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Polymerization

Polynuclear Olefin Polymerization Catalysis: Proximity and Cocatalyst Effects Lead to Significantly Increased Polyethylene Molecular Weight and Comonomer Enchainment Levels**

*Hongbo Li, Liting Li, and Tobin J. Marks**

Abiotic attempts to mimic certain advantageous enzyme characteristics have recently focused on construction of multimetallic catalytic centers capable of achieving cooperative recognition/activation/reactivity effects between proximate transition-metal ions.[1] Regarding such effects in single-site polymerization catalysis,[2–4] we recently reported that a constrained geometry binuclear catalyst and binuclear cocatalyst combination (**C2-Zr$_2$** + **B$_2$**) affords, through the modification of chain-transfer pathways, significantly enhanced branching in ethylene homopolymerization and enhanced comonomer incorporation in ethylene and 1-hexene copolymerization versus a mononuclear combination of **Zr$_1$** + **B$_1$**.[3c]

Nevertheless, constrained-geometry catalysts (CGC) of Zr typically produce unacceptably low-$\bar{M}_w$ polyolefins,[4c,d,5] ($\bar{M}_w$ is the weight-average molar mass) raising the intriguing question of what effects closer metal–metal proximity and alternative cocatalysts might have. Here we communicate that in ethylene homopolymerizations under identical reaction conditions, methylene-bridged **C1-Zr$_2$** affords significantly higher molecular weight products than -CH$_2$CH$_2$-bridged **C2-Zr$_2$** (≈70× $\bar{M}_w$ increase) and mononuclear **Zr$_1$** (≈130× $\bar{M}_w$ increase). Furthermore, with MAO (methylaluminoxane) as cocatalyst, very large increases in polyethylene molecular weight are achieved with both **C2-Zr$_2$Cl$_4$** and **C1-**

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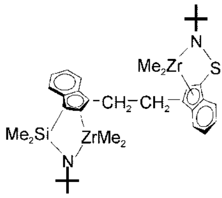
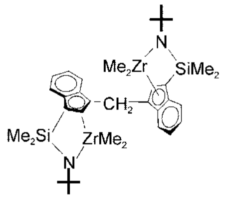


C2-Zr$_2$



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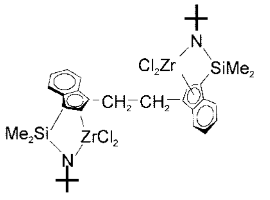

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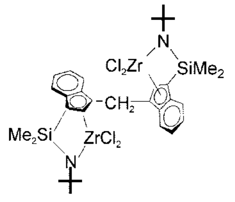
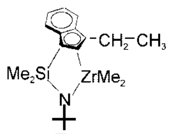


C1-Zr$_2$Cl$_4$

$Ph_3C^+B(C_6F_5)_4^-$

B$_1$



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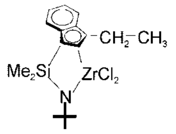
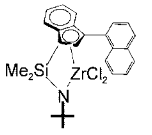
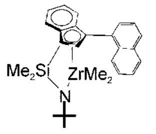


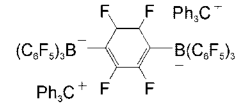
Zr$_1$Cl$_2$



N-Zr$_1$Cl$_2$

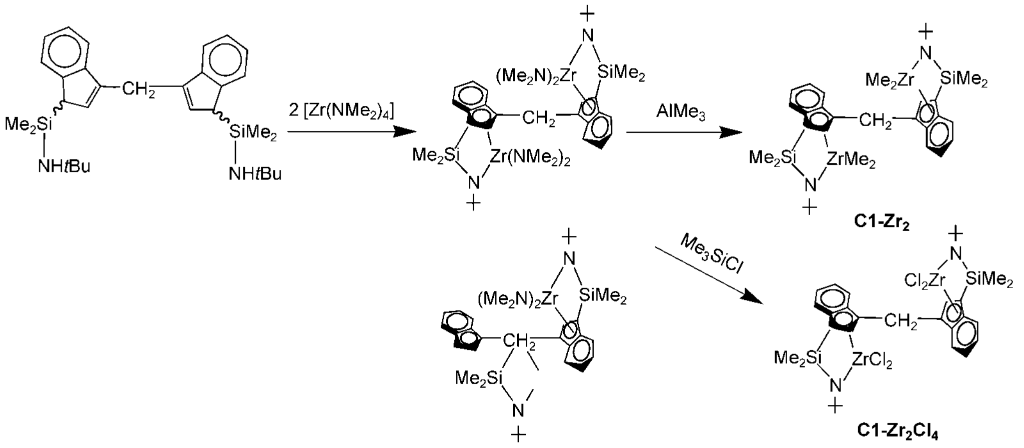


N-Zr$_1$



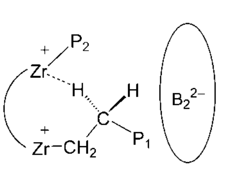
B$_2$

Zr$_2$Cl$_4$ versus mononuclear **Zr$_1$Cl$_2$** ($\approx 600\times \bar{M}_w$ increase), while for ethylene + 1-hexene copolymerization, the shorter bridge enhances both product $\bar{M}_w$ ($\approx 40\times$ increase) and selectivity for α-olefin enchainment ($\approx 3\times$ increase). Results from ligand-substituent and solvent experiments support the argument that the role of the proximate metal centers is not merely steric.



Scheme 1. Synthetic routes to complexes **C1-Zr$_2$** and **C1-Zr$_2$Cl$_4$**.

C1-Zr$_2$ was synthesized as shown in Scheme 1, while sterically encumbered naphthyl derivative **N-Zr$_1$**[6] was prepared to probe ligand steric effects. New compounds were characterized by conventional methodologies, and polymerizations were carried out under rigorously anhydrous, anaerobic conditions with attention to exotherm and mass-transfer effects.[3a,b] Ethylene homopolymerization results are summarized in Table 1. Entries 1–3 show that 70× and 130× increases in $\bar{M}_w$ are achieved with **C1-Zr$_2$** verus **C2-Zr$_2$** and **Zr$_1$**, respectively, under identical polymerization conditions (**B$_2$** cocatalyst). As in the case of **C2-Zr$_2$**,[3c] a combination of **C1-Zr$_2$** with **B$_2$** produces polyethylene with ethyl branching as a distinctive microstructural feature, and the $\bar{M}_w$ is found to be essentially independent of ethylene pressure. Chain transfer to monomer[7] is therefore the most probable source of branching in these polymerizations,[3c] with the $\approx 8\times$ greater ethyl branching per 1000 C atoms for **C2-Zr$_2$** versus **C1-Zr$_2$**, which correlates with the lower product $\bar{M}_w$ arising from the former. For single-site polymerization, $\bar{M}_{n,w}$ ($\bar{M}_n$ is the number-average molar mass) are typically proportional to the net rate of chain propagation divided by the net rate of chain termination. Since **C1-Zr$_2$** polymerization activity is $\approx 20\%$ that of **C2-Zr$_2$** (Table 1), reasonably assuming comparable percentages of active catalytic centers[8] (in situ ^{1}H NMR indicates rapid, quantitative Ph_3CCH_3 formation upon catalyst activation) infers that the net rate of **C1-Zr$_2$** propagation is $\approx$ 20% that of **C2-Zr$_2$**, hence, the **C1-Zr$_2$** termination rate must be dramatically depressed to obtain the large observed $\bar{M}_w$ enhancement. These effects are likely to reflect differences in achievable Zr–Zr proximity[9] and possible access to bridged structures (e.g., **1**). Note that the results with more sterically congested mononuclear **N-Zr$_1$** (Table 1, compare entries 1, 2, 4) support the argument that the effect of the proximate metal center is not simply steric in origin, while polymerization experiments in more polar, ion-pairing-weakening[10] C_6H_5Cl



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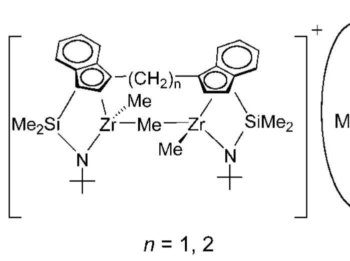

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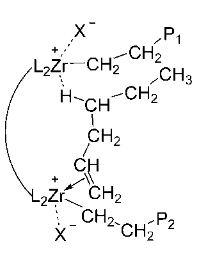

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Table 1: Ethylene and ethylene + 1-hexene polymerization data for CGCZr catalysts with various nuclearities and cocatalysts.[a]

Entry no	Catalyst	Monomer	μmol of catalyst	Reaction time [h]	Polymer yield [g]	Activity [$\times 10^3$][b]	Ethyl branches per 1000C	*n*-Butyl branches per 1000 C	$\bar{M}_n$ [$\times 10^2$][c]	$\bar{M}_w/\bar{M}$[c]
1	**Zr$_1$ + B$_2$**[d]	E	10	1.16	1.08	93 (11)	6.5	0.6	6.3	1.1
2	**C1-Zr$_2$ +B$_2$**	E	5.0	1.50	0.19	13 (3)	1.6	≈ 0	326	2.7
3	**C2-Zr$_2$ + B$_2$**[d]	E	5.0	1.50	0.94	63 (7)	12	1.0	11	1.2
4	**N-Zr$_1$ + B$_2$**	E	10	1.50	0.51	34 (7)	≈ 0	≈ 0	25	2.3
5	**Zr$_1$ + B$_2$**[e]	E	10	0.025	0.17	680 (20)	1.7	1.1	17	1.4
6	**C1-Zr$_2$ +B$_2$**[e]	E	5.0	0.025	0.16	640 (20)	2.8	1.4	15	1.5
7	**Zr$_1$Cl$_2$ + MAO**[f]	E	10	1.50	0.37	25 (5)	≈ 0	≈ 0	9.5	1.3
8	**C1-Zr$_2$Cl$_4$ + MAO**[f]	E	5.0	1.50	0.38	25 (3)	≈ 0	≈ 0	2440	2.7
9	**C2-Zr$_2$Cl$_4$ + MAO**[f]	E	5.0	1.50	0.35	23 (5)	≈ 0	≈ 0	2680	2.8
10	**N-Zr$_1$Cl$_2$ + MAO**[f]	E	10	1.50	0.35	23 (5)	≈ 0	≈ 0	56	2.2
11	**Zr$_1$ + B$_2$**[d]	E/H	10	0.75	1.00	133 (13)	6.0	3.2	7.3	1.1
12	**C1-Zr$_2$ +B$_2$**	E/H	5.0	1.50	0.13	8.6(5)	1.3	17.2	221	2.3
13	**C2-Zr$_2$ + B$_2$**[d]	E/H	5.0	1.25	1.09	87 (9)	10	5.5	11	1.2
14	**Zr$_1$Cl$_2$ + MAO**[f]	E/H	10	1.50	0.46	15 (3)	≈ 0	5.4	3.4	1.3
15	**C1-Zr$_2$Cl$_4$ + MAO**[f]	E/H	5.0	1.50	0.33	11 (2)	≈ 0	22.8	1130	2.9
16	**C2-Zr$_2$Cl$_4$ + MAO**[f]	E/H	5.0	3.00	0.27	8.9 (6)	≈ 0	19.4	872	2.9

[a] Polymerizations carried out on high vacuum line at 24 °C in 100 mL of toluene under 1.0 atm ethylene pressure, [hexene] = 0.8 M. [b] (g polymer) (mol cationic metallocene)$^{-1}$ (atm)$^{-1}$ h^{-1}. [c] From GPC versus polystyrene standards.[d] from reference [3c] (other low-$\bar{M}_w$ samples have a similarly low polydispersity pattern, reflecting imprecision in calibration). [e] Polymerizations carried out in chlorobenzene. [f] Al:Zr = 1000:1. MAO dried in vacuo for 48 h to remove excess Al$_2$Me$_6$.

In regard to cocatalyst effects, note that while the homopolymerization behavior of the combination of **Zr$_1$Cl$_2$** or **N-Zr$_1$Cl$_2$** + MAO approximately parallels that of **Zr$_1$** + **B$_2$** (Table 1, entries 1,7,10), the combinations of **C1-Zr$_2$Cl$_4$** + MAO and **C2-Zr$_2$Cl$_4$** + MAO both afford comparable polyethylenes of very high $\bar{M}_w$, with $\bar{M}_w$ increased up to $\approx 600\times$ versus **Zr$_1$Cl$_2$** + MAO (entries 8,9 versus 7).[11,12] From Table 1, note that the activities **C1-Zr$_2$Cl$_4$** and **C2-Zr$_2$Cl$_4$** + MAO are similar to that of **Zr$_1$Cl$_2$** + MAO, so by using the arguments outlined above, chain-transfer rates must be dramatically depressed in the binuclear catalysts. Comparing entries 8,9, and 2, we note that the MAO-activated species produce polyethylene witj even higher molecular weight than **C1-Zr$_2$** + **B$_2$**; the lower ethyl-branch content suggests a scenario in which the relative chain-termination rate is even slower for **Zr$_2$Cl$_4$** + MAO than for **C1-Zr$_2$** + **B$_2$** (assuming that ethyl branch formation requires chain transfer to monomer and subsequent α-olefin/polyolefin reinsertion[3c]). For the MAO with **C1-Zr$_2$Cl$_4$** and **C2-Zr$_2$Cl$_4$** catalysts, we observe Zr(μ-CH$_3$)Zr species by in situ NMR, which confirms that the two Zr centers can approach closely,[12,13] and the bulky[14] MAO cocatalyst/counteranion may stabilize this structure, (for example, **2;** as encumbered H$_3$CB(perfluorobiphenyl)$_3^-$ stabilizes cationic M(μ-CH$_3$)M$^+$ species).[13a] Note that bridge length plays, at most, a minor role when MAO is the cocatalyst (entries 8, 9).

Regarding cooperativity effects in copolymerization, experiments that involve a mixture of ethylene and 1-hexene indicate that a combination of **C1-Zr$_2$** + **B$_2$** incorporates $\approx 3\times$ more 1-hexene than does **C2-Zr$_2$** + **B$_2$** (Table 1 entries 11–13). The homopolymerization results are paralleled; the copolymer $\bar{M}_w$ is $\approx 40\times$ greater for **C1-Zr$_2$** + **B$_2$** than for **C2-Zr$_2$** + **B$_2$**. Interestingly, ^{13}C NMR data also reveal that the copolymer derived from **C1-Zr$_2$** + **B$_2$** contains similar quantities of ethyl branches to those obtained in the above ethylene homopolymerizations, which suggests that the same chain-transfer mechanism is again operative. With MAO as the copolymerization cocatalyst, **C1-Zr$_2$Cl$_4$** incorporates $4.2\times$ more, and **C2-Zr$_2$Cl$_4$** $3.5\times$ more, 1-hexene than does **Zr$_1$Cl$_2$** and with comparable polymerization activities. Paralleling the homopolymerizations, the copolymer $\bar{M}_w$ from the **C1-Zr$_2$Cl$_4$**- and **C2-Zr$_2$Cl$_4$**-mediated polymerizations is again significantly greater ($\approx 600\times$) than in the **Zr$_1$Cl$_2$**-catalyzed process. These comonomer-enchainment-selectivity data implicate differences in achievable Zr–Zr proximity and structures likely to facilitate comonomer enchainment (e.g., **3**).

The present results significantly expand what is known about metal–metal proximity and cocatalyst/counteranion effects in binuclear CGC olefin polymerization catalysis. In ethylene homopolymerization, a large increase in product $\bar{M}_w$ is achieved with **C1-Zr$_2$** + **B$_2$** versus **C2-Zr$_2$** + **B$_2$** and **Zr$_1$** + **B$_2$**. In ethylene + 1-hexene copolymerizations, a combination of **C1-Zr$_2$** + **B$_2$** incorporates significantly more 1-hexene than does **C2-Zr$_2$** + **B$_2$**. When MAO is the cocatalyst, very large increases in $\bar{M}_w$ occur with both **C1-Zr$_2$Cl$_4$** and **C2-Zr$_2$Cl$_4$** compared with **Zr$_1$Cl$_2$**, and in ethylene + 1-hexene copolymerization, both **C2-Zr$_2$Cl$_4$** and **C1-Zr$_2$Cl$_4$** enchain more 1-hexene than does **Zr$_1$Cl$_2$** to yield products with far higher molecular weights. These results support the argument that Zr–Zr cooperativity effects can decrease chain-transfer rates as well as increase selectivity for comonomer enchainment, and that such effects are highly sensitive to ion pairing. Ligand-substituent and solvent-control experiments reveal that the role of proximate metal centers is not merely steric.

Experimental Section

All manipulations were performed as described elsewhere with rigorous exclusion of O$_2$ and H$_2$O.[3a] Ethylene polymerizations[3c] were carried out on a high vacuum line in round-bottom three-neck Morton flasks. In typical experiments, dry toluene was vacuum-were carried out on a high vacuum line in round-bottom three-neck Morton flasks. In typical experiments, dry toluene was vacuum-transferred into the reaction flask from Na/K and presaturated with 1.0 atm of ethylene. Catalytically active species were freshly generated by mixing measured amounts of precatalyst and cocatalyst in 1,2-difluorobezene in septum-capped vials in the glove box (with MAO, the mixture was stirred vigorously for 30 min before use). The catalyst solution was then quickly injected into the rapidly stirred reaction flask. After a measured time interval, polymerization was quenched by the addition of 2% acidified methanol.

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[9] Approximate modeling at the Spartan level reveals that the minimum Zr···Zr approach distance in **C1-Zr$_2$** with **B$_2$** is ≈0.25 Å shorter than in **C2-Zr$_2$** with **B$_2$**.

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[11] A combination of **C1-Zr$_2$** + MAO exhibits polymerization behavior indistinguishable from that of **C1-Zr$_2$Cl$_4$** + MAO, excluding artifacts due to Zr−Cl linkages.

[12] In situ ^{1}H NMR of the reactions of **C2-Zr$_2$Cl$_4$** with MAO and **C1-Zr$_2$Cl$_4$** + MAO reveals a $\delta = -2.13$ ppm resonance, assignable to a Zr(μ-methyl)Zr moiety.[13] Such a feature is not detectable in either **Zr$_1$Cl$_2$** + MAO, **C1-Zr$_2$** + **B$_2$**, or **C2-Zr$_2$** + **B$_2$** reaction mixtures, but can also be detected in **C2-Zr$_2$** + tris(perfluorobiphenyl)borane (**PBB)** reaction mixtures, a system known to readily form Zr(μ-methyl)Zr moieties.[13a] After the introduction of ethylene into the **C2-Zr$_2$Cl$_4$** with MAO mixture, the intensity of the $\delta = -2.13$ ppm peak decreases dramatically, consistent with μ-methyl dissociation and subsequent activation of the Zr centers, analogous to previous observations on other MAO-activated μ-methyl systems.[13c]

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