

## Zwitterionic Aluminabenzene-Alkylzirconium Complex Having Half-Zirconocene Structure: Synthesis and Application for an Additive-Free Ethylene Polymerization

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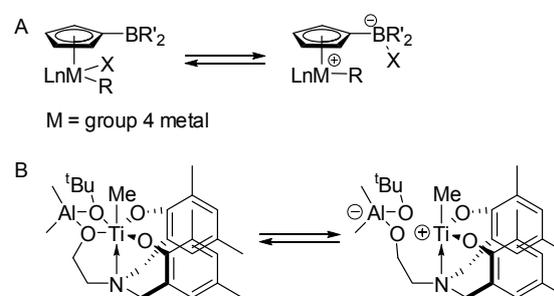
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**The aluminabenzene-alkylzirconium complex having half-zirconocene structure was synthesized. X-ray crystallographic analysis of this complex revealed a zwitterionic structure consisting of cationic alkylzirconium chloride and four-coordinated aluminabenzene. In the presence of catalytic amount of this complex, ethylene polymerization could proceed without any additives to form ultra-high molecular weight polyethylene.**

In homogeneous catalytic polymerization of olefins, an admixture of group 4 transition-metal complex, such as metallocene or half-metallocene complexes, and Lewis acidic additive, have been known to construct an effective catalyst system, represented as Kaminsky catalyst.<sup>1</sup> The Lewis acidic additive, such as methylalumoxane (MAO), plays a crucial role for the generation of catalytically active species. Generally, a large excess of the additive is required to form the active catalyst effectively.<sup>1</sup> Using an excess of additive causes side reactions, such as catalyst degradation by contaminated  $\text{AlMe}_3$  and chain transfer that decreases the molecular weight of the resulting polymer.<sup>2</sup> Thus, the catalytic polymerization system with stoichiometric amount of Lewis acidic additive or with an isolation of catalytically active cationic complex has been developed.<sup>3</sup> As an alternative strategy, Reetz and Bochmann reported group 4 metal complexes with pendent Lewis acid functionality, which could capture an anionic ligand from metal centre to generate catalytically active cationic metal centre (Scheme 1A).<sup>4</sup> After these findings, several examples of such complexes possessing a boron-based Lewis acidic moiety have been reported to be applied as an active catalyst for ethylene polymerization.<sup>5</sup> For example, Piers reported catalytic activity of zwitterionic complex synthesized by the reaction of "tuck-in" zirconocene with  $\text{HB}(\text{C}_6\text{F}_5)_2$  or  $\text{B}(\text{C}_6\text{F}_5)_3$ . In this case, the

resulting zwitterionic complexes catalyses ethylene polymerization as a highly active single-component catalyst.<sup>5b</sup> However, the reported group 4 metal catalyst systems with a pendent aluminum-based Lewis acidic moiety were limited,<sup>6</sup> while the aluminum additives have been commonly used in Kaminsky catalyst. Nomura reported utilization of titanium complex bearing  $\text{Me}_2\text{Al}(\text{O}^t\text{Bu})(\text{OR})$  moiety as a single-component catalyst for ethylene polymerization (Scheme 1B).<sup>6a,b</sup> In their plausible mechanism, the dissociation of  $\text{Me}_2\text{Al}(\text{O}^t\text{Bu})(\text{OR})$  moiety as an anion generates zwitterionic complex involving cationic titanium centre. This catalyst system can form high molecular weight PE ( $> 1,000,000$ ) due to the suppression of chain transfer by taking advantages of the absence of external Lewis acid. These reports indicate that incorporation of Lewis acidic aluminum on an ancillary ligand will be unique strategy for the active catalyst for high molecular weight polyethylene (PE). In this context, common catalysts, such as metallocene/half-metallocene type complex, bearing aluminum moiety should be mentioned. However, in our knowledge, no example of metallocene or half-metallocene-type olefin polymerization catalyst bearing a Lewis acidic  $\text{sp}^2$  aluminum moiety incorporated in the ancillary Cp type ligand have been reported.<sup>7,8</sup>

Recently, we reported synthesis and characterization of anionic aluminabenzene, which has aromatic **1** and ambiphilic **1'** resonance contributions (Scheme 2).<sup>9</sup> Due to the resonance

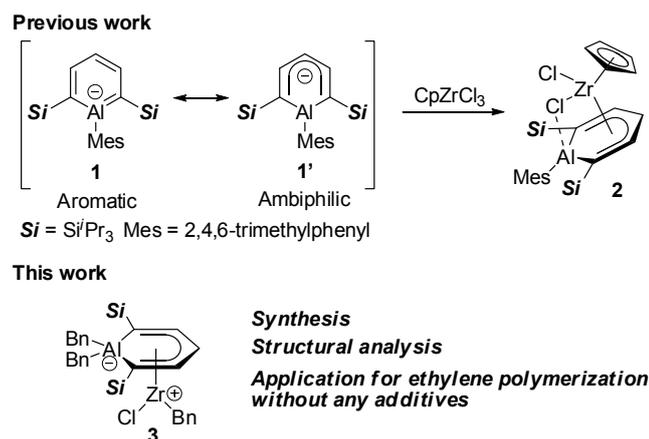


**Scheme 1** (A) Formation of active catalyst by intramolecular ligand migration proposed by Reetz and Bochmann. (B) Reported single-component olefin polymerization catalyst based on intra-molecular combination of aluminum and titanium

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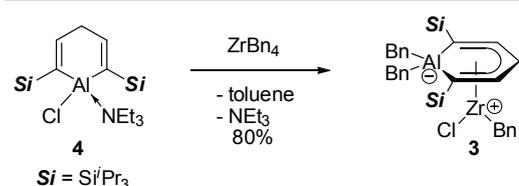
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**Scheme 2** Complexation of aluminabenzene with zirconium

contribution of **1'**, the aluminum atom act as Lewis acid to accept the coordination of Lewis base. In addition, anionic aluminabenzene can coordinate to early and late transition metals in  $\eta^5$ -fashion with retaining the Lewis acidity of the aluminum atom in aluminabenzene ligand.<sup>10</sup> In fact, aluminabenzene-chlorozirconium complex **2** exhibited intramolecular interaction between the aluminum atom and chloride ligand on zirconium. If anionic aluminabenzene would coordinate to alkylzirconium complex, one could expect that aluminum atom on the aluminabenzene ligand would abstract an alkyl ligand from zirconium to generate cationic zirconium centre, which would be capable for the olefin polymerization. Herein, we report the synthesis of the alkylzirconium complex having aluminabenzene ligand **3**. The X-ray crystallographic analysis of **3** revealed a zwitterionic structure bearing anionic aluminate and cationic alkylzirconium moieties. Catalytic activity of **3** toward ethylene polymerization in the absence of additive was also investigated.

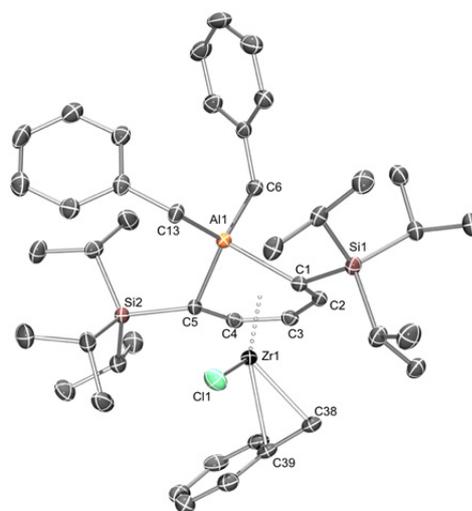
Although we initially attempted synthesis of aluminabenzene-alkylzirconium complex by an alkylation of the previously reported aluminabenzene-zirconium chloride, such as **2**,<sup>10</sup> the alkylation did not proceed probably due to the steric hindrance around zirconium centre. In contrast, red-crystalline aluminabenzene-alkylzirconium complex **3** could be synthesized by the reaction of aluminacyclohexadiene **4**<sup>11</sup> with tetrabenzylzirconium in 80% yield (Scheme 3). Although no intermediate was observed during this reaction, the mechanism for the formation of complex **3** would be explained by the complexation of aluminabenzene ligand with zirconium followed by the ligand redistribution between zirconium and aluminum atoms.<sup>12</sup> The formation of Zr-Cl might be preferable due to the presence of the  $\pi\pi$ - $d\pi$  interaction between a lone pair



**Scheme 3** Synthesis of aluminabenzene-alkylzirconium complex **3**

on Cl and the  $d^0$ -Zr centre. The <sup>1</sup>H NMR spectrum of **3** in C<sub>6</sub>D<sub>6</sub> exhibited broadened signals probably due to a change in hapticity of the Zr-attached Bn group or exchanging Bn groups between Al and Zr atoms. The complex **3** was unstable in solution at room temperature even under argon atmosphere (45% of **3** was converted to unidentified product after 24 h in C<sub>6</sub>D<sub>6</sub>). Single-crystal X-ray diffraction analysis of **3** revealed a zwitterionic half-metallocene structure involving dibenzylaluminate and cationic zirconium moieties (Fig. 1). The Al1–Zr1 distance [2.9686(9) Å] is longer than the sum of the covalent radii (2.70 Å), indicating no tangible interaction between Al and Zr atoms.<sup>13</sup> The aluminabenzene ligand coordinated to zirconium in  $\eta^5$ -fashion at pentadienyl moiety, which had almost same C–C bond lengths [1.407(4)–1.423(4) Å]. The Zr–C1 and Zr1–C5 distances [2.204(3), 2.292(3) Å] were shorter compared to those of the previously reported aluminabenzene zirconium chloride.<sup>10a</sup> This result would attribute to the strong interaction between cationic zirconium and most negatively charged *ortho*-carbon atoms due to the substitution of electropositive aluminum and silicon atoms. The aluminum atom adopts tetrahedral geometry with two benzyl ligands. The Al–C1 and Al–C5 distances [2.188(3), 2.112(3) Å] were longer compared to those of **1** [1.922(2)–1.930(2) Å] due to the disappearance of unsaturated character of Al–C bonds upon coordination. The Zr1–C38 and Zr1–C39 distances [2.293(3), 2.693(2) Å] indicated  $\eta^2$ -coordination mode of benzyl ligand to Zr because they were comparable to those of  $\eta^2$ -Bn ligand in the previously reported cationic zirconium complex [ZrBn<sub>3</sub>]<sup>+</sup>[BnB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>–</sup>.<sup>14</sup>

To obtain further insight into the electronic structure of **3**, we performed DFT calculations at the M06L/[LanL2DZ for Zr, 6-31G(d) for Al, Si, Cl, C, H] level of theory.<sup>15</sup> The optimized structure of **3** is comparable to the experimentally observed structure determined by X-ray crystallography. The HOMO and LUMO of the optimized **3** are shown in Fig. 2. The HOMO localizes around the AlBn<sub>2</sub> moiety, while the LUMO was located around zirconium atom. The localization of HOMO and LUMO would be reasonable to the zwitterionic character of



**Fig. 1** Crystal structure of **3** (50% thermal ellipsoid probability). Hydrogen atoms are omitted for clarity.

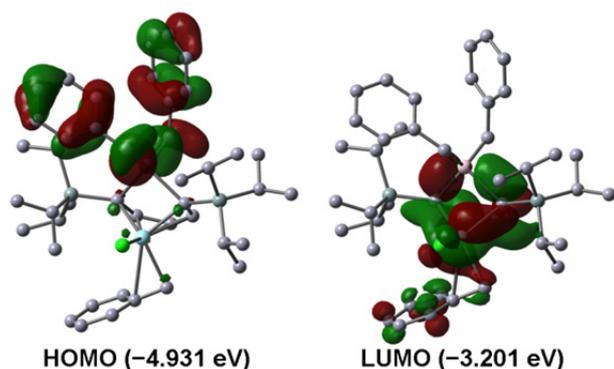


Fig. 2 HOMO and LUMO of **3**. Hydrogen atoms are omitted for clarity.

complex **3** having tetracoordinate aluminate and cationic zirconium. Based on the Wiberg bond index (WBI) between zirconium and the coordinated carbon atoms, which attached on *ortho*-, *meta*-, and *para*-positions in aluminabenzene ligand, the interactions between Zr and *ortho*-carbon atoms, C1 and C5 (0.882/0.733) are larger than those of *meta*- and *para*-carbon atoms (0.141/0.142 for Zr–C2/Zr–C4 and 0.234 for Zr–C3). According to the result of natural population analysis (NPA), the *ortho*-carbon atoms, C1 and C5, have the most negative charges (–1.16, –1.20) compared to those of *meta*- (–0.167/–0.177 for C2 and C4) and *para*-carbon atom (–0.353 for C3).

The complex **3** was applied as a catalyst for polymerization of ethylene (Table 1). In a benzene solution of **3**, ethylene was polymerized without any additive. Polymerization under 1.0 MPa of ethylene for 6 h gave polyethylene (PE) with an activity of 8.6 kg(PE)/mol(Zr)·h·MPa (entry 1). Longer reaction time of 24 h improved the yield but gave lower activity (entry 2).

Table 1 Ethylene polymerization using complex **3**

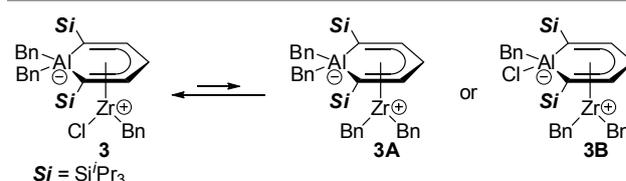
Entry	Reaction conditions		Yield /mg	Activity <sup>b</sup>	$M_w^c$ × 10 <sup>-6</sup>	$M_w/M_n^c$	$M_w^d$ × 10 <sup>-6</sup>
	Pressure /MPa	Time /h					
1	1.0	6	413	8.6	-	-	>7
2	1.0	24	868	4.5	-	-	>7
3	3.9	24	5094	6.8	-	-	>7
4	1.0	0.25	2.8	1.4	3.4 <sup>e</sup>	10.4 <sup>e</sup>	-
5	1.0	0.5	11.6	2.9	10.2 <sup>e</sup>	8.9 <sup>e</sup>	-
6 <sup>f</sup>	1.0	6	163	3.4	-	-	-

<sup>a</sup> Reaction condition: catalyst **3** (8  $\mu$ mol), benzene (4 mL), room temperature, 300 mL autoclave. <sup>b</sup> activity: kg(PE)/mol(Zr)·h·MPa. <sup>c</sup> estimated by high-temperature GPC analysis. <sup>d</sup> estimated by intrinsic viscosity measurement. <sup>e</sup> potentially inaccurate values due to partial exceeding of exclusion limit of the column. <sup>f</sup> complex **3** (8  $\mu$ mol) after standing at room temperature for 24 h was used for the ethylene polymerization.

Higher pressure of ethylene resulted in higher yield and activity of 6.8 kg(PE)/mol(Zr)·h·MPa (entry 3). All the obtained PEs were not soluble in solvent for GPC analysis, probably due to their high molecular weight. Therefore, we tried the ethylene polymerization in shorter time to carry out the GPC analysis (entries 4 and 5). The  $M_w$  of the resulting PEs in entry 4 and 5 were estimated to be about  $3.4 \times 10^6$  and  $10.2 \times 10^6$  by high-temperature GPC analysis, although the edge on the higher molecular weight of GPC chromatogram exceeded the exclusion limit of the column ( $4.0 \times 10^6$ ). Instead of GPC analysis, the intrinsic viscosity measurement provided viscosity average molecular weight ( $M_v > 7,000,000$ ;  $[\eta] > 35$ ) for entries 1-3. Thus, all the obtained PEs are classified as ultra-high molecular weight PE (UHMW-PE). While UHMW-PEs were formed in the presence of **3**, the catalytic activity was low, suggesting that the catalytically active specie was not **3** itself.<sup>16</sup> Although the active species is not clear at the present stage, the formation of active aluminabenzene-zirconium complex, such as dibenzylzirconium complex **3A** or **3B** bearing aluminabenzene ligand, via intra- or intermolecular ligand exchange might be plausible (Scheme 4). In the recently reported Al/Zr hybrid catalyst system, it was proposed that the ethylene polymerization could proceed on a single metal centre even in the presence of active aluminum moiety.<sup>8c</sup> Thus, in the case of **3A** or **3B**, the Zr atom would also be active centre. The ethylene polymerization using a partially decomposed mixture of **3** decreased the catalytic activity (Table 1, entry 6), suggesting the decomposition of **3** was not crucial for the ethylene polymerization. On the other hand, the polymerization of 1-hexene in the presence of **3** did not proceed even heating conditions. This result would attribute to the steric bulkiness of the aluminabenzene ligand.

In summary, the zwitterionic alkylzirconium complex **3** having aluminabenzene ligand was synthesized by the reaction of aluminacyclohexadiene with ZrBn<sub>4</sub>. X-ray crystallographic analysis revealed that **3** involved cationic alkylzirconium chloride and four-coordinate aluminate. Reflecting the presence of cationic alkylzirconium centre, this complex could catalyse polymerization of ethylene without any additives to result in the formation of UHMW-PE.

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Scheme 4 Possible generation of catalytically active cationic dibenzylzirconium complexes

measurement. We also thank Drs. S. Ishii and T. Fujita (Mitsui Chemicals, Inc.) for intrinsic viscosity measurement. Theoretical calculations were carried out using resources of the Research Centre for Computational Science, Okazaki, Japan.

### Conflicts of interest

There are no conflicts to declare.

### Notes and references

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