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Dual Catalyst System for Asymmetric Alternating Copolymerization of Carbon Dioxide and Cyclohexene Oxide with Chiral Aluminum Complexes: Lewis Base as Catalyst Activator and Lewis Acid as Monomer Activator

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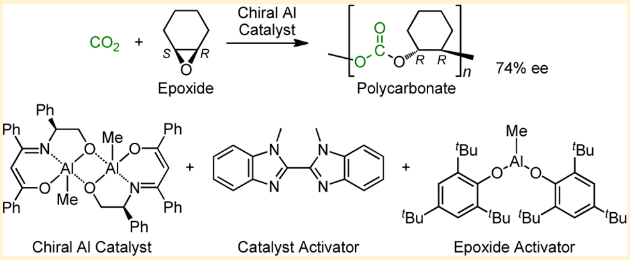
Supporting Information



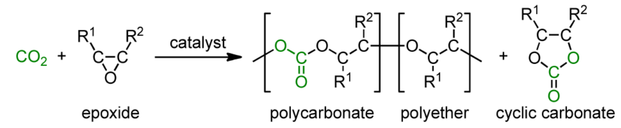
ABSTRACT: Optically active aluminum complexes such as Schiff base, binuclear β-ketoiminate, and bisprolinol complexes were found to promote asymmetric alternating copolymerizations of carbon dioxide and cyclohexene oxide. The aluminum Schiff base complexes−tetraethylammonium acetate afforded isotactic poly(cyclohexene carbonate)s with low enantioselectivities. Lewis bases having two coordinating sites were utilized to enhance activity and selectivity based on the binuclear structure of the aluminum β-ketoiminate clarified by X-ray crystallography. [**2g**AlMe]$_2$−bulky bisimidazole produced the alternating copolymer with high enantioselectivity (62% ee). The polymerization is considered to preferentially proceed at more crowded, enantioselective site owing to coordination of bulky Lewis bases to aluminums in less enantioselective sites. **3**$_2$AlMe−2-picoline also exhibited a high enantioselectivity (67% ee). Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) was applied to perform faster and more enantioselective copolymerizations at low temperature (82% ee). The asymmetric copolymerizations were found to be significantly dependent on size of epoxide, temperature, and kind/amount of activators.

INTRODUCTION

As carbon dioxide (CO_2) has been considered as one of principal substrates giving rise to global warming since the late 1980s, the reduction of CO_2 emission and its concentration in the atmosphere have been required. On the contrary, CO_2 is the most fundamental substance related in origin of life. Namely, CO_2 is an indispensable carbon source for living organisms in nature via the transformation of CO_2 to useful chemicals through photosynthesis.[1] In the field of industrial chemistry, CO_2 has attracted chemists as a C_1 feedstock alternative to fossil resources because CO_2 is abundant in nature, harmless, nonflammable, inexpensive, and easy to handle.[2] The transformation of CO_2 on a commercial scale has been limited to the productions of urea, methanol, salicylic acid and carbonates. Therefore, useful processes for converting CO_2 into chemicals are of great attractive and interest.[3]

Polymeric synthesis using CO_2 as a monomer is one of the most desirable processes to effectively incorporate CO_2 into polymeric main chains and to exhibit remarkable properties. The first example is alternating copolymerization of CO_2 and epoxide reported by Inoue, Koinuma, and Tsuruta in 1969 to give aliphatic polycarbonates (Scheme 1).[4,5] An equimolar mixture of Et_2Zn and H_2O was used as the catalyst. Since this discovery, many heterogeneous and homogeneous catalysts based on various metals were developed for alternating copolymerization of CO_2 and epoxides.[6−34] Chemists have focused their attentions on development of discrete complexes as catalysts for investigating reaction mechanism or controlling chemoselectivity, regioselectivity, stereoselectivity (tacticity), molecular weight, molecular weight distribution, and sequential arrangement in copolymer.

Scheme 1. Copolymerization of CO_2 and Epoxide



Because organoaluminum systems are known to be effective catalytic systems for homopolymerization of epoxide,[35] a Et_3Al-H_2O system (instead of the Et_2Zn-H_2O system) and a $Et_3Al-PPh_3$ system were utilized for copolymerization of CO_2 and epoxide in the early investigation by Koinuma in 1977 to afford a copolymer with low content of carbonate linkages.[18a] Since then, aluminum complexes have been applied for the copolymerization by research groups.[16−18] Our former

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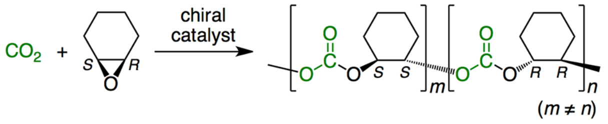
group reported the first successful alternating copolymerization of CO_2 and epoxide with aluminum porphyrin complex−quaternary phosphonium or ammonium salts.[16b] Our group[17a] and Darensbourg's group[17b] separately demonstrated aluminum salen-type Schiff-base complex−quaternary ammonium salt or Lewis base systems catalyzing alternating copolymerization of CO_2 and cyclohexene oxide (CHO). In our system, the copolymerization proceeded in a living fashion, and the selectivities for the products (polycarbonate, polyether, and cyclic carbonate) significantly depended on the combination of the catalyst and cocatalyst.[17a] For instance, an *achiral* aluminum salen-type Schiff base complex ((Salophen)AlMe (**4**AlMe); Salophen = *N*,*N*′-bis(salicylidene)-1,2-phenylenediamine, see Results and Discussion) in conjunction with tetraethylammonium acetate (Et_4NOAc) or pyridine predominantly generated the alternating copolymer (polycarbonate), whereas the same aluminum complex−Et_4NBr induced the production of cyclic carbonate in 30% against total products.[17a]

There are a few examples of CO_2 fixation in asymmetric synthesis though there are a lot of processes, in which CO_2 with substrates is transformed into chemicals, including alternating copolymerization of CO_2 and epoxide. The first is a nickel-catalyzed enantioselective, carboxylative cyclization of bis-1,3-dienes.[36] The second is a silver-catalyzed enantioselective CO_2 incorporation into symmetrical bispropargylic alcohols to generate monopropargylic cyclic carbonates.[37] The third is an enantioselective alternating copolymerization of CO_2 and *meso*-epoxides with enantiopure catalysts to afford polycarbonates.[14,25a,d,30f,j] These three reactions are categorized as asymmetric induction transformation. The fourth is an enantiomer-selective alternating copolymerization or cycloaddition of CO_2 and racemic epoxides with enantiopure catalysts to give polycarbonates[25b,c,30a−e,g−i,k] or cyclic carbonates.[38] This reaction is classified into enantiomer-selective transformation (kinetic resolution). Although these catalyst systems are needed to exhibit high activities and enantioselectivities, asymmetric CO_2 incorporation is still one of the challenging areas.

An asymmetric alternating copolymerization of CO_2 and CHO being one of asymmetric induction polymerizations (Scheme 2) was first accomplished using an optically active binuclear zinc aminoalkoxide complex by Nozaki (Figure 1A).[14a−c] The complex copolymerized CO_2 and CHO into isotactic poly(cyclohexene carbonate) (PCHC) which was quantitatively converted into *trans*-1,2-cyclohexanediol with 80% ee (enantiomeric excess) by alkali-catalyzed hydrolysis. Since then, Coates (Figure 1B),[14d] Ding (Figure 1C),[14e] and Lu (Figure 1D)[30f] reported a chiral zinc imine-oxazoline complex (up to 76% ee), a chiral zinc bisprolinol complex (18% ee), and a chiral cobalt salen-type Schiff base complex−bis(triphenylphosphine)iminium chloride system (up to 38% ee), respectively. Most recently, Lu and co-workers reported an unsymmetrical chiral salen cobalt complex−(*S*)-2-methyltetrahydrofran system for the production of PCHC composed of 1,2-cyclohexanediol units with 96%ee (*R*,*R*) (Figure 1E).[30j]

Scheme 2. Alternating Copolymerization of CO_2 and CHO with Asymmetric Induction



In this paper, we describe asymmetric alternating copolymerization of CO_2 and CHO with C_2-symmetric optically active aluminum complexes easily synthesized from an inexpensive aluminum reagent and chiral compounds. To our knowledge, chiral aluminum complexes for asymmetric copolymerization of CO_2 and *meso*-epoxides have never been reported. The complexes used in this study were the aluminum salen-type Schiff base complexes (**1a**AlMe−**1f**AlMe),[39,40] aluminum *β*-ketoiminate complexes ([**2a**AlMe]$_2$−[**2i**AlMe]$_2$),[41] and aluminum aminoalkoxide complex (**3**$_2$AlMe),[42] (Figure 2). The details will be described hereinafter.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Aluminum Complexes. Three series of optically active aluminum complexes, aluminum chiral Schiff base complexes (**1a**AlMe−**1f**AlMe),[39,40] aluminum chiral *β*-ketoiminato complexes ([**2a**AlMe]$_2$−[**2i**AlMe]$_2$),[41] and aluminum prolinol complex (**3**$_2$AlMe)[42] were synthesized according to Schemes 3, 4, and 5, respectively. (1*R*,2*R*)-1,2-Diphenyl-1,2-ethanediamine[43] and (1*R*,2*R*)-1,2-cyclohexanediamine[44] were obtained by optical resolutions of the *rac*-diamines with L-tartaric acid and the subsequent removal of L-tartaric acid with potassium carbonate. The enantiopure diamines were mixed with salicylaldehyde derivatives (salicylaldehyde, 3-phenylsalicylaldehyde,[45] and 3,5-di-*tert*-butylsalicylaldehyde) to afford six salen-type Schiff base compounds (**1a**H_2−**1f**H_2),[46−48] respectively (Scheme 3). The reactions of two *β*-diketones (2,4-pentanedione and 1,3-diphenyl-1,3-propanedione) with seven amino alcohols (glycinol, L-alaninol, L-valinol, L-leucinol, L-isoleucinol, L-phenylalaninol, and L-phenylglycinol)[49] generated the corresponding *β*-ketoimine compounds (**2a**H_2−**2i**H_2),[41,50] respectively (Scheme 4). After *N*-ethoxycarbonyl L-proline methyl ester

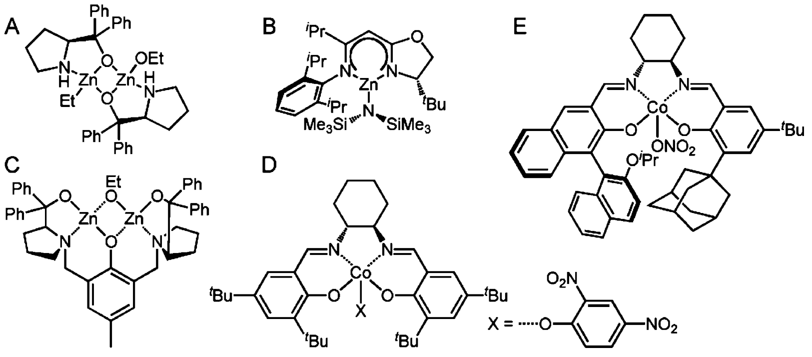


Figure 1. Metal complexes used as catalysts for alternating copolymerization of CO_2 and *meso*-epoxides with asymmetric induction.

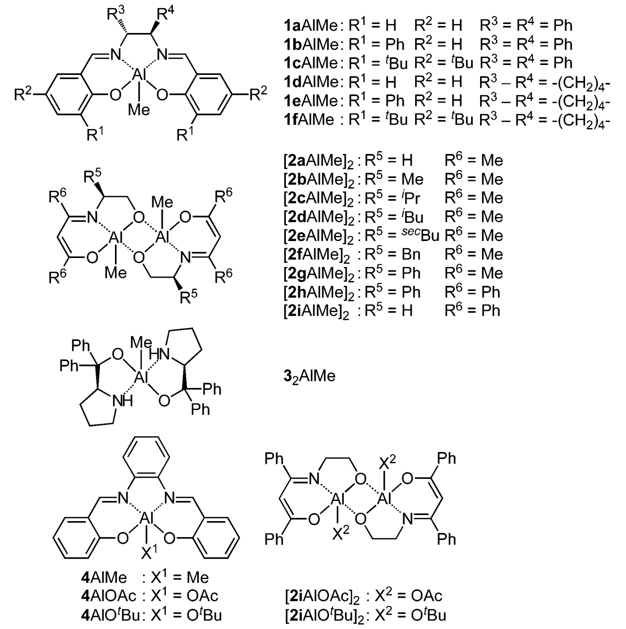


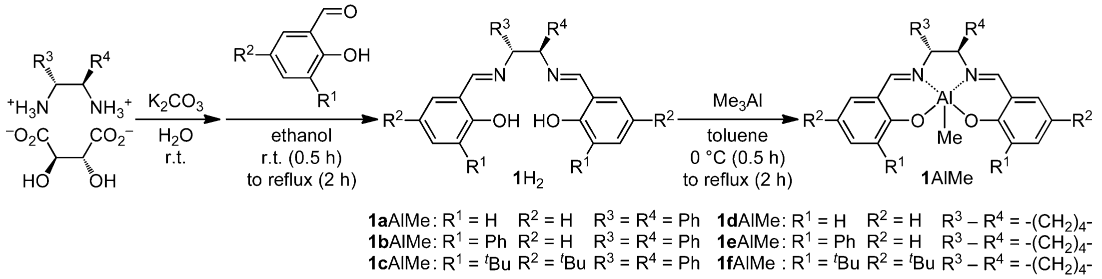
Figure 2. Structures of aluminum complexes: aluminum salen-type Schiff base complexes (**1a**AlMe−**1f**AlMe and **4**AlX^{1}s), bimetallic *β*-ketoiminate complexes ([**2a**AlMe]$_2$−[**2i**AlMe]$_2$ and [**2i**AlX^2]$_2$s, and aminoalkoxide complex (**3**$_2$AlMe)).

was synthesized via a spontaneous protection of the amino and carboxyl groups of L-proline, the ester was converted into (*S*)-diphenyl(pyrrolidine-2-yl)methanol (**3**H) by the coupling with phenylmagnesium bromide and the subsequent base-catalyzed hydrolysis (Scheme 5).[51] Each reaction of **1a**H$_2$−**1f**H$_2$, **2a**H$_2$−**2i**H$_2$, or **3**H, with trimethylaluminum (Me$_3$Al) was followed by ^{1}H NMR spectroscopy; the signals assignable to the phenol (at 13−15 ppm for **1a**H$_2$−**1f**H$_2$), enol (at 10−12 ppm for **2a**H$_2$−**2i**H$_2$), or alcohol (at 4.6 ppm for **3**H) disappeared, whereas novel signals assignable to methyl groups vertically connected to the aluminums (Al−Me) appeared at −2 to −1 ppm. These results indicated the formation of the aluminum complexes (**1a**AlMe−**1f**AlMe,[39,40] [**2a**AlMe]$_2$−[**2i**AlMe]$_2$,[41] and **3**$_2$AlMe[42]).

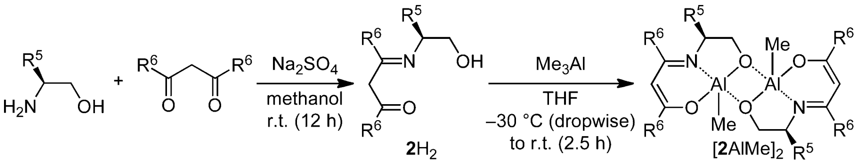
The structures of [**2g**AlMe]$_2$ and **3**$_2$AlMe were investigated by X-ray crystallography because the complexes were obtained as suitable single crystals for X-ray crystallographic analysis (the X-ray data of **3**$_2$AlMe is described before polymerization results). The single crystal X-ray analysis of [**2g**AlMe]$_2$ revealed the formation with the 2:2 stoichiometric ratio of aluminum ion with the tridentate dianion derived from the *β*-ketoimine **2g**H$_2$ (Figure 3, Table 1). The chelation of the [O,N,O] atoms in one dianion to one aluminum ion induced the formation of the 1:1 complex having the five- and six-membered chelate rings. Two 1:1 complexes were then dimerized via *μ*-O bridges between two aluminums of each other: the distances in the range of 1.82−1.88 Å (for Al−O), 1.99−2.00 Å (for Al−N), and 1.94−1.95 Å (for Al−C) and the angles in the range of 105−116° (for C−Al−O or C−Al−N), 75−91° (for O−Al−O or O−Al−N, *cis*), and 138−144° (for O−Al−O or O−Al−N, *trans*).[52] This result exhibited that the aluminum complex adopted a five-coordinate, distorted square-pyramidal geometry. Both methyl groups were connected to the aluminums in a *syn* arrangement. The "*syn*-arrangement" is denoted as an arrangement of the substituents and functional groups in the same direction against the plane formed by two aluminums and two tridentate units. In addition, two phenyl groups in [**2g**AlMe]$_2$ were also aligned in the *syn* arrangement the directions whose were the same as those of the methyl groups on the aluminums. These observations indicated the bimetallic aluminum complex adopted a C_2-symmetric structure similar to a truncated trapezoid (Figure 3B). The R^5 substituents in [**2b**AlMe]$_2$−[**2h**AlMe]$_2$ (e.g., R^5 = Ph for [**2g**AlMe]$_2$) are denoted as "wall" to regulate the direction of CHO approaching the aluminums. The spatial region surrounded by the R^5 substituents is abbreviated as "inside walls" and the opposite region of "inside walls" against the coordination plane formed by two aluminums and two [O,N,O] chelating units is named as "outside walls". When a nucleophilic reagent (e.g., alkoxide) attacks a C_s-symmetric *meso*-epoxide coordinated to the aluminum in the region "inside walls", the approaching directions of the regent to two tertiary carbons of the epoxide are differentiated by the phenyl groups attached on the asymmetric tetrahedral carbons. The asymmetric ring-opening of the *meso*-epoxide in the enantioselective site ("inside walls") may generate the optically active oxycarbonyloxy-*trans*-cyclohexane-1,2-diyl repeating units.

A coordination geometry of [**2g**AlMe]$_2$ in solution was investigated by ^{27}Al NMR analysis in noncoordinating solvent (Figure S2A in the Supporting Information).[53] Only one signal assignable to the aluminums of [**2g**AlMe]$_2$ was observed in the range of 40−100 ppm at the center of 70 ppm. This suggests that the four-coordinated complex in the monomeric state was dimerized to adopt the more stable, five-coordinated complex in C_6D_6 (Scheme S1, Figure S3 in the Supporting Information).[54] This result was in good agreement with that from X-ray crystallographic analysis. Such a formation of bimetallic five-coordinated aluminum complexes via dimerization was confirmed by Doherty and co-workers:[41] a dimeric structure of a complex [**2a**AlCl]$_2$ in solution was confirmed by ^{27}Al NMR analysis. Therefore, the structures of other [**2**AlMe]$_2$ complexes are considered to be similar to that of the complex [**2g**AlMe]$_2$ though the complexes ([**2**AlMe]$_2$) except for

Scheme 3. Synthesis of Aluminum Chiral Schiff Base Complexes (1aAlMe−1fAlMe)

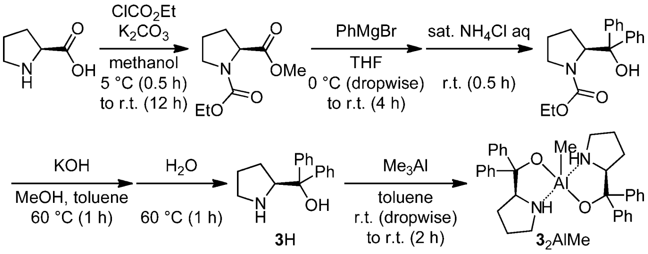


Scheme 4. Synthesis of Bimetallic Aluminum β-Ketoiminate Complexes ([2aAlMe]$_2$−[2iAlMe]$_2$)



[**2a**AlMe]$_2$: R^5 = H R^6 = Me [**2d**AlMe]$_2$: R^5 = ^{i}Bu R^6 = Me [**2g**AlMe]$_2$: R^5 = Ph R^6 = Me
[**2b**AlMe]$_2$: R^5 = Me R^6 = Me [**2e**AlMe]$_2$: R^5 = ^{sec}Bu R^6 = Me [**2h**AlMe]$_2$: R^5 = Ph R^6 = Ph
[**2c**AlMe]$_2$: R^5 = ^{i}Pr R^6 = Me [**2f**AlMe]$_2$: R^5 = Bn R^6 = Me [**2i**AlMe]$_2$: R^5 = H R^6 = Ph

Scheme 5. Synthesis of Aluminum Chiral Aminoalkoxide Complex (3$_2$AlMe)



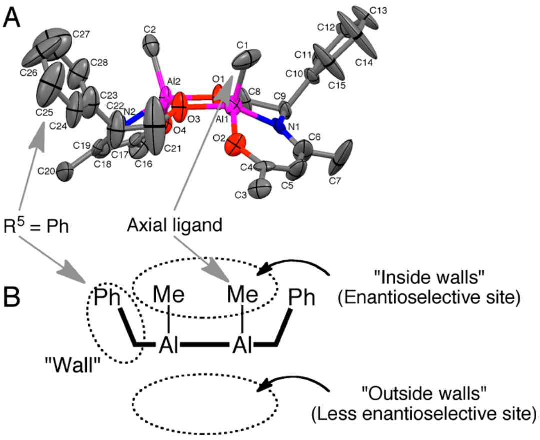


Figure 3. (A) Ball-and-stick drawings of [**2g**AlMe]$_2$ with thermal ellipsoids at 50% probability (carbon, gray; nitrogen, blue; oxygen, red; aluminum, pink). Hydrogen atoms are omitted for clarity. (B) Model of bimetallic aluminum complex [**2g**AlMe]$_2$.

[**2g**AlMe]$_2$ were not crystallized as suitable single crystals for X-ray crystallographic analysis.

In the crystal, the aluminum bisprolinol complex **3**$_2$AlMe formed a five-coordinate, C_2-symmetric structure similar to the reported literature (Figures 4 and S1 and Table S2 in the Supporting Information).[42] The complex **3**$_2$AlMe had two regions: one region is "inside walls" enclosed by two phenyl and two pyrroridyl groups as "wall" and the other is "outside walls" surrounded by two remaining phenyl groups alone. Since phenyl groups and pyrroridyl groups in the complex **3**$_2$AlMe are denoted as "wall" to regulate the direction of CHO approaching the aluminum, the spatial region encircled by "walls" (two phenyl and two pyrroridyl groups) are abbreviated as "inside walls" and the opposite region of "inside walls" against the coordination plane formed by one aluminum and two [N,O] chelating units are named as "outside walls".

Asymmetric Alternating Copolymerization of CO$_2$ and CHO with Aluminum Salen-Type Schiff Base Complexes−Et$_4$NOAc. A series of optically active salen-type Schiff base complex[25,30,55] (**1a**AlMe−**1f**AlMe) having (1*R*,2*R*)-1,2-diphenylethane-1,2-diyl or (1*R*,2*R*)-cyclohexane-1,2-diyl group−Et$_4$NOAc catalytic systems were first employed for alternating copolymerization of CO$_2$ and CHO with asymmetric induction (Table 2). The copolymerization was carried out with the complex **1a**AlMe in the presence of Et$_4$NOAc (1 equiv to **1a**AlMe) at 80 °C under 50 atm of CO$_2$ at an initial mole ratio ([CHO]$_0$/[**1**AlMe]$_0$) of 250 in toluene. The **1a**AlMe−Et$_4$NOAc system gave the alternating copolymer in 73% yield for 24 h (the content of carbonate linkages = 98%, the number-averaged molecular weight (M_n) = 6800, the molecular weight distribution (M_w/M_n) = 1.22; Table 2, run 1). The obtained copolymer was converted into *trans*-1,2-cyclohexanediol in 85% yield by alkali-catalyzed hydrolysis. The enantiomeric excess (ee) of the diol was estimated to be 8% (for (*R*,*R*)-isomer) by optical rotation measurement ($[\alpha]_D$ −3.1° (*c* 1.4, H$_2$O)).[56] This value shows the ratio of (*R*,*R*) and (*S*,*S*) units ((*R*,*R*) units: (*S*,*S*) units = 54: 46) in the main chain of the copolymer.

To investigate effect of substituents connected to the phenolate rings on enantioselectivity of the catalysts, aluminum complexes (**1b**AlMe and **1c**AlMe) having one phenyl group at

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for Complex [2gAlMe]$_2$

Length/Å			
Al(1)−C(1)	1.942(9)	Al(2)−C(2)	1.954(9)
Al(1)−O(1)	1.855(4)	Al(2)−O(3)	1.878(5)
Al(1)−N(1)	1.985(7)	Al(2)−N(2)	2.003(7)
Al(1)−O(2)	1.831(5)	Al(2)−O(4)	1.822(5)
Al(1)−O(3)	1.878(5)	Al(2)−O(1)	1.868(5)
Angle/deg			
O(1)−Al(1)−C(1)	113.3(4)	O(3)−Al(2)−C(2)	115.8(3)
C(1)−Al(1)−N(1)	109.6(4)	C(2)−Al(2)−N(2)	111.0(3)
O(2)−Al(1)−C(1)	106.9(4)	O(4)−Al(2)−N(2)	105.6(3)
O(3)−Al(1)−C(1)	104.8(4)	O(1)−Al(2)−C(2)	104.1(3)
O(1)−Al(1)−N(1)	81.0(2)	O(3)−Al(2)−N(2)	79.8(3)
O(2)−Al(1)−N(1)	90.1(2)	O(4)−Al(2)−N(2)	89.8(3)
O(2)−Al(1)−O(3)	90.5(3)	O(4)−Al(2)−O(1)	91.4(2)
O(1)−Al(1)−O(3)	75.3(2)	O(1)−Al(2)−O(3)	75.0(2)
O(2)−Al(1)−O(1)	139.6(3)	O(4)−Al(2)−O(3)	138.3(3)
O(3)−Al(1)−N(1)	143.8(3)	O(1)−Al(2)−N(2)	143.2(3)
Al(1)−O(1)−Al(2)	105.5(2)	Al(1)−O(3)−Al(2)	104.2(3)

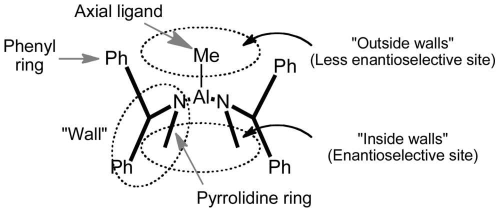


Figure 4. Model of aluminum complex **3**$_2$AlMe.

Table 2. Asymmetric Alternating Copolymerization of CO_2 and CHO with Aluminum Salen-Type Schiff Base Complexes−Et_4NOAc.[a]

				copolymerization					hydrolysis	
run	complex	temp/°C	time/h	yield[b]/%	TOF[c]/h^{-1}	C.L.[d]/%	M_n[e]	M_w/M_n[e]	yield of diol/%	%ee[f] (*R*,*R*)
1	**1a**AlMe	80	24	73	6.2	98	6800	1.22	85	8
2	**1b**AlMe	80	24	24	2.1	94	1900	1.60	91	12
3	**1c**AlMe	80	24	29	2.5	97	4400	1.14	88	14
4	**1d**AlMe	80	24	26	2.2	94	5300	1.23	90	5
5	**1e**AlMe	80	24	20	1.7	96	3100	1.29	78	10
6	**1f**AlMe	80	24	31	2.6	94	2800	1.40	95	9
7	**1a**AlMe	80	6	21	8.8	94	2000	1.23	93	9
8	**1a**AlMe	60	24	32	2.7	99	6700	1.26	89	13
9	**1a**AlMe	40	24	58	6.0	70	5800	1.98	79	20
10	**1c**AlMe	60	6	8	3.3	97	2200	1.66	88	23

[a] In 1 mL of toluene, 80 °C, 50 atm of CO_2, complex **1**AlMe (0.1 mmol), Et_4NOAc (0.1 mmol), and CHO (25 mmol). [b] On the basis of isolated copolymer. [c] Turnover frequency = (mol of reacted CHO)·(mol of cat.)$^{-1}$·h^{-1}. [d] Content of carbonate linkages (C.L.) = (carbonate unit)·((carbonate unit) + (ether unit))$^{-1}$, estimated by ^{1}H NMR ($CDCl_3$). [e] Estimated by GPC calibrated with polystyrene standard in THF at 40 °C. [f] Estimated from optical rotation of *trans*-1,2-cyclohexanediol in H_2O.

the 3-position (for **1b**AlMe) and two *tert*-butyl groups at the 3- and 5-positions (for **1c**AlMe) of the phenolate ring were employed for the copolymerization (Table 2, runs 2 and 3). The introduction of the bulky groups to the phenolate was expected to improve enantioselectivity. The complexes **1b**AlMe and **1c**AlMe produced alternating copolymers with more than 94% content of carbonate linkages (M_n = 1900, M_w/M_n = 1.60 (for **1b**AlMe) and M_n = 4400, M_w/M_n = 1.14 (for **1c**AlMe)) and slightly higher enantioselectivities (12% ee (for **1b**AlMe) and 14% ee (for **1c**AlMe)) than that (8% ee) by **1a**AlMe. In contrast, the turnover frequencies (TOFs) were significantly reduced (2.1 h^{-1} (for **1b**AlMe) and 2.5 h^{-1} (for **1c**AlMe)), meaning that the rates of the copolymerizations with **1b**AlMe and **1c**AlMe were slower than that by **1a**AlMe. These results indicate that the introduction of the bulky substituents around the active aluminums in the catalysts led to not only the expected improvement of the enantioselectivity (H < Ph ≈ ^{t}Bu) but also the undesirable lowering of the copolymerization rate (H > Ph ≈ ^{t}Bu).

The effect of diimine backbones ((1*R*,2*R*)-1,2-diphenylethane-1,2-diyldiimino (**1a**AlMe−**1c**AlMe) and (1*R*,2*R*)-cyclohexane-1,2-diyldiimino (**1d**AlMe−**1f**AlMe) groups) on enantioselectivity was next investigated using the complexes **1d**AlMe−**1f**AlMe (Table 2, runs 4−6). The complexes **1d**AlMe−**1f**AlMe showed lower enantioselectivities (5−10% ee) than those of the complexes **1a**AlMe−**1c**AlMe (8−14% ee), while other polymerization data (TOF, content of carbonate linkages, M_n, and M_w/M_n) with **1d**AlMe−**1f**AlMe were similar to those with **1a**AlMe−**1c**AlMe. These results revealed that the *trans*-1,2-diphenylethane-1,2-diyldiimino backbone was more effective for asymmetric alternating copolymerization of CO_2 and CHO with chiral aluminum complex than the *trans*-cyclohexane-1,2-diyldiimino one.

Other conditions (time and temperature) affecting enantioselectivity, content of carbonate linkages, and so on were refined for the copolymerization of CO_2 and CHO with the complexes **1a**AlMe−**1c**AlMe. At 6 h for the copolymerization with **1a**AlMe−Et_4NOAc, the enantioselectivity and content of carbonate linkages were 9% ee and 94%, respectively (Table 2, run 7), indicating that enantioselectivity and content of carbonate linkages are independent of polymerization time. In general, asymmetric reactions with high enantioselectivities have been achieved at low temperature because enantioselectivities in asymmetric reactions are significantly dependent on temperature.[57] Thus, the copolymerizations with **1a**AlMe−Et_4NOAc were performed at 60 and 40 °C (Table 2, runs 8 and 9). The enantioselectivities expectedly increased with lowering of the temperature; 13% ee (for 60 °C) and 20% ee (for 40 °C). However, the copolymer synthesized at 40 °C had a low content of carbonate linkages ([carbonate linkages]:[ether linkages] = 70: 30). The highest enantioselectivity of 23% was achieved among the asymmetric copolymerizations with the catalysts **1a**AlMe−**1f**AlMe as the complex **1c**AlMe was used at 60 °C instead of **1a**AlMe (Table 2, run 10).

In the cases except for runs 1 and 9 in Table 2, the polymer yields were relatively low (8−32%). This is because the polymerizations were quenched at the predetermined time regardless of the conversion of CHO on the basis of the results in Table 2, runs 1 and 7. In addition, the observed M_n values were smaller than the calculated ones (e.g., Table 2, run 1; the observed M_n = 6800, the calculated M_n = 13000). This disagreement is due to the contamination of water into the reaction system.[58]

Asymmetric Alternating Copolymerization of CO_2 and CHO with Aluminum β-Ketoiminate Complexes−Et_4NOAc. The chiral aluminum Schiff-base complexes (**1a**AlMe−**1f**AlMe) for the asymmetric alternating copolymerization of CO_2 and CHO were considered to be less effective as described above. Thus, aluminum complexes having chiral skeletons, which have never been used for the asymmetric alternating copolymerization of CO_2 and epoxide, are needed to afford a more highly enantioenriched copolymer. Metal complexes exhibiting catalytic activity for ring-opening polymerization of lactide are known to be effective for alternating copolymerization of CO_2 and epoxide.[59] In fact, aluminum salen-type ligand complexes including **1f**AlMe have been known as active catalysts for polymerizations of lactide and for copolymerization of CO_2 and epoxide.[60] Doherty and co-workers reported that aluminum β-ketoiminate complexes including [**2a**AlCl]$_2$ functioned as catalysts for ring-opening polymerization of *rac*-lactide by an addition of PO or CHO.[41] In addition, achiral and racemic cobalt β-ketoiminate complexes were recently reported as effective catalysts for alternating copolymerization of CO_2 and epoxide (in particular, ethylene oxide) by Yamada.[32] However, aluminum β-ketoiminate complexes have been never employed as catalyst for

Table 3. Asymmetric Alternating Copolymerization of CO_2 and CHO with Aluminum β-Ketoiminate Complexes−Et_4NOAc.[a]

		copolymerization					hydrolysis	
run	complex	yield[b]/%	TOF[c]/h^{-1}	C.L.[d]/%	M_n[e]	M_w/M_n[e]	yield of diol/%	%ee[f] (*R*,*R*)
1	[**2a**AlMe]$_2$	36	15.0	97	4200	1.21	89	–
2	[**2b**AlMe]$_2$	26	10.8	96	2700	1.29	88	10
3	[**2c**AlMe]$_2$	16	6.7	96	2500	1.22	94	15
4	[**2d**AlMe]$_2$	19	7.9	98	4900	1.24	90	14
5	[**2e**AlMe]$_2$	20	8.3	96	3100	1.14	79	18
6	[**2f**AlMe]$_2$	28	11.7	97	3600	1.27	87	20
7	[**2g**AlMe]$_2$	18	7.5	99	2000	1.18	95	26
8	[**2h**AlMe]$_2$	32	13.3	98	8800	1.38	93	24

[a] In 1 mL of toluene, 60 °C, 6 h, 50 atm of CO_2, complex [**2**AlMe]$_2$ (0.1 mmol), Et_4NOAc (0.2 mmol), and CHO (25 mmol). [b] On the basis of isolated copolymer. [c] Turnover frequency = (mol of reacted CHO)·(mol of cat.)$^{-1}$·h^{-1}. [d] Content of carbonate linkages (C.L.) = (carbonate unit)·((carbonate unit) + (ether unit))$^{-1}$, estimated by ^{1}H NMR ($CDCl_3$). [e] Estimated by GPC calibrated with polystyrene standard in THF at 40 °C. [f] Estimated from optical rotation of *trans*-1,2-cyclohexanediol in H_2O.

Table 4. Asymmetric Alternating Copolymerization of CO_2 and CHO with Aluminum β-Ketoiminate Complexes−Lewis Bases.[a]

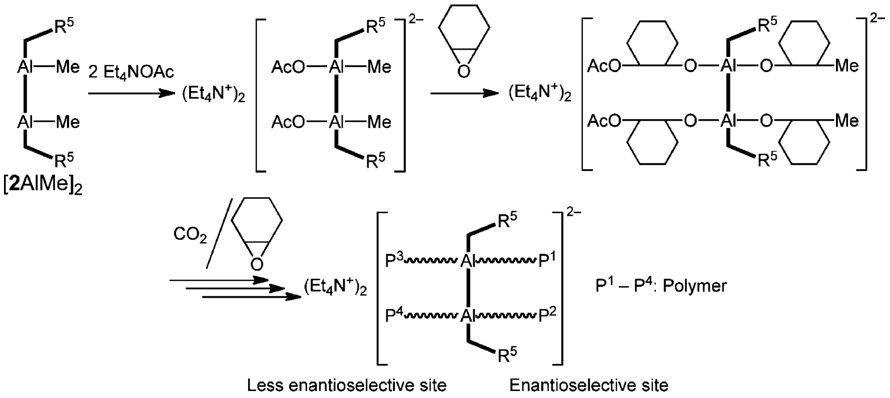
			copolymerization					hydrolysis	
run	complex	Lewis base	yield[b]/%	TOF[c]/h^{-1}	C.L.[d]/%	M_n[e]	M_w/M_n[e]	yield of diol/%	%ee[f] (*R*,*R*)
1	[**2g**AlMe]$_2$	pyridine	12	5.0	99	2900	1.18	89	22
2	[**2g**AlMe]$_2$	*N*-MeIm[g]	10	4.2	90	1900	2.27	87	19
3	[**2g**AlMe]$_2$	DMAP	12	5.0	97	1600	1.26	94	39
4	[**2h**AlMe]$_2$	DMAP	16	6.7	99	4300	1.18	91	49

[a] In 1 mL of toluene, 60 °C, 6 h, 50 atm of CO_2, complex [**2g**AlMe]$_2$ and [**2h**AlMe]$_2$ (0.1 mmol), Lewis base (0.2 mmol), and CHO (25 mmol); *N*-MeIm = *N*-methylimidazole, DMAP = *N*,*N*-dimethyl-4-aminopyridine. [b] On the basis of isolated copolymer. [c] Turnover frequency = (mol of reacted CHO)·(mol of cat.)$^{-1}$·h^{-1}. [d] Content of carbonate linkages (C.L.) = (carbonate unit)·((carbonate unit) + (ether unit))$^{-1}$, estimated by ^{1}H NMR ($CDCl_3$). [e] Estimated by GPC calibrated with polystyrene standard in THF at 40 °C. [f] Estimated from optical rotation of *trans*-1,2-cyclohexanediol in H_2O. [g] 0.5 mmol.

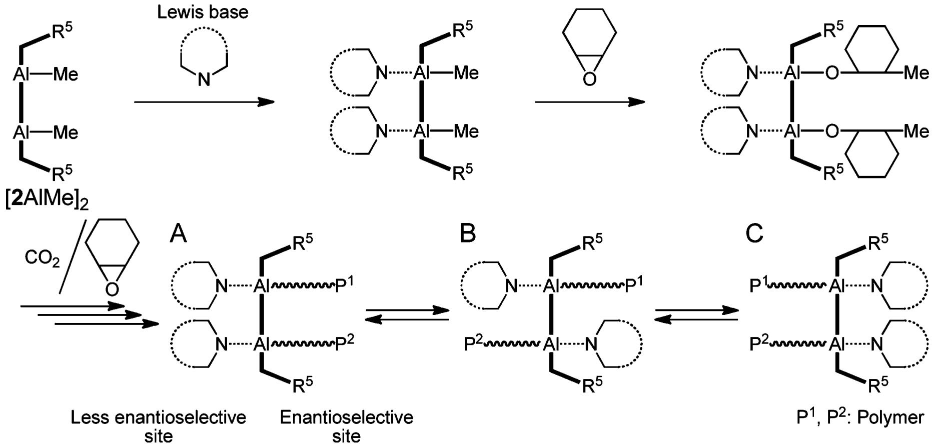
(asymmetric) copolymerization of CO_2 and epoxide Thus, an achiral aluminum β-ketoiminate complex [**2a**AlMe]$_2$ was first attempted for alternating copolymerization of CO_2 and CHO. The copolymerization of CO_2 and CHO with [**2a**AlMe]$_2$ in the presence of Et_4NOAc (1 equiv to Al) was carried out at 60 °C for 6 h under 50 atm of CO_2 at an initial mole ratio ([CHO]$_0$/[[**2a**AlMe]$_2$]$_0$) of 250 in toluene. The [**2a**AlMe]$_2$−tetraethylammonium acetate (Et_4NOAc) system gave the alternating copolymer with the narrow molecular weight distribution in 36% yield (content of carbonate linkages = 97%, M_n = 4200, M_w/M_n = 1.21; Table 3, run 1). The TOF (15.0 h^{-1}) was larger than that using **1a**AlMe−**1f**AlMe (1.7−8.8), meaning that the polymerization with [**2a**AlMe]$_2$ were faster than those with **1a**AlMe−**1f**AlMe.

On the basis of the structure of the achiral complex [**2a**AlMe]$_2$ being active for the copolymerization, optically active β-ketoiminate complexes ([**2b**AlMe]$_2$−[**2h**AlMe]$_2$) were designed. Chiral β-ketoiminate complexes consist of aluminum compounds (trialkylaluminums or aluminum halides) and chiral β-ketoimines readily prepared from β-diketones and chiral amino alcohols. The amino alcohols were obtained by reduction of amino acids. Since chiral amino acids are easily available as enantiomerically pure forms from naturally abundant sources or by using asymmetric synthetic methods,[61] chiral β-ketoimines and their metal complexes are attractive as ligands and catalysts. The copolymerizations with the aluminum chiral β-ketoiminate complexes having different R^5 substituents (R^5 = Me ([**2b**AlMe]$_2$), ^{i}Pr ([**2c**AlMe]$_2$), ^{i}Bu ([**2d**AlMe]$_2$), ^{sec}Bu ([**2e**AlMe]$_2$), Bn ([**2f**AlMe]$_2$), Ph ([**2g**AlMe]$_2$)) were performed under the same condition as that with [**2a**AlMe]$_2$ (Table 3, runs 2−7). The alternating copolymers (content of carbonate linkages = 96−99%) were generated by using all complexes, and the ees of the diols obtained by alkali-hydrolysis of the polymers increased with increasing the sizes of the R^5 substituents (ee = 10%, 15%, 14%, 18%, 20%, 26%; size = Me < ^{i}Pr < ^{i}Bu < ^{sec}Bu < Bn < Ph). The TOFs of the copolymerizations with [**2b**AlMe]$_2$−[**2g**AlMe]$_2$ (6.7−11.7 h^{-1}) were smaller than that with [**2a**AlMe]$_2$ (15.0 h^{-1}), meaning the slower polymerizations with [**2b**AlMe]$_2$−[**2g**AlMe]$_2$ than that with [**2a**AlMe]$_2$. This is considered to be due to the steric repulsion between the R^5 groups and CHO in spite of no observation of relationship between the TOFs and the sizes of the R^5s. The M_ns were in the range of 2000−4900, which were independent of the structures of the R^5s. The observed M_ns were significantly lower than the calculated values, resulting in the contamination of water into the polymerization systems similar to those with the aluminum salen-type Schiff base complexes (**1a**AlMe−**1f**AlMe). Subsequently, a complex [**2h**AlMe]$_2$ (R^6 = Ph) having a more bulky β-diketone skeleton than that of [**2g**AlMe]$_2$ (R^6 = Me) was applied for the copolymerization of CO_2 and CHO to afford a more highly enantioenriched copolymer (Table 3, run 8). Contrary to expectations, the catalyst showed an enantioselective ability similar to [**2g**AlMe]$_2$ (26% (for [**2g**AlMe]$_2$) and 24% (for [**2h**AlMe]$_2$) ees). On the other hand, the TOF of [**2h**AlMe]$_2$ (13.3 h^{-1}) was high as compared with that of [**2g**AlMe]$_2$ (7.5 h^{-1}), meaning the higher catalytic activity of [**2h**AlMe]$_2$ than that of [**2g**AlMe]$_2$. In addition, the M_n of the copolymer obtained with [**2h**AlMe]$_2$ was higher than that with [**2g**AlMe]$_2$. These results indicate that the introduction of the bulky substituents to the ketoimine skeleton (R^6−C(OH)=CH−C(=N)−R^6) is valid to improve the catalytic activity but not the enantioselectivity.

Scheme 6. Active Propagating Species Generated in Copolymerization of CO_2 and CHO with Aluminum β-Ketoiminate Complexes and Et_4NOAc



Scheme 7. Active Propagating Species Generated in Copolymerization of CO_2 and CHO with Aluminum β-Ketoiminate Complexes and Lewis Bases (Monoamines)



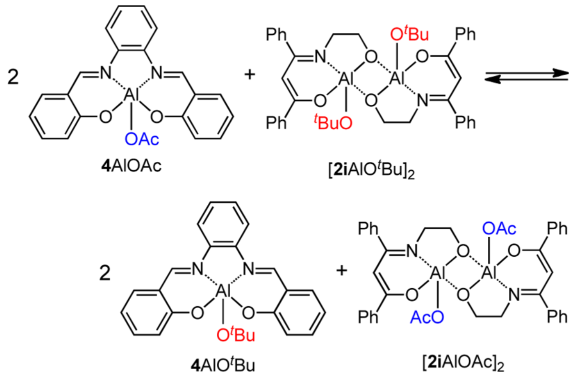
Asymmetric Alternating Copolymerization of CO_2 and CHO with Aluminum β-Ketoiminate Complexes–Lewis Bases. To find out condition suitable for asymmetric alternating copolymerization of CO_2 and CHO with optically active aluminum β-ketoiminate complexes, *N*-containing Lewis bases such as pyridine, *N*-methylimidazole (*N*-MeIm), and *N*,*N*-dimethyl-4-aminopyridine (DMAP) instead of Et_4NOAc were employed as cocatalysts in the presence of the complexes [**2g**AlMe]$_2$ and [**2h**AlMe]$_2$ (Table 4). The utilizations of pyridine and *N*-MeIm led to the decreases of the catalytic activities (TOF: 5.0 h^{-1} (for pyridine), 4.2 h^{-1} (for *N*-MeIm) vs 7.5 h^{-1} (for OAc)), the enantioselectivities (ee: 22% (for pyridine), 19% (for *N*-MeIm) vs 26% (for OAc)), and the content of carbonate linkages (C.L.: 90% (for *N*-MeIm)) (Table 4, runs 1, 2). In contrast, the alternating copolymer generated with DMAP was comprised of the repeating units with 39% ee (C.L., 97%; M_n, 1600; M_w/M_n, 1.26) (Table 4, run 3) being the largest value among those obtained with Lewis bases. Hence, DMAP was used to the copolymerization with the complex [**2h**AlMe]$_2$ to afford the alternating copolymer with high enantioselectivity of 49% ee (C.L., 99%; M_n, 4300; M_w/M_n, 1.18) (Table 4, run 4). These results suggest that the pK_a of Lewis base and acetate affects the enantioselective ring-opening of CHO (pK_a: 4.76 for OAc; 5.19 for pyridine; 7.06 for *N*-MeIm; 9.70 for DMAP).[62]

Mechanism of Asymmetric Alternating Copolymerization of CO_2 and CHO with Aluminum β-Ketoiminate Complexes. We previously described the following two points regarding alternating copolymerizations of CO_2 and CHO with an *achiral* aluminum Schiff base complex (**4**AlMe)–Et_4NOAc system. One is that the anion species assignable to the ammonium salt is coordinated to the aluminum to adopt a six-coordinated ate complex having two axial ligands (the methyl anion of the original five-coordinated aluminum complex and the counteranion derived from the ammonium salt). The other is that both two anionic species on the aluminum independently served as the initiators to allow the propagation of two polymeric chains on both axial sites.[17a] On the basis of our knowledge, the initiation and propagation mechanism of the polymerization with the chiral bimetallic aluminum β-ketoiminate complexes–Et_4NOAc was proposed as shown in Scheme 6. The coordination of two acetate ions to two aluminums in the single complex brings about the formation of two six-coordinated ate structures having four anionic ligands. Four anionic species on the aluminums severally function as the initiators on the axial sites to permit the propagation of four polymeric chains: two chains are placed in the same direction as the R^5 substituents and two remaining chains are placed in the opposite direction as the R^5s. The enantioselective ring-opening of CHO most likely proceeds in the region "inside walls" as the R^5s regulate the orientation of CHO approaching the aluminum. On the other hand, the less enantioselective ring-opening of CHO probably advances in the opposite direction as the R^5s.

Furthermore, a mechanism of the polymerization with the chiral bimetallic aluminum β-ketoiminate complexes–monoamines was described in Scheme 7. Both two methyl anionic species connected to the aluminums independently act as the initiators to allow the propagation of two polymeric chains. The behavior of aluminum–alkoxide and –carboxylate bonds in the growing step of the polymer chains is assumed to cause the formation of three active species of the aluminum β-ketoiminate complex ([**2g**AlMe]$_2$)–Lewis base system as follow (Scheme 7): (A) form is a active species having two alkoxide groups of the chain's terminal in the region "inside walls", (B) form is that having one alkoxide group in "inside walls" and the other in "inside walls", and (C) form is that having two alkoxide groups of the chain's terminal in "outside walls".

As shown in Scheme 7, the exchange between alkoxide and carboxylate groups on the aluminums is presumed to proceed during the copolymerization of CO_2 and epoxide. This is because the exchange of alkoxide and carboxylate groups as the growing species on the aluminum porphyrin was previously observed in the polymerizations of epoxide or β-lactone.[63] To clarify the behavior of the aluminum–alkoxide and –carboxylate bonds in the aluminum complexes, an equimolar mixture of two aluminum complexes with different axial groups from each other, **4**AlOAc and [**2i**AlO^{t}Bu]$_2$, was investigated by ^{1}H NMR analysis (Scheme 8, Figures 5 and S4 in the Supporting Information). The ^{1}H NMR spectrum of the complex [**2i**AlO^{t}Bu]$_2$ showed a single signal at 1.25 ppm due to the *tert*-butoxide group in [**2i**AlO^{t}Bu]$_2$. At 10 min after mixing of two aluminum complexes, a new signal appeared at 1.26 ppm assignable to the methyl protons of the *tert*-butoxide group in **4**AlO^{t}Bu. The intensity of the signal at 1.26 ppm gradually increased with time and reached a constant value (approximately 25% mole fraction based on the signal area) at 60 min (Figure 6). This result is in agreement with the exchange between the polymeric species in more enantioselective and less enantioselective sites.

Scheme 8. Exchange of Axially-Coordinated Alkoxide (O^{t}Bu) and Carboxylate Groups (OAc) Between Two Different Aluminum Complexes (4AlOAc and [2iAlO^{t}Bu]$_2$)



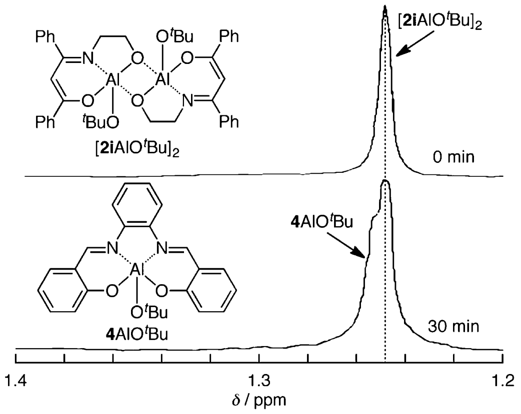


Figure 5. ^{1}H NMR spectra of the equimolar mixture of **4**AlOAc and [**2i**AlO^{t}Bu]$_2$ at 30 °C in $CDCl_3$ at 0 (upper) and 30 (lower) min after mixing.

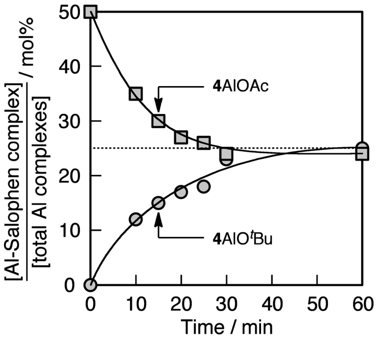


Figure 6. Relationship between the mole fractions of **4**AlOAc (squares) and **4**AlO^{t}Bu (circles) and the reaction time in the equimolar mixture of **4**AlOAc and [**2i**AlO^{t}Bu]$_2$ in $CDCl_3$ at 30 °C.

Asymmetric Alternating Copolymerization of CO_2 and CHO with Aluminum β-Ketoiminate Complexes–Bidentate Lewis Bases. The aluminum β-ketoiminate complexes ([**2a**AlMe]$_2$–[**2i**AlMe]$_2$) are presumed to have kept the dimeric structures even during the copolymerization. If diamines having two nitrogens in parallel in one molecule are applied instead of monoamines as Lewis bases, the diamines are expected to be coordinated to two aluminums in the complexes with the molar ratio of 1:1 (Scheme 9).[64] The (B) form of the aluminum β-ketoiminate/diamine complex is the forbidden structure. In addition, the steric hindrance between the diamines and the complexes most likely induces the formation of the (A) form rather than the (C) one to promote the copolymerization at the more enantioselective site. An enantioselective reaction by using coordination of a Lewis base to restrict reaction sites was reported by Inoue et al.[65] On the basis of our strategy, a bisimidazole (two *N*-MeIms are linked at the 2-positions of each other, bis-*N*-MeIm[66]) was employed for the copolymerization with the complex [**2g**AlMe]$_2$ or [**2h**AlMe]$_2$ (Table 5, runs 1 and 2).[67] The complex [**2g**AlMe]$_2$ or [**2h**AlMe]$_2$–bis-*N*-MeIm systems produced alternating copolymers (96–97% for contents of carbonate linkages) with the molar ratios of 78.5: 21.5 (57% ee (*R*,*R*)) and 77: 23 (54% ee (*R*,*R*)), respectively. When more bulky bisbenzimidazole (two *N*-methylbenzimidazoles are coupled similarly, bis-*N*-MeBzIm[66]) was used with the complex [**2g**AlMe]$_2$ and [**2h**AlMe]$_2$ (Scheme 10), the obtained copolymers had higher contents of carbonate linkages (98% for [**2g**AlMe]$_2$ and 96% for [**2h**AlMe]$_2$) and higher enantioselectivities (62% ee for [**2g**AlMe]$_2$ and 60% ee for [**2h**AlMe]$_2$) than those with bis-*N*-MeIm (Table 5, runs 3 and 4). In particular, the M_n of the copolymer generated with the complex [**2g**AlMe]$_2$–bis-*N*-MeBzIm was close to the calculated one.

Scheme 9. Active Propagating Species Generated in Copolymerization of CO_2 and CHO with [2aAlMe]$_2$−[2iAlMe]$_2$ and Bis-*N*-MeIm (Diamine)

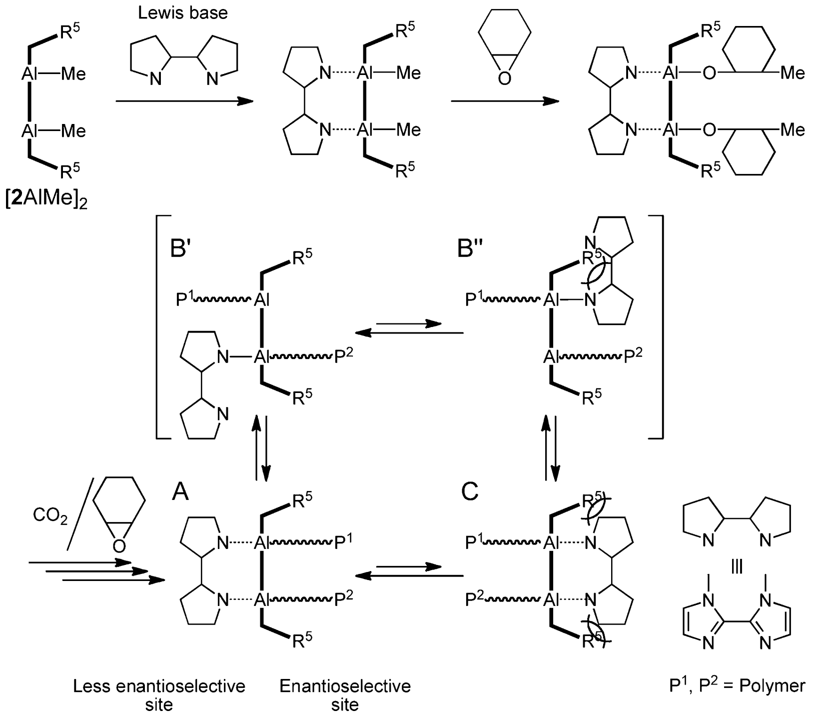


Table 5. Asymmetric Alternating Copolymerization of CO_2 and CHO with Aluminum β-Ketoiminate Complexes−Bisimidazoles.[a]

			copolymerization					hydrolysis	
run	complex	Lewis base	yield[b]/%	TOF[c]/h^{-1}	C.L.[d]/%	M_n[e]	M_w/M_n[e]	yield of diol/%	%ee[f] (*R*,*R*)
1	[**2g**AlMe]$_2$	bis-*N*-MeIm	10	4.2	97	3200	1.29	90	57
2	[**2h**AlMe]$_2$	bis-*N*-MeIm	20	8.3	96	5800	1.17	97	54
3	[**2g**AlMe]$_2$	bis-*N*-MeBzIm	12	5.0	98	3900	1.41	87	62
4	[**2h**AlMe]$_2$	bis-*N*-MeBzIm	19	7.9	96	5700	1.24	91	60

[a] In 1 mL of toluene, 60 °C, 6 h, 50 atm of CO_2, complex [**2g**AlMe]$_2$ and [**2h**AlMe]$_2$ (0.1 mmol), Lewis base (0.1 mmol), and CHO (25 mmol); bis-*N*-MeIm = *N*-methyl-2-(*N*′-methylimidazol-2-yl)imidazole, bis-*N*-MeBzIm = *N*-methyl-2-(*N*′-methylbenzimidazol-2-yl)benzimidazole. [b] On the basis of isolated copolymer. [c] Turnover frequency = (mol of reacted CHO)·(mol of cat.)$^{-1}$·h^{-1}. [d] Content of carbonate linkages (C.L.) = (carbonate unit)·((carbonate unit) + (ether unit))$^{-1}$, estimated by ^{1}H NMR ($CDCl_3$). [e] Estimated by GPC calibrated with polystyrene standard in THF at 40 °C. [f] Estimated from optical rotation of *trans*-1,2-cyclohexanediol in H_2O.

To investigate whether the Lewis bases are coordinated to the bimetallic aluminum β-ketoiminate complexes in solution or not, the mixture of [**2g**AlMe]$_2$ and bis-*N*-MeIm (1 equiv to [**2g**AlMe]$_2$) in C_6D_6 was measured by ^{27}Al NMR analysis (Figure S2B in the Supporting Information). Two signals assignable to the aluminums of [**2g**AlMe]$_2$ were observed at 68 and 12 ppm in the range of 40−100 ppm. One signal is due to the five-coordinated aluminum species without bis-*N*-MeIm, whereas the other is assignable to the six-coordinated aluminum species generated via the coordination of bis-*N*-MeIm. In addition, the observation of two signals means the slow ligand exchange on the NMR time scale. Moreover, the area of the former is larger than that of the latter regardless of the equimolar mixture of [**2g**AlMe]$_2$ and bis-*N*-MeIm in C_6D_6. This suggests a part of the binuclear aluminum complexes forms the active species with the Lewis base under the condition.

Asymmetric Alternating Copolymerization with Aluminum β-Ketoiminate Complex−Lewis Bases−Lewis Acid. To enhance enantioselectivities for copolymerizations of CO_2 and CHO with optically active aluminum complexes, lowering temperature is one of effective methods. In addition, utilization of accelerator allows improvement of yield within predetermined time because reaction generally tends to become slow at lower temperature. In our previous research,[68] a ring-opening polymerization of propylene oxide with an aluminum porphinate complex was substantially accelerated 460-folds by addition of 0.5 equiv of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD[69]). This is owing to the coordinative activation of epoxide by MAD. According to this knowledge, MAD was applied for alternating copolymerization of CO_2 and CHO with [**2g**AlMe]$_2$− or [**2h**AlMe]$_2$−bis-*N*-MeBzIm systems. First, the increase of the feed ratio of MAD to the catalyst [**2g**AlMe]$_2$ (0 to 1 equiv) was related to the following changes: not only the increase of the TOF (4.2 to >10.4 h^{-1}; 1.1 to 2.7-folds to that with [**2g**AlMe]$_2$−bis-*N*-MeBzIm: 3.9 h^{-1}) but also the decreases of the ee (61 to 39% ee; 63% ee for [**2g**AlMe]$_2$−bis-*N*-MeBzIm) and the content of carbonate linkages (93 to 35%; > 98% for [**2g**AlMe]$_2$−bis-*N*-MeBzIm) and the increase of the M_w/M_n (1.51 to 1.93; 1.31 for [**2g**AlMe]$_2$−bis-*N*-

Scheme 10. Active Propagating Species Generated in Copolymerization of CO_2 and CHO with $[2gAlMe]_2$– or $[2hAlMe]_2$–bis-*N*-MeBzIm (Bulky Diamine)

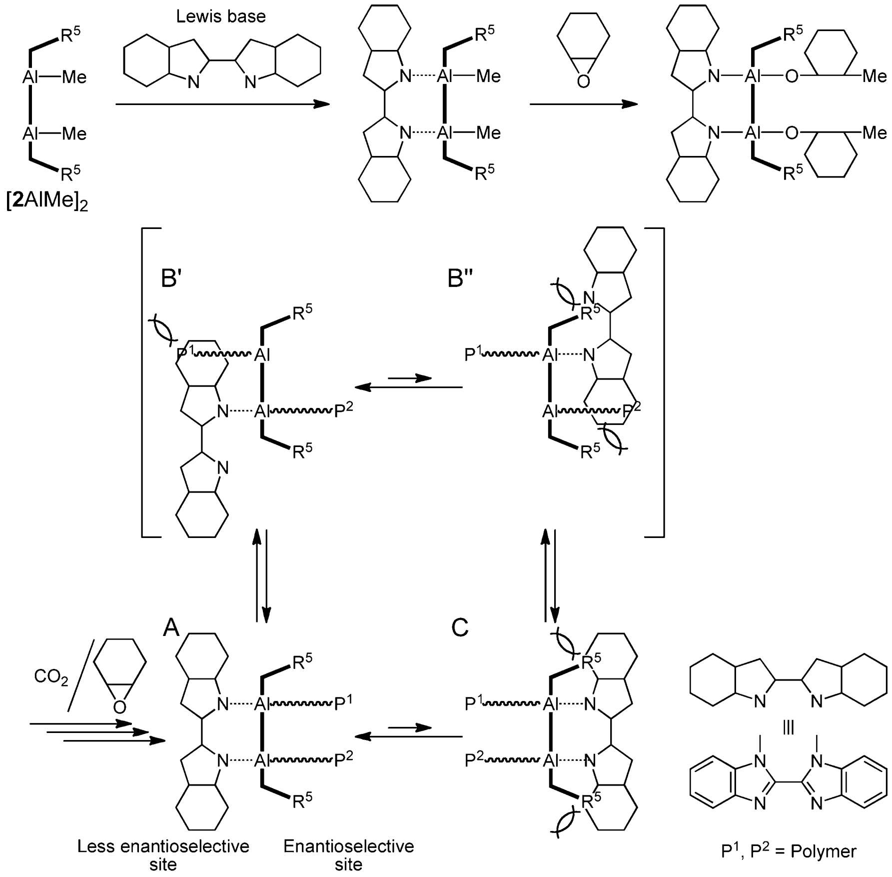


Table 6. Asymmetric Alternating Copolymerization of CO_2 and CHO with $[2gAlMe]_2$–bis-*N*-MeBzIm–MAD.[a]

				copolymerization					hydrolysis	
run	$[2gAlMe]_2$/equiv	bis-*N*-Me BzIm/equiv	MAD/equiv	yield[b]/%	TOF[c]/h^{-1}	C.L.[d]/%	M_n[e]	M_w/M_n[e]	yield of diol/%	%ee[f] (*R*,*R*)
1	1	0.5	0	37	3.9	98	7900	1.31	92	63
2	1	0.5	0.1	40	4.2	93	6900	1.51	94	61
3	1	0.5	0.3	61	6.4	90	11 300	1.42	86	59
4	1	0.5	0.5	76	7.9	70	13 800	1.91	89	51
5	1	0.5	1	>99	>10.4	35	12 600	1.93	96	39
6	1	1	0.3	52	5.4	95	9100	1.32	93	62
7	1	1	1	90	9.4	63	17 500	2.01	91	47

[a] In 1 mL of toluene, 60 °C, 24 h, 50 atm of CO_2, complex $[2gAlMe]_2$ (0.1 mmol), and CHO (25 mmol); bis-*N*-MeBzIm = *N*-methyl-2-(*N*′-methylbenzimidazol-2-yl)benzimidazole, MAD = methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide). [b] On the basis of isolated copolymer. [c] Turnover frequency = (mol of reacted CHO)·(mol of cat.)$^{-1}$·h^{-1}. [d] Content of carbonate linkages (C.L.) = (carbonate unit)·((carbonate unit) + (ether unit))$^{-1}$, estimated by ^{1}H NMR ($CDCl_3$). [e] Estimated by GPC calibrated with polystyrene standard in THF at 40 °C. [f] Estimated from optical rotation of *trans*-1,2-cyclohexanediol in H_2O.

MeBzIm) (Table 6, runs 1–5). Furthermore, various ratios of $[2gAlMe]_2$–bis-*N*-MeBzIm–MAD were attempted to establish the catalytic system which produces the copolymer in a high yield with a high content of carbonate linkages and an enantioselectivity. The optimized ratio was $[2gAlMe]_2$/[bis-*N*-MeBzIm]/[MAD] = 1/1/0.3. The system produced the alternating copolymer in 52% yield (TOF: 5.4 h^{-1}; the slight acceleration) with the content of carbonate linkages (95%) and the enantioselectivity (62% ee) (Table 6, run 6) similar to those of the polymer obtained by an MAD-free catalytic system (98% and 62% ee, respectively) in Table 5, run 3. The effect of MAD on the copolymerization is described afterward (in section of copolymerization with 3_2AlMe).

The copolymerizations with the $[2gAlMe]_2$–bis-*N*-MeBzIm–MAD (1: 1: 0.3) system were performed at lower temperature (60 °C to 0–40 °C) (Table 7, runs 1–4). The decrease of the temperature expectedly caused the increase of the ee value of the *trans*-(*R*,*R*)-1,2-diol. In contrast, the content of carbonate linkages unexpectedly decreased with lowering of the temperature. The decrease of the content of carbonate linkages may be owing to decrease of reactivity of CO_2 at low temperature as shown in Table 2, run 9 or increase of reactivity of epoxide upon the addition of MAD as observed in Table 7. For example, at 0 °C the catalytic system produced the copolymer with a low content of carbonate linkages (42%) (M_n = 2300, M_w/M_n = 1.93) in 19% yield. The copolymer was

Table 7. Asymmetric Alternating Copolymerization of CO_2 and CHO with $[\mathbf{2g}AlMe]_2$ or $[\mathbf{2h}AlMe]_2$−bis-*N*-MeBzIm−MAD at Various Temperatures.[a]

			copolymerization					hydrolysis	
run	complex	temp. /°C	yield[b]/%	TOF[c]/h^{-1}	C.L.[d]/%	M_n[e]	M_w/M_n[e]	yield of diol/%	%ee[f] (*R*,*R*)
1	$[\mathbf{2g}AlMe]_2$	60	52	5.4	95	9100	1.32	93	62
2	$[\mathbf{2g}AlMe]_2$	40	41	4.3	88	6500	1.51	89	69
3	$[\mathbf{2g}AlMe]_2$	25	37	3.9	59	6000	1.54	84	74
4	$[\mathbf{2g}AlMe]_2$	0	19	2.0	42	2300	1.93	80	80
5	$[\mathbf{2h}AlMe]_2$	60	62	6.5	94	10 200	1.47	89	64
6	$[\mathbf{2h}AlMe]_2$	40	49	5.1	86	7300	1.29	90	74
7	$[\mathbf{2h}AlMe]_2$	25	40	4.2	63	6400	1.60	85	75
8	$[\mathbf{2h}AlMe]_2$	0	21	2.2	47	2500	1.55	86	80

[a] In 1 mL of toluene, 24 h, 50 atm of CO_2, complex $[\mathbf{2g}AlMe]_2$ or $[\mathbf{2h}AlMe]_2$ (0.1 mmol), bis-*N*-MeBzIm (0.1 mmol), MAD (0.03 mmol), and CHO (25 mmol); bis-*N*-MeBzIm = *N*-methyl-2-(*N*′-methylbenzimidazol-2-yl)benzimidazole, MAD = methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide). [b] On the basis of isolated copolymer. [c] Turnover frequency = (mol of reacted CHO)·(mol of cat.)$^{-1}$·h^{-1}. [d] Content of carbonate linkages (C.L.) = (carbonate unit)·((carbonate unit) + (ether unit))$^{-1}$, estimated by ^1H NMR ($CDCl_3$). [e] Estimated by GPC calibrated with polystyrene standard in THF at 40 °C. [f] Estimated from optical rotation of *trans*-1,2-cyclohexanediol in H_2O.

Table 8. Asymmetric Alternating Copolymerization of CO_2 and CHO with $\mathbf{3}_2AlMe$−Lewis Bases.[a]

		copolymerization					hydrolysis	
run	Lewis base	yield[b]/%	TOF[c]/h^{-1}	C.L.[d]/%	M_n[e]	M_w/M_n[e]	yield of diol/%	%ee[f] (*R*,*R*)
1	DMAP	10	0.35	>99	28 800	1.92	82	59
2	2-picoline	8	0.28	96	25 600	2.10	97	67

[a] In 1 mL of toluene, 60 °C, 72 h, 50 atm of CO_2, complex $\mathbf{3}_2AlMe$ (0.1 mmol), Lewis base (0.1 mmol), and CHO (25 mmol); DMAP = *N*,*N*-dimethyl-4-aminopyridine. [b] On the basis of isolated copolymer. [c] Turnover frequency = (mol of reacted CHO)·(mol of cat.)$^{-1}$·h^{-1}. [d] Content of carbonate linkages (C.L.) = (carbonate unit)·((carbonate unit) + (ether unit))$^{-1}$, estimated by ^1H NMR ($CDCl_3$). [e] Estimated by GPC calibrated with polystyrene standard in THF at 40 °C. [f] Estimated from optical rotation of *trans*-1,2-cyclohexanediol in H_2O.

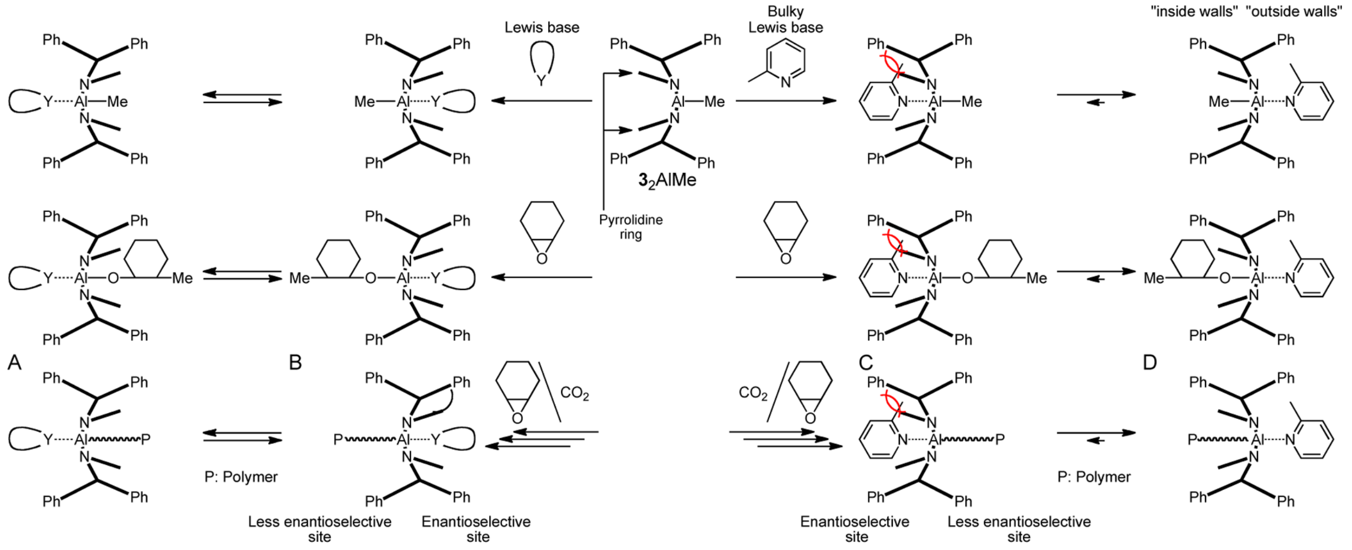
transformed to the *trans*-1,2-diol with 80% ee[70] and the oligo- or polyether chains with an optical activity ($[\alpha]_D$ −16.7° (*c* 0.6, benzene)) by alkaline hydrolysis.[71]

Furthermore, the replacement of the aluminum complex in the catalytic system ($[\mathbf{2g}AlMe]_2$ to $[\mathbf{2h}AlMe]_2$) slightly affects the copolymerization behavior (Table 7, runs 5−8). At 0 °C the catalytic system generated the copolymer with a low content of carbonate linkages (47%) (M_n = 2500, M_w/M_n = 1.55) in 21% yield. The copolymer comprised of the *trans*-1,2-diol with 80% ee[70] and the oligo- or polyether chains with an optical activity ($[\alpha]_D$ −17.6° (*c* 0.6, benzene)).[71] These results indicate the polymerization is significantly dependent on temperature regardless of the kinds of the catalytic systems.

Asymmetric Alternating Copolymerization of CO_2 and CHO with Aluminum Aminoalkoxide Complex−Lewis Bases. Bulky prolinol derivatives synthesized from L-proline with ease have been used as organocatalysts[72] and ligands[73] of metal complexes for asymmetric synthesis. A bulky prolinol **3**H[51] is known to be one of powerful organocatalysts and ligands. The **3**H was applied as [N,O]-ligands and chelating units of catalysts for asymmetric copolymerization of CO_2 and epoxide by Nozaki[14a−c] and Ding[14e,15] separately. The former catalyst was an intermolecular bimetallic zinc prolinol complex and the latter was an intramolecular bimetallic zinc or magnesium multidentate bisprolinol complex. These complexes are binuclear zinc complexes composed of two zincs and two prolinol units. Although a mixture of **3**H and organoaluminum instead of Et_2Zn was expected to form a binuclear aluminum complex via *μ*-C or -O linkage similar to the complexes[14a−c,e,15] and $[\mathbf{2}AlMe]_2$, a mononuclear aluminum bisprolinol complex ($\mathbf{3}_2AlMe$) was obtained. The complex $\mathbf{3}_2AlMe$ has two bidentate prolinol skeletons and forms a pyramidal geometry similar to aluminum porphyrinate and salen-type Schiff base complexes[16,17] showing activity for the copolymerization of CO_2 and epoxide (Table 8, run 1). Thus, the copolymerization of CO_2 and CHO with $\mathbf{3}_2AlMe$ in the presence of DMAP (1 equiv to $\mathbf{3}_2AlMe$) was carried out at 60 °C for 72 h under 50 atm of CO_2 at an initial mole ratio ($[CHO]_0/[\mathbf{3}_2AlMe]_0$) of 250 in toluene. The obtained copolymer had perfect carbonate linkages (over 99%) with a higher enantioselectivity of 59% ee ((*R*,*R*) units: (*S*,*S*) units =79.5: 20.5) than those with the complexes **1a**AlMe−**1f**AlMe and $[\mathbf{2a}AlMe]_2$−$[\mathbf{2h}AlMe]_2$ (Tables 2−4). However, the copolymerization was relatively slower (TOF = 0.35 h^{-1}) than those with the complexes **1a**AlMe−**1f**AlMe and $[\mathbf{2a}AlMe]_2$−$[\mathbf{2h}AlMe]_2$ (Tables 2−4). Compared with the calculated M_n (3500), the observed molecular weight was 28800. It is presumed that the large M_n and broad M_w/M_n are due to action of a part of $\mathbf{3}_2AlMe$ as the catalyst for the copolymerization, that is, the slow initiation and the fast propagation of the polymerization. Furthermore, utilization of 2-picoline instead of DMAP led to the enhancement of the enantioselectivity (67% ee) though the TOF, content of carbonate linkages, and M_w/M_n were slightly degraded (Table 8, run 2).

Mechanism of Asymmetric Alternating Copolymerization of CO_2 and CHO with Aluminum Aminoalkoxide Complex−Lewis Bases. When CHO approaches the aluminum in the region “inside walls” of the complex $\mathbf{3}_2AlMe$, an enantioselective ring-opening of CHO will likely advance. In contrast, a coordination of a Lewis base such as pyridine to the aluminum in “inside walls” brings about the approach of CHO to the aluminum in “outside walls”, probably causing a less enantioselective ring-opening of CHO. If Lewis base having bulky substituents around the coordination site collides with the walls (two pyrrolidine and two phenyl rings)

Scheme 11. Mechanism of Asymmetric Copolymerization with 3_2AlMe−2-picoline



of “inside walls”, the Lewis base may be coordinated to the aluminum in “outside walls”. The steric repulsion may accelerate the preferential approach of CHO to the aluminum in “inside walls”. In fact, the enantioselectivity of the copolymerization was improved by the utilization of 2-picoline as the Lewis base based on the concept (Table 8, run 2). The polymerization is considered to proceed through the process as described in Scheme 11D.

Asymmetric Alternating Copolymerization with Aluminum Aminoalkoxide Complex−Lewis Bases−Lewis Acid. To perform the fast copolymerization with high enantioselectivity, MAD was applied for alternating copolymerization of CO_2 and CHO with 3_2AlMe−Lewis bases on the basis of [**2g**AlMe]$_2$− or [**2h**AlMe]$_2$−bis-*N*-MeBzIm systems (Figure 7). First, MAD (1 equiv to aluminum) accelerated the copolymerization (conversion of CHO = 77%) to produce the copolymer (content of carbonate linkages = 90%, M_n = 23000, M_w/M_n = 3.10) in 72% yield for 24 h, meaning the 21-folds-acceleration of the copolymerization (Table 9, run 1). The increase of the feed ratio of MAD to the catalyst 3_2AlMe (1 to 5 equiv) was related to the following changes: not only the increase of the TOF (7.5 to 14.8 h^{-1}; 21- to 42-folds to that with 3_2AlMe−DMAP 0.35 h^{-1}) but also the decreases of the ee (53 to 39% ee; 59% ee for 3_2AlMe−DMAP) and the content of carbonate linkages (91 to 83%; > 99% for 3_2AlMe−DMAP) and the increase of the M_w/M_n (3.10 to 5.44; 1.92 for 3_2AlMe−DMAP) (Table 9, runs 1−5).

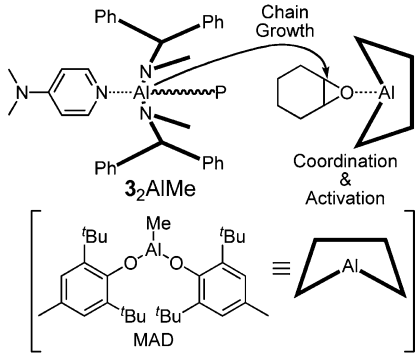


Figure 7. Coordinative activation of CHO with MAD and chain growth from active chain terminal to CHO.

Even if MAD alone catalyzes the copolymerization, the large M_w/M_n is explicable because multiple active species (at least two kinds (3_2AlMe and MAD)) work as catalysts in the polymerization system. Therefore, the copolymerization with MAD alone was carried out in the absence of other aluminum complexes or additives. MAD alone generated the copolymer with a low content of carbonate linkages ([carbonate linkages]:[ether linkages] = 37: 63) and a very broad distribution (M_w/M_n = 6.43) (Table 9, run 9). The 1:1 mixture of MAD and DMAP was inactive for the copolymerization of CO_2 and CHO (Table 9, run 10). MAD and DMAP were originally expected to act as a monomer activator and a catalyst activator, respectively. These results, however, disclosed that MAD not only catalyzed the polymerization of CO_2 and CHO but also directly reacted with DMAP. The interactions between CHO or DMAP and MAD were examined by using ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of an equimolar mixture of CHO and MAD in $CDCl_3$ at 30 °C showed all signals due to CHO clearly shifted from those of CHO alone (Figure 8). In particular, the signal assignable to O−CH of CHO was shifted most significantly (52.1 ppm for CHO alone; 66.1 ppm for CHO−MAD). This result indicates that CHO is coordinated to the aluminum of MAD. Furthermore, an equimolar mixture of MAD and DMAP in $CDCl_3$ at 30 °C was investigated in the same manner (Figure 9). Two signals due to the carbons at the 2- and 4-positions on the pyridine ring of DMAP were remarkably shifted: 154.3 to 155.9 ppm (for C at the 2-position) and 150.0 to 147.6 ppm (for C at the 4-position). This result suggests that DMAP also coordinates to the aluminum of MAD.

Various ratios of 3_2AlMe−DMAP−MAD were attempted to establish the catalytic system which produces the copolymer in a high yield with a high content of carbonate linkages and an enantioselectivity (Table 9, run 1−8). The optimized ratio was [3_2AlMe]/[DMAP]/[MAD] = 1/3/2 (Table 9, run 6). The system quantitatively generated the copolymer (TOF = over 10.4 h^{-1}; the degree of acceleration was approximately 30-folds) with the content of carbonate linkages (95%) and the enantioselectivity (55% ee) similar to those of the polymer yielded by an MAD-free catalytic system (>99% and 59% ee,

Table 9. Asymmetric Alternating Copolymerization of CO_2 and CHO with $\mathbf{3}_2$AlMe–DMAP–MAD System.[a]

					copolymerization					hydrolysis	
run	$\mathbf{3}_2$AlMe/equiv	DMAP/equiv	MAD/equiv	time/h	yield[b]/%	TOF[c]/h^{-1}	C.L.[d]/%	M_n[e]	M_w/M_n[e]	yield of diol/%	%ee[f] (*R*,*R*)
1	1	1	1	24	72	7.5	90	23 000	3.10	94	53
2	1	1	2	18	70	9.7	91	20 600	3.33	96	54
3	1	1	3	18	81	11.3	88	26 100	4.92	89	49
4	1	1	4	18	>99	13.9	83	24 700	3.72	86	40
5	1	1	5	12	71	14.8	85	15 500	5.44	94	39
6	1	3	2	24	>99	10.4	95	32 700	1.74	91	55
7	1	2	2	24	89	9.3	94	27 000	2.29	94	48
8	1	2	3	24	>99	10.4	89	29 200	2.50	90	46
9	0	0	1	24	82	8.5	37	3500	6.43	88	0
10	0	1	1	24	–	–	–	–	–	–	–

[a] In 1 mL of toluene, 60 °C, 50 atm of CO_2, complex $\mathbf{3}_2$AlMe (0.1 mmol), and CHO (25 mmol); DMAP = *N*,*N*-dimethyl-4-aminopyridine, MAD = methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide). [b] On the basis of isolated copolymer. [c] Turnover frequency = (mol of reacted CHO)·(mol of cat.)$^{-1}$·h^{-1}. [d] Content of carbonate linkages (C.L.) = (carbonate unit)·((carbonate unit) + (ether unit))$^{-1}$, estimated by ^{1}H NMR ($CDCl_3$). [e] Estimated by GPC calibrated with polystyrene standard in THF at 40 °C. [f] Estimated from optical rotation of *trans*-1,2-cyclohexanediol in H_2O.

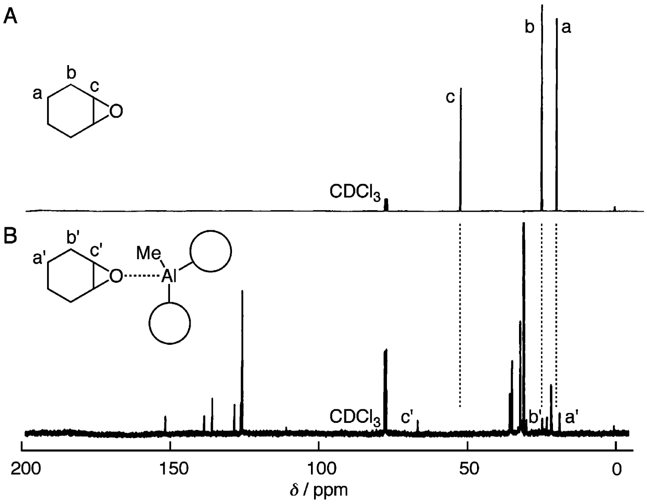


Figure 8. ^{13}C NMR spectra of CHO in the absence (A) and presence (B) of MAD in $CDCl_3$ at 30 °C. [CHO]/[MAD] = 1.

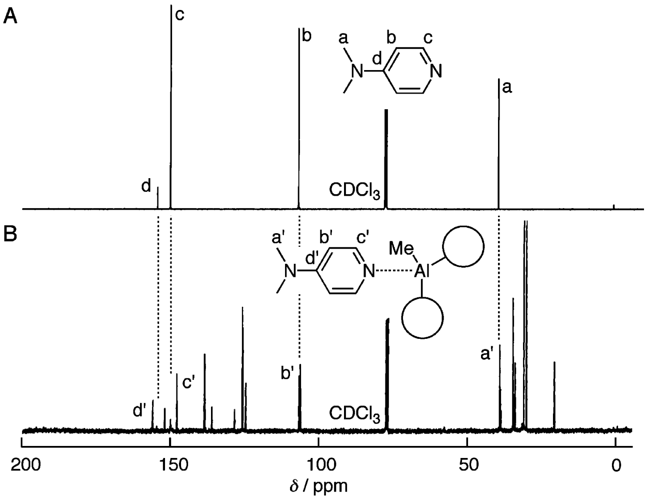


Figure 9. ^{13}C NMR spectra of DMAP in the absence (A) and presence (B) of MAD in $CDCl_3$ at 30 °C. [DMAP]/[MAD] = 1.

respectively) in Table 8, run 1. On the other hand, the copolymers obtained with other catalytic ratios had low contents of carbonate linkages and enantioselectivities and large M_w/M_n values (Table 9, runs 7 and 8).

To improve further enantioselectivities in the asymmetric copolymerization of CO_2 and CHO, MAD was added to the $\mathbf{3}_2$AlMe–2-picoline system producing the copolymer with 67% ee being the highest value among the ees of the *trans*-1,2-diols obtained with MAD-free catalytic systems at 60 °C. The $\mathbf{3}_2$AlMe/2-picoline/MAD (= 1/3/2, molar ratio) produced the alternating copolymer in a quantitative yield with a high enantioselectivity of 66% ee (Table 10, run 1), which was higher than those with $\mathbf{3}_2$AlMe–DMAP–MAD system (Table 9, run 6). In addition, the temperature was lowered from 60 °C to 0–40 °C (Table 8, runs 2–4). Lowering the temperature expectedly led to the improvement of the enantioselectivities. On the other hand, the contents of carbonate linkages of the polymers were significantly decreased with the decrease of temperature. For instance, at 0 °C the catalytic system generated the copolymer with a low content of carbonate linkages (37%) (M_n = 2100, M_w/M_n = 2.09) in 15% yield. The copolymer was alkali-hydrolyzed to afford the *trans*-1,2-diol with 82% ee and the oligo- or polyether chains. The enantiomeric excess of the *trans*-1,2-diol was the highest among those of the copolymers synthesized with the catalytic systems in this work.[70] Furthermore, the polyether exhibited an apparent optical activity ($[\alpha]_D$ −18.9° (*c* 0.6, benzene)).[71] These results indicate that the asymmetric ring-opening of *meso*-epoxide, CHO, proceeded throughout the copolymerization together with no insertion of CO_2 to alkoxide terminal.

Asymmetric Alternating Copolymerization of CO_2 and *meso*-Epoxides by Aluminum Complex–Lewis Base–MAD Systems. The most enantioselective systems ([**2g**AlMe]$_2$– and [**2h**AlMe]$_2$–bis-*N*-MeBzIm–MAD (1: 1: 0.3) and $\mathbf{3}_2$AlMe–2-picoline–MAD (1: 3: 2)) were applied for copolymerizations of CO_2 and other *meso*-epoxides such as cyclopentene oxide (CPO)[74] and cyclooctene oxide (COO) at 60 °C for 24 h (Table 11). CPO was transformed under CO_2 with the catalytic systems into the corresponding alternating copolymer, poly(cyclopentene carbonate), with 90–97% contents of carbonate linkages (Table 11, runs 1–3). The copolymers were independently converted into *trans*-1,2-cyclopenatanediol with 15% (for [**2g**AlMe]$_2$), 15% (for [**2h**AlMe]$_2$), and 21% (for $\mathbf{3}_2$AlMe) ee.[56] These data exhibit that $\mathbf{3}_2$AlMe–2-picoline–MAD (1: 3: 2) is more preferential for the copolymerization of CPO and CO_2. On the other hand,

Table 10. Asymmetric Alternating Copolymerization of CO_2 and CHO with $\mathbf{3}_2$AlMe−2-Picoline−MAD at Various Temperatures.[a]

		copolymerization					hydrolysis	
run	temp/°C	yield[b]/%	TOF[c]/h^{-1}	C.L.[d]/%	M_n[e]	M_w/M_n[e]	yield of diol/%	%ee[f] (*R*,*R*)
1	60	>99	10.4	91	26 600	2.11	97	66
2	40	69	7.2	67	14 100	2.01	89	67
3	25	28	2.9	52	6000	1.57	96	74
4[g]	0	15	0.9	37	2100	2.09	95	82

[a] In 1 mL of toluene, 24 h, 50 atm of CO_2, complex $\mathbf{3}_2$AlMe (0.1 mmol), 2-picoline (0.3 mmol), MAD (0.2 mmol), and CHO (25 mmol); MAD = methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide). [b] On the basis of isolated copolymer. [c] Turnover frequency = (mol of reacted CHO)·(mol of cat.)$^{-1}$·h^{-1}. [d] Content of carbonate linkages (C.L.) = (carbonate unit)·((carbonate unit) + (ether unit))$^{-1}$, estimated by ^{1}H NMR ($CDCl_3$). [e] Estimated by GPC calibrated with polystyrene standard in THF at 40 °C. [f] Estimated from optical rotation of *trans*-1,2-cyclohexanediol in H_2O. [g] 60 atm of CO_2 and CHO (15 mmol).

Table 11. Asymmetric Alternating Copolymerization of CO_2 and *meso*-Epoxides with Complex [**2g**AlMe]$_2$, [**2h**AlMe]$_2$, and $\mathbf{3}_2$AlMe.[a]

			copolymerization					Hydrolysis	
run	complex	epoxide	yield[b]/%	TOF[c]/h^{-1}	C.L.[d]/%	M_n[e]	M_w/M_n[e]	yield of diol/%	%ee[f] (*R*,*R*)
1	[**2g**AlMe]$_2$	CPO	27	1.1	97	1500	1.41	91	15
2	[**2h**AlMe]$_2$	CPO	30	1.3	90	1700	1.37	93	15
3	$\mathbf{3}_2$AlMe	CPO	24	1.0	91	1000	1.83	85	21
4	[**2g**AlMe]$_2$	COO	10	0.4	94	910	1.27	90	21
5	[**2h**AlMe]$_2$	COO	11	0.5	92	880	1.53	89	23
6	$\mathbf{3}_2$AlMe	COO	7	0.3	88	1300	1.99	91	10

[a] In 1 mL of toluene, 60 °C, 24 h, 50 atm of CO_2, complex [**2g**AlMe]$_2$ or [**2h**AlMe]$_2$ (0.1 mmol), bis-*N*-MeBzIm (0.1 mmol), MAD (0.03 mmol), and CHO (25 mmol) or complex $\mathbf{3}_2$AlMe (0.1 mmol), 2-picoline (0.3 mmol), MAD (0.2 mmol), and epoxide (10 mmol); MAD = methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide), bis-*N*-MeBzIm = *N*-methyl-2-(*N*′-methylbenzimidazol-2-yl)benzimidazole. [b] On the basis of isolated copolymer. [c] Turnover frequency = (mol of reacted CHO)·(mol of cat.)$^{-1}$·h^{-1}. [d] Content of carbonate linkages (C.L.) = (carbonate unit)·((carbonate unit) + (ether unit))$^{-1}$, estimated by ^{1}H NMR ($CDCl_3$). [e] Estimated by GPC calibrated with polystyrene standard in THF at 40 °C. [f] Estimated from optical rotation of *trans*-1,2-cyclohexanediol in EtOH or $CHCl_3$.

COO was converted into poly(cyclooctene carbonate) with 88−94% contents of carbonate linkages (Table 11, runs 4−6) under the same conditions as those of CPO and CHO. The copolymers had the repeating units composed of *trans*-1,2-cyclooctanediol with 21 (for [**2g**AlMe]$_2$), 23 (for [**2h**AlMe]$_2$), and 10% (for $\mathbf{3}_2$AlMe) ee. These show that [**2h**AlMe]$_2$−bis-*N*-MeBzIm−MAD (1: 1: 0.3) is more superior for the copolymerization of COO and CO_2. The contents of carbonate linkages (88−97%) of the copolymers synthesized from CPO or COO and CO_2 were on the same level as those (91−95%) from CHO, whereas the ees of the *trans*-1,2-diols converted from the copolymers are significantly smaller than those from PCHC: 15−21% (for CPO) and 10−23% (for COO) vs 62−66% (for CHO) ee.[56] This result suggests that the asymmetric copolymerization is significantly dependent on the structure (size, conformation, etc.) of epoxide. In addition, the TOF data (1.0−1.3 (for CPO) and 0.4−0.5 (for COO) vs 5.4−10.4 (for CHO)) indicate that the reactivity of *meso*-epoxide decreased in order of CHO ≫ CPO > COO. This tendency was similar to the reactivity of homopolymerization of *meso*-epoxide with Et_3Al reported by Bacskai.[75]

CONCLUSION

We have explored a series of optically active aluminum complexes (salen-type Schiff base, *β*-ketoiminate, and amino-alkoxide complexes) for alternating copolymerization of CO_2 and CHO with asymmetric induction. The aluminum salen-type Schiff base complex−Et_4NOAc systems afforded alternating copolymers with low enantioselectivities (up to 23% ee). On the basis of the binuclear structure of the aluminum *β*-ketoiminate complex disclosed by single crystal X-ray analysis, Lewis bases having two coordinating nitrogens coordinated to two aluminums were designed and employed as catalyst activator. In particular, bis-*N*-MeBzIm assisted the preferential production of the copolymer with high enantioselectivity (up to 62% ee). In addition, the aluminum bisprolinol complex−2-picoline system generated the copolymer with high enantioselectivity (up to 67% ee) despite of the relatively slow copolymerization. MAD was subsequently employed as monomer activator in order to perform faster and more enantioselective copolymerizations at low temperature. The enantiomeric excess of *trans*-1,2-diol comprising the copolymer was improved up to 82% ee though the copolymer partially included oligo- or polyether sequences showing optical activities. The design and utilization of catalyst and monomer activator for asymmetric alternating polymerization are expected to allow improvement of not only asymmetric ring-opening polymerizations but also asymmetric syntheses related to ring-opening of cyclic substrates. The related work is under investigation in our laboratory.

EXPERIMENTAL SECTION

Materials. The reactions involving air- and/or moisture-sensitive compounds were performed under nitrogen. Toluene, THF, and C_6D_6 were distilled over sodium benzophenone ketyl in a nitrogen atmosphere. $CDCl_3$ was distilled over CaH_2 under nitrogen. 1,2-Epoxycyclohexane (CHO) and 1,2-epoxycyclopentane (CPO) was dried over KOH pellet and distilled over CaH_2 and KOH under reduced pressure and stored under nitrogen prior to use. 1,2-Epoxycyclooctane (COO) was recrystallized from benzene. *N*-MeIm, pyridine, and 2-picoline were distilled over CaH_2 under reduced pressure and stored under nitrogen. *tert*-Butanol was distilled over Mg/I_2 and stored under nitrogen. Acetic acid was distilled over P_2O_5 and stored under nitrogen. Me_3Al was distilled under reduced pressure and stored in a nitrogen atmosphere. Et_4NOAc was azeotropically dehydrated with benzene using a Dean−Stark apparatus. DMAP was recrystallized from toluene. CO_2 was used without further purification. Other reagents were used as received. Following materials were commercially obtained: 2,4-pentanedione, 1,3-diphenyl-1,3-propanedione, *tert*-butanol, pyridine, *N*-MeIm, DMAP, 2-picoline, CHO, COO (from TCI); Me_3Al, Et_4NOAc (from Aldrich). Following materials were synthesized according to the reported literatures: salen-type Schiff bases [(1*R*,2*R*)-*N*,*N*′-bissalicylidene-1,2-diphenylethane-1,2-diamine (**1a**H_2),[46] (1*R*,2*R*)-*N*,*N*′-bis(3-phenylsalicylidene)-1,2-diphenylethane-1,2-diamine (**1b**H_2),[47] (1*R*,2*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diphenylethane-1,2-diamine (**1c**H_2),[46] (1*R*,2*R*)-*N*,*N*′-bissalicylidene-1,2-cyclohexanediamine (**1d**H_2),[47] (1*R*,2*R*)-*N*,*N*′-bis(3-phenylsalicylidene)-1,2-cyclohexanediamine (**1e**H_2),[47] and (1*R*,2*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine (**1f**H_2)[48]], amino alcohols [(*S*)-2-amino-1-propanol, (*S*)-2-amino-3-methyl-1-butanol, (*S*)-2-amino-4-methyl-1-pentanol, (2*S*,3*S*)-2-amino-3-methyl-1-pentanol, (*S*)-2-amino-3-phenyl-1-propanol, (*S*)-2-amino-2-phenylethanol, and (*R*)-2-amino-2-phenylethanol],[49] *β*-ketoimines [4-(2-hydroxyethylimino)pent-2-en-2-ol (**2a**H_2)[41] and 4-((*S*)-1-hydroxypropan-2-ylimino)pent-2-en-2-ol (**2b**H_2)[50]], (*S*)-diphenyl(pyrrolidine-2-yl)methanol (**3**H),[51] aluminum complexes [**1c**AlMe,[39] **1d**AlMe,[40] **1f**AlMe,[39] [**2a**AlMe]$_2$,[41] **3**$_2$AlMe,[42] and **4**AlMe[17a]], bis-*N*-MeIm,[66] bis-*N*-MeBzIm,[66] MAD,[69] and CPO.[74]

4-((*S*)-1-Hydroxy-3-methylbutan-2-ylimino)pent-2-en-2-ol (2cH_2).[50] Na_2SO_4 (2.5 g) was added to acetylacetone (1.0 g, 10 mmol) in methanol (10 mL) in a 100-mL two-necked round-bottomed flask equipped with a dropping funnel. (*S*)-2-Amino-3-methyl-1-butanol (1.03 g, 10.0 mmol) in methanol (20 mL) was added dropwise over 1 h while the solution turned yellow, and the resulting mixture was then stirred for 12 h at room temperature. After dilution with CH_2Cl_2 (10 mL), the mixture was filtered and concentrated to dryness under reduced pressure to leave a yellow solid. The residue was purified by silica gel column chromatography with ethyl acetate/hexane (2/3, vol/vol) to afford a colorless oil (1.44 g, 78% yield). $[\alpha]_D$ −14° (*c* 3.9, $CHCl_3$). ^1H NMR ($CDCl_3$): *δ* 10.9−10.8 (br, 1H), 4.98 (s, 1H), 4.26−4.02 (br, 1H), 3.61−3.56 (t, 1H), 3.45−3.40 (m, 1H), 1.96−1.95 (d, 6H), 1.88−1.82 (m, 1H), 0.99−0.91 (d, 6H). ^{13}C NMR ($CDCl_3$): *δ* 194.1, 164.8, 95.4, 63.8, 61.0, 29.7, 28.1, 19.6, 19.3, 17.6. FAB−MS *m*/*z*: 186 [for $C_{10}H_{20}NO_2$ $[M + H]^+$]. Compounds **2d**H_2−**2f**H_2 were also synthesized according to the similar procedure to **2c**H_2.

4-((*S*)-1-Hydroxy-4-methylpentan-2-ylimino)pent-2-en-2-ol (2dH_2). This was purified by silica gel column chromatography with ethyl acetate/hexane (5/1, vol/vol) to afford a colorless viscous oil (62% yield). $[\alpha]_D$ −31° (*c* 5.5, $CHCl_3$). ^1H NMR ($CDCl_3$): *δ* 10.8−10.7 (br, 1H), 4.96 (s, 1H), 4.00−3.63 (d, 2H), 3.51−3.46 (t, 1H), 1.99−1.95 (d, 6H), 1.68−1.66 (m, 1H), 1.36−1.33 (t, 2H), 0.93−0.89 (d, 6H). ^{13}C NMR ($CDCl_3$): *δ* 194.3, 164.0, 95.3, 66.1, 53.9, 41.1, 28.4, 24.8, 23.1, 22.2, 19.4. FAB−MS *m*/*z*: 200 [for $C_{11}H_{22}NO_2$ $[M + H]^+$].

4-((2*S*,3*R*)-1-Hydroxy-3-methylpentan-2-ylimino)pent-2-en-2-ol (2eH_2). This was purified by silica gel column chromatography with ethyl acetate/hexane (5/1, vol/vol) to afford a colorless viscous oil (75% yield). $[\alpha]_D$ −51° (*c* 2.2, CH_2Cl_2). ^1H NMR ($CDCl_3$): *δ* 10.8−10.7 (br, 1H), 5.01 (s, 1H), 4.00−3.63 (d, 2H), 3.51−3.46 (t, 1H), 1.99−1.95 (d, 6H), 1.68−1.66 (m, 1H), 1.36−1.33 (t, 2H) 0.95−0.90 (d, 6H). ^{13}C NMR ($CDCl_3$): *δ* 194.4, 163.9, 95.4, 63.7, 60.7, 41.1, 28.4, 24.8, 19.6, 15.2, 11.4. FAB−MS *m*/*z*: 200 [for $C_{11}H_{22}NO_2$ $[M + H]^+$].

4-((*S*)-1-Hydroxy-3-phenylpropan-2-ylimino)pent-2-en-2-ol (2fH_2). This was purified by silica gel column chromatography with ethyl acetate/hexane (3/1, vol/vol) to afford a slightly yellowish viscous oil (58% yield). $[\alpha]_D$ −310° (*c* 4.7, $CHCl_3$). ^1H NMR ($CDCl_3$): *δ* 10.89 (br, 1H), 7.29−7.07 (m, 5H), 4.82 (s, 1H), 4.14−3.67 (m, 3H), 3.62−3.58 (m, 1H), 2.92−2.87 (d, 1H), 2.74−2.68 (t, 1H), 1.95 (s, 3H), 1.60 (s, 3H). ^{13}C NMR ($CDCl_3$): *δ* 194.6, 164.0, 137.9, 129.3, 129.2, 128.5, 126.5, 95.5, 64.7, 57.8, 39.1, 28.4, 18.9, 18.2. FAB−MS *m*/*z*: 234 [for $C_{14}H_{20}NO_2$ $[M + H]^+$].

4-((*S*)-2-Hydroxy-1-phenylethylimino)pent-2-en-2-ol (2gH_2). This was purified by recrystallization from ethanol to afford a white crystal (88% yield). $[\alpha]_D$ −878° (*c* 1.6, $CHCl_3$). ^1H NMR ($CDCl_3$): *δ* 11.43 (br, 1H), 7.37−7.28 (m, 5H), 5.03 (s, 1H), 4.73−4.68 (m, 1H), 3.87−3.78 (m, 2H), 3.25−3.21 (t, 1H), 2.07 (s, 3H), 1.87 (s, 3H). ^{13}C NMR ($CDCl_3$): *δ* 195.4, 163.9, 139.3, 128.9, 128.6, 127.7, 126.5, 96.4, 67.2, 60.1, 28.5, 19.4. FAB−MS *m*/*z*: 220 [for $C_{13}H_{18}NO_2$ $[M + H]^+$]. 4-((*R*)-2-Hydroxy-1-phenylethylimino)pent-2-en-2-ol was also prepared from D-phenylglycinol; $[\alpha]_D$ +860° (*c* 1.5, $CHCl_3$).

3-((*S*)-2-Hydroxy-1-phenylethylimino)-1,3-diphenylprop-1-en-1-ol (2hH_2).[76] L-Phenylglycinol (2.19 g, 10.0 mmol) and dibenzoylmethane (2.24 g, 10.0 mmol) were dissolved in toluene (50 mL) in a 100-mL round-bottomed flask equipped with a reflux condenser. After one drop of formic acid was added to this solution, the mixture was heated under reflux for 48 h. The mixture was concentrated under reduced pressure to leave a yellow oil. The crude oil was purified by silica gel column chromatography with ethyl acetate to afford a yellow viscous oil (1.65 g, 48% yield). $[\alpha]_D$ −366° (*c* 1.8, $CHCl_3$). ^1H NMR ($CDCl_3$): *δ* 12.16−11.98 (br, 1H), 7.91−7.85 (d, 2H), 7.42−7.11 (m, 13H), 5.75 (s, 1H), 4.67−4.58 (m, 1H), 4.04−3.90 (br, 1H), 3.87−3.81 (m, 2H). ^{13}C NMR ($CDCl_3$): *δ* 188.9, 167.4, 140.1, 139.6, 135.4, 130.9, 129.5, 128.8, 128.4, 128.3, 127.8, 127.6, 127.2, 126.5, 94.6, 67.4. FAB−MS *m*/*z*: 344 [for $C_{23}H_{22}NO_2$ $[M + H]^+$]. Compound **2i**H_2 was also synthesized according to a procedure similar to that used for **2h**H_2.

3-(2-Hydroxyethylimino)-1,3-diphenylprop-1-en-1-ol (2iH_2). This was purified by recrystallization from ethanol to afford a white crystals (87% yield). ^1H NMR ($CDCl_3$): *δ* 12.11−11.93 (br, 1H), 7.91−7.85 (d, 2H), 7.42−7.11 (m, 8H), 5.78 (s, 1H), 4.01−3.95 (t, 2H), 3.54−3.41 (t, 2H). ^{13}C NMR ($CDCl_3$): *δ* 194.4,189.5, 177.6, 164.8, 160.7, 140.7, 139.2, 136.7, 133.2, 131.1, 129.0, 128.8, 127.9, 127.0, 126.8, 126.0, 125.5, 69.3, 68.7, 65.1, 58.8, 58.2. FAB−MS *m*/*z*: 268 [for $C_{17}H_{18}NO_2$ $[M + H]^+$].

Complex 1aAlMe.[39,40] After **1a**H_2 (0.21 g, 0.50 mmol) was dissolved in dry toluene (10 mL) in a 50-mL two-necked round-bottomed flask equipped with a reflux condenser under dry nitrogen, the mixture was cooled at 0 °C. Me_3Al (0.06 mL, 0.6 mmol) was carefully added to the solution by a hypodermic syringe in a nitrogen stream. After gas evolution ceased, the resulting mixture was stirred at 0 °C for 30 min and then heated under reflux for 2 h. The mixture was cooled at room temperature, and the volatile components were then removed under reduced pressure to leave a yellow powder in an almost quantitative yield. The crude product was purified by recrystallization form CH_2Cl_2/hexane to afford a pale yellow powder (0.20 g, 87% yield). ^1H NMR ($CDCl_3$): *δ* 8.32 (s, 2H), 7.40−7.10 (m, 14H), 6.90 (d, 2H), 6.77 (d, 2H), 4.73 (s, 2H), −1.01 (s, 3H). Compounds **1b**AlMe and **1e**AlMe were also synthesized according to the similar procedure to **1a**AlMe.

Complex 1bAlMe. 93% yield as a pale yellow powder. ^1H NMR ($CDCl_3$): *δ* 8.54 (s, 2H), 7.65−7.40 (m, 8H), 7.37−7.30 (m, 4H), 7.23−7.11 (m, 12H), 6.87 (m, 2H), 4.78 (s, 2H), −0.97 (s, 3H).

Complex 1eAlMe. 92% yield as a pale yellow powder. ^1H NMR ($CDCl_3$): *δ* 8.47 (s, 2H), 7.70−7.10 (m, 16H), 6.94 (m, 2H), 6.85−6.60 (m, 2H), 3.49−3.34 (m, 2H), 2.11−1.29 (m, 8H), −1.02 (s, 3H).

Complex [2bAlMe]$_2$.[41] After **2b**H_2 (0.16 g, 1.0 mmol) was dissolved in dry THF (10 mL) in a 50-mL two-necked round-bottomed flask equipped with a three-way stopcock under dry nitrogen, the mixture was cooled at −30 °C. Me_3Al (0.12 mL, 1.2 mmol) was carefully added to the solution by a hypodermic syringe in a nitrogen stream. After gas evolution ceased, the resulting mixture was allowed to warm to room temperature and then stirred for 2.5 h. The volatile components were then removed under reduced pressure to leave a white solid. The crude product was purified by recrystallization form THF/hexane to afford a colorless crystal (0.18 g, 90% yield). ^1H NMR ($CDCl_3$): *δ* 5.00 (s, 2H), 3.78−3.69 (m, 2H), 3.63−3.43 (m, 4H), 2.02 (s, 6H), 1.93 (s, 6H), 1.25−1.19 (d, 6H), −0.88 (s, 3H), −0.95 (s, 3H). Complexes [**2c**AlMe]$_2$−[**2c**AlMe]$_2$ were also synthesized according to the similar procedure to [**2b**AlMe]$_2$.

Complex [2cAlMe]$_2$. 86% yield as a colorless solid. ^{1}H NMR ($CDCl_3$): δ 4.78 (s, 2H), 3.77−3.61 (t, 2H), 3.55−3.47 (m, 2H), 1.97−1.94 (d, 12H), 1.85−1.83 (m, 2H), 1.02−0.90 (d, 12H), −0.78 (s, 3H), −0.82 (s, 3H).

Complex [2dAlMe]$_2$. 79% yield as a colorless crystal. ^{1}H NMR ($CDCl_3$): δ 5.01 (s, 2H), 4.09−3.88 (d, 4H), 3.31−3.20 (t, 2H), 1.99−1.93 (d, 12H), 1.47−1.39 (m, 2H), 1.26−1.19 (t, 4H), 1.02−0.89 (d, 12H), −0.84 (s, 3H), −0.96 (s, 3H).

Complex [2eAlMe]$_2$. 77% yield as a colorless solid. ^{1}H NMR ($CDCl_3$): δ 5.12 (s, 2H), 3.98−3.63 (d, 4H), 3.21−3.10 (t, 2H), 2.01−1.92 (d, 12H), 1.71−1.66 (m, 2H), 1.29−1.23 (t, 4H), 0.94−0.80 (d, 12H), −0.91(s, 3H), −1.01 (s, 3H).

Complex [2fAlMe]$_2$. 69% yield as a colorless powder. ^{1}H NMR ($CDCl_3$): δ 7.40−7.02 (m, 10H), 5.01 (s, 2H), 4.21−3.67 (m, 6H), 3.60−3.50 (m, 2H), 3.00−2.87 (d, 2H), 2.84−2.69 (t, 2H), 2,00 (s, 6H), 1.40 (s, 6H), −0.65 (s, 3H), −0.88 (s, 3H).

Complex [2gAlMe]$_2$. 90% yield as a colorless crystal. ^{1}H NMR ($CDCl_3$): δ 7.50−7.20 (m, 10H), 5.21 (s, 2H), 4.70−4.39 (m, 2H), 3.90−3.61 (m, 4H), 3.10−2.99 (t, 2H), 2.00 (s, 6H), 1.80 (s, 3H), −0.99 (s, 3H), −1.10 (s, 3H).

Complex [2hAlMe]$_2$. 80% yield as a colorless powder. ^{1}H NMR ($CDCl_3$): δ 8.00−7.97 (d, 4H), 7.60−7.01 (m, 26H), 5.86 (s, 2H), 4.67−4.59 (m, 4H), 3.90−3.81 (m, 4H), −0.88 (s, 3H), −0.97 (s, 3H).

Complex [2iAlMe]$_2$. 77% yield as a colorless crystal. ^{1}H NMR ($CDCl_3$): δ 7.90−7.82 (d, 4H), 7.32−7.00 (m, 16H), 5.87 (s, 2H), 4.20−4.15 (t, 4H), 3.50−3.40 (t, 4H), −0.97 (s, 6H).

Complex [2iAlO^{t}Bu]$_2$.[17a] After [**3i**AlMe]$_2$ (0.614 g, 1.00 mmol) was dissolved in dry toluene (10 mL) in a 50-mL two-necked round-bottomed flask equipped with a three-way stopcock under dry nitrogen, *tert*-butanol (5 mL) was added to the mixture at room temperature. After the mixture was heated under reflux for 12 h, the volatile compounds were removed under reduced pressure to obtain a slightly yellow powder. The powder was purified by recrystallization from THF/hexane to afford a slight yellow crystal (0.46 g, 62% yield). ^{1}H NMR ($CDCl_3$): δ 7.93−7.86 (d, 4H), 7.45−7.30 (m, 16H), 5.86 (s, 2H), 4.01−3.95 (t, 4H), 3.64−3.63 (m, 4H), 1.25 (s, 18H).

Complex 4AlOAc.[17a] After **4**AlMe (0.349 g, 1.00 mmol) was dissolved in dry toluene (10 mL) in a 50-mL two-necked round-bottomed flask equipped with a three-way stopcock under dry nitrogen, acetic acid (60 μL, 1.0 mmol) was added to the mixture at room temperature. After stirred for 12 h, the mixture changed to a yellow suspension. The yellow solid was collected by filtration of the suspension, washed with cooled toluene, and dried in vacuo to afford a colorless crystal (0.22 g, 54% yield). ^{1}H NMR ($CDCl_3$): δ 8.58 (s, 2H), 7.65−7.00 (m, 12H), 2.08 (s, 3H).

X-ray Crystallography. The aluminum complexes [**2g**AlMe]$_2$ (*R*-form was used) and **3**$_2$AlMe were obtained as X-ray-quality crystals. Crystallographic data for [**2g**AlMe]$_2$ and **3**$_2$AlMe were summarized in the Supporting Information.

Representative Copolymerization of CO_2 and CHO. The aluminum complex [**2g**AlMe]$_2$ (51.8 mg, 0.10 mmol), bis-*N*-MeBzIm (26.2 mg, 0.10 mmol, 1 equiv to Al), toluene (1.0 mL), and CHO (2.5 mL, 25 mmol) were placed in a well-dried 150-mL stainless autoclave in a nitrogen stream. The autoclave was pressurized to 50 atm of CO_2, and left stirred at 60 °C for 24 h. The reactor was cooled to ambient temperature and the CO_2 pressure was slowly released. A small aliquot of the resulting mixture was subjected to analysis. To the remaining mixture was added methanol. The mixture was dissolved in $CHCl_3$ (30 mL) and washed with HCl(aq) (1 M, 10 mL), water (10 mL). The organic layer was concentrated to about 3 mL. This solution was added to methanol (300 mL) with stirring to precipitate the white solid. This solid was collected and dried in vacuo at 120 °C for 6 h (1.3 g, 37% yield).

Copolymerization in the Presence of MAD. The aluminum complex [**2g**AlMe]$_2$ (51.8 mg, 0.10 mmol), bis-*N*-MeBzIm (26.2 mg, 0.10 mmol, 1 equiv to Al), toluene (0.5 mL), and CHO (2.5 mL, 25 mmol) were placed in a well-dried 150-mL stainless autoclave in a nitrogen stream and the mixture was stirred for 30 min. A solution of MAD (14.4 mg, 0.030 mmol) in toluene (0.5 mL) was added to the mixture. The autoclave was pressurized to 50 atm of CO_2, and left stirred at 60 °C for 24 h. Following operations were identical with the copolymerization in the absence of MAD (1.8 g, 52% yield).

Alkali-Catalyzed Hydrolysis of Poly(cyclohexene carbonate)..[14a,b] PCHC (0.14 g, corresponding to 1 mmol of diol) obtained with [**2g**AlMe]$_2$−bis-*N*-MeBzIm−MAD (Table 7, run 1) was dissolved in THF (30 mL) and methanol (10 mL) in a 100-mL round-bottomed flask equipped with reflux condenser. After NaOH(aq) (2 M, 5 mL) was added to the solution, the resulting solution was heated to reflux for 6 h. When the reaction mixture was neutralized with 1 M HCl(aq), a white precipitate was generated. The precipitate was filtered off and the filtrate was then concentrated to approximately 20 mL under reduced pressure. The solution diluted with water (10 mL) was washed with ethyl acetate (10 mL) three times. After the combined organic layer was dried over $MgSO_4$, the solvent was evaporated to dryness to afford a white solid. The solid was purified by silica gel column chromatography with ethyl acetate as an eluent (0.093 g, 93% yield). The obtained diol was subjected to an optical rotation measurement. $[\alpha]_D$ −24° (*c* 1.0, H_2O). (lit.[56] $[\alpha]_D^{20}$ −39° (*c* 1.6, H_2O)). ^{1}H NMR ($CDCl_3$): δ 4.30 (s, 2H), 3.35 (s, 2H), 1.95 (m, 2H), 1.69 (m, 2H), 1.26 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 75.6, 33.0, 24.5. IR (KBr, cm^{-1}): 3371, 3278, 2934, 1632, 1470, 1404, 1351, 1233, 1165, 1080, 1058, 930, 866, 668. Poly(cyclopentene carbonate) and poly(cyclooctene carbonate) were hydrolyzed with the same procedure, respectively.

Hydrolysis of Poly(cyclopentene carbonate). 91% yield as a white solid (Table 11, run 1). $[\alpha]_D$ −3.2° (*c* 0.11, $CHCl_3$). (lit.[56] $[\alpha]_D^{20}$ −21° (*c* 1.0, $CHCl_3$)). Mp: 54−55 °C (lit.[56] 54−56 °C (racemic), 47−51 °C (enantiopure)). ^{1}H NMR ($CDCl_3$): δ 4.35 (s, 2H), 3.92 (t, 2H), 2.05−1.90 (m, 2H), 1.81−1.62 (m, 2H), 1.59−1.40 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 79.0, 31.2, 19.6. IR (KBr, cm^{-1}): 3382, 3261, 3201, 2924, 1674, 1455, 1374, 1230, 1155, 1100, 1028, 918, 886.

Hydrolysis of Poly(cyclooctene carbonate). Purification by distillation to yield a colorless oil, which was spontaneously solidified to give a white solid (90%) (Table 11, run 4). $[\alpha]_D$ −3.2° (*c* 0.10, EtOH). (lit.[56] $[\alpha]_D^{22}$ +16.9° (*c* 1.33, EtOH) for (1*S*,2*S*)-1,2-cyclooctanediol). Mp: 31−32 °C (lit.[56] 32 °C). ^{1}H NMR ($CDCl_3$): δ 3.75 (s, 2H), 3.70 (s, 2H), 1.92−1.20 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 76.2, 31.9, 26.2, 23.8. IR (neat, cm^{-1}): 3350, 3220, 2919, 1620, 1429, 1410, 1323, 1251, 1175, 1083, 930, 876, 845, 660.

Alkali-Catalyzed Hydrolysis of Ether-Containing Copolymer. The copolymer (0.28 g (52% content of carbonate linkages), corresponding to 1 mmol of diol) obtained from the complex [**2g**AlMe]$_2$−bis-*N*-MeBzIm−MAD (Table 10, run 3) was dissolved in THF (30 mL) and methanol (10 mL) in a 100-mL round-bottomed flask. After NaOH(aq) (2 M, 5 mL) was added to the solution, the resulting solution was heated to reflux for 12 h. After the reaction mixture was neutralized by 1 M HCl(aq), the aqueous solution diluted with water (20 mL) was washed with $CHCl_3$ (20 mL) three times. After the combined organic layer was washed with water (10 mL) twice, the solvent was evaporated to approximately 2 mL under reduced pressure. The residue was poured into methanol (100 mL) to yield a white suspension. The white solid was collected by filtration and dried in vacuo at 120 °C for 6 h (0.13 g). $[\alpha]_D$ −14.3° (*c* 0.8, benzene). ^{1}H NMR (C_6D_6): δ 4.10−3.76 (br, 2H), 2.34−2.12 (br, 4H), 1.80−1.59 (br, 4H). ^{1}H NMR (C_6D_6): δ 78.9−73.0, 32.0−30.0, 23.3−21.0. IR (KBr, cm^{-1}): 3371, 3278, 1470, 1461, 1350, 1165, 1080, 1063, 912, 836, 768.

The filtrate was evaporated to dryness and the residue was dissolved in water (10 mL). The insoluble part was removed by filtration and the filtrate was extracted with ethyl acetate (10 mL) three times. The combined organic layer was dried over $MgSO_4$ and the solvent was evaporated to yield a white solid, which was purified by silica gel column chromatography with ethyl acetate as an eluent (0.11 g, 96% yield). $[\alpha]_D$ −28.8° (*c* 0.11, H_2O). (lit.[56] $[\alpha]_D^{20}$ −39° (*c* 1.6, H_2O)). The ^{1}H NMR ($CDCl_3$), ^{13}C NMR ($CDCl_3$), IR (KBr), and mp data were identical with those described above.

^{1}H NMR Observation of Exchange of Axial Ligands Between Two Types of Aluminum Complexes.[63] A $CDCl_3$ (10 mL) solution of **4**AlOAc (100 mg, 0.25 mmol) was mixed to a $CDCl_3$ (5.0

mL) solution of $[\mathbf{2i}AlO^tBu]_2$ (77 mg, 0.125 mmol) with stirring in a 50-mL flask equipped with a three-way stopcock at room temperature. An aliquot (0.5 mL) of the above reaction mixture was transferred into a glass tube (o.d. = 5 mm) by a syringe under N_2. After, the glass tube was then sealed under N_2, ^{1}H NMR spectrum of the sample was measured at predetermined times.

Measurements. ^{1}H and ^{13}C NMR measurements were performed with $CDCl_3$ as the solvent at 30 °C on a Bruker DPX-300 (300 MHz) or DPX-400 spectrometer (400 MHz). Chemical shifts were determined with respected to tetramethylsilane (δ = 0.00 ppm) and $CHCl_3$ (δ = 7.26 ppm) for ^{1}H NMR, and $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR as the internal standard. ^{27}Al NMR measurements were performed with external referencing method using the saturated C_6D_6 solution of the sample ($[\mathbf{2g}AlMe]_2$ or $[\mathbf{2g}AlMe]_2$−bis-*N*-MeIm (1:1)) in the outer tube and the D_2O solution (0.5 M) of $Al(NO_3)_3$ (δ = 0.0 ppm) as the external reference in the inset tube at 30 °C on a Bruker DPX-400 spectrometer (400 MHz). IR spectra were recorded with a Horiba FT-720 spectrometer. Optical rotations were measured on a Horiba SEPA-300 polarimeter using 1-dm cell at room temperature (25−27 °C). Mass spectra were recorded on a JEOL JMS-SX102A spectrometer. Single crystal X-ray diffraction was performed on a Bruker AXS SMART APEX system at 100 or 173 K. The intensity data were collected on a Bruker SMART CCD diffractometer. The structure was solved by direct method and refined with SHELXTL program package (*SAINT-Plus*, version 6.02, *SHELXS-97*: *Program for Crystal Structure Solution, SHELXL-97*: *Program for Crystal Structure Refinement*, *SHELXTL*, version 5.0).[77] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions with isotropic thermal parameters. Gel Permeation chromatography (GPC) was performed at 40 °C on a Tosoh model HLC-8220 high-speed liquid chromatograph equipped with two series-connected TSK-GEL GMH_{HR}-H columns, a differential refractometer detector with THF as an eluent at a flow rate of 1.0 mL min^{-1}. The molecular weight calibration curve was obtained with standard polystyrenes (TSK standard polystyrene from Tosoh Co.); M_ws by light scattering (M_w/M_n by GPC) were as follows: 1.89×10^5 (1.04), 9.89×10^4 (1.01), 3.72×10^4 (1.01), 1.71×10^4 (1.01), 9.83×10^3 (1.02), 5.87×10^3 (1.02), 2.5×10^3 (1.05).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, spectral data of the copolymer, ^{1}H NMR study of alkoxide and carboxylate exchange, a ^{27}Al NMR study, optimized structures, and crystallographic data and tables giving full details of the complexes $[\mathbf{2g}AlMe]_2$ and $\mathbf{3}_2AlMe$ including crystallographic information files (cif). This material is available free of charge via Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Reszko, A. E.; Kasumov, T.; Pierce, B. A.; David, F.; Hoppel, C. L.; Stanley, W. C.; Rosiers, C. D.; Brunengraber, H. *J. Biol. Chem.* **2003**, *278*, 34959−34965.

(2) For comprehensive reviews on utilization of CO_2 as feedstock, see: (a) Inoue, S.; Yamazaki, N. *Organic and Bioorganic Chemistry of Carbon Dioxide*: Kodansha: Tokyo, Japan, 1981. (b) *Utilization of Greenhouse Gases*; Liu, C.-J., Mallinson, R. G., Aresta, M., Eds.; ACS Symposium Series 852; American Chemical Society: Washington, DC, 2003. (c) *Advances in CO_2 Conversion and Utilization*; Hu, Y. H. ed.; ACS Symposium Series 1056; American Chemical Society: Washington, DC, 2010. (d) *Carbon Dioxide as Chemical Feedstock*; Aresta, M., Ed.; Wiley-VCH Verlag: Weinheim, Germany, 2010.

(3) For reviews on transformation of CO_2 into chemicals via C−C bond formation, see: (a) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661−678. (b) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747−764. (c) Leitner, W. *Angew. Chem., Int. Ed.* **1995**, *34*, 2207−2221. (d) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953−996. (e) Aresta, M.; Dibenedetto, A. *Dalton Trans.* **2007**, 2975−2992. (f) Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365−2387. (g) Sakakura, T.; Kohno, K. *Chem. Commun.* **2009**, 1312−1330. (h) Riduan, S. N.; Zhang, Y.-G. *Dalton Trans.* **2010**, *39*, 3347−3357. (i) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kühn, F. E. *Angew. Chem., Int. Ed.* **2011**, *50*, 8510−8537.

(4) For reviews on alternating copolymerization of CO_2 and epoxide, see: (a) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155−174. (b) Kuran, W. *Prog. Polym. Sci.* **1998**, *23*, 919−992. (c) Nozaki, K. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 215−221. (d) Sugimoto, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5561−5573. (e) Darensbourg, D. J.; Mackiewicz, R. M.; Phelps, A. L.; Billodeaux, D. R. *Acc. Chem. Res.* **2004**, *37*, 836−844. (f) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618−6639. (g) Sugimoto, H.; Inoue, S. *Pure Appl. Chem.* **2006**, *78*, 1823−1834. (h) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388−2410. (i) Luinstra, G. A. *Polym. Rev.* **2008**, *48*, 192−219. (j) Coates, G. W.; Jeske, R. C. Homogeneous Catalyst Design for the Synthesis of Aliphatic Polycarbonates and Polyesters. *In Handbook of Green Chemistry, Vol. 1: Homogeneous Catalysis*; Crabtree, R. H., Ed.; Wiley-VCH Verlag: Weinheim, Germany, 2009; Chapter 15, pp 343−373. (k) Darensbourg, D. J. *Inorg. Chem.* **2010**, *49*, 10765−10780. (l) Kember, M. R.; Buchard, A.; Williams, C. K. *Chem. Commun.* **2011**, *47*, 141−163. (m) Klaus, S.; Lehenmeier, M. W.; Anderson, C. E.; Rieger, B. *Coord. Chem. Rev.* **2011**, *255*, 1460−1479. (n) Lu, X.-B.; Darensbourg, D. J. *Chem. Soc. Rev.* **2012**, *41*, 1462−1484.

(5) (a) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B: Polym. Lett.* **1969**, *7*, 287−292. (b) Inoue, S.; Koinuma, H.; Tsuruta, T. *Makromol. Chem.* **1969**, *130*, 210−220.

(6) Diethylzinc−dihydric or trihydric compounds systems, see: (a) Kobayashi, M.; Inoue, S.; Tsuruta, T. *Macromolecules* **1971**, *4*, 658−659. (b) Inoue, S.; Kobayashi, M.; Koinuma, H.; Tsuruta, T. *Makromol. Chem.* **1972**, *155*, 61−73. (c) Kobayashi, M.; Tang, Y.-L.; Tsuruta, T.; Inoue, S. *Makromol. Chem.* **1973**, *169*, 69−81. (d) Kuran, W.; Pasynkiewicz, S.; Skupinska, J.; Rokicki, A. *Makromol. Chem.* **1976**, *177*, 11−20. (e) Kuran, W.; Pasynkiewicz, S.; Skupinska, J. *Makromol. Chem.* **1976**, *177*, 1283−1292. (f) Kuran, W.; Pasynkiewicz, S.; Skupinska, J. *Makromol. Chem.* **1977**, *178*, 47−54. (g) Kuran, W.; Pasynkiewicz, S.; Skupinska, J. *Makromol. Chem.* **1977**, *178*, 2149−2158. (h) Kuran, W.; Rokicki, A.; Wilinska, E. *Makromol. Chem.* **1979**, *180*, 361−366. (i) Rokicki, A.; Kuran, W. *Makromol. Chem.* **1979**, *180*,

2153–2161. (j) Kuran, W.; Listos, T. *Macromol. Chem. Phys.* **1994**, *195*, 977–984.

(7) Zinc carboxylate systems, see: (a) Soga, K.; Uenishi, K.; Hosoda, S.; Ikeda, S. *Makromol. Chem* **1977**, *178*, 893–897. (b) Soga, K.; Hyakkoku, K.; Ikeda, S. *Makromol. Chem* **1978**, *179*, 2837–2843. (c) Soga, K.; Uenishi, K.; Ikeda, S. *J. Polym. Sci.: Polym. Chem. Ed.* **1979**, *17*, 415–423. (d) Super, M.; Berluche, E.; Costello, C.; Beckman, E. *Macromolecules* **1997**, *30*, 368–372. (e) Sarbu, T.; Beckman, E. J. *Macromolecules* **1999**, *32*, 6904–6912. (f) Darensbourg, D. J.; Zimmer, M. S. *Macromolecules* **1999**, *32*, 2137–2140. (g) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C. *Inorg. Chem.* **2002**, *41*, 973–980.

(8) Zinc dicarboxylate systems, see: (a) Kobayashi, M.; Inoue, S.; Tsuruta, T. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 2383–2385. (b) Hino, Y.; Yoshida, Y.; Inoue, S. *Polym. J.* **1984**, *16*, 159–163. (c) Soga, K.; Imai, E.; Hattori, I. *Polym. J.* **1981**, *13*, 407–410. (d) Darensbourg, D. L.; Stafford, N. W.; Katsurao, T. *J. Mol. Catal. A: Chem.* **1995**, *104*, L1–L4. (e) Ree, M.-H.; Bae, J. Y.; Jung, J. H.; Shin, T. J. *J. Polym. Sci.; Part A: Polym. Chem.* **1999**, *37*, 1863–1876. (f) Kim, J.-S.; Ree, M.-H.; Shin, T. J.; Han, O. H.; Cho, S. J.; Hwang, Y.-T.; Bae, J. Y.; Lee, J. M.; Ryoo, R.; Kim, H.-S. *J. Catal.* **2003**, *218*, 209–219. (g) Ree, M.-H.; Hwang, Y.-T.; Kim, J.-S.; Kim, H.-C.; Kim, G.-H.; Kim., H.-S. *Catal. Today* **2006**, *115*, 134–145. (h) Chisholm, M. H.; Navarro-Llobet, D.; Zhou, Z. *Macromolecules* **2002**, *35*, 6494–6504. (i) Meng, Y. Z.; Du, L. C.; Tiong, S. C.; Zhu, Q.; Hay, A. S. *J. Polym. Sci.; Part A: Polym. Chem.* **2002**, *40*, 3579–1876. (j) Gao, L. J.; Xiao, M.; Wang, S. J.; Du, F. G.; Meng, Y. Z. *J. Appl. Polym. Sci.* **2007**, *104*, 15–20. (k) Eberhardt, R.; Allmendinger, M.; Zintl, M.; Troll, C.; Luinstra, G. A.; Rieger, B. *Macromol. Chem. Phys.* **2004**, *205*, 42–47. (l) Klaus, S.; Lehenmeier, M. W.; Herdtweck, E.; Deglmann, P.; Ott, A. K.; Rieger, B. *J. Am. Chem. Soc.* **2011**, *133*, 13151–13161 and references cited therein..

(9) Double metal cyanides, see: (a) Darensbourg, D. J.; Adams, M. J.; Yarbrough, J. C. *Inorg. Chem.* **2001**, *40*, 6543–6544. (b) Darensbourg, D. J.; Adams, M. J.; Yarbrough, J. C.; Phelps, A. L. *Inorg. Chem.* **2003**, *42*, 7809–7818. (c) Chen, S.; Qi, G.-R.; Hua, Z.-J.; Yan, H.-Q. *J. Polym. Sci., Part A: Polym. Chem* **2004**, *42*, 5284–5291. (d) Chen, S.; Hua, Z.-J.; Fang, Z.; Qi, G.-R. *Polymer* **2004**, *45*, 6519–6524. (e) Sun, X.-K.; Zhang, X.-H.; Liu, F.; Chen, S.; Du, B.-Y.; Wang, Q.; Fan, Z.-Q.; Qi, G.-R. *J. Polym. Sci., Part A: Polym. Chem* **2008**, *46*, 3128–3139. (f) Kim, I.; Yi, M. J.; Byun, S. H.; Park, D. W.; Kim, B. U.; Ha, C. S. *Macromol. Symp.* **2005**, *224*, 181–191. (g) Robertson, N. J.; Qin, Z.-Q.; Dallinger, G. C.; Lobkovsky, E. B.; Lee, S.; Coates, G. W. *Dalton Trans.* **2006**, 5390–5395.

(10) Zinc phenoxide complexes, see: (a) Kuran, W. *Appl. Organomet. Chem.* **1991**, *5*, 191–194. (b) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577–7579. (c) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 107–116. (d) Darensbourg, D. J.; Zimmer, M. S.; Rainey, P.; Larkins, D. L. *Inorg. Chem.* **2000**, *39*, 1578–1585. (e) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 12487–12496. (f) Koning, C.; Wildeson, J.; Parton, R.; Plum, B.; Steeman, P.; Darensbourg, D. J. *Polymer* **2001**, *42*, 3995–4004. (g) Dinger, M. B.; Michael, J.; Scott, M. J. *Inorg. Chem.* **2001**, *40*, 1029–1036.

(11) Zinc β-diiminate complexes, see: (a) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018–11019. (b) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749. (c) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Angew. Chem., Int. Ed.* **2002**, *41*, 2599–2602. (d) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 14284–14285. (e) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2003**, *125*, 11911–11924. (f) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 11404–11405. (g) Kim, J. G.; Cowman, C. D.; LaPointe, A. M.; Wiesner, U.; Coates, G. W. *Macromolecules* **2011**, *44*, 1110–1113. (h) Eberhardt, R.; Allmendinger, M.; Luinstra, G. A.; Rieger, B. *Organometallics* **2003**, *22*, 211–214. (i) Yu, K.-Q.; Jones, C. W. *Organometallics* **2003**, *22*, 2571–2580. (j) Kröger, M.; Folli, C.; Walter, O.; Döring, M. *Adv. Synth. Catal.* **2005**, *347*, 1325–1328. (k) Kröger, M.; Döring, M. *Catal. Today* **2006**, *115*, 146–150. (l) Kröger, M.; Folli, C.; Walter, O.; Döring, M. *Adv. Synth. Catal.* **2006**, *348*, 1908–1918. (m) Kröger, M.; Folli, C.; Walter, O.; Döring, M. *J. Organomet. Chem.* **2006**, *691*, 3397–3402. (n) van Meerendonk, W. J.; Duchateau, R.; Koning, C. E.; Gruter, G.-J. M. *Macromol. Rapid Commun.* **2004**, *25*, 7306–7313.

(12) Zinc other ligand complexes, see: (a) Darensbourg, D. J.; Rainey, P.; Yarbrough, J. C. *Inorg. Chem.* **2001**, *40*, 986–993. (b) Walther, M.; Wermann, K.; Lutsche, M.; Günther, W.; Görls, H.; Anders, E. *J. Org. Chem.* **2006**, *71*, 1399–1406. (c) Liu, B.-Y.; Tian, C.-Y.; Zhang, L.; Yan, W.-D.; Zhang, W.-J. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 6243–6251. (d) Sugimoto, H.; Yamazaki, H. *Koubunshi Ronbunshu* **2007**, *64*, 676–682. (in Japanese). (e) Orchard, K. L.; Harris, J. E.; White, A. J. P.; Shaffer, M. S. P.; Williams, C. K. *Organometallics* **2011**, *30*, 2223–2229.

(13) Discrete bimetallic zinc complexes, see: (a) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S.; Yun, H.; Lee, H.; Park, Y. W. *J. Am. Chem. Soc.* **2005**, *127*, 3031–3037. (b) Bok, T.; Yun, H.; Lee, B. Y. *Inorg. Chem.* **2006**, *45*, 4228–4237. (c) Sugimoto, H.; Ogawa, A. *React. Funct. Polym.* **2007**, *67*, 1277–1283. (d) Pilz, M. F.; Limberg, C.; Lazarov, B. B.; Hultzsch, K. C.; Ziemer, B. *Organometallics* **2007**, *26*, 3668–3676. (e) Piesik, D. F.-J.; Range, S.; Harder, S. *Organometallics* **2008**, *27*, 6178–6187. (f) Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams., C. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 931–933. (g) Kember, M. R.; White, A. J. P.; Williams., C. K. *Inorg. Chem.* **2009**, *48*, 9535–9542. (h) Jutz, F.; Buchard, A.; Kember, M. R.; Fredriksen, S. B.; Williams., C. K. *J. Am. Chem. Soc.* **2011**, *133*, 17395–17405. (i) Lehenmeier, M. W.; Bruckmeier, C.; Klaus, S.; Dengler, J. E.; Deglmann, P.; Ott, A.-K.; Rieger, B. *Chem.—Eur. J.* **2011**, *17*, 8858–8869.

(14) Zinc chiral ligand complexes for asymmetric polymerizations, see: (a) Nozaki, K.; Nakano, K.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 11008–11009. (b) Nakano, K.; Nozaki, K.; Hiyama, T. *J. Am. Chem. Soc.* **2003**, *125*, 5501–5510. (c) Nakano, K.; Hiyama, T.; Nozaki, K. *Chem. Commun.* **2005**, 1871–1873. (d) Cheng, M.; Darling, N. A.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun.* **2000**, 2007–2008. (e) Xiao, Y.; Wang, Z.; Ding, K. *Chem.—Eur. J.* **2005**, *11*, 3668–3678.

(15) Magnesium complexes, see: Xiao, Y.; Wang, Z.; Ding, K. *Macromolecules* **2006**, *39*, 128–137.

(16) Aluminum porphinate complexes, see: (a) Takeda, N.; Inoue, S. *Makromol. Chem.* **1978**, *179*, 1377–1381. (b) Aida, T.; Ishikawa, M.; Inoue, S. *Macromolecules* **1986**, *19*, 8–13. (c) Jung, J. H.; Ree, M.; Chang, T. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3329–3336. (d) Chatterjee, C.; Chisholm, M. H. *Inorg. Chem.* **2011**, *50*, 4481–4492.

(17) Aluminum Schiff base complexes, see: (a) Sugimoto, H.; Ohtsuka, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 4172–4186. (b) Darensbourg, D. J.; Billodeaux, D. R. *Inorg. Chem.* **2005**, *44*, 1433–1442. (c) Chen, P.; Chisholm, M. H.; Gallucci, J. C.; Zhang, X.-Y.; Zhou, Z.-P. *Inorg. Chem.* **2005**, *44*, 2588–2595. (d) Alvaro, M.; Baleizao, C.; Carbonell, E.; El Ghoul, M.; García, H.; Gigante, B. *Tetrahedron* **2005**, *61*, 12131–12139.

(18) Aluminum other additive systems, see: (a) Koinuma, H.; Hirai, H. *Makromol. Chem* **1977**, *178*, 1283–1294. (b) Kuran, W.; Listos, T.; Abramczyk, M.; Dawidek, A. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **1998**, *35*, 427–437. (c) Zevaco, T. A.; Janssen, A.; Sypien, J.; Dinjus, E. *Green Chem.* **2005**, *7*, 659–666. (d) Zevaco, T. A.; Sypien, J.; Janssen, A.; Walter, O.; Dinjus, E. *Catal. Today* **2006**, *115*, 151–161.

(19) Titanium, germanium, and tin complexes, see: Nakano, K.; Kobayashi, K.; Nozaki, K. *J. Am. Chem. Soc.* **2011**, *133*, 10720–10723.

(20) Chromium porphinate complexes, see: (a) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. *Macromolecules* **2000**, *33*, 303–308. (b) Stamp, L. M.; Mang, S. A.; Holmes, A. B.; Knights, K. A.; de Miguel, Y. R.; McConvey, I. F. *Chem. Commun.* **2001**, 2502–2503.

(21) Chromium tetraazaannulene complexes, see: (a) Darensbourg, D. J.; Fitch, S. B. *Inorg. Chem.* **2007**, *46*, 5474−5476. (b) Darensbourg, D. J.; Fitch, S. B. *Inorg. Chem.* **2008**, *47*, 11868−11878. (c) Darensbourg, D. J.; Fitch, S. B. *Inorg. Chem.* **2009**, *48*, 8668−8677.

(22) Chromium Schiff base complexes, see: (a) Darensbourg, D. J.; Yarbrough, J. C.; Ortiz, C.; Fang, C. C. *J. Am. Chem. Soc.* **2003**, *125*, 7586−7591. (b) Darensbourg, D. J.; Rodgers, J. L.; Fang, C. C. *Inorg. Chem.* **2003**, *42*, 4498−4500. (c) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Phelps, A. L. *Inorg. Chem.* **2004**, *43*, 1831−1833. (d) Darensbourg, D. J.; Rodgers, J. L.; Mackiewicz, R. M.; Phelps, A. L. *Catal. Today* **2004**, *98*, 485−492. (e) Darensbourg, D. J.; Bottarelli, P.; Andreatta, J. R. *Macromolecules* **2007**, *40*, 7727−7729. (f) Hongfa, C.; Tian, J.-H.; Andreatta, J.; Darensbourg, D. J.; Bergbreiter, D. E. *Chem. Commun.* **2008**, 975−977. (g) Darensbourg, D. J.; Moncada, A. I. *Inorg. Chem.* **2008**, *47*, 10000−10008. (h) Darensbourg, D. J.; Ulusoy, M.; Karroonnirum, O.; Poland, R. R.; Reibenspies, J. H.; Çetinkaya, B. *Macromolecules* **2009**, *42*, 6992−6998. (i) Alvaro, M.; Baleizao, C.; Das, D.; Carbonell, E.; García, H. *J. Catal.* **2004**, *228*, 254−258. (j) Luinstra, G. A.; Haas, G. R.; Molnar, F.; Bernhart, V.; Eberhardt, R.; Rieger, B. *Chem.−Eur. J.* **2005**, *11*, 6298−6314. (k) Xu, X.-Q.; Wang, C.-M.; Li, H.-R.; Wang, Y.; Sun, W.-L.; Shen, Z.-Q. *Polymer* **2007**, *48*, 3921−3924. (l) Eberhardt, R.; Allmendinger, M.; Rieger, B. *Macromol. Rapid Commun.* **2003**, *24*, 194−196.

(23) Discrete bimetallic chromium complexes, see: (a) Vagin, S. I.; Reichardt, R.; Klaus, S.; Rieger, B. *J. Am. Chem. Soc.* **2010**, *132*, 14367−14369. (b) Klaus, S.; Vagin, S. I.; Lehenmeier, M. W.; Deglmann, P.; Brym, A. K.; Rieger, B. *Macromolecules* **2011**, *44*, 9508−9516.

(24) Chromium chiral Schiff base complexes, see: (a) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124*, 6335−6342. (b) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Fang, C. C.; Billodeaux, D. R.; Reibenspies, J. H. *Inorg. Chem.* **2004**, *43*, 6024−6034. (c) Darensbourg, D. J.; Mackiewicz, R. M.; Billodeaux, D. R. *Organometallics* **2005**, *24*, 144−148. (d) Darensbourg, D. J.; Phelps, A. L. *Inorg. Chem.* **2005**, *44*, 4622−4629. (e) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 14026−14038. (f) Rao, D.-Y.; Li, B.; Zhang, R.; Wang, H.; Lu, X.-B. *Inorg. Chem.* **2009**, *48*, 2830−2836. (g) Guo, L.-P.; Wang, C.-M.; Zhao, W.-J.; Li, H.-R.; Sun, W.-L.; Shen, Z.-Q. *Dalton Trans.* **2009**, 5406−5410.

(25) Chromium chiral Schiff base complexes for asymmetric polymerizations, see: (a) Li, B.; Zhang, R.; Lu, X.-B. *Macromolecules* **2007**, *40*, 2303−2307. (b) Niu, Y.-S.; Zhang, W.-X.; Pang, X.; Chen, X.-S.; Zhuang, X.-L.; Jing, X.-B. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5050−5056. (c) Li, B.; Wu, G.-P.; Ren, W.-M.; Wang, Y.-M.; Rao, D.-Y.; Lu, X.-B. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6102−6113. (d) Nakano, K.; Nakamura, M.; Nozaki, K. *Macromolecules* **2009**, *42*, 6972−6980.

(26) Manganese complexes, see: (a) Sugimoto, H.; Ohshima, H.; Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3549−3555. (b) Darensbourg, D. J.; Ganguly, P.; Billodeaux, D. R. *Organometallics* **2004**, *23*, 6025−6030. (c) Darensbourg, D. J.; Frantz, E. B. *Inorg. Chem.* **2007**, *46*, 5967−5978.

(27) Iron complexes, see: (a) Buchard, A.; Kember, M. R.; Sandemanb, K. G.; Williams, C. K. *Chem. Commun.* **2011**, *47*, 212−214. (b) Dengler, J. E.; Lehenmeier, M. W.; Klaus, S.; Anderson, C. E.; Herdtweck, E.; Rieger, B. *Eur. J. Inorg. Chem.* **2011**, 336−343.

(28) Cobalt Schiff base complexes, see: (a) Nakano, K.; Kamada, T.; Nozaki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 7274−7277. (b) Noh, E. K.; Na, S. J.; S, S.; Kim, S.-W.; Lee, B. Y. *J. Am. Chem. Soc.* **2007**, *129*, 8082−8083. (c) S, S.; Min, J. K.; Seong, J. E.; Na, S. J.; Lee, B. Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 7306−7309. (d) Na, S. J.; S, S.; Cyriac, A.; Kim, B. E.; Yoo, J.; Kang, Y. K.; Han, S. J.; Lee, C.; Lee, B. Y. *Inorg. Chem.* **2009**, *48*, 10455−10465. (e) Seong, J. E.; Na, S. J.; Cyriac, A.; Kim, B.-W.; Lee, B. Y. *Macromolecules* **2010**, *43*, 903−908. (f) Yoo, J.; Na, S. J.; Park, H. C.; Cyriac, A.; Lee, B. Y. *Dalton Trans.* **2010**, *39*, 2622−2630. (g) Cyriac, A.; Lee, S. H.; Varghese, J. K.; Park, E. S.; Park, J. H.; Lee, B. Y. *Macromolecules* **2010**, *43*, 7398−7401. (h) Cyriac, A.; Lee, S. H.; Lee, B. Y. *Polym. Chem.* **2011**, *2*, 950−956. (i) Ren, W.-M.; Liu, Z.-W.; Wen, Y.-Q.; Zhang, R.; Lu, X.-B. *J. Am. Chem. Soc.* **2009**, *131*, 11509−11518. (j) Liu, B.-Y.; Zhao, X.; Guo, H.-F.; Gao, Y.-H.; Yang, M.; Wang, X.-H. *Polymer* **2009**, *50*, 5071−5075.

(29) Cobalt chiral Schiff base complexes, see: (a) Cohen, C. T.; Thomas, C. M.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. *Dalton Trans.* **2006**, 237−249. (b) Niu, Y.-S.; Zhang, W.-X.; Pang, X.; Chen, X.-S.; Zhuang, X.-L.; Jing, X.-B. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 5050−5056. (c) Darensbourg, D. J.; Wilson, S. J. *J. Am. Chem. Soc.* **2011**, *133*, 18610−18613. (d) Ren, W.-M.; Zhang, X.; Liu, Y.; Li, J.-F.; Wang, H.; Lu, X.-B. *Macromolecules* **2010**, *43*, 1396−1402. (e) Wu, G.-P.; Wei, S.-H.; Lu, X.-B.; Ren, W.-M.; Darensbourg, D. J. *Macromolecules* **2010**, *43*, 9202−9204. (f) Wu, G.-P.; Wei, S.-H.; Ren, W.-M.; Lu, X.-B.; Xu, T.-Q.; Darensbourg, D. J. *J. Am. Chem. Soc.* **2011**, *133*, 15191−15199.

(30) Cobalt chiral Schiff base complexes for asymmetric polymerizations: (a) Qin, Z.-Q.; Thomas, C. M.; Lee, S.; Coates, G. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5484−5487. (b) Cohen, C. T.; Chu, T.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869−10878. (c) Cohen, C. T.; Coates, G. W. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5182−5191. (d) Lu, X.-B.; Wang, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3574−3577. (e) Lu, X.-B.; Shi, L.; Wang, Y.-M.; Zhang, R.; Zhang, Y.-J.; Peng, X.-J.; Zhang, Z.-C.; Li, B. *J. Am. Chem. Soc.* **2006**, *128*, 1664−1674. (f) Shi, L.; Lu, X.-B.; Zhang, R.; Peng, X.-J.; Zhang, C.-Q.; Li, J.-F.; Peng, X.-M. *Macromolecules* **2006**, *39*, 5679−5685. (g) Ren, W.-M.; Zhang, W.-Z.; Lu, X.-B. *Sci. China* **2010**, *53*, 1646−1652. (h) Ren, W.-M.; Liu, Y.; Wu, G.-P.; Liu, J.; Lu, X.-B. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4894−4901. (i) Wu, G.-P.; Wei, S.-H.; Ren, W.-M.; Lu, X.-B.; Li, B.; Zu, Y.-P.; Darensbourg, D. J. *Energy Environ. Sci.* **2011**, *4*, 5084−5092. (j) Wu, G.-P.; Ren, W.-M.; Luo, Y.; Li, B.; Zhang, W.-Z.; Lu, X.-B. *J. Am. Chem. Soc.* **2012**, *134*, 5682−5688. (k) Paddock, R. L.; Nguyen, S. T. *Macromolecules* **2005**, *38*, 6251−6253. (l) Nakano, K.; Hashimoto, S.; Nakamura, M.; Kamada, T.; Nozaki, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 4868−4871.

(31) Cobalt porphinate complexes, see: (a) Sugimoto, H.; Kuroda, K. *Macromolecules* **2008**, *41*, 312−317. (b) Qin, Y.-S.; Wang, X.-H.; Zhang, S.-B.; Zhao, X.-J.; Wang, F.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5959−5967.

(32) Cobalt β-ketoiminate complexes, see: Okada, A.; Kikuchi, S.; Nakano, K.; Nishioka, K.; Nozaki, K.; Yamada, T. *Chem. Lett.* **2010**, *39*, 1066−1068.

(33) Bimetallic cobalt complexes, see: (a) Nakano, K.; Hashimoto, S.; Nozaki, K. *Chem. Sci.* **2010**, *1*, 369−373. (b) Kember, M. R.; White, A. J. P.; Williams, C. K. *Macromolecules* **2010**, *43*, 2291−2298.

(34) Rare-earth-metal complexes, see: (a) Chen, X.-H.; Shen, Z.-Q.; Zhang, Y.-F. *Macromolecules* **1991**, *24*, 5305−5308. (b) Tan, C.-S.; Hsu, T.-J. *Macromolecules* **1997**, *30*, 3147−3150. (c) Hsu, T.-J.; Tan, C.-S. *Polymer* **2001**, *42*, 5143−5150. (d) Liu, B.-Y.; Zhao, X.-J.; Wang, X.-H.; Wang, F.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2751−2754. (e) Quan, Z.-L.; Min, J.-D.; Zhou, Q.-H.; Xie, D.; Liu, J.-J.; Wang, X.-H.; Zhao, X.-J.; Wang, F.-S. *Macromol. Symp.* **2003**, *195*, 281−286. (f) Liu, B.-Y.; Zhao, X.-J.; Wang, X.-H.; Wang, F.-S. *Polymer* **2003**, *44*, 1803−1808. (g) Quan, Z.-L.; Wang, X.-H.; Zhao, X.-J.; Wang, F.-S. *Polymer* **2003**, *44*, 5605−5610. (h) Nikitinskii, A. V.; Bochkarev, L. N.; Khorshev, S. Y.; Bochkarev, M. N. *Russ. J. Gen. Chem.* **2004**, *74*, 1197−1200. (i) Cui, D.-M.; Nishiura, M.; Hou, Z.-M. *Macromolecules* **2005**, *38*, 4089−4095. (j) Cui, D.-M.; Nishiura, M.; Tardif, O.; Hou, Z.-M. *Organometallics* **2008**, *27*, 2428−2435. (k) Zhang, Z.-C.; Cui, D.-M.; Liu, X.-L. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 6810−6818. (l) Vitanova, D. V.; Hampel, F.; Hultzsch, K. C. *J. Organomet. Chem.* **2005**, *690*, 5182−5197. (m) Lazarov, B. B.; Hampel, F.; Hultzsch, K. C. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2367−2373. (n) Kobayashi, S.; Akiyama, R.; Suzuki, K.; Fujimoto, K. Jpn. Kokai Tokkyo Koho JP2009242794, 2009.

(35) Jedliñski, Z. J.; Bero, M.; Kasperczyk, J.; Kowalczuk, M. Polymerization of Substituted Oxiranes, Epoxy Aldehydes, and Derived Oxacyclic Monomers. In *Ring-Opening Polymerization: Kinetics, Mechanisms, and Synthesis*; McGrath, J. E., Ed.; ACS Symposium Series 286; American Chemical Society: Washington, DC, 1986; Chapter 16, pp 205−217.

(36) (a) Takimoto, M.; Nakamura, Y.; Kimura, K.; Mori, M. *J. Am. Chem. Soc.* **2004**, *126*, 5956−5957. (b) Mori, M. *Eur. J. Org. Chem.* **2007**, 4981−4993.

(37) (a) Yoshida, S.; Fukui, K.; Kikuchi, S.; Yamada, T. *J. Am. Chem. Soc.* **2010**, *132*, 4072−4073. (b) Kikuchi, S.; Yoshida, S.; Sugawara, Y.; Yamada, W.; Cheng, H.-M.; Fukui, K.; Sekine, K.; Iwakura, I.; Ikeno, T.; Yamada, T. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 698−717.

(38) (a) Tanaka, H.; Kitaichi, Y.; Sato, M.; Ikeno, T.; Yamada, T. *Chem. Lett.* **2004**, *33*, 676−677. (b) Lu, X.-B.; Liang, B.; Zhang, Y.-J.; Tian, Y.-Z.; Wang, Y.-M.; Bai, C.-X.; Wang, H.; Zhang, R. *J. Am. Chem. Soc.* **2004**, *126*, 3732−3733. (c) Paddock, R. L.; Nguyen, S. T. *Chem. Commun.* **2004**, 1622−1623. (d) Berkessel, A.; Brandenburg, M. *Org. Lett.* **2006**, *8*, 4401−4404. (e) Chen, S.-W.; Kawthekar, R. B.; Kim, G.-J. *Tetrahedron Lett.* **2007**, *48*, 297−300. (f) Yamada, W.; Kitaichi, Y.; Tanaka, H.; Kojima, T.; Sato, M.; Ikeno, T.; Yamada, T. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1391−1401. (g) Jin, L.-L.; Huang, Y.-Z.; Jing, H.-W.; Chang, T.; Yan, P. *Tetrahedron: Asym.* **2008**, *19*, 1947−1953. (h) Chan, T.; Jin, L.-L.; Jing, H.-W. *ChemCatChem* **2009**, *1*, 379−383. (i) Yan, P.; Jing, H.-W. *Adv. Synth. Catal.* **2009**, *351*, 1325−1332.

(39) Alaaeddine, A.; Roisnel, T.; Thomas, C. M.; Carpentier, J.-F. *Adv. Synth. Catal.* **2008**, *350*, 731−740.

(40) Duxbury, J. P.; Warne, J. N. D.; Mushtaq, R.; Ward, C.; Thornton-Pett, M.; Jiang, M.; Greatrex, R.; Kee, T. P. *Organometallics* **2000**, *19*, 4445−4457.

(41) Doherty, S.; Errington, R. J.; Housley, N.; Clegg, W. *Organometallics* **2004**, *23*, 2382−2388.

(42) (a) Gelbrich, T.; Hecht, E.; Thiele, K.-H.; Sieler, J. *J. Organomet. Chem.* **2000**, *595*, 21−30. (b) Hecht, E.; Gelbrich, T.; Thiele, K.-H.; Sieler, J. *Z. Anorg. Allg. Chem.* **2000**, *626*, 180−186.

(43) Williams, O. F.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 4464−4469.

(44) Galsbøl, F.; Steenbøl, P.; Sørensen, B. S. *Acta Chem. Scand.* **1972**, *26*, 3605−3611.

(45) Veldhuizen, J. J. V.; Gillingham, D. G.; Garber, S. B.; Kataoka, O.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 12502−12508.

(46) (a) Pan, W.; Feng, X.; Gong, L.; Hu, W.; Li, Z.; Mi, A.; Jiang, Y. *Synlett* **1996**, 337−338. (b) Jiang, Y.; Gong, L.; Feng, X.; Hu, W.; Pan, W.; Li, Z.; Mi, A. *Tetrahedron* **1997**, *53*, 14327−14338.

(47) Bryliakov, K. P.; Talsi, E. P. *Eur. J. Org. Chem.* **2008**, 3369−3376.

(48) Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X.; Zepp, C. M. *J. Org. Chem.* **1994**, *59*, 1939−1942.

(49) McKennon, M. J.; Meyers, A. I.; Drauz, K.; Schwarm, M. *J. Org. Chem.* **1993**, *58*, 3568−3571.

(50) Lim, S.; Choi, B.; Min, Y.-S.; Kim, D.; Yoon, I.; Lee, S. S.; Lee, I.-M. *J. Organomet. Chem.* **2004**, *689*, 224−237.

(51) Bhaskar Kanth, J. V.; Periasamy, M. *Tetrahedron* **1993**, *49*, 5127−5132.

(52) Examples of binuclear aluminum complexes formed via μ-O linkages effective for cyclic carbonate synthesis from CO_2 and epoxide, see: (a) Meléndez, J.; North, M.; Pasquale, R. *Eur. J. Inorg. Chem.* **2007**, 3323−3326. (b) Meléndez, J.; North, M.; Villuendas, P. *Chem. Commun.* **2009**, 2577−2579. (c) Clegg, W.; Harrington, R. W.; North, M.; Pasquale, R. *Chem.−Eur. J.* **2010**, *16*, 6826−6843.

(53) (a) Delpuech, J. J. In *NMR of Newly Accessible Nuclei*; Lazlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, pp 153−195. (b) Benn, R.; Rufińska, A.; Lehmkuhl, H.; Janssen, E.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 779−780. (c) Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufińska, A. *J. Organomet. Chem.* **1987**, *333*, 155−168. (d) Wang, Y.; Parkin, S.; Atwood, D. *Inorg. Chem.* **2002**, *41*, 558−565.

(54) To investigate dimer structure of the complex [**2g**AlMe]$_2$ in solution, geometry optimizations of dimeric structures were performed using the DMol^3 module as implemented in the Material Studio software (version 5.5: Accerlys Inc.) (Figure S3 in the Supporting Information). On the basis of the dimeric structure (A) of [**2g**AlMe]$_2$ (*R*-form) clarified by single crystal X-ray analysis, we first focused our attention on the structure A and other two structures (B and C): two methyl groups in the *syn* arrangement (A), one methyl and the other in the *syn* and *anti* arrangements, respectively, (B), and two methyl groups in the *anti* arrangement (C) against two phenyl groups. The structures are expectedly formed under kinetic (but not thermodynamic) control after the mixture of Me_3Al and **2g**H. This is owing to no observation of an exchange between axial alkyl ligands of two different aluminum porphyrin complexes, see: (a) Aida, T.; Sugimoto, H.; Kuroki, M.; Inoue, S. *J. Phys. Org. Chem.* **1995**, *8*, 249−257. The geometry optimizations of the structures (A−C) resulted in small differential energies between the structures (less than −1 kcal/mol), suggesting that the formations of the structures A−C are possible. In addition, the structure A may be stabilized through CH$\cdots\pi$ interaction between methyl and phenyl groups (the distance = 3.5−4 Å) though the structure A seems to be unfavorable due to steric repulsion. We previously reported an example that the *syn* form (the direction of one methyl group is the same as those of four phenyl groups) of the methylaluminum tetrakis(2′-phenylphenyl)porphyrinate is more stable than the anti form (the direction of one methyl group is opposite to those of four phenyl groups), see: (b) Sugimoto, H.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1411−1412 . Subsequently, the types (structures A and D−F) of the μ-O linkages were examined. The structure A was the most stable by over 10 kcal/mol among four structures in relation with dimer formation via two μ-O linkages (A, D−F) (in the *syn* arrangement against two phenyl groups). This shows that the structure A is more favorable than the structures D−F.

(55) Reviews, see: (a) Jacobsen, E. N.; Wu, M. H. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds., Springer: Berlin, 1999; Vol. 2, Chapter 18.2, pp 649−677. (b) Katsuki, T. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed., Wiley-VCH: Ney York, 2000; Chapter 6B, pp 287−325. (c) Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33*, 421−431. (d) Katsuki, T. *Chem. Soc. Rev.* **2004**, *33*, 437−444.

(56) Estimated by comparing with specific rotations of commercially available optically active diols [(1*R*,2*R*)-*trans*-1,2-cyclopentanediol ($[\alpha]_D^{20}$ −21° (*c* 1.0, $CHCl_3$)), (1*R*,2*R*)-*trans*-1,2-cyclohexanediol ($[\alpha]_D^{20}$ −39° (*c* 1.6, H_2O)), and (1*R*,2*R*)-*trans*-1,2-cyclooctanediol ($[\alpha]_D^{22}$ +16.9° (*c* 1.33, EtOH) for (1*S*,2*S*)-isomer] as the references, see: (a) Sigma-Aldrich catalog 2009−2010. (b) Corey, E. J.; Shulman, J. I. *Tetrahedron Lett.* **1968**, *33*, 3655−3658.

(57) Recent examples of asymmetric reaction on temperature effect, see: (a) Czarnecki, P.; Plutecka, A.; Gawroñski, J.; Kacprzak, K. *Green Chem.* **2011**, *13*, 1280−1287. (b) Huynh, K.-D.; Ibrahim, H.; Kolodziej, E.; Toffano, M.; Vo-Thanh, G. *New J. Chem.* **2011**, *35*, 2622−2631. (c) Wu, R.; Chang, X.; Lu, A.; Wang, Y.; Wu, G.; Song, H.; Zhou, Z.; Tang, C. *Chem. Commun.* **2011**, *47*, 5034−5036.

(58) (a) Aida, T. *Prog. Polym. Sci.* **1994**, *19*, 469−528. (b) Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39−48. (c) Inoue, S. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2861−2871.

(59) Reviews on polymerization of lactide with metal complexes, see: (a) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *Dalton Trans.* **2001**, 2215−2224. (b) Chisholm, M. H.; Zhou, Z. *J. Mater. Chem.* **2004**, *14*, 3081−3092. (c) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147−6176. (d) Wu, J.; Yu, T.-L.; Chen, C.-T.; Lin, C.-C. *Coord. Chem. Rev.* **2006**, *250*, 602−626. (e) Dove, A. P. *Chem. Commun.* **2008**, 6446−6470.

(60) (a) Spassky, N.; Wisniewski, M.; Pluta, C.; Le Borgne, A. *Macromol. Chem. Phys.* **1996**, *197*, 2627−2637. (b) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *J. Am. Chem. Soc.* **2003**, *125*, 11291−11298. (c) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; Pugh, R. I.; White, A. J. P. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15343−15348.

(61) Reviews, see: (a) Drauz, K.; Kleeman, A.; Martens, J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 584−608. (b) Ager, D. J.; Prakash, I.; Schaad, D. R. *Chem. Rev.* **1996**, *96*, 835−875. (c) Gennari, C.; Piaruli, U. *Chem. Rev.* **2003**, *103*, 3071−3100. (d) Jandeleit, B.; Schaefer, D. J.; Powers, T. S.; Turner, H. W.; Weinberg, W. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2494−2532. (e) Davie, E. A. C.; Mennen, S. M.; Xu, Y.; Miller, S. J. *Chem. Rev.* **2007**, *107*, 5759−5812. (f) Paradowska, J.; Stodulski, M.; Mlynarski, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 4288−4297.

(62) (a) John, A. *Dean Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill: New York, 1999. (b) Kaljurand, I.; Kütt, A.; Sooväli, L.;

Rodima, T.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2005**, *70*, 1019−1028.

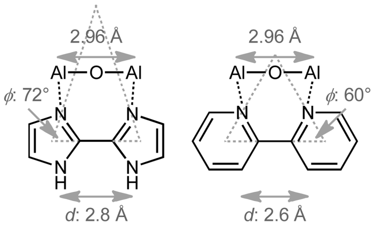
(63) Asano, S.; Aida, T.; Inoue, S. *Macromolecules* **1985**, *18*, 2057−2061.

(64) To investigate whether the (A) or (C) form of optimized geometries of [**2g**AlMe]$_2$−bisimidazoles (bis-*N*-MeIm and bis-*N*-MeBzIm) is stable, geometry optimizations of the systems were performed using the Forcite module as implemented in the Material Studio software (version 5.5: Accerlys Inc.) (Figure S5 in the Supporting Information). Both (A) forms of [2gAlMe]$_2$−bis-*N*-MeIm and −bis-*N*-MeBzIm) (*R*-form) are more stable than the (C) forms.

(65) Konishi, K.; Oda, K.; Nishida, K.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1992**, *114*, 1313−1317.

(66) Park, S. B.; Alper, H. *Org. Lett.* **2003**, *5*, 3209−3212.

(67) Although DMAP was the most preferential ligands among Lewis bases utilized for asymmetric alternating copolymerization of CO_2 and CHO, bisimidazole was chosen as a following reason. The distance (Al−O−Al) between two aluminums via μ-O linkages is 2.96 Å based on X-ray data of [**2g**AlMe]$_2$. The angle (ϕ) of the lone pairs on nitrogens on the imidazole or the pyridine ring against the extension line of the bond linking two rings and the distance (d) between the nitrogens are important factors for the coordination of the diamine to the aluminum complex (vide infra). The angle (ϕ) of bipyridine is smaller (ca. 10°) than that of bisimidazole and the distance (d) of bipyridine (2.6 Å) is shorter (ca. 0.2 Å) than that of bisimidazole (2.8 Å). On the basis of these data, the coordination of bisimidazole was expected to be more facile than that of bipyridine. An example on the coordination of bisimidazole to two rheniums via μ-O linkages, see: (a) Fortin, S.; Beauchamp, A. L. *Inorg. Chem.* **2000**, *39*, 4886−4893. Recent examples on the coordination of 2,2′-bipyridine to two metals via μ-O linkages, see: (b) Moreira, F. F.; Hasegawa, T.; Evans, D. J.; Nunes, F. S. *J. Coord. Chem.* **2007**, *60*, 185−191. (c) Pang, H.-J.; Sha, J.-Q.; Peng, J.; Tian, A.-X.; Zhang, C.-J.; Zhang, P.-P.; Chen, Y.; Zhu, M.; Wang, Y.-H. *Inorg. Chem. Commun.* **2009**, *12*, 735−738. Structures discussed.



(68) Sugimoto, H.; Kawamura, C.; Kuroki, M.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 2013−2018.

(69) (a) Strowieyski, K. B.; Pasynkiewicz, S.; Skowronska-Ptasinska, M. *J. Organomet. Chem.* **1975**, *90*, C43−C44. (b) Maruoka, K.; Itoh, T.; Sakurai., M.; Nonoshita, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 3588−3597.

(70) Our research on this theme has preliminarily been presented in an international symposium: Nishioka, K. and Sugimoto H. preliminarily presented at Pacifichem 2005, Honolulu (HI), December, 2005. Since then, we have prepared our manuscript. Before submission of our manuscript, Lu, X.-B. and co-workers reported the synthesis of poly(cyclohexene carbonate) composed of 96%ee (*R*,*R*) of 1,2-cyclohexanediol units via the alternating copolymerization of CO_2 and CHO with enantiopure cobalt(III)-salen complexes in optically pure (*S*)-2-methyltetrahydrofuran as the solvent.[30j]

(71) Oligo- or poly(cyclohexene oxide) comprised of enantiometically pure monomeric units ((1*R*,2*R*)- or (1*S*,2*S*)-oxycyclohexane-1,2-diyl units) has never been reported though asymmetric synthesis polymerization of *meso*-epoxide (CHO) with chiral initiator systems was performed. This is owing to no way for estimating the enantiomeric excess of the monomeric units. We were also not able to investigate the ees of the repeating units composing of oligo- or polyethers. Spassky, N.; Momtaz, A.; Kassamaly, A.; Sepulchre, M. *Chirality* **1992**, *4*, 295−299.

(72) Reviews, see: (a) Mukherjee, S.; Yang, J. W.; Hoffmann, S.; List, B. *Chem. Rev.* **2007**, *107*, 5471−5569. (b) Moyano, A.; Rios, R. *Chem. Rev.* **2011**, *111*, 4703−4832. (c) Jensen, K. L.; Dickmeiss, G.; Jiang, H.; Albrecht, L.; Jorgensen, K. A. *Acc. Chem. Rev.* **2012**, *45*, 248−264.

(73) (a) Braun, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *5*, 519−522. (b) Trost, B. M.; Ito, H. *J. Am. Chem. Soc.* **2000**, *122*, 12003−12004. (c) Trost, B. M.; Ito, H.; Silcoff, E. R. *J. Am. Chem. Soc.* **2001**, *123*, 3367−3368. (d) Cho, B. T. *Chem. Soc. Rev.* **2009**, *38*, 443−452.

(74) Murata, S.; Suzuki, M.; Noyori, R. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 247−254.

(75) Bacskai, R. *J. Polym. Sci., Part A: Gen. Pap.* **1963**, *1*, 2777−2790.

(76) Landers, A. E.; Phillips, D. J. *Inorg. Chim. Acta* **1979**, 32, 53−58.

(77) (a) *SHELXS-97: Program for the Solution of Crystal Structures*: Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *A46*, 467−473. (b) Sheldrick, G. M. *Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.