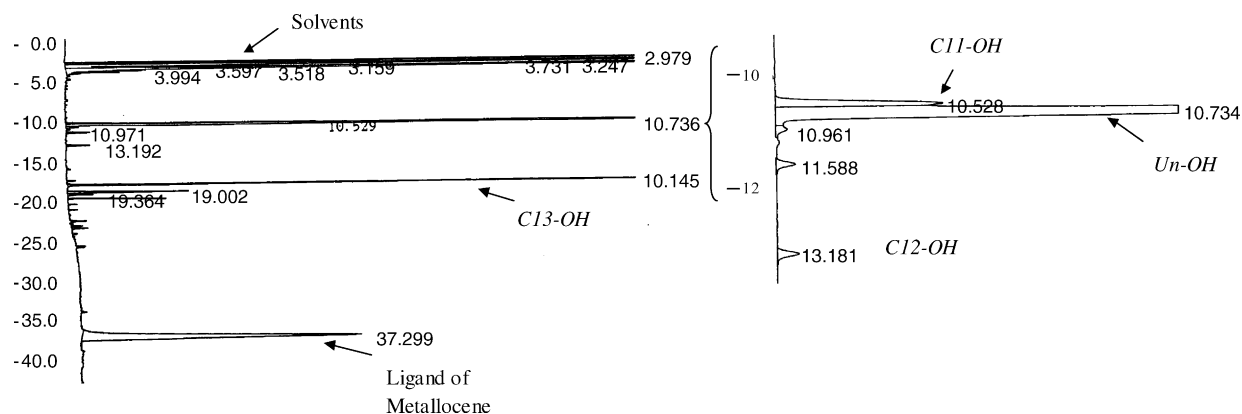
[c] Estimated by NMR analysis.

Fig. 1. GC chart of compounds resulting from TEAL (after 5 min).

3. Results and discussion

3.1. Confirmation of incorporation of Un-O-AlR_2 in polyethylene

In this study, $En(Ind)_2ZrCl_2$ activated with MAO was used as a metallocene catalyst. First, to confirm the insertion of $Un-O-AlR_2$ into the metallocene active center, copolymer-izations of Un-OH protected with trialkylaluminum (Un-$O-AlR_2$) were carried out in the presence of an ethylene monomer using an $En(Ind)_2ZrCl_2$/MAO catalyst system in toluene under atmospheric pressure. The resulting polymers were analyzed by NMR and GPC referring to previous papers [17,21]. Table 1 shows the results of copolymerization conducted using different trialkylaluminums. The incorporation of Un-O-AlR_2 into polyethylene was confirmed in each
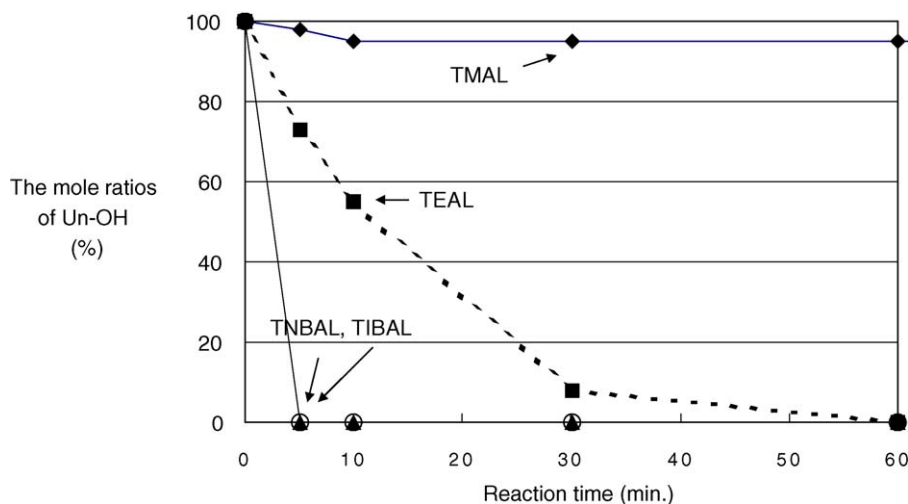

Fig. 2. Relations of mole ratios of Un-OH and reaction time.

Table 2
Mol% of identified alcohol compounds formed by the reaction of 10-undecen-1-ol protected with alkylaluminum in En(Ind)$_2$ZrCl$_2$/MAO catalyst system[a]

Entry	AlR$_3$	Reaction time (min)	Undecenol Un-OH (A)	Undecanol C$_{11}$-OH (B)	Dodecenol C$_{12}''$-OH (C)	Dodecanol C$_{12}$-OH (D)	Tridecanol C$_{13}$-OH (E)	Pentadecanol C$_{15}$-OH (F)
1	TMAL	5	97	1	Trace[b]	2	0	0
2		10	95	1	1	3	0	0
3		30	95	1	1	3	0	0
4		60	95	1	1	3	0	0
5		120	95	1	1	3	0	0
6	TEAL	5	73	7	Trace[b]	1	19	0
7		10	55	12	Trace[b]	1	32	0
8		30	8	20	Trace[b]	1	71	0
9		60	0	21	Trace[b]	1	78	0
10		120	0	21	Trace[b]	1	78	0
11	TNBAL	5	0	45	Trace[b]	1	0	54
12		10	0	45	Trace[b]	1	0	54
13		30	0	45	Trace[b]	1	0	54
14		60	0	45	Trace[b]	1	0	54
15		120	0	45	Trace[b]	1	0	54
16	TIBAL	5	1	91	Trace[b]	1	0	7
17		10	0	91	Trace[b]	1	0	8
18		30	0	91	Trace[b]	1	0	8
19		60	0	91	Trace[b]	1	0	8
20		120	0	91	Trace[b]	1	0	8

[a] Estimated by GC analysis.
[b] Less than 0.5 mol%.

copolymer, indicating that the Un-O-AlR$_2$ was inserted into the examined metallocene active center in the presence of olefin monomer.

3.2. Insertion reaction of Un-O-AlR$_2$ into the metallocene active center in the absence of olefin monomers

The investigation of the insertion reaction of Un-O-AlR$_2$ into the metallocene active center was conducted using En(Ind)$_2$ZrCl$_2$ activated with MAO in the absence of olefin monomers. Un-OH was selected as the monomer in this study because of the tendency preventing monomer propagation reaction compared with other higher α-olefins [21,25]. Un-OH (1.0 mmol) was pretreated with 2.0 mmol of trialkylaluminum compounds, which were trimethylaluminum (TMAL), triethylaluminum (TEAL), tri-n-butylaluminum (TNBAL) and triisobutylaluminum (TIBAL), to protect the hydroxyl group. En(Ind)$_2$ZrCl$_2$ was pretreated with MAO for 30 min to prepare the alkyl complex of metallocene. The prepared Un-O-AlR$_2$ and excess trialkylaluminum were treated with the En(Ind)$_2$ZrCl$_2$/MAO system in toluene (15.3 mmol[Zr]/L). The molar ratios of [OH]/[Zr] were 10/1 in this reaction. After quenching the reactant with hydrochloric acid, the organic phase was separated. The resulting alcohol compounds were identified by GC analysis through the comparison with authentic samples. GC–MS was also used to distinguish saturated and unsaturated ones. The GC chart in the case of TEAL is shown as a typical example in Fig. 1. The results are summarized in Table 2.

All alcohol compounds were saturated ones except Un-OH (starting material). Those were undecanol (C$_{11}$-OH; saturated Un-OH) and other alcohol compounds in which alkyl groups derived from trialkylaluminum were incorporated into Un-OH. Namely, for TMAL and TEAL, C$_{12}$-OH and C$_{13}$-OH were produced, respectively. For TNBAL and TIBAL, C$_{15}$-
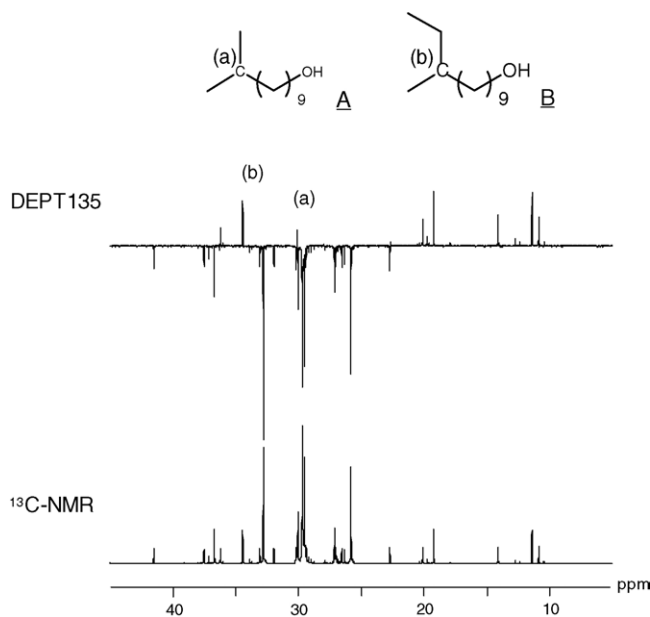

Fig. 3. Expanded ^{13}C and DEPT NMR spectra (recorded in CDCl$_3$ at 27 °C) between 5 and 45 ppm of entry 10.
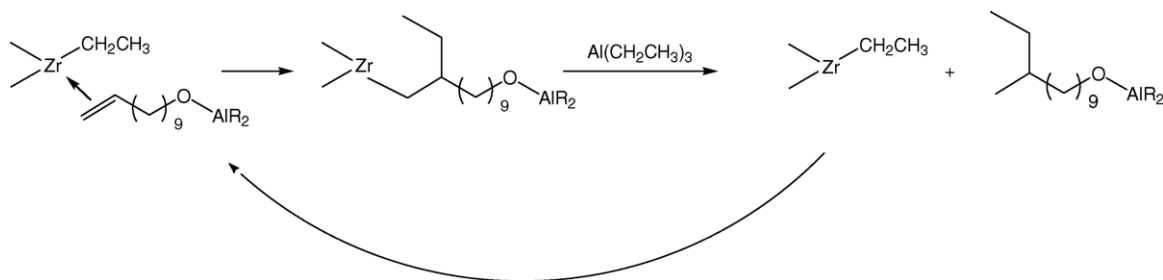
Fig. 4. Alkyl exchange reaction in the case of TEAL.

OH was produced. Neither dimer nor oligomers of Un-OH were detected.

Fig. 2 shows the relations of the molar ratios of Un-OH and reaction time. This figure indicates the consumption rates of Un-O-AlR$_2$ for each alkylaluminum, and the order was TNBAL, TIBAL $\rangle$ TEAL $\rangle\rangle$ TMAL. For TNBAL and TIBAL, almost all of Un-O-AlR$_2$ was consumed in 5 min. For TMAL, however, its consumption was limited. For TEAL, it was consumed gradually. Although 10 times as much amount of Un-OH (or resulting Un-O-AlR$_2$) as En(Ind)$_2$ZrCl$_2$ was used, all of Un-O-AlR$_2$ was completely consumed for TEAL, TNBAL and TIBAL, indicating that Un-O-AlR$_2$ was reacted catalytically.

In expanded ^{13}C and DEPT NMR spectra of entry 10 for TEAL (Fig. 3), the signals assigned as the methine carbon appeared around 30.0 and 34.5 ppm. Those peaks would be due to branched alkyl groups as like structures **A** and **B**. It would be considered that those branched alcohol com-

pounds were formed by the insertion of Un-O-AlR$_2$ followed by alkyl exchange reactions with trialkylaluminum as shown in Fig. 4.

Each alcohol compound would be formed via the insertion reaction of Un-O-AlR$_2$ into the metallocene active center as shown in Fig. 5. Compounds **D**, **E**, and **F**, which were the alkyl-added ones to Un-OH, would be formed via route 6 after an insertion of Un-O-AlR$_2$ into the Zr-R (a) active center formed by the reaction of En(Ind)$_2$ZrCl$_2$ with MAO or by alkyl exchange reaction. Undecanol (**B**) would be formed via route 7 after an insertion of Un-O-AlR$_2$ into Zr-H (c) active center formed by the elimination of alkene from Zr-R (route 2). The compound **C** produced from (b) (route 5) was negligible. Neither dimer nor oligomers of Un-OH were produced, indicating that further insertion of Un-O-AlR$_2$ would not occur at (b) and (d).

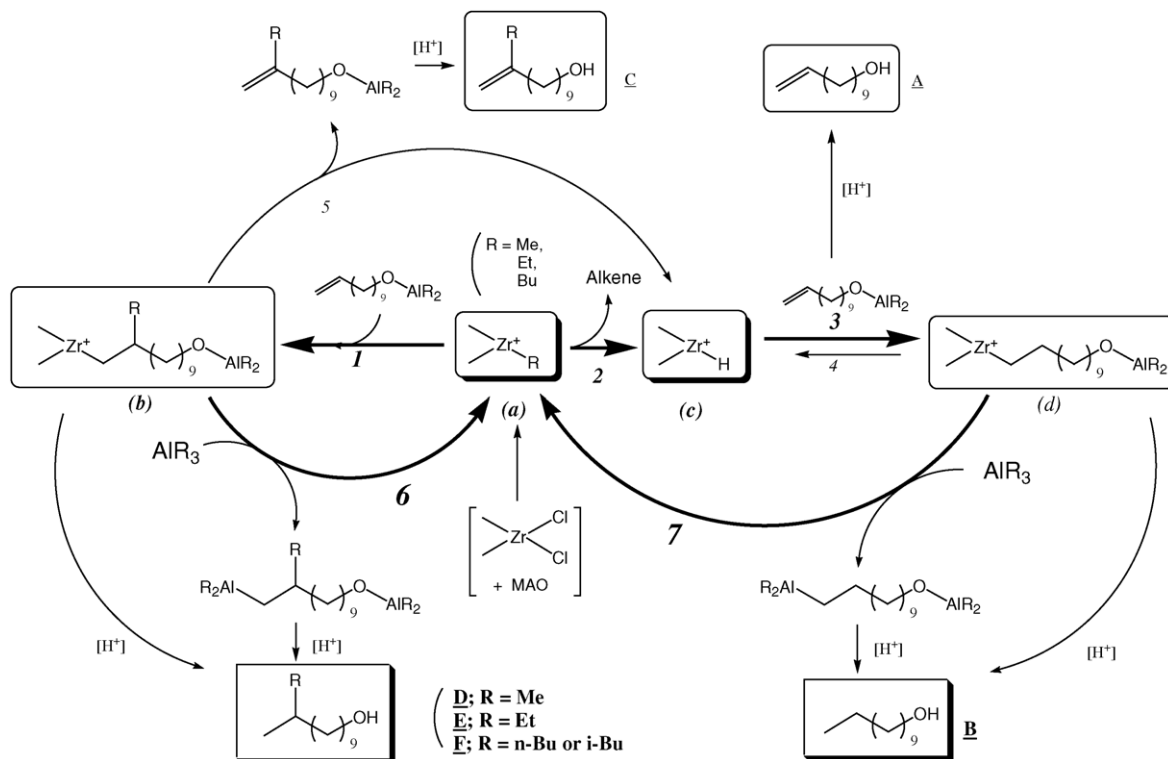In the case of TMAL, the consumption of Un-OH was low. The reason might be that the alkyl exchange reaction

Fig. 5. Possible mechanism of the formation of alcohol compounds.

after the insertion of Un-O-AlR$_2$ hardly occur or that the insertion of Un-O-AlR$_2$ is prevented due to coordination of the oxygen atom of the monomer to the metallocene active center because TMAL is not bulky enough. For TEAL, **E** was found mainly, indicating that the reaction progressed via route 1–6. In the case of TNBAL, **B** and **F** were found in the same amounts, which would indicate that reactions both via route 1–6 and via route 2–3–7 might occur competitively. For TIBAL, since **B** was formed mainly, the reaction via route 2–3–7 would progress dominantly. In all examples, **D** was hardly detected although MAO was used in large amounts, therefore, the alkyl exchange reaction (route 6) with MAO would hardly occur.

Thus, for TEAL, TNBAL and TIBAL, the insertion reaction of Un-O-AlR$_2$ would progress catalytically via route 1–6 or route 2–3–7. The priority of the routes might depend on the ease of the elimination of alkene from Zr-R (route 2), namely the ease of the proton transfer to active center; $-CH_2CH(CH_3)_2$ in TIBAL $> -CH_2CH_2CH_2CH_3$ in TNBAL $> -CH_2CH_3$ in TEAL.

4. Conclusion

Insertion reaction of 10-undecen-1-ol protected with TMAL, TEAL, TNBAL or TIBAL (Un-O-AlR$_2$; R = Me, Et, *n*-Bu, *i*-Bu) into the metallocene active center of En(Ind)$_2$ZrCl$_2$/MAO was confirmed in the absence of olefin monomers by GC and NMR analyses for the first time. In the case of TEAL, TNBAL and TIBAL, the identified compounds in which alkyl groups derived from trialkylaluminum were incorporated into Un-OH. It could be concluded that Un-O-AlR$_2$ was inserted into the metallocene active center catalytically with an alkyl exchange reaction in the absence of olefin monomers.

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