

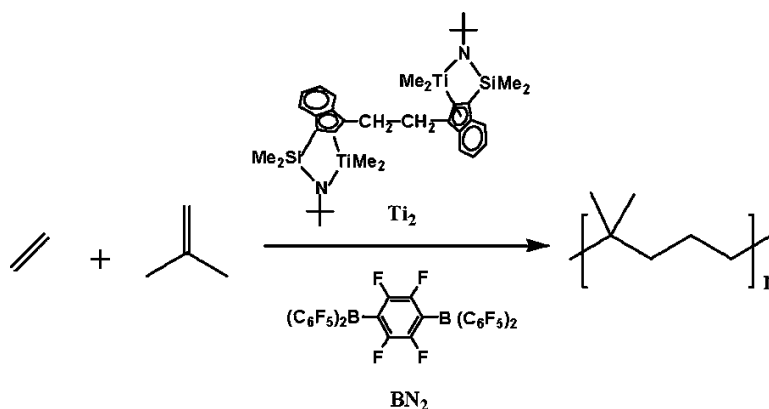
Communication

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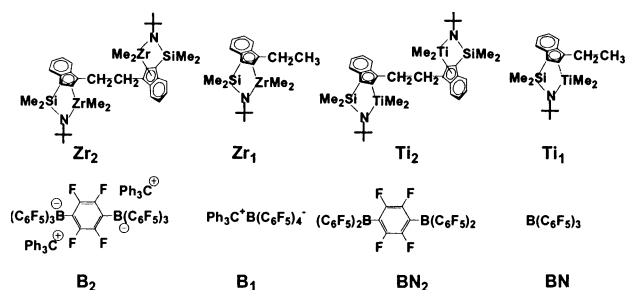
Catalyst/Cocatalyst Nuclearity Effects in Single-Site Olefin Polymerization. Significantly Enhanced 1-Octene and Isobutene Comonomer Enchainment in Ethylene Polymerizations Mediated by Binuclear Catalysts and Cocatalysts

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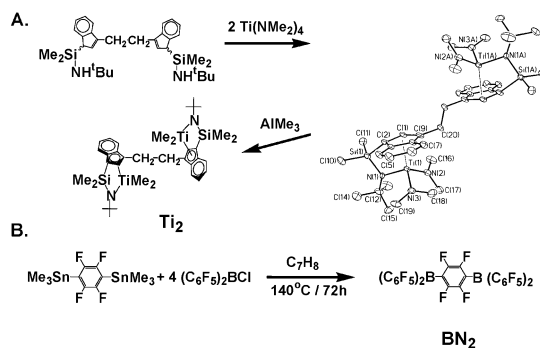
Enzymatic catalysts achieve superior reactivity and selectivity, in part due to high local reagent concentrations and conformationally advantageous spatial proximities/interactions.¹ In this regard, the possibility of unique/more efficient catalytic transformations based on cooperative effects between active centers in multinuclear complexes is being intensively investigated.² For single-site olefin polymerization catalysts,^{3–5} two connectivity strategies (electrostatic and covalent) for bringing catalyst centers into spatial proximity have been pursued to achieve cooperative effects via multinuclear “CGC” structures.^{4a,b} Regarding electrostatic approaches, it was recently shown^{4a} that bisborate cocatalyst **B**₂ dramatically increases



the efficiency of heterobimetallic enchainment processes by bringing cationic Me₂Si(‘BuN)(η⁵-C₅Me₄)TiMe⁺ (producing high-molecular-weight polyethylene with high activity) and 1-Me₂Si(3-ethylindenyl)(‘BuN)]ZrMe⁺ (producing low-molecular-weight polyethylene with low activity, **Zr**₁) centers into proximity, thereby increasing selectivity for branched LLDPE formation. Regarding covalent approaches, it was recently reported^{4b} that bimetallic **Zr**₂^{4b} + **B**₂^{4b,6} affords enhanced branching in ethylene homopolymerization and enhanced comonomer incorporation in ethylene + 1-pentene copolymerization vs **Zr**₁ + **B**₁. Nevertheless, CGCZr catalysts produce low-molecular-weight polyolefins with low activity and low α-olefin cochainment efficiency,^{4b,7} raising the intriguing question of what properties bimetallic CGCTi catalysts might exhibit, since mononuclear CGCTi catalysts typically produce high-molecular-weight polyolefins with high activity and high α-olefin cochainment efficiency.^{4a,5} Here we report that a new binuclear organotitanium catalyst + binuclear activators affords, vs mononuclear analogues, high-molecular-weight polyethylenes with significantly enhanced α-olefin comonomer incorporation and, in particular, significantly enhanced incorporation of traditionally unreactive isobutene.

Bimetallic catalyst precursor EBICGC(TiMe₂)₂ (**Ti**₂) was synthesized by Al₂(CH₃)₆ alkylation of EBICGC[Ti(NMe₂)₂]₂ (Scheme 1A),⁸ while monometallic [1-Me₂Si(3-CH₂CH₃indenyl)(‘BuN)]-

Scheme 1. Synthetic Routes to Binuclear Catalyst and Cocatalyst



TiMe₂ (**Ti**₁) was synthesized in a similar manner for control experiments.⁸ Binuclear bisborane activator 1,4-(C₆F₅)₂BC₆F₄B-(C₆F₅)₂ (**BN**₂) was synthesized via reaction of 1,4-Me₃SnC₆F₄SnMe₃ and excess (C₆F₅)₂BCl (Scheme 1B). All new compounds were characterized by standard spectroscopic/analytical/diffraction methodologies.⁸

As benchmarks, ethylene + 1-octene copolymerizations with four combinations of CGCTi catalysts and cocatalysts of varying nuclearity (**Ti**₁ + **B**₁, **Ti**₁ + **B**₂, **Ti**₂ + **B**₁, **Ti**₂ + **B**₂) were first examined under identical anhydrous/anaerobic reaction conditions.^{4a,b} The polymerization data (Table 1) indicate that, under identical conditions, the catalyst derived from bimetallic **Ti**₂ and bifunctional cocatalyst **B**₂ enchains ~11 times more 1-octene⁹ than that derived from mononuclear **Ti**₁ and **B**₁, while **Ti**₁ + **B**₂ and **Ti**₂ + **B**₁ each incorporate ~2 times more. The activity of these CGCTi catalysts activated by the trityl borates is ~100 times greater, and the product molecular weight is ~100 times greater than previously achieved with the Zr analogues.^{4b}

Efficient isobutene + ethylene coordinative copolymerization presents a daunting challenge from both academic and technological perspectives.^{10a,b} Recently, ethylene + isobutylene copolymers with moderate comonomer contents were prepared using modified mononuclear CGCTi catalysts and *very large* isobutene stoichiometric excesses (isobutene:ethylene up to 150:1).^{10c} In the present work, ethylene + isobutene polymerization was examined with several CGC catalysts and cocatalysts of varying nuclearity. It is found that CGCZr catalysts (**Zr**₁ or **Zr**₂) in combination with any of the cocatalysts introduce negligible quantities of the isobutene comonomer. With Ti, the results are sensitive to cocatalyst. Trityl borate activators (**B**₁ or **B**₂) alone initiate *cationic* isobutene homopolymerization,^{10d} affording physical mixtures of polyethylene and polyisobutene homopolymers in the presence of **Ti**₁ or **Ti**₂. MAO avoids this problem but yields copolymers with low activity. With MAO, **Ti**₂ incorporates ~2 times more isobutene than **Ti**₁. Next, polymerizations were carried out with bisborane cocatalyst **BN**₂, affording ethylene–isobutene copolymers with reasonable

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Table 1. Ethylene + α -Olefin Copolymerization Results for Catalysts **Ti₂**, **Ti₁** and Cocatalysts **B₂**, **B₁**, **BN₂**, **BN**

entry	cat.	cocat.	comonomer	comonomer concn (M)	μ mol of cat.	reaction time (min)	polymer yield (g)	activity ^b	$10^{-3} M_n^c$	M_w/M_n^c	comonomer incorporation (%) ^e
1	Ti₁	B₁	1-octene	0.64	10	5	8.43	1.0×10^7	155	2.33	0.6
2	Ti₁	B₂	1-octene	0.64	10	5	3.20	3.9×10^6	147	1.99	1.1
3	Ti₂	B₁	1-octene	0.64	5	5	4.30	5.1×10^6	157	2.75	1.0
4	Ti₂	B₂	1-octene	0.64	5	5	2.50	3.0×10^6	161	2.73	7.0
5	Ti₁	BN	isobutene	1.2	10	5	0.80	9.6×10^5	577	2.13	3.1
6	Ti₁	BN₂	isobutene	1.2	10	5	0.37	4.4×10^5	305	2.16	9.5
7	Ti₂	BN	isobutene	1.2	5	10	0.61	3.6×10^5	490	2.41	7.3
8	Ti₂	BN₂	isobutene	1.2	5	10	0.47	2.8×10^5	168	3.67	15.2
9	Ti₁	MAO^d	isobutene	1.2	10	60	0.39	3.9×10^4	487	2.52	2.9
10	Ti₂	MAO^d	isobutene	1.2	5	240	0.44	1.1×10^4	355	2.87	6.2

^a Polymerizations carried out on a high-vacuum line at 24 °C in 100 mL of toluene under 1.0 atm ethylene pressure. ^b Gram polymer/[mol cationic metallocene]·atm·h]. ^c From GPC vs polystyrene standards; all distributions are monomodal. ^d Al:Ti = 1000:1. ^e For ethylene + 1-octene copolymer, calculated from ¹³C NMR spectra;^{9a,b} for ethylene + isobutene copolymer, calculated from ¹³C NMR spectra.^{10c}

activity (Table 1).¹¹ Importantly, under identical, stoichiometrically conservative polymerization conditions (isobutene:ethylene = 8.8:1), binuclear **Ti₂** + bifunctional **BN₂** incorporates ~5 times more isobutene than the mononuclear analogues (~30-fold increase in isobutene:ethylene reactivity ratio), while product molecular weight and polymerization activities decline only moderately with increased catalyst/cocatalyst nuclearity. ¹³C NMR analysis of the copolymer microstructure⁸ reveals that most enchainment units are separated by two or more ethylene units, with small quantities separated by a single ethylene unit. The ¹H spectrum reveals vinylidene endgroups derived from β -methyl elimination. Steric congestion is known to play an important role in metallocenium β -methyl elimination processes.^{10d,e,12} The present results show that the sterically open CGC structure favors ethylene + isobutene copropagation by decreasing the relative rate of chain termination.

In conclusion, new types of binuclear CGCTi catalysts and bifunctional activators have been investigated. They exhibit greatly enhanced polymerization activity, polyolefin molecular weight, and comonomer incorporation efficiency vs the Zr analogues. Particularly noteworthy is the increased selectivity for highly encumbered comonomer enchainment, presumably facilitated via cooperative comonomer capture/binding/delivery by the proximate cationic centers.^{4a,b,13}

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Supporting Information Available: Details of catalyst, cocatalyst syntheses, 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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