

## Reaction Properties of Dinuclear Metallocenes

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### Introduction

Linear low-density polyethylenes (LLDPE) are 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.<sup>1</sup> Compared to Ziegler-Natta catalysts, metallocenes can produce higher comonomer incorporation and narrower molecular weight and composition distribution.<sup>2,3</sup> The modification of metallocene structure and the nature of cocatalyst (MAO, perfluoroaryl borane, borate, and fluoroaluminate reagents)<sup>4,5</sup> have a pronounced effect on copolymerization behavior including activity, molecular weight, and comonomer incorporation. Group 4 "constrained geometry catalysts" (CGC)<sup>6,7</sup> are well-known single-site polymerization catalysts that produce branched polyethylene under various conditions. One of the specialties is the highly enhanced  $\alpha$ -olefin copolymerizability of CGC comparing with normal metallocene catalysts. Recently, dinuclear compounds,<sup>8,9</sup> which contain two mechanically linked metallocene units, have been prepared to study the multinuclear cooperation effects on the enchainment processes. Marks' group reported<sup>10</sup> synthesis of the ethylene bridged dinuclear CGC to probe copolymerization of ethylene and  $\alpha$ -olefin. They attributed the higher comonomer incorporation capability to the nuclearity effects of the dinuclear CGC due to the close spatial proximity between two active sites.

In view of the great scientific interest in the dinuclear metallocene multinuclearity effects and the corresponding intermolecular processes, we report here the preparations of a series of polymethylene bridged dinuclear CGC as a new dinuclear metallocene and the results of cationic ethylene/1-Hexene copolymerization using these catalysts. The counteranion 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 drierite (8 mesh). Tetrahydrofuran, diethyl ether, hexane, and toluene were distilled from sodiumbenzophenone ketyl prior to use. Ethylene (Matheson, polymerization grade) was purified by passage through a supported MnO oxygen-removal column and an activated Davison 4 Å molecular sieve column. Comonomer 1-hexene was dried over Na and vacuum-transferred into storage tubes. 1,2-difluorobenzene, purchased from Aldrich, was distilled from calcium hydride prior to use. The reagents  $\text{Ph}_3\text{C}^+\text{B}^-(\text{C}_6\text{F}_5)_4$  (**B<sub>1</sub>**) and  $\text{B}(\text{C}_6\text{F}_5)_3$  (**B<sub>2</sub>**) purchased from TCI was used without further purification.  $\text{Ph}_3\text{C}^+(\text{C}_6\text{F}_5)_3\text{B}^-\text{C}_6\text{F}_4\text{B}^-(\text{C}_6\text{F}_5)_3\text{Ph}_3\text{C}^+$  (**B<sub>2</sub>**) and  $[\text{Zr}(\eta^5\text{-C}_9\text{H}_7\text{SiMe}_2\text{N}(\text{CMe}_3)\text{Cl}_2)_2[(\text{CH}_2)_n]]$  [ $n=6, 9, 12$ ] were prepared according to literature procedure. <sup>1</sup>H(300 MHz) NMR and <sup>13</sup>C(75.46 MHz) NMR spectra were recorded using a Bruker DPX-300 FT-NMR spectrometer. <sup>13</sup>C NMR assays of polymer microstructure were conducted in mixture (1:1 in volume) of 1,2,4-trichlorobenzene (containing 0.1 M Cr(acac)<sub>3</sub> solution) and 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at 120 °C, the pulse interval was 5.2 s and the acquisition time was 0.8 s. The polymer solutions were prepared by dissolving polymers in solvent up to 10 wt%. Signals were assigned according to the literature for polyethylene and copolymers. Elemental analysis was recorded by EA1108 (FISONIS Instrument, Italy). Molecular weight and molecular weight distribution were measured by Waters Alliance GPC 2000 high temperature instrument with a polystyrene gel column (Styragel HT 3,4,5) at 145 °C. A flow rate of 1.0 mL/min was used, and HPLC grade 1,2,4-trichlorobenzene (TCB) was employed as the eluent.

**Preparation of  $[\text{Zr}(\eta^5\text{-C}_9\text{H}_7\text{SiMe}_2\text{N}(\text{CMe}_3)\text{Cl}_2)_2[(\text{CH}_2)_n]]$ .** A drybox, 0.625g (0.7 mmol)  $[\text{Zr}(\eta^5\text{-C}_9\text{H}_7\text{SiMe}_2\text{N}(\text{CMe}_3)\text{Cl}_2)_2[(\text{CH}_2)_n]]$  was dissolved in 40 mL of Et<sub>2</sub>O. To this solution, 2.8mL (2.8mmol) of MeMgBr (1 M in THF) was added dropwise at room temperature. After stirring for 3 h, the solvent was removed under reduced pressure and the

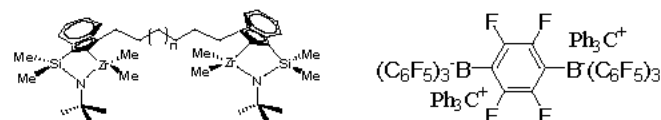
residue was extracted with hexane. The solution was filtered celite, and the filtrate was evaporated to dryness under reduced pressure. Final product was purified by the recrystallization from hexane to give 0.49 g (86% yield) of yellow crystalline. <sup>1</sup>H NMR( 300 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>): 87.59(d, 2H, C<sub>9</sub>H<sub>5</sub>), 7.45(d, 2H, C<sub>9</sub>H<sub>5</sub>), 7.10(t, 2H, C<sub>9</sub>H<sub>5</sub>), 6.95 (t, 2H, C<sub>9</sub>H<sub>5</sub>), 6.26(s, 2H, C<sub>9</sub>H<sub>5</sub>), 2.80(m, 4H, CH<sub>2</sub>), 1.61(m, 4H, CH<sub>2</sub>), 1.34 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.25(m, 4H, CH<sub>2</sub>), 0.64(s, 6H, Si-CH<sub>3</sub>), 0.46(s, 6H, Si-CH<sub>3</sub>), 0.20 (s, 6H, Zr-Me), -0.71(s, 6H, Zr-Me).<sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): 8 133.7(C.Ind), 130.0(C.Ind), 126.1(CH.Ind), 125.4(C.Ind), 124.7(CH.Ind), 124.7(CH.Ind), 124.2(CH.Ind), 123.6(CH.Ind), 86.1(C.Ind), 55.4(NCMe<sub>3</sub>), 40.5(Zr-Me), 39.0(Zr-Me), 34.3(NCMe<sub>3</sub>), 30.8(CH<sub>2</sub>), 29.6(CH<sub>2</sub>), 28.1(CH<sub>2</sub>), 4.5(SiMe<sub>2</sub>), 2.8(SiMe<sub>2</sub>). Anal. Calcd for C<sub>40</sub>H<sub>64</sub>N<sub>2</sub>Si<sub>2</sub>Zr<sub>2</sub>: C, 59.20%; H, 7.95%; N, 3.45%. Found C, 58.98%; H, 8.20%; N, 2.87%. The brown solid **2** (88%). <sup>1</sup>H NMR( 300 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>): 87.60(d, 2H, C<sub>9</sub>H<sub>5</sub>), 7.47(d, 2H, C<sub>9</sub>H<sub>5</sub>), 7.09(t, 2H, C<sub>9</sub>H<sub>5</sub>), 6.95 (t, 2H, C<sub>9</sub>H<sub>5</sub>), 6.29(s, 2H, C<sub>9</sub>H<sub>5</sub>), 2.82(m, 4H, CH<sub>2</sub>), 1.67(m, 4H, CH<sub>2</sub>), 1.34 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.25(m, 10H, CH<sub>2</sub>), 0.64(s, 6H, Si-CH<sub>3</sub>), 0.46(s, 6H, Si-CH<sub>3</sub>), 0.22 (s, 6H, Zr-Me), -0.70(s, 6H, Zr-Me).<sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): 8 133.7(C.Ind), 130.1(C.Ind), 126.1(CH.Ind), 125.4(C.Ind), 124.7(CH.Ind), 124.3(CH.Ind), 123.7(CH.Ind), 86.0(C.Ind), 55.4(NCMe<sub>3</sub>), 40.5(Zr-Me), 39.0(Zr-Me), 34.3(NCMe<sub>3</sub>), 31.0(CH<sub>2</sub>), 29.9(CH<sub>2</sub>), 28.3(CH<sub>2</sub>), 4.5(SiMe<sub>2</sub>), 2.8(SiMe<sub>2</sub>). Anal. Calcd for C<sub>43</sub>H<sub>70</sub>N<sub>2</sub>Si<sub>2</sub>Zr<sub>2</sub>: C, 60.50%; H, 8.26%; N, 3.28%. Found C, 60.24%; H, 8.57%; N, 2.67%. The brown solid **3** (84%). <sup>1</sup>H NMR( 300 MHz, 25 °C, C<sub>6</sub>D<sub>6</sub>): 87.60(d, 2H, C<sub>9</sub>H<sub>5</sub>), 7.48(d, 2H, C<sub>9</sub>H<sub>5</sub>), 7.09(t, 2H, C<sub>9</sub>H<sub>5</sub>), 6.95 (t, 2H, C<sub>9</sub>H<sub>5</sub>), 6.28(s, 2H, C<sub>9</sub>H<sub>5</sub>), 2.85(m, 4H, CH<sub>2</sub>), 1.69(m, 4H, CH<sub>2</sub>), 1.34 (s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.27(m, 16H, CH<sub>2</sub>), 0.64(s, 6H, Si-CH<sub>3</sub>), 0.45(s, 6H, Si-CH<sub>3</sub>), 0.21 (s, 6H, Zr-Me), -0.70(s, 6H, Zr-Me).<sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): 8 133.7(C.Ind), 130.0(C.Ind), 126.1(CH.Ind), 125.4(C.Ind), 124.7(CH.Ind), 124.3(CH.Ind), 123.6(CH.Ind), 86.0(C.Ind), 55.4(NCMe<sub>3</sub>), 40.5(Zr-Me), 39.0(Zr-Me), 34.3(NCMe<sub>3</sub>), 31.0(CH<sub>2</sub>), 29.9(CH<sub>2</sub>), 28.3(CH<sub>2</sub>), 4.6(SiMe<sub>2</sub>), 2.8(SiMe<sub>2</sub>). Anal. Calcd for C<sub>46</sub>H<sub>76</sub>N<sub>2</sub>Si<sub>2</sub>Zr<sub>2</sub>: C, 61.68%; H, 8.55%; N, 3.13%. Found C, 61.97%; H, 8.96%; N, 2.57%.

**Ethylene polymerization experiments.** Ethylene polymerization was carried out in a 250 mL glass reactor. In a typical experiment, 50 mL dry toluene (freeze-pump-thaw degassed three times) was injected into the flask, pre-saturated under 1.0 atm of rigorously purified ethylene, and equilibrated at the desired reaction temperature using an external bath. The catalytically active species were freshly generated in 1.5 mL of dry 1,2-difluorobenzene. The catalyst solution was then quickly injected into the rapidly stirred flask. After a measured time interval, the polymerization was quenched by the addition of 25 mL 2% acidified methanol. Another 200 mL of methanol was then added and the polymer was collected by filtration, washed with methanol, and dried on the high vacuum line overnight to constant weight.

### Results and Discussion

**Synthesis.** The reactions of the tetrachloride dinuclear Zirconium CGC complexes  $[\text{Zr}(\eta^5\text{-C}_9\text{H}_7\text{SiMe}_2\text{N}(\text{CMe}_3)\text{Cl}_2)_2[(\text{CH}_2)_n]]$  [ $n=6, 9, 12$ ] with MeMgBr in diethyl ether at room temperature yield the corresponding desired tetramethyl complexes  $[\text{Zr}(\eta^5\text{-C}_9\text{H}_7\text{SiMe}_2\text{N}(\text{CMe}_3)\text{Me}_2)_2[(\text{CH}_2)_n]]$  [ $n=6(1), 9(2), 12(3)$ ] (Figure 1.) in over 80% isolated yields respectively. The product work-up and purification involve only routine extraction and filtration to produce the spectroscopically and analytically pure precatalysts. Unlike the ethylene bridged dinuclear CGC complex that has been reported, the <sup>1</sup>H NMR spectrum of **1**, **2**, and **3** show no diastereomer consisted. Further more, all these polymethylene bridged dinuclear complexes (**1-3**) have high solubility in toluene and pentane comparing with ethylene bridged complex. The observations indicate the different nature between polymethylene bridged dinuclear CGC (longer and flexible structures) and the ethylene bridged complex (shorter and rigid structure).

The reactions of dimethyl metallocenes with  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{Ph}_3\text{C}^+\text{B}^-(\text{C}_6\text{F}_5)_4$  often generate the corresponding cationic complexes which are highly active catalysts for the polymerization of ethylene and olefin.<sup>4</sup> Not surprisingly, all polymethylene tetramethyl dinuclear Zirconium CGC complexes (**1-3**) undergo rapid activation with  $\text{Ph}_3\text{C}^+\text{B}^-(\text{C}_6\text{F}_5)_4$  (**B<sub>1</sub>**),  $\text{Ph}_3\text{C}^+(\text{C}_6\text{F}_5)_3\text{B}^-\text{C}_6\text{F}_4\text{B}^-(\text{C}_6\text{F}_5)_3\text{Ph}_3\text{C}^+$  (**B<sub>2</sub>**) or  $\text{B}(\text{C}_6\text{F}_5)_3$  (**B<sub>3</sub>**) in C<sub>7</sub>D<sub>8</sub> at room temperature within minutes to form  $\text{Ph}_3\text{CMe}$  (by *in situ* <sup>1</sup>H NMR).



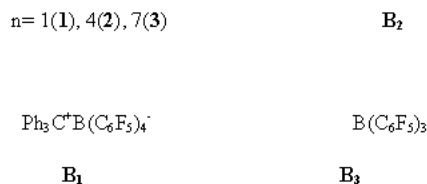


Figure 1. Catalysts and Cocatalysts

**Polymerization studies.** Polymerizations with the three combinations of metallocene catalysts and borane/borate cocatalysts were carried out at room temperature in 250 mL flamed, round-bottomed flasks equipped with magnetic stirring bars and attached to the high-vacuum line. **Table 1** summarizes ethylene polymerization activities as well as the properties of the resulting polymers. Considering the catalysts activity, the prime feature is that the activity increases as the bridge between two active centers becomes longer (follows the order of  $1 < 2 < 3$ ). As shown in **Table 1**, this tendency has been maintained throughout ethylene homopolymerization, regardless of the counteranions. This behavior is in accord with the activity behaviors observed on the dinuclear metallocenes using MAO as the activator to generate the catalytical active species. This could be understood by the idea that the more electron density delivered by the adoption of longer polymethylene group would stabilize the electron deficient active site more efficiently, thus lead the polymerization rate acceleration consequently. This observation may imply that the length of the bridging ligand does play an important role in determining polymerization activity of the dinuclear CGC. The steric factor was also believed to contribute to direct the polymerization behavior as a consequence of coming into close two active sites.

**Table 1: Results of Ethylene polymerization<sup>a</sup> by precursor [Zr( $\eta^5$ - $\eta$ -1-C<sub>9</sub>H<sub>7</sub>SiMe<sub>2</sub>NCMe<sub>3</sub>)Me<sub>2</sub>]<sub>2</sub>[(CH<sub>2</sub>)<sub>n</sub>] [n=6(1), 9(2), 12(3)] with various cocatalysts**

precursor	Cocatalyst <sup>b</sup>	Activity <sup>c</sup>	T <sub>m</sub> (°C)	M <sub>w</sub> ( $\times 10^{-4}$ ) <sup>d</sup>
1	B <sub>1</sub>	309	135.9	63.9
1	B <sub>2</sub>	141	132.7	36.5
1	B <sub>3</sub>	226	125.6	40.1
2	B <sub>1</sub>	346	137.2	56.5
2	B <sub>2</sub>	154	131.6	56.1
2	B <sub>3</sub>	248	128.3	57.4
3	B <sub>1</sub>	373	136.1	41.5
3	B <sub>2</sub>	173	134.2	56.0
3	B <sub>3</sub>	266	126.7	51.8
Marks' Cat (Zr <sub>2</sub> )	B <sub>1</sub> <sup>e</sup>	87	NA	0.076
Marks' Cat (Zr <sub>2</sub> )	B <sub>2</sub> <sup>f</sup>	67	NA	0.12

(a) Polymerization conditions: C<sub>2</sub>H<sub>4</sub>=1 atm, Toluene=50 mL, t=15 min, [precursor]=15  $\mu$  mol; T<sub>p</sub>=30 °C (b) B<sub>1</sub> 30  $\mu$  mol; B<sub>2</sub> 15  $\mu$  mol; B<sub>3</sub> 30  $\mu$  mol. (c) Activity: Kg-Polymer/ mol cationic metallocene  $\cdot$  h  $\cdot$  atm. (d) By GPC vs polystyrene standards, broad MWD (e) C<sub>2</sub>H<sub>4</sub>=1 atm, Toluene=100 mL, T<sub>p</sub>=24 °C, [precursor]=5  $\mu$  mol; (f) B<sub>1</sub> 10  $\mu$  mol, t=1.25 h; (f) B<sub>2</sub> 5  $\mu$  mol, t=10 min.

#### Nuclearity Effects of polymethylene bridged dinuclear cation.

According to the reported studies it turned out that the ethylene bridged dinuclear metallocene with the dinuclear borate anion was found to be effective to form LLDPE with the significantly enhanced chain branching due to the improved  $\alpha$ -olefin comonomer 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 CGC 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 close spatial proximity. Presumably, there are two pathways for the preferential formation of cation/anion active ion pairs by activation of B<sub>2</sub> to form two kinds of active species which would both act as active center in the enchainment processes. And hence led to reverse nuclearity effect when activated by B<sub>2</sub> and produced polymer with broad MWD.

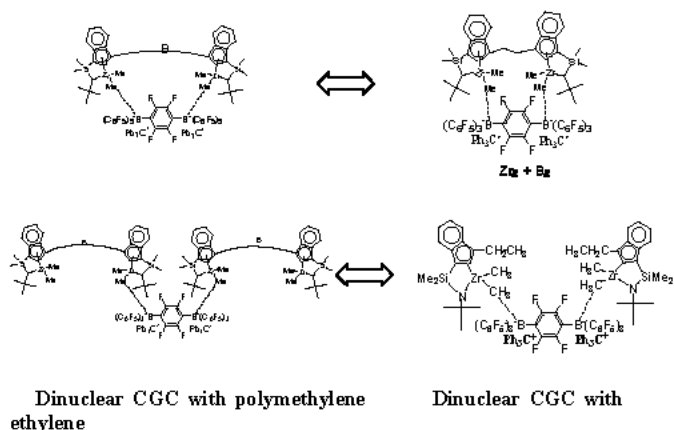


Figure 2. Cationic dinuclear metallocene with various anions.

#### Conclusion.

New polymethylene bridged dinuclear cationic CGC complexes have been prepared to study polymerization effects as well as the counteranion effects in the ethylene polymerization. Regarding the ethylene polymerization activity, increased activity is observed upon increasing the length of the bridging ligand. Counteranion studies demonstrate there was the significant influence on catalytic activity following the order of B<sub>2</sub> < B<sub>3</sub> < B<sub>1</sub>. The comonomer incorporation capability shows no apparent dependence on the length of the bridging ligand. Ethylene polymerization results suggest that polymethylene bridged dinuclear CGC complexes represented a different, complicate pathway that was distinguished from the ethylene bridged dinuclear complexes in  $\alpha$ -olefins polymerization process.

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