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Highly stable methylaluminum dimer complex with chiral tridentate ligand

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ABSTRACT

The dimeric aluminum complex containing fully deprotonated 4-{[(1*S*,2*R*)-2-hydroxyindan-1-yl]amino}-pent-3-en-2-one was synthesized and characterized. X-ray analysis revealed that the two five-coordinate aluminum centers possess ideal tetragonal pyramid geometry and two methyl groups are located in *cis* position. It is found to be stable in the presence of isopropanol at room temperature. The compound was used as a catalyst for the ring opening polymerization of lactide accompanying lactide epimerization.

A large variety of aluminum complexes has been reported, and their performance in many applications including catalysis and organic light-emitting diodes was studied [1–3]. In particular, they have been used as efficient catalytic systems for the controlled ring opening polymerization of lactide (LA), which provides high activity at low reaction temperature.

Aluminum prefers 5 or 6 coordination geometry around a metal center. For example, monoanionic bidentate ligands can easily form AlX_3 type aluminum complex, such as Alq_3 (tris(8-hydroxyquinolinato)aluminum) [4–8]. Aluminum can easily be ligated by tetradentate ligands such as salen (N,N′-ethylenebis(salicylimine)) [3,9–12] or triethanolamine ligands to form an Al complex with 5 coordination geometry. Although a number of aluminum complexes bearing *mer*-type ligand have been reported [13], aluminum complexes containing *mer*-type tridentate ligands are relatively rare due to the structural preference of Al metal. Recently, Darensbourg and Karroonnirun reported dimeric ethylaluminum complexes with tridentate half-salen-type ligands, in which complexes existed as two isomeric sets in an ethyl group attached to aluminum metal, resulting in the epimerization of D- and L-LA to meso-LA in the ring opening polymerization [14]. They also revealed that complexes which existed as only *trans* isomer produced isotactic polylactide (PLA) without any epimerization in the ring opening polymerization. Inspired by the lack of ring opening polymerization studies using aluminum catalysts in which alkyl groups existed in *cis* formation only, we designed a new chiral tridentate dianionic ligand derived from chiral aminoindanol and its aluminum complex.

As a new ONO-type tridentate dianionic chelating ligand, complex **1** was synthesized by the reaction of 2,4-pentanedione with (1*S*,2*R*)-(−)-*cis*-amino-2-indanol [15]. Recently, we reported its solid-state structure [16]. The simple addition of $AlMe_3$ to the CH_2Cl_2 solution of complex **1** yields aluminum complex **2** (Scheme 1), which was characterized by nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry, and elemental analysis [17]. By the reaction, the ^{1}H NMR spectrum was significantly changed from that of ligand **1** and well-defined resonances were observed. A proton peak of a phenolate group at 11 ppm was removed and a methyl group belonging to Al metal appeared at −1.8 ppm. More importantly, unlike previously reported aluminum complexes by Darensbourg and Karroonnirun [14], the spectrum showed that there was a major one species in the solution, which was further confirmed to be a *cis* isomeric complex in methyl groups attached to aluminum metal by X-ray crystallography [18]. To check the presence of *trans* isomer, ^{1}H NMR experiments at variable temperatures were performed. Although a small shift in the spectrum was derived from thermal motion, no appearance of new signals or large shifts in spectral peaks was observed, suggesting the presence of a *cis* isomer mainly in solution even at the high temperature (see Fig. 1).

It was crystallized in CH_2Cl_2 at a refrigerator with a space group $P2_12_12_1$ (Fig. 2). A reasonably low Flack parameter (0.10 (s.u.9))

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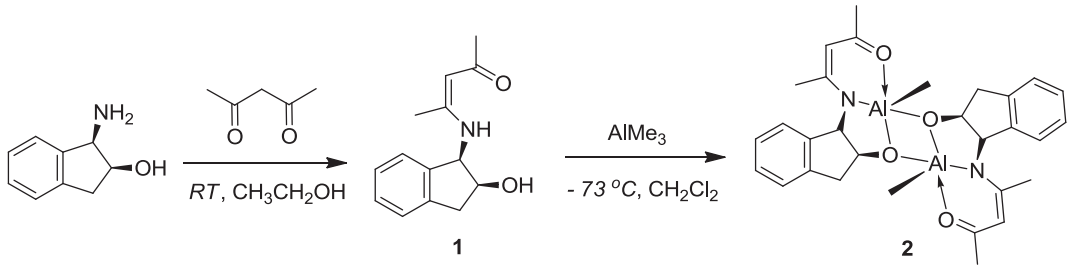

Scheme 1. Synthesis of ligand **1** and complex **2**.

indicates that the absolute configuration of structure is correct in complex **2**. Two aluminum metal centers are linked by two bridging oxygen atoms belonging to indanol. It is noteworthy that there were no large differences between the bond lengths of $Al-O_{bridging}$ and $Al-O_{other}$. The distance between the two Al metal atoms was relatively short (2.9721(6) Å) and the bond lengths of Al – O and Al – N were in the range of 1.8288(10)–1.8864(10) Å and 1.9888(12)–1.9969(12), respectively, similar to those observed for other structurally characterized aluminum complexes [14].

The distortion of the coordination around Al metal was determined by the trigonality parameter τ (τ = [α − β] / 60, where α and β are the largest and next-largest interligand bond angle) [19] and Δ (dihedral angle method) [20]. For the regular trigonal–bipyramidal complexes, the trigonality parameter τ is 1.0, while Δ is zero for trigonal–bipyramidal compounds and 1.0 for square–pyramidal complexes. The calculated τ and Δ values are 0.03 and 0.98 for Al_1 and 0.05 and 0.95 for Al_2, indicating nearly ideal tetragonal pyramid geometry. Methyl groups and ligand parts including bridging oxygen are located in the axial and basal positions, respectively.

Sugimoto and co-workers [21] also reported a similar chiral aluminum complex and its application in the copolymerization of cyclohexene oxide and carbon dioxide. In their research, the tridentate ligand was described as a "wall" that protected the aluminum metal center and its alkyl group. Ligand **1** can also be considered as "wall" that may sterically provide a more shielding effect. To check its stability, complex **2** was dissolved in $CDCl_3$, which contains iso-propyl alcohol (1 wt.%). Even in the presence of iso-propyl alcohol, the methyl group of the aluminum metal center was not decomposed. This result proves that complex **2** is a quite stable species.

Methyl aluminum complex **2** has been tested as a catalyst for ring opening polymerization of LA in the presence of iso-propyl alcohol as an initiator [22]. Because complex **2** is somewhat stable in the presence of iso-propyl alcohol at RT, polymerization was tested at a higher temperature (130 °C) with various [LA]/[Al] ratios. Catalytic activity was assessed in terms of number average molecular weight (M_n) and polydispersity index (PDI, M_w/M_n) (see Table 1). The M_n values of the polymers were calculated by ^1H NMR and determined by gel permeation chromatography, which was corrected by the Mark–Houwink correction factor (0.58 for PLA) [23]. In the L-LA polymerization, as the monomer-to-catalyst molar ratio [LA]/[Al] increases from 50 to 125, M_n increases linearly from 3900 to 11,700 while the PDI values of PLA remain unchanged within the range of 1.01–1.04 under the condition of the same conversion (>96%), implying the presence of a substantially controlled living polymerization process (see Figs. 3 and 4 and Table 1, entries 1–4). It is noteworthy that complex **2** polymerized L-LA to atactic or isotactic-rich PLA, accompanying LA epimerization. As the monomer-to-catalyst molar ratio [LA]/[Al] increases, the isotactic enchainment, P_m, increases from 0.54 to 0.63. This may result from the high polymerization/epimerization rate at the high LA concentration. The polymerization of D-lactide also produced atactic PLA with relatively low M_n and P_m value (0.59) (Table 1, entry 5). The *rac*-LA polymerization provided a lower P_m value (0.44) than those of L-LA (0.61) and D-LA (0.59) (Table 1, entry 6). This observation is in accord with the result by Darensbourg et al. [14] in which a *trans* isomeric complex produced

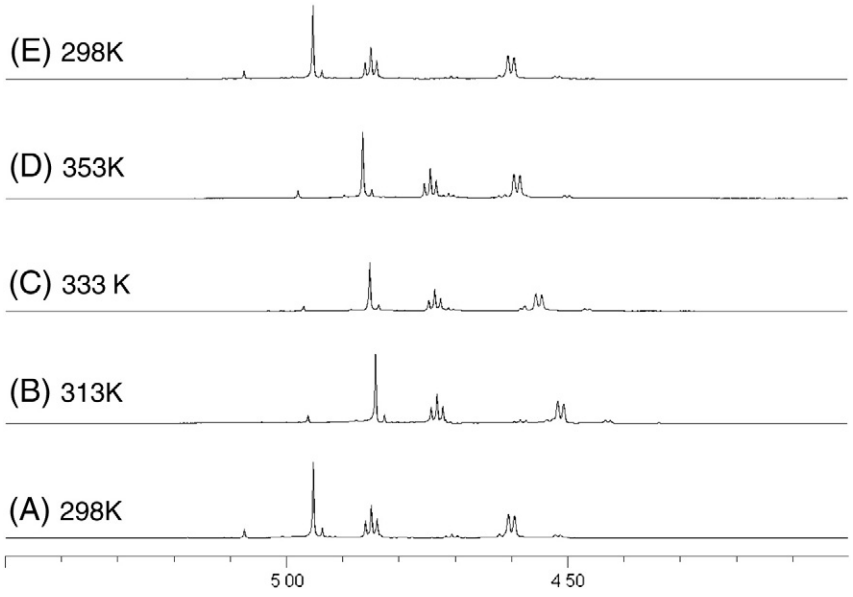

Fig. 1. Variable-temperature ^1H NMR spectra of complex **2** in toluene-d_8 at different temperatures: (A) 298 K; (B) 313 K; (C) 333 K; (D) 353 K; (E) cooled from 353 K to 298 K.