

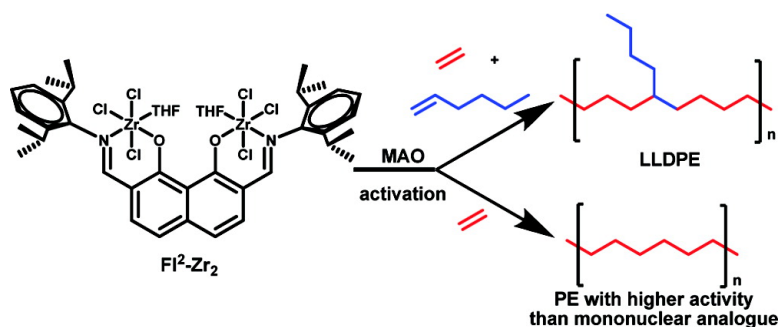
Communication

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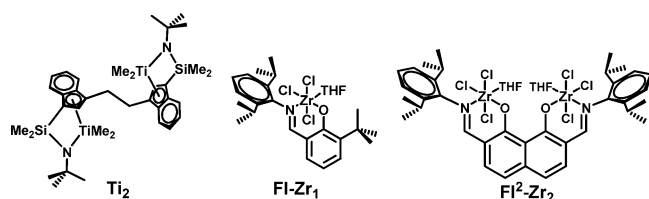
## Synthesis, Characterization, and Marked Polymerization Selectivity Characteristics of Binuclear Phenoxyiminato Organozirconium Catalysts

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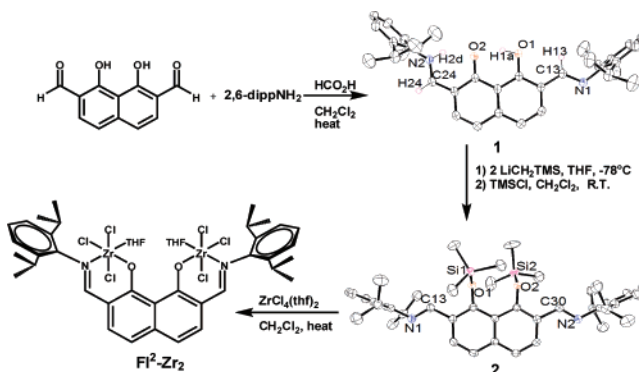
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Recently, binuclear organo group 4 polymerization catalysts<sup>1</sup> based on constrained geometry catalyst (CGC) structures have been reported (e.g., **Ti**<sub>2</sub>),<sup>2</sup> and cooperativity effects between adjacent catalytic centers were shown to induce significant rate and selectivity enhancements in ethylene and ethylene +  $\alpha$ -olefin (co)-polymerizations. Even traditionally unreactive hindered olefins are readily enchainment in the presence of these catalysts.<sup>2c,d</sup> In the nonmetallocene area, new families of group 4 bis-<sup>3</sup> and monophenoxyiminato<sup>4</sup> olefin polymerization catalysts have attracted attention due to ease of preparation,<sup>3a</sup> ability to support living polymerizations,<sup>3b,5</sup> and utility in producing new polyolefin architectures.<sup>6</sup> However, despite these attractions, monophenoxyiminato group 4 catalysts generally exhibit surprisingly limited efficiencies for ethylene +  $\alpha$ -olefin copolymerizations.<sup>4</sup> In view of the aforementioned results in which binuclear CGC complexes enhance comonomer incorporation selectivity, the intriguing question arises as to whether two phenoxyiminato catalytic centers could be poised in close proximity and whether copolymers and other new macromolecular architectures might then be accessible. Here we communicate the first binuclear phenoxyiminato zirconium polymerization catalyst and show that it exhibits significantly enhanced polymerization activity in ethylene homopolymerizations versus a mononuclear analogue. Furthermore, the catalyst produces high molecular weight 1-hexene/ethylene copolymers, while the mononuclear analogue yields only traces of copolymer under identical reaction conditions.



Binuclear ligand (Scheme 1) precursor **1** was synthesized<sup>7</sup> by condensation of 2,7-diformyl-1,8-dihydroxynaphthalene<sup>8</sup> and 2,6-diisopropylaniline (2,6-dippNH<sub>2</sub>) in refluxing dichloromethane.<sup>7,9</sup> The asymmetric proton arrangement in the crystal structure<sup>10</sup> of **1** is consistent with solution NMR data.<sup>11</sup> The reagent 2,7-di(2,6-diisopropylphenyl)imino-1,8-di(trimethylsiloxy)naphthalene (**2**) was synthesized by LiCH<sub>2</sub>TMS deprotonation of **1** followed by TMSCl silylation.<sup>4</sup> In agreement with previous reports,<sup>4b</sup> direct addition of ZrCl<sub>4</sub> to lithiated phenoxyimine ligands proceeds with poor selectivity. Therefore, bimetallic precursor **FI**<sup>2</sup>-Zr<sub>2</sub> was synthesized by TMSCl elimination from **2** + ZrCl<sub>4</sub>(THF)<sub>2</sub> in dichloromethane. The shift of the imine proton in the <sup>1</sup>H NMR spectrum from  $\delta$  8.76 to 12.95 ppm is consistent with Zr<sup>4+</sup> coordination to N.<sup>4</sup> All new compounds were characterized by standard spectroscopic and analytical techniques, with elemental analysis and MALDI-MS<sup>7</sup> confirming the **FI**<sup>2</sup>-Zr<sub>2</sub> bimetallic constitution. Note that the **FI**<sup>2</sup>

**Scheme 1.** Synthetic Routes to Ligand Precursors and Bimetallic Catalyst **FI**<sup>2</sup>-Zr<sub>2</sub>



coordination geometry confers significantly more rigidity on the M...M interaction than in binuclear CGC structures<sup>2</sup> and reduces the minimum estimated<sup>12</sup> M...M approach distance to  $\sim$ 5.9 Å from  $\sim$ 7.4–8.7 Å.<sup>2d</sup>

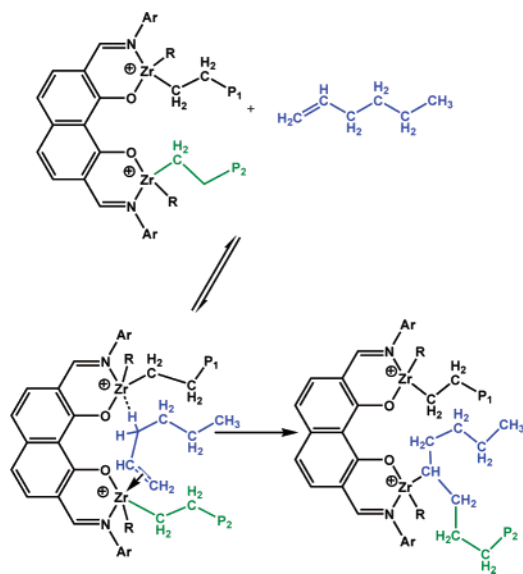
Ethylene homopolymerizations<sup>13</sup> using **FI**<sup>2</sup>-Zr<sub>2</sub> activated with MAO afford high molecular weight linear polyethylenes with activities (Table 1) which are  $\sim$ 8 $\times$  that of mononuclear **FI-Zr**<sub>1</sub> (Table 1, entry 1 vs entry 3). The importance of linear low-density polyethylenes (LLDPEs)<sup>14</sup> led us to also investigate ethylene + 1-hexene copolymerizations with **FI**<sup>2</sup>-Zr<sub>2</sub>. It is found that efficient 1-hexene co-enchainment is achieved under mild reaction conditions.<sup>7</sup> The copolymers were characterized by <sup>1</sup>H and <sup>13</sup>C NMR<sup>16</sup> spectroscopy and melting point (125–126 °C), and comonomer incorporation is found to increase incrementally over a 5.5-fold 1-hexene concentration range (Table 1, entries 5–7). In marked contrast to these results, mononuclear control catalyst **FI-Zr**<sub>1</sub> yields only traces of copolymer under identical reaction conditions (Table 1, entry 8).<sup>7</sup> It has been postulated<sup>2</sup> that two proximate, activated CGC centers facilitate comonomer enchainment via multinuclear interactions involving both metal centers. This CGC-centered picture is clearly more general than previously thought, and Scheme 2 shows a possible scenario for binuclear phenoxyiminato Zr-mediated comonomer enchainment selectivity. In the case of **FI-Zr**<sub>1</sub>, 1-hexene appears to inhibit polymerization activity, while **FI**<sup>2</sup>-Zr<sub>2</sub> displays moderate activity with substantial selectivity for copolymerization. Furthermore, at most only minor depression in **FI**<sup>2</sup>-Zr<sub>2</sub> polymerization activity is observed on 5.5-fold increase in 1-hexene concentration (Table 1, entries 5–7).<sup>15</sup> Meaningful GPC data could not be obtained for entries 1, 3, and 4 due to limited polymer solubility.

These results show that binuclear group 4 phenoxyiminato polymerization catalysts are accessible and that, compared to a mononuclear control, multinuclearity substantially enhances ethylene homopolymerization activity and comonomer enchainment

**Table 1.** Ethylene and Ethylene-co-1-Hexene Polymerization Results for Catalysts **FI<sup>2</sup>-Zr<sub>2</sub>** and **FI-Zr<sub>1</sub>**<sup>a</sup>

entry	cat	comonomer	temperature (°C)	comonomer conc. (M)	μmol Zr	polymer yield (g)	activity <sup>b</sup> (×10 <sup>3</sup> )	10 <sup>3</sup> M <sub>w</sub> <sup>c</sup>	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	comonomer incorporation (%) <sup>d</sup>
1	<b>FI<sup>2</sup>-Zr<sub>2</sub></b>	N/A	24	N/A	10.2	0.167	16(1)	too insol.	too insol.	N/A
2	<b>FI<sup>2</sup>-Zr<sub>2</sub></b>	N/A	40	N/A	10.2	0.230	23(1)	155	3.92	N/A
3	<b>FI-Zr<sub>1</sub></b>	N/A	24	N/A	10.1	0.019	2.1(4)	too insol.	too insol.	N/A
4	<b>FI-Zr<sub>1</sub></b>	N/A	40	N/A	10.1	0.036	3.6(5)	too insol.	too insol.	N/A
5	<b>FI<sup>2</sup>-Zr<sub>2</sub></b>	1-hexene	40	0.72	10.1	0.196	16(1)	53	4.21	2.1
6	<b>FI<sup>2</sup>-Zr<sub>2</sub></b>	1-hexene	40	1.6	10.1	0.178	14(1)	93	3.33	5.8
7	<b>FI<sup>2</sup>-Zr<sub>2</sub></b>	1-hexene	40	4.0	10.1	0.150	12(1)	98	3.31	11
8	<b>FI-Zr<sub>1</sub></b>	1-hexene	24	0.72	10.1	<0.001	N/A	N/A	N/A	N/A

<sup>a</sup> Polymerizations carried out on a high-vacuum line with MAO as cocatalyst (Al:Zr = 1000:1) in 50 mL of toluene under 1.0 atm ethylene pressure. Ethylene homopolymerizations and ethylene-1-hexene copolymerizations carried out for 60 and 75 min, respectively. Each entry is the average of at least two runs. <sup>b</sup> Gram polymer/[mol Zr]·atm·h; estimated uncertainties indicated in parentheses. <sup>c</sup> From GPC vs polystyrene standards. <sup>d</sup> Comonomer incorporations calculated by the method of Pooter et al.<sup>16</sup> N/A = not applicable.

**Scheme 2.** Possible Pathway for Multi-Metal-Assisted Comonomer Enchainment in Bimetallic **FI<sup>2</sup>-Zr<sub>2</sub>** Catalyst (Ar = 2,6-Diisopropylphenyl; R = H, Alkyl; Anion Omitted for Clarity)

selectivity in ethylene + 1-hexene copolymerizations. The ability to produce copolymers presumably reflects the influence of the proximate metal center in promoting comonomer enchainment.

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**Supporting Information Available:** Details of ligand, catalyst synthesis, polymerization experiments, and crystal structures (PDF, CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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