

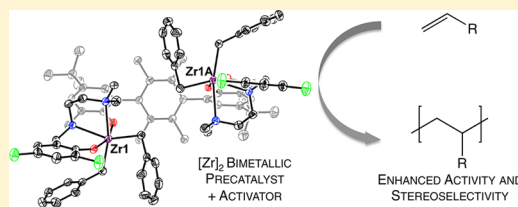
Bimetallic Zirconium Amine Bis(phenolate) Polymerization Catalysts: Enhanced Activity and Tacticity Control for Polyolefin Synthesis

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Supporting Information

ABSTRACT: Binucleating multidentate amine bis(phenolate) ligands with rigid terphenyl backbones were designed to support two zirconium centers locked in close proximity. Polymerizations of propylene or 1-hexene with the synthesized bimetallic precatalysts resulted in polymers with significantly higher isotacticity (up to 79% *mmmm*) in comparison to the stereoirregular polymers produced with previously reported C_s -symmetric monometallic analogues. The bimetallic precatalysts also display higher activity (up to 124 kg of poly(1-hexene) (mmol of Zr)⁻¹ h⁻¹), in comparison to the monometallic analogues, and among the highest activities reported for nonmetallocene catalysts. The stereocontrol is consistent with a bimetallic mechanism involving remote steric interactions with the ligand sphere of the second metal center.



The mechanisms responsible for stereoregulation in the homogeneous polymerization of propylene and α -olefins have been studied extensively.¹ *ansa*-Zirconocene catalysts are the most successful systems for pairing high activity and stereoselectivity, though the development of new classes of catalysts with different selectivity and stability profiles is desirable.^{1b,c,g,2} Thus, the design of stable and inexpensive nonmetallocene catalysts with high activity, regioselectivity, stereoselectivity, and comonomer incorporation is an active area of study.^{1b,g,3} Numerous nonmetallocene catalysts have been reported that exhibit either high activity or stereoselectivity, but rarely both.^{1b,4} Although bimetallic catalysts for olefin polymerization display a variety of beneficial effects, they have received only limited attention as a strategy for tacticity control.⁵ Improved syndiospecificity in styrene polymerization has been reported with linked ditanium systems relative to their monometallic analogues.⁶ Dipalladium catalysts have been shown to produce moderately isotactic CO/styrene copolymers, whereas the monometallic Pd system yielded stereoirregular polymers.⁷ Dizirconium bis-propagators, in the presence of ZnEt₂ as a chain transfer agent, retained the stereoselectivity generally observed with the analogous monometallic catalysts in the absence of ZnEt₂, thereby overcoming a limitation of chain transfer polymerization with these systems.⁸

Recently we reported dinickel bisphenoxyiminato polymerization catalysts based on a rigid terphenyl ligand framework with a permethylated central arene.⁹ The locked conformation of these complexes allowed the isolation and purification of syn and anti atropisomers.^{9a} Early-metal-based dinuclear catalysts are of interest for higher activity, α -olefin incorporation, and tacticity control. For the present work, the terphenyl backbone was utilized with altered donor sets to target the synthesis of bis[amine bis(phenolate)] dizirconium systems analogous to C_s -symmetric monometallic systems reported by Kol and co-

workers.¹⁰ This ligand design was selected for its versatility, ease of synthesis, and interesting catalytic properties of related monometallic Zr complexes. Highly active C_s -symmetric tetradentate amine bis(phenolate) Zr complexes produce up to 10² kg of poly(1-hexene) (mmol of Zr)⁻¹ h⁻¹ or 10¹ kg of polypropylene (mmol of Zr)⁻¹ h⁻¹ of stereoirregular polymer.^{4b,10b} C_2 -symmetric complexes supported by related ligands show increased isospecificity, albeit with significantly lower activity.¹¹ C_1 -symmetric versions displayed enhanced activity and selectivity by exploiting both steric and electronic effects.^{4c,h,12}

Only the syn atropisomers of the binucleating ligand precursors ($H_4^{R2R'2}$ -L) were studied, with the focus on examining the effect of a proximal metal center (Figure 1; see the Supporting Information (SI) for detailed ligand synthesis). A series of compounds was prepared with variation of donor L (methoxy or dimethylamino) and substituents R and R' for steric and electronic tuning (chloride, bromide, methyl, or *tert*-butyl). The dizirconium complexes ($Zr_2^{R2R'2}$ -L) were synthesized by the addition of 1 equiv of the tetraphenol $H_4^{R2R'2}$ -L to 2 equiv of ZrBn₄. In all cases, two major species (in a ratio of 1:1) were observed in the reaction mixture by ¹H NMR spectroscopy, and isolation of one of these species in analytically pure form was achieved via recrystallization. The ¹H NMR spectrum of this isolated species displays eight doublets corresponding to benzylic protons, consistent with either a pseudo- C_2 -symmetric species in which the C_2 axis runs through the center of the central arene of the terphenyl backbone or a pseudo- C_s -symmetric species in which the mirror plane cuts perpendicularly through the central arene and the terphenyl vector (Figure 1). X-ray-quality crystals

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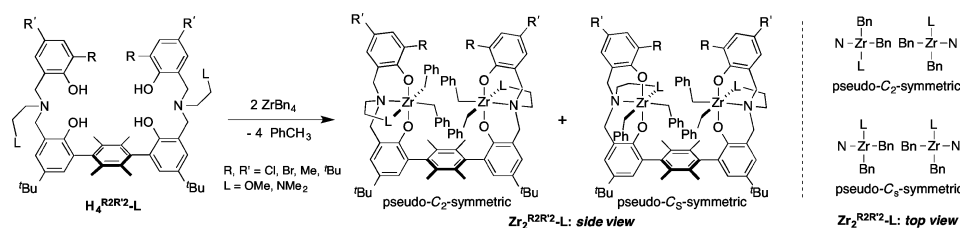


Figure 1. Synthesis of $\text{Zr}_2^{\text{R}2\text{R}'2}\text{-L}$ (left) and representations of the possible metalation isomers of $\text{Zr}_2^{\text{R}2\text{R}'2}\text{-L}$ (right).

were obtained for $\text{Zr}_2^{\text{Cl}4}\text{-OMe}$ and $\text{Zr}_2^{\text{Cl}4}\text{-NMe}_2$. Solid-state characterization by single crystal X-ray diffraction (XRD) showed structures of pseudo- C_2 symmetry for the isolated isomer of $\text{Zr}_2^{\text{Cl}4}\text{-OMe}$ (Figure 2) and $\text{Zr}_2^{\text{Cl}4}\text{-NMe}_2$ (Figure S82 (SI)). Isolation of the second major product was possible only for compound $\text{Zr}_2^{\text{Me}4}\text{-OMe}$ by successive recrystallizations. An XRD study revealed a solid-state structure of pseudo- C_s symmetry (Figure 2). Crystal structures were correlated with ^1H NMR spectra to identify diagnostic benzyl peaks for each metalation isomer in the ^1H NMR spectra between 3 and 4 ppm. No isomerization between the two isomers was observed by ^1H NMR spectroscopy in solution at room temperature with the isolated pseudo- C_2 -symmetric species or with different ratios of the two isomers. As the racemic mixtures of the pseudo- C_2 -symmetric complexes were isolable in all cases, these species were utilized in polymerization trials, except when stated otherwise.

Monometallic (Chart 1) and bimetallic precatalysts were highly active for 1-hexene polymerization, causing significant heating upon stoichiometric activation with a solution of $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ in chlorobenzene (PhCl). Polymerizations run for 10 min led to greater than 80% conversion of 1-hexene to poly(1-hexene).¹³ As expected, the literature complexes $\text{Zr}_1^{\text{tBu}4}\text{-L}^{10c}$ produced stereoirregular polymers with <10% *mmmm*. In contrast, the bimetallic complexes produced polymers with increased isotacticity (17–50% *mmmm*). The polymer isotacticity varied in the bimetallic systems, with the systems bearing amino ethers ($\text{L} = \text{OMe}$) being more selective than those with diamines ($\text{L} = \text{NMe}_2$): $\text{Zr}_2^{\text{Cl}4}\text{-OMe} > \text{Zr}_2^{\text{Br}4}\text{-OMe} > \text{Zr}_2^{\text{Cl}4}\text{-NMe}_2 > \text{Zr}_2^{\text{Br}4}\text{-NMe}_2 > \text{Zr}_2^{\text{Me}4}\text{-OMe} > \text{Zr}_2^{\text{H}2\text{tBu}2}\text{-OMe}$. For the same L , precatalysts with the smallest substituent in the position ortho to the phenoxide moiety, $\text{R} = \text{Cl}$, resulted in the highest tacticity, while the large ^tBu substituent led to the lowest tacticity. Precatalysts bearing diamine ligands were more active. Using mixtures of the two metalation isomers (C_s and C_2 symmetric) did not alter either the activity or the stereoselectivity of the complexes (Table S1 (SI), entries 9 and 12). Similarly, for $\text{Zr}_2^{\text{Me}4}\text{-OMe}$, which is the only ligand system where the C_s -symmetric isomer was isolated and purified, polymerizations with each isomer could be compared and were found to be very similar in activity and stereoselectivity (Table S1, entry 16). These results suggest that, although the presence of the second metal site significantly affects tacticity, its relative conformation is less consequential.

The complexes $\text{Zr}_2^{\text{Cl}4}\text{-L}$, $\text{Zr}_1^{\text{Cl}2\text{tBu}2}\text{-L}$, and $\text{Zr}_1^{\text{Cl}2\text{tBuAr}}\text{-L}$ were tested with temperature control (Table 1). The bimetallic catalysts are more active than the monometallic analogues by up to several orders of magnitude. $\text{Zr}_2^{\text{Cl}4}\text{-NMe}_2$ generated a catalyst that is 1 order of magnitude more active than $\text{Zr}_2^{\text{Cl}4}\text{-OMe}$. Upon optimization of polymerization conditions, activities of up to 124 kg of poly(1-hexene) ($\text{mmol of Zr}^{-1} \text{ h}^{-1}$ (ambient temperature)) were achieved for $\text{Zr}_2^{\text{Cl}4}\text{-NMe}_2$. This is among the highest olefin

polymerization activities reported for nonmetallocene catalysts.^{1b,g,4} At low temperatures (-30°C), poly(1-hexene) with 79% *mmmm* (Figure S79 (SI)) was obtained at an activity of 2.7 kg of poly(1-hexene) ($\text{mmol of Zr}^{-1} \text{ h}^{-1}$). This polymer also exhibited a high molecular weight of 1.2×10^6 Da and low polydispersity ($\text{PDI} = 1.1$), as determined by size exclusion chromatography. Under the same conditions, the best of the monometallic catalysts produced 0.054 kg of poly(1-hexene) ($\text{mmol of Zr}^{-1} \text{ h}^{-1}$ with 33% *mmmm*). Although propylene polymerizations with the bimetallic complexes showed lower activity and isoselectivity (Table S4 (SI)) in comparison to 1-hexene, similar trends were observed. The most active catalyst was again $\text{Zr}_2^{\text{Cl}4}\text{-NMe}_2$ with 47 kg of polypropylene ($\text{mmol of Zr}^{-1} \text{ h}^{-1}$ and 43% *mmmm*). In contrast, the monometallic catalyst $\text{Zr}_1^{\text{Cl}2\text{tBuAr}}\text{-NMe}_2$ (vide infra), showed significantly lower activity (2.9 kg of polypropylene ($\text{mmol of Zr}^{-1} \text{ h}^{-1}$)) and polymer tacticity (31% *mmmm*). The present results indicate that the bimetallic catalysts display considerably enhanced activity and tacticity control in comparison to the monometallic analogues.

The expected stereoerror distribution for enantiomorphic site control primarily includes the following pentads: *mmmr*, *mmrr*, and *mrrm*. The bimetallic zirconium precatalysts produce polymers with these stereoerrors as the most common, but the distribution includes the remaining possible stereoerrors as well. A model displaying a combination of enantiomorphic site control and chain end is most consistent with the data.¹⁴ Comparative studies between the bimetallic and the monometallic systems were performed to gain insight into the structural features responsible for stereocontrol. A series of new monometallic C_1 -symmetric complexes was synthesized (Chart 1; see the SI for detailed synthetic procedures and characterization). XRD studies of $\text{Zr}_1^{\text{Cl}2\text{tBu}2}\text{-OMe}$ revealed a structure very similar to those of the C_s -symmetric complexes in the literature (Figure S85 (SI)).^{10a,c} These monometallic complexes produce poly(1-hexene) of varied isotacticity, from stereoirregular with $\text{Zr}_1^{\text{tBu}4}\text{-L}$ to 10–35% *mmmm* with $\text{Zr}_1^{\text{Cl}2\text{tBu}2}\text{-L}$ and $\text{Zr}_1^{\text{Cl}2\text{tBuAr}}\text{-L}$. The tacticity control increases from the C_s -symmetric to the C_1 -symmetric precatalysts.

The increase in isotacticity is improved further by the incorporation of a second metal site. Each metal center in the bimetallic systems has local C_1 symmetry (Scheme 1). The two sites available for polymeryl coordination are very different in the bimetallic vs the monometallic species. The site pointing toward the second metal is considerably more hindered by the distal steric bulk in both C_s -symmetric and C_2 -symmetric structures (Figure 2). This steric effect is proposed to favor a polymeryl location away from this position (species A vs C), lowering the degrees of freedom available for the polymeryl chain and the monomer compared to the monometallic species. Although the site pointing toward the second metal may also disfavor olefin binding (D), this effect is expected to be lower, due to the lower steric profile of the olefin with the substituent residing in the

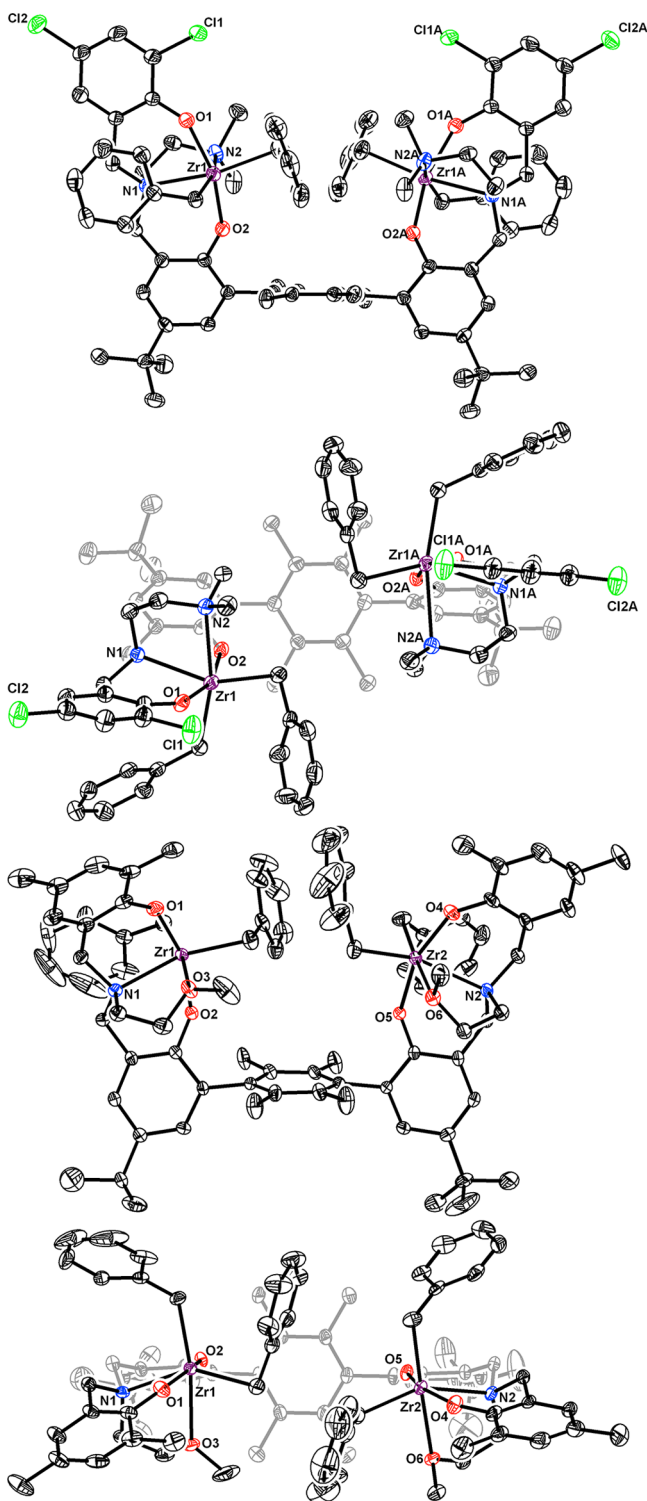


Figure 2. Side-on and top-down views of the solid-state structures of $\text{Zr}_2\text{Cl}_4\text{-NMe}_2$ (pseudo- C_2 -symmetric, top) and $\text{Zr}_2\text{Cl}_4\text{-OMe}$ (pseudo- C_s -symmetric, bottom) with thermal ellipsoids at the 50% probability level. Solvent molecules and H atoms have been omitted for clarity.

Chart 1. Monometallic Zirconium Complexes

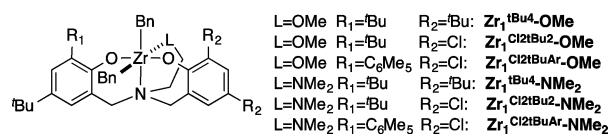
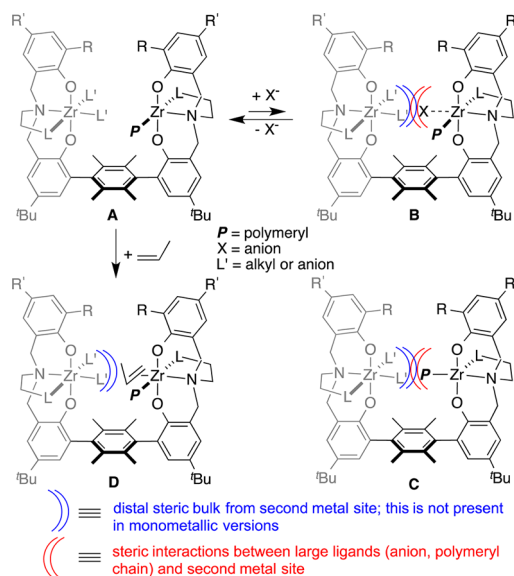


Table 1. 1-Hexene Polymerizations^a

| | complex | <i>T</i> (°C) | time (min) | yield (g) | activity ^b | <i>mmmm</i> (%) ^c |
|-----------------|---|---------------|------------|-----------|-----------------------|------------------------------|
| 1 | $\text{Zr}_2\text{Cl}_4\text{-OMe}$ | room temp | 10 | 0.75 | 2.3 | 50 |
| 2 | $\text{Zr}_2\text{Cl}_4\text{-OMe}$ | 60 | 10 | 0.67 | 2.0 | 37 |
| 3 | $\text{Zr}_2\text{Cl}_4\text{-OMe}$ | 25 | 10 | 0.68 | 2.0 | 47 |
| 4 | $\text{Zr}_2\text{Cl}_4\text{-OMe}$ | 0 | 480 | 0.78 | 0.05 | 57 |
| 5 | $\text{Zr}_2\text{Cl}_4\text{-OMe}$ | −30 | 480 | 0.01 | 0.0007 | 76 |
| 6 | $\text{Zr}_2\text{Cl}_4\text{-NMe}_2$ | room temp | 1 | 1.17 | 35 | 38 |
| 7 | $\text{Zr}_2\text{Cl}_4\text{-NMe}_2$ | 60 | 1 | 0.65 | 19 | 33 |
| 8 | $\text{Zr}_2\text{Cl}_4\text{-NMe}_2$ | 25 | 2 | 1.28 | 19 | 33 |
| 9 | $\text{Zr}_2\text{Cl}_4\text{-NMe}_2$ | 0 | 2 | 1.42 | 21 | 38 |
| 10 | $\text{Zr}_2\text{Cl}_4\text{-NMe}_2$ | −20 | 5 | 1.51 | 9.0 | 58 |
| 11 ^d | $\text{Zr}_2\text{Cl}_4\text{-NMe}_2$ | room temp | 1 | 0.82 | 124 | 41 |
| 12 ^d | $\text{Zr}_2\text{Cl}_4\text{-NMe}_2$ | 60 | 2 | 0.58 | 43 | 34 |
| 13 ^d | $\text{Zr}_2\text{Cl}_4\text{-NMe}_2$ | 25 | 2 | 0.62 | 46 | 41 |
| 14 ^d | $\text{Zr}_2\text{Cl}_4\text{-NMe}_2$ | 0 | 8 | 1.39 | 26 | 48 |
| 15 ^d | $\text{Zr}_2\text{Cl}_4\text{-NMe}_2$ | −30 | 10 | 0.18 | 2.7 | 79 |
| 16 | $\text{Zr}_1\text{Cl}_2\text{iBu}_2\text{-OMe}$ | 0 | 480 | 0.11 | 0.007 | 9 |
| 17 | $\text{Zr}_1\text{Cl}_2\text{iBuAr-OMe}$ | 0 | 480 | 0.04 | 0.003 | 23 |
| 18 ^d | $\text{Zr}_1\text{Cl}_2\text{iBu}_2\text{-NMe}_2$ | 0 | 60 | 0.03 | 0.09 | 11 |
| 19 ^d | $\text{Zr}_1\text{Cl}_2\text{iBuAr-NMe}_2$ | 0 | 30 | 0.61 | 3.0 | 35 |
| 20 ^d | $\text{Zr}_1\text{Cl}_2\text{iBuAr-NMe}_2$ | −30 | 480 | 0.17 | 0.01 | 33 |

^aPolymerizations were run with 2.5 mL of 1-hexene in 2.5 mL of PhCl with 2 μmol of [Zr], 1 equiv of $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$, and 5 equiv of Al^iBu_3 . Room temperature polymerizations were run without temperature control and varied in the strength of their exotherms. ^bActivity in kg of poly(1-hexene) ($\text{mmol of Zr}^{-1} \text{ h}^{-1}$). ^cDetermined from ^{13}C NMR spectra. ^dPolymerizations were run with 2.5 mL of 1-hexene in 2.5 mL of PhCl with 0.4 μmol of [Zr], 3 equiv of $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$, and 15 equiv of Al^iBu_3 .

Scheme 1. Proposed Steric Interactions Due to the Bimetallic Nature of the Catalysts



plane perpendicular to the Zr–olefin bond. The highest level of tacticity control is observed for $\text{Zr}_2\text{Cl}_4\text{-L}$, which has substituents

ortho to the phenoxide moiety for each metal site ($R = \text{Cl}$ vs $\text{C}_6\text{Me}_4\text{Ar}$) that have significantly different steric profiles. The reduced isotacticity observed for the polymerization of propylene relative to that for 1-hexene may be caused by the smaller size of the polymer chain, leading to lower levels of steric repulsion and orientation preference.

The steric profiles of the bimetallic catalysts outlined here suggest that tacticity could be controlled by a distal steric interaction unique to these rigid systems. This effect is more pronounced with the larger 1-hexene monomer, which leads to a more sterically demanding polymer chain. A similar distal steric interaction is proposed to engender high catalytic activities by weakening metal–anion interactions (**B**). A related mechanism was evidenced for the copolymerization of ethylene with amino olefins by nickel phenoximine bimetallic catalysts; in the absence of the bimetallic effect, little activity and polar monomer incorporation was observed.^{9b,c} Without a strong interaction with the counterion, the metal center is more electrophilic and reactive in olefin polymerization catalysis.

In summary, we have synthesized a series of dizirconium bis[amine bis(phenolate)] precatalysts that are effective for the polymerization of propylene and 1-hexene with very high activities and significant stereocontrol. 1-Hexene polymers with >75% *mmmm* content and remarkable activities exceeding 120 kg of poly(1-hexene) ($\text{mmol of Zr}^{-1} \text{ h}^{-1}$) were obtained. Studies of related monometallic systems show that the bimetallic character is required for the increased activity and isoselectivity. The distal steric interactions caused by the presence of the second metal site are proposed to lead to increased activity and stereocontrol. Ongoing efforts are focused on expanding the applicability of the distal steric effect in bimetallic and monometallic catalysts toward the synthesis of stereoregular materials with other nonpolar as well as functionalized monomers.

■ ASSOCIATED CONTENT

■ Supporting Information

Text, figures, tables, and CIF files giving experimental procedures, characterization data, crystallographic details for complexes $\text{Zr}_2^{\text{Cl}^4}\text{-NMe}_2$, $\text{Zr}_2^{\text{Me}^4}\text{-OMe}$, $\text{Zr}_2^{\text{Cl}^4}\text{-OMe}$, and $\text{Zr}_1^{\text{Cl}^2\text{Bu}^2}\text{-OMe}$, and additional polymerization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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