Reaction Properties of Dinuclear Metalloccenes
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Introduction
Linear low-density polyethylene (LLDPE) is a class of materials of commercial and academic importance. The physical properties and processing characteristics of these materials have been found to depend on the number and distribution of branching. Compared to Ziegler-Natta catalysts, metallocones can produce higher comonomer incorporation and narrower molecular weight and composition distribution. The modification of the metalocene structure and the nature of comonomer (MAO, perfluoroproplene oxide, butene, and fluoroolefinic co-reactants) have a pronounced effect on copolymerization behavior including activity, molecular weight, and comonomer incorporation. Group 4 "constrained geometry catalysts" (CGCs) are well-known site-specific polymerization catalysts that produce branched polyethylene under various conditions. One of the specialties is the highly enhanced ability of copolymerization of COCl compared to the vast steric hindrance of CGCs. This chapter describes the recent development of the CGC technology for the production of ethylene oligomerization, using these catalysts. The copolymerization effects are also described.

Experimental
General Consideration. All reactions were carried out under a dry, oxygen-free atmosphere using standard Schlenk techniques with a double manifold vacuum line. Nitrogen gas was purified by passage through a column of molecular sieve (4 Å) and driers (2 Å). Tetrahydrofuran, diethyl ether, hexane, and toluene were distilled from sodium benzenophenone ketyl prior to use. Ethylene (Matheson, polymerization grade) was purified by passage through a supported MnCl washco washing column and an activated Davison 4 A molecular sieve column. Commercially obtained and vacuum-dried into storage tubes 1,2-dichloroethene, purchased from Aldrich, was distilled from calcium hydride prior to use. The reagents F_{2}COBF_{3} (RC=CF_{2}) (B) and COBF_{3} (B) were purchased from PCI and used without further purification. F_{2}COBF_{3} was used as the co-reactant and 2,2-dimethoxypropane (DM) was used as the solvent. The reaction was performed in a Schlenk flask and the reaction mixture was degassed by two freeze-pump-thaw cycles. The pressure was maintained at 0.1 Torr throughout the reaction. The reaction mixture was then heated to 80 °C for 1 h. The crude product was then purified by column chromatography on silica gel (silica gel 60, 40-63 nm) using dichloromethane (DCM) as the eluent. The purified product was then further purified by reprecipitation from methanol to obtain the final product.

Preparation of [Zn(η₃-C₅H₅]_2(CH₃CN)(MeCN)Me] (CH₃CN)₄

A solution of 0.20 mmol of [Zn(η₃-C₅H₅]_2(CH₃CN)(MeCN)Me] in 5 mL of CH₃CN was treated with 5 mL of MeCN, and the mixture was stirred at room temperature for 24 h. The mixture was then evaporated under reduced pressure, and the residue was extracted with hexane. The solution was filtered, and the filtrate was evaporated to dryness under reduced pressure. The resulting solid was then washed with hexane and dried.

Results and Discussion
Synthesis. The reaction of the tetrahydrofuran dimeric Zirconium GC complex [Zn(η₃-C₅H₅]_2(CH₃CN)(MeCN)Me] (CH₃CN)₄ with MeCN in diethyl ether at room temperature yields the corresponding dimeric tetramethyl zirconocene [Zn(η₃-C₅H₅]_2(CH₃CN)(MeCN)Me] (CH₃CN)₄. The X-ray structure of this complex is shown in Figure 1. The crystal structure is monoclinic, space group P2₁/c, with Z = 4. The molecule consists of two Zr atoms, each coordinated by two C₅H₅ ligands, one MeCN ligand, and one CH₃CN ligand. The Zr-Zr distance is 3.41 Å, and the C₅H₅-Zr-C₅H₅ angle is 70.4°. The molecule is held together by weak CH···π interactions.

The reaction of dinitrobenzene with Zn(η₃-C₅H₅]_2(CH₃CN)(MeCN)Me] yields the corresponding dimeric dinitrobenzene complex [Zn(η₃-C₅H₅]_2(CH₃CN)(MeCN)Me] (CH₃CN)₄(N), which is a yellow solid. The X-ray structure of this complex is shown in Figure 2. The crystal structure is monoclinic, space group P2₁/c, with Z = 4. The molecule consists of two Zr atoms, each coordinated by two C₅H₅ ligands, one MeCN ligand, and one CH₃CN ligand. The Zr-Zr distance is 3.41 Å, and the C₅H₅-Zr-C₅H₅ angle is 70.4°. The molecule is held together by weak CH···π interactions.

The reaction of dinitrobenzene with Zn(η₃-C₅H₅]_2(CH₃CN)(MeCN)Me] yields the corresponding dimeric dinitrophenyl complex [Zn(η₃-C₅H₅]_2(CH₃CN)(MeCN)Me] (CH₃CN)₄(N), which is a yellow solid. The X-ray structure of this complex is shown in Figure 3. The crystal structure is monoclinic, space group P2₁/c, with Z = 4. The molecule consists of two Zr atoms, each coordinated by two C₅H₅ ligands, one MeCN ligand, and one CH₃CN ligand. The Zr-Zr distance is 3.41 Å, and the C₅H₅-Zr-C₅H₅ angle is 70.4°. The molecule is held together by weak CH···π interactions.

The reaction of dinitrobenzene with Zn(η₃-C₅H₅]_2(CH₃CN)(MeCN)Me] yields the corresponding dimeric dinitrophenyl complex [Zn(η₃-C₅H₅]_2(CH₃CN)(MeCN)Me] (CH₃CN)₄(N), which is a yellow solid. The X-ray structure of this complex is shown in Figure 4. The crystal structure is monoclinic, space group P2₁/c, with Z = 4. The molecule consists of two Zr atoms, each coordinated by two C₅H₅ ligands, one MeCN ligand, and one CH₃CN ligand. The Zr-Zr distance is 3.41 Å, and the C₅H₅-Zr-C₅H₅ angle is 70.4°. The molecule is held together by weak CH···π interactions.
Polymerization studies: Polymerization with the three combinations of metalloene catalysts and boronate ester co-catalysts were carried out at room temperature in 250 mL, round-bottomed flasks equipped with magnetic stirring bars and sealed with the high vacuum line.

**Table 1: Results of Ethylene polymerization**

<table>
<thead>
<tr>
<th>precursor</th>
<th>Cocatalyst</th>
<th>Activity</th>
<th>T&lt;sub&gt;n&lt;/sub&gt; (°C)</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; (10&lt;sup&gt;4&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zr(η5-C₅H₅)₂Cl₂(C₆H₄OCH₂CH₂OCH₂C₆H₄)]</td>
<td>B₃</td>
<td>309</td>
<td>135.9</td>
<td>63.9</td>
</tr>
<tr>
<td>[Zr(η5-C₅H₅)₂Cl₂(C₆H₄OCH₂CH₂OCH₂C₆H₄)]</td>
<td>B₄</td>
<td>141</td>
<td>127.1</td>
<td>36.5</td>
</tr>
<tr>
<td>[Zr(η5-C₅H₅)₂Cl₂(C₆H₄OCH₂CH₂OCH₂C₆H₄)]</td>
<td>B₅</td>
<td>226</td>
<td>125.6</td>
<td>40.1</td>
</tr>
<tr>
<td>[Zr(η5-C₅H₅)₂Cl₂(C₆H₄OCH₂CH₂OCH₂C₆H₄)]</td>
<td>B₆</td>
<td>346</td>
<td>137.2</td>
<td>56.5</td>
</tr>
<tr>
<td>[Zr(η5-C₅H₅)₂Cl₂(C₆H₄OCH₂CH₂OCH₂C₆H₄)]</td>
<td>B₇</td>
<td>154</td>
<td>131.6</td>
<td>56.1</td>
</tr>
<tr>
<td>[Zr(η5-C₅H₅)₂Cl₂(C₆H₄OCH₂CH₂OCH₂C₆H₄)]</td>
<td>B₈</td>
<td>248</td>
<td>123.8</td>
<td>37.4</td>
</tr>
<tr>
<td>[Zr(η5-C₅H₅)₂Cl₂(C₆H₄OCH₂CH₂OCH₂C₆H₄)]</td>
<td>B₉</td>
<td>373</td>
<td>135.1</td>
<td>41.5</td>
</tr>
<tr>
<td>[Zr(η5-C₅H₅)₂Cl₂(C₆H₄OCH₂CH₂OCH₂C₆H₄)]</td>
<td>B₁₀</td>
<td>173</td>
<td>134.2</td>
<td>56.0</td>
</tr>
<tr>
<td>[Zr(η5-C₅H₅)₂Cl₂(C₆H₄OCH₂CH₂OCH₂C₆H₄)]</td>
<td>B₁₁</td>
<td>266</td>
<td>136.7</td>
<td>51.8</td>
</tr>
</tbody>
</table>

**Nuclearity Effects of polymethylene bridged dinuclear cation.** According to the reported study, it turned out that the ethylene bridged dinuclear metalloene with the dinuclear borate anion was found to be effective to form LLDEE with the significantly enhanced chain branching due to the improved α-definit忠诚 incorporation capability of the ethylene bridged dinuclear complex originated from the close spatial proximity between two active sites. As shown in Figure 2, polymethylene bridged dinuclear C3G complex differ from ethylene bridged dinuclear complex in that the former contained a long and flexible bridge. The related far distance between two metal center make them difficult to get to the same spatial proximity. Presumably, there are two pathways for the preferred formation of coordination active ions by activation of B₃ to form two kinds of active species which would both act as active centers in the encapsulation processes. Hence, it led to reverse nucleation effect when activated by B₃ and produced polymer with broad MWD.

![Figure 1: Catalysts and Cofactors](image1)

![Figure 2: Cationic dinuclear metalloene with various anions](image2)

**References**


