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Investigation of Dynamic Intra- and Intermolecular Processes within a Tether-Length Dependent Series of Group 4 Bimetallic Initiators for Stereomodulated Degenerative Transfer Living Ziegler–Natta Propene Polymerization

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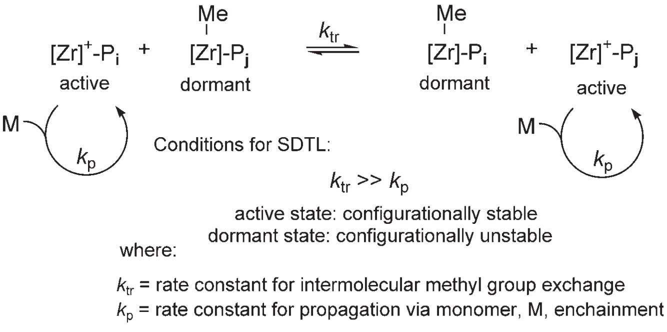
Abstract: The series of bimetallic complexes, $[(\eta^5\text{-}C_5Me_5)Zr(Me)_2]_2$ $[N(t\text{-}Bu)C(Me)N{-}(CH_2)_n{-}NC(Me)N(t\text{-}Bu)]$ **3** ($n=8$), **4** ($n=6$), and **5** ($n=4$) were prepared in high yield through a simple, one-pot synthesis involving 2 equiv. of *in situ* generated $(\eta^5\text{-}C_5Me_5)Zr(Me)_3$ and the corresponding bis-carbodiimide, $(t\text{-}Bu)NCN{-}(CH_2)_n{-}NCN(t\text{-}Bu)$. Compounds **3–5** were found to be highly isoselective for the living Ziegler–Natta polymerization of propene upon 100% activation using 2 equiv. of the borate co-initiator, $[PhNHMe_2]$ $[B(C_6F_5)_4]$ (**2**), with the degree of stereoselectivity decreasing slightly as the two metal centers are brought closer together [*cf.*, **3** ($\sigma=0.92$) > **4** ($\sigma=0.91$) > **5** ($\sigma=0.89$)]. Under conditions of sub-stoichiometric activation by **2**, all three bimetallic initiators, **3–5**, were found to engage in degenerative transfer living Ziegler–Natta polymerization involving rapid and reversible methyl group transfer between active, (cationic) and dormant, (neutral) methyl, polymeryl zirconium centers. Under these conditions, the frequency of *mr* triad stereoerror incorporation into the polypropene (PP) microstructure decreases as the two metal centers are brought closer together as a result of increasing barriers for metal-centered epimerization within the neutral metal site due to correspondingly greater non-bonded steric interactions *vis-à-vis* mononuclear **1**.

Keywords: bimetallic catalyst; living polymerization; polypropene; stereoselectivity; Ziegler–Natta catalysis

Introduction

Crucial to world-wide efforts to expand the range of commercially viable polyolefins that can be produced through the Ziegler–Natta polymerization of ethene, propene, and higher α-olefins are the identification, investigation, and exploitation of chemical processes that can be used as mechanistic control points by which new fundamental forms of polyethene (PE), polypropene (PP), and other polyolefin materials can be envisioned and subsequently realized.[1–3] In this regard, the tethering of two active metal propagating centers within a bimetallic molecular framework has long been a strategy pursued with the expectation that nuclearity and cooperativity effects between two metal centers that are physically held in close proximity to one another might serve to provide access to different mechanistic processes that are competitive with propagation, and thereby, increase the scope of polyolefin compositions that are available through modulation of their relative rates .[4–8] However, only very recently have Marks and co-workers[4], and subsequently, Noh and co-workers[5] succeeded in achieving this goal for PE-based co-polymers.[6] In the case of propene polymerization, one can easily imagine that, within bimetallic-based catalysts, proximity effects between two propagating centers might also be capable of influencing the stereochemical course of alkene insertion into the metal-carbon bond of the pendant polymer chain and, thereby, provide new PP microstructures that are not achievable with the corresponding mononuclear system. Unfortunately, results obtained to date with such systems have been far less encouraging, and more specifically, to the best of our knowledge, only one bimetallic species has ever been reported that is catalytically active for the production of PP beyond formation of oligomeric or low molecular weight products.[7,8] However, neither the existence of proximity effects nor their possible influence on PP stereochemical microstructure were mentioned or examined for this systems.[8]

For our part, we recently discovered, and then developed, stereomodulated degenerative transfer living (SDTL) Ziegler–Natta polymerization as a means by which to design and prepare, with an unprecedented level of control: (1) an unlimited variety of new polyolefin materials and, in particular, PP microstructural forms – including those possessing an architecturally diverse range of well-defined and discrete isotactic-atactic stereoblock and stereogradient profiles and (2), an infinite range of new PP materials based on the programmed introduction of various levels and patterns of *mmrm* pentad stereoerrors.[3] Importantly, given the living nature of this polymerization process, all these new polyolefin and PP-based materials can be obtained with a pre-selected number-average degree of polymerization, X_n, and with a very narrow molecular weight polydispersity index, $D = M_w/M_n \approx 1.1$–1.2.[9,10] A further important feature of SDTL Ziegler–Natta polymerization is that this entire aforementioned portfolio of new microstructural classes of polyolefin and PP materials can be prepared using a *single* C_1-symmetrical, group 4 metal initiator. In the examples published to date, the dimethyl(monocyclopentadienyl)(monoamidinate)zirconium complex, $(\eta^5\text{-}C_5Me_5)Zr(Me)_2[N(Et)C(Me)N(t\text{-}Bu)]$ (**1**), was employed in combination with varying stoichiometries of the borate, $[PhNMe_2H]$ $[B(C_6F_5)_4]$ (**2**), that serves as the 'activating' co-initiator through methyl group protonolysis to produce the zirconocenium species, $\{(\eta^5\text{-}C_5Me_5)ZrMe[N(Et)C(Me)N(t\text{-}Bu)]\}$ $[B(C_6F_5)_4]$ which, in the absence of SDTL conditions (i.e., 100% activation, or [**1**]/[**2**] = 1), has been shown to be a highly active and stereoselective initiator for the living Ziegler–Natta polymerization of propene and higher α-olefins.[11] As schematically presented in Scheme 1, at the heart of SDTL Ziegler–Natta polymerization, which is in effect at all values of [**1**]/[**2**] > 1, is the rapid and reversible bimolecular *methyl group* exchange, defined by the rate, ν_{tr}, that occurs between active (configurationally stable) cationic metal centers that engage in stereoselective polyolefin chain growth and dormant (configurationally unstable) neutral metal centers that undergo facile metal-centered epimerization[12] with a rate, ν_{epi}, that must be several orders of magnitude faster than the rate of propagation, ν_p, (i.e., $\nu_{epi} \geqslant \nu_p$).[10] Modulation of the PP stereochemical microstructure using **1** then simply resides with the ability to directly influence the magnitude of ν_{tr}, relative to ν_p in a programmed fashion by adjusting the relative and absolute concentrations of both the active and the dormant species, and optionally for stereoblock or stereogradient microstructures, as a function of time.[3d,e]

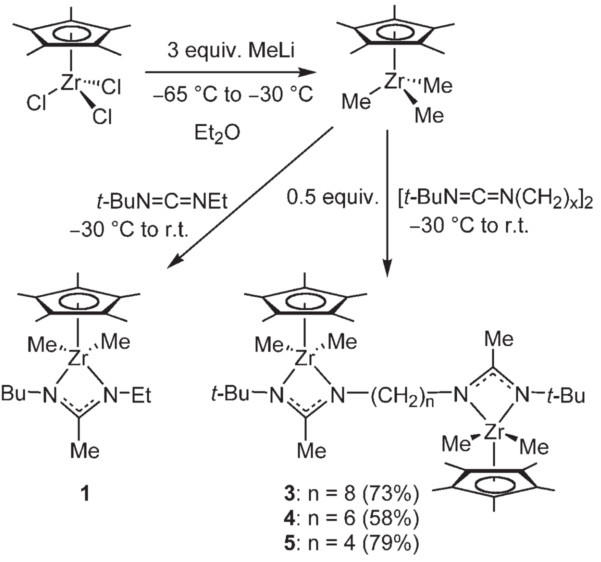


Scheme 1.

Under the SDTL Ziegler–Natta polymerization conditions just described, it can be anticipated that the tethering of dormant and active sites within bimetallic molecular frameworks now introduces the possibility of additional control points that can potentially be used to influence polyolefin microstructure in terms of manipulating either: (1) the relative rates of ν_{epi}, *vs.* ν_p, which might be governed more easily through steric control within a bimetallic rather than a mononuclear species, and (2) the relative rates for unimolecular (intramolecular) *vs.* bimolecular (intermolecular) methyl group degenerative transfer, $\nu_{tr(intra)}$, and $\nu_{tr(inter)}$, respectively; the latter of which can be directly manipulated through adjustments to the experimental conditions (e.g., concentration). Herein, we now report the results of our first investigative study of the possible existence and influence of such proximity effects on the stereochemical course of propene polymerization as carried out with a tether-length series of well-defined group 4 metal bimetallic initiators related to **1** under both SDTL and non-SDTL conditions.

Results and Discussion

Scheme 2 presents the direct one-pot, high-yielding procedure that was previously used to synthesize **1**, and currently, the linked bimetallic complexes, **3**–**5**, possessing different *n*-alkyl tether lengths [that is, $-(CH_2)_n-$ for $n = 8$, 6, and 4, respectively].[11,12] All of these new crystalline compounds were fully characterized, including a determination of their solid-state structure by single-crystal X-ray analysis and, as presented in Figure 1, none of these static structures appear to display any significant deviations within the geometrical parameters associated with each of the metal centers when compared to the corresponding values obtained for the solid-state structure of **1**.[13] This observation suggests that no substantial nonbonded steric interactions between the two metal centers have been introduced as the result of the presence of the *n*-alkyl tethering link, and indeed, variable temperature ^1H NMR (500 MHz, toluene-d_8, 183–



Scheme 2.

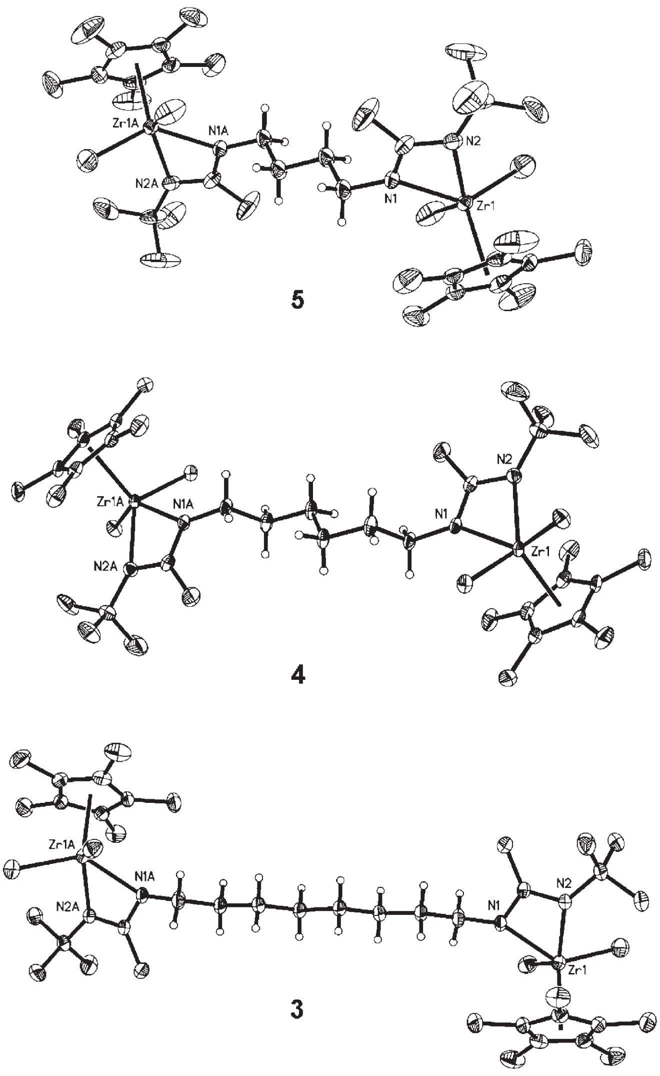


Figure 1. Molecular structures (30% thermal ellipsoids) (from bottom to top) of the binuclear initiators **3**–**5**. Hydrogen atoms have been removed for the sake of clarity, except for those associated with the *n*-alkyl tethers.

298 K) spectroscopy of **3**–**5** revealed that, for each bimetallic complex, rapid interconversion between the *meso* and racemic (*rac)* diastereomeric configurations of the two metal centers is rapidly occurring on the NMR time scale as the result of facile metal-centered epimerizations that have associated barriers of $\Delta G_c^{\ddagger} < 10$ kcal mol^{-1} at the coalescence temperature, $T_c = 203$ K. When compared to a similar barrier determined for metal-centered racemization in **1**,[3a] these observations suggest that, in the *absence* of any additional proximity effects that might arise after initiation and propagation, it is reasonable to expect *a priori* that the same range of stereomodulation of the PP microstructure can be achieved with **3**–**5** under SDTL conditions as previously demonstrated for **1**.

Propene polymerizations were conducted with **1** and the bimetallic initiators **3**–**5** in chlorobenzene at $-10\,°C$ according to previously published procedures using **2** as the activating co-initiator.[3,11] As an initial screen of behaviour under both standard and SDTL conditions, propene polymerizations were further conducted keeping the total initial concentration of zirconium centers, $[Zr]_{tot}$, constant while varying only the initial concentration of the borate, $[\mathbf{2}]_0$, in order to establish 50, 70, 90, and 100% levels of activation, i.e., $[Zr]_{tot}/[\mathbf{2}]_o = 2.0$, 1.43, 1.11, and 1.0, respectively. Polymerization time, t_p, was varied between 2–7 h, depending upon both the identity of the initiator and the level of activation, in order to ensure that a substantial quantity of PP material (~0.3–0.6 g) could be isolated for characterization. In this manner, all three bimetallic initiators, **3**–**5**, proved to be competent for propene polymerization at all levels of activation, with propagation activities being comparable in magnitude to those established for mononuclear **1** under identical conditions. In keeping with prior observations and expectations,[3] ν_p for all the bimetallic initiators was also seen to decrease with decreasing levels of activation, e.g., for **5**: ν_p (75% activation) ≈ 2 ν_p (50% activation), and gel permeation chromatography (GPC) analyses further confirmed that, in all cases, the molecular weight distributions of the PP materials obtained were monomodal in nature and characterized by very narrow polydispersities; with the number average molecular weight index, M_n, being on the order of 45,000–50,000 g mol^{-1} and $D \sim 1.1$–1.2. Finally, detailed kinetic analyses conducted with the bimetallic initiator **5** at 50 and 75% levels of activation confirmed a steady linear increase in M_n as a function of time, and these data are in keeping with the conclusion that, just as with **1**, propagation with **3**–**5** occurs in living fashion at all values of $[Zr]_{tot}/[\mathbf{2}]_o$.[9,10,14] Finally, ^1H NMR (500 MHz, 1,1,2,2-$C_2D_2Cl_4$, 70 °C) spectra of the isolated PP materials obtained from these studies routinely revealed the absence of any vinyl resonances that might arise from chain termination through β-hydride elimination, and these results provide further support for the living character of propene polymerization utilizing **3**-**5**.

Detailed ^{13}C NMR (125 MHz, 1,1,2,2-$C_2D_2Cl_4$, 70 °C) stereochemical analyses of the PP materials obtained from **3**–**5** under both standard and SDTL conditions provide considerable information regarding both the initial extent of activation of the two metal centers in the bimetallic species and the nature of any dynamic stereochemical processes that were competitive with propagation during chain growth.[14,15] Figure 2 presents a subset of the ^{13}C NMR spectra for the methyl resonances of these PP samples along with those obtained by employing mononuclear **1** under identical conditions, and in particular, $[Zr]_{tot}/[\mathbf{2}]_o$. At first glance, these data clearly reveal that significant differences in PP stereochemical microstructures have indeed arisen as the result of both the level of activation, which is expected on the basis of previous results obtained for **1** under degenerative transfer conditions,[3] and, perhaps more gratifyingly, as a result of the length of the tether within the bimetallic initiators. Charts presented in Figure 3 serve to provide a more detailed quantitative look at these microstructural differences which become fairly apparent and informative through side-by-side comparisons of the levels of incorporation of a selected subset (i.e.,

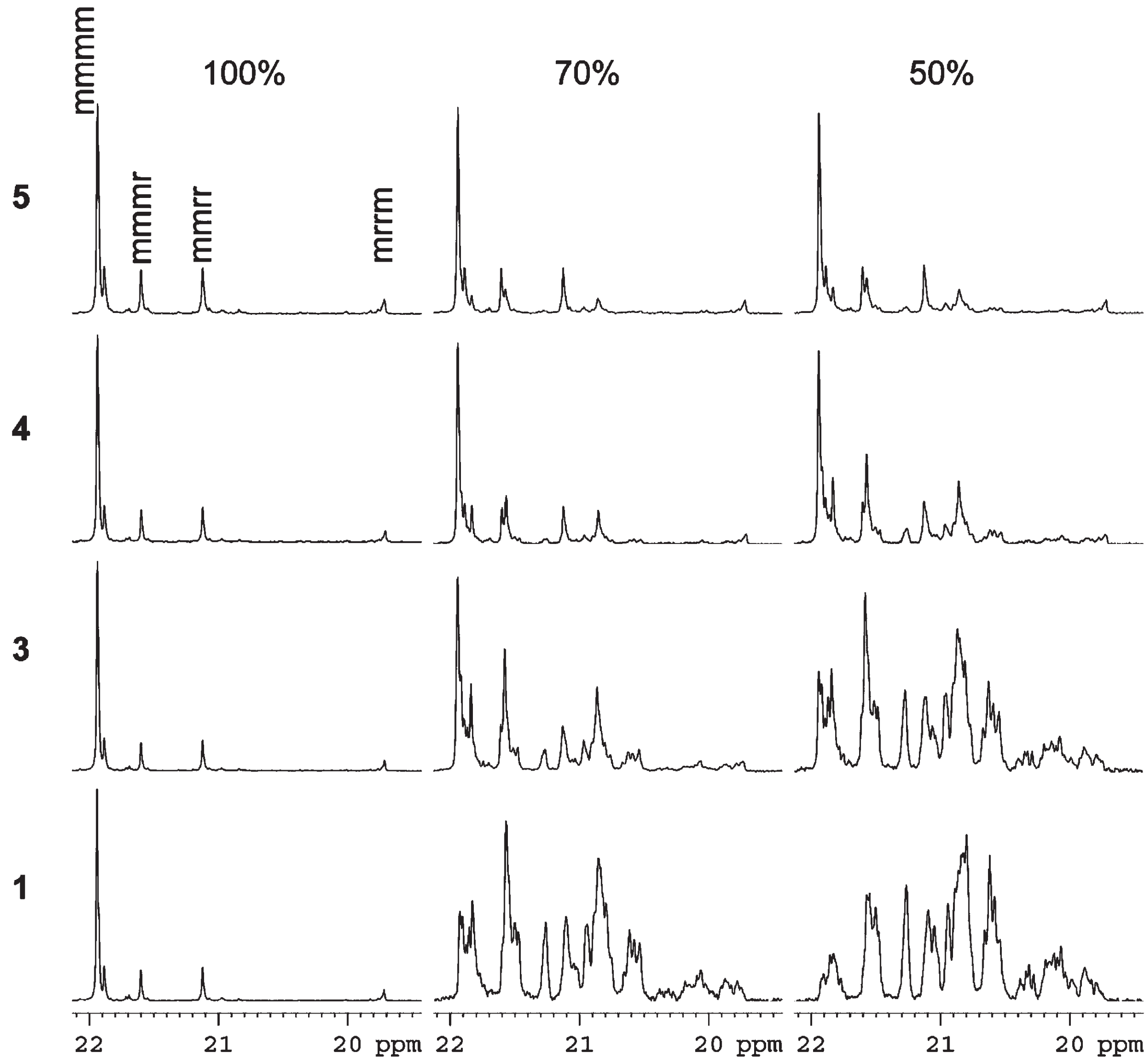


Figure 2. $^{13}C\{^1H\}$ NMR (125 MHz, 1,1,2,2-$C_2D_2Cl_4$, 70 °C) spectra for the methyl resonances of PP samples obtained from (bottom to top) the mononuclear and binuclear complexes, **1** and **3**–**5**, respectively, using **2** as the activating co-initiator. Polymerization conditions: (from left to right): $[Zr]_{tot}/[\mathbf{2}]_o = 1.0$, 1.43, and 2.0; $[Zr]_{tot} = 1.25$ mM; –10 °C; C_6H_5Cl, 34.5 kPa propene).

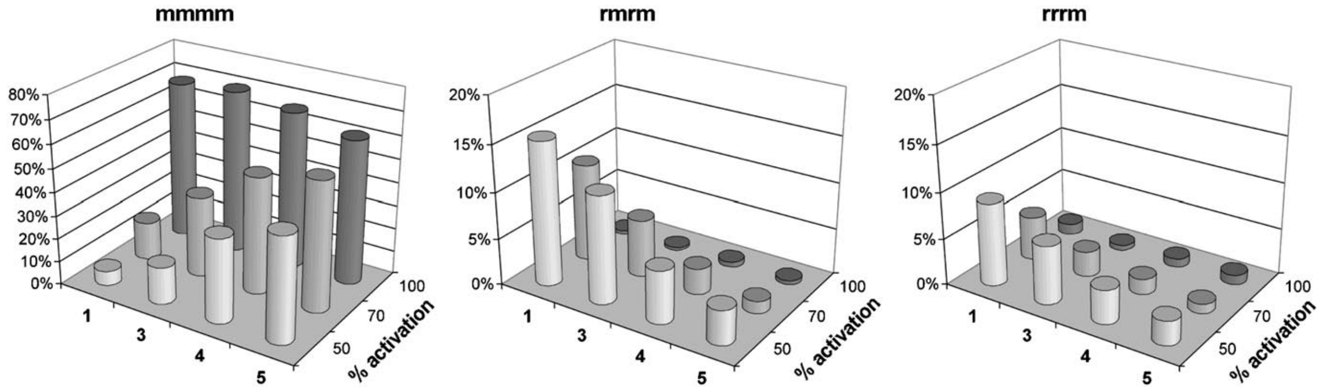


Figure 3. Dependence of (from left to right) % *mmmm*, *rmrm*, and *rrrm* pentad content on level of activation and length of *n*-alkyl tether for PP produced using the mononuclear and binuclear complexes, **1** and **3–5**, respectively, and **2** as the activating co-initiator.

mmmm, *rmrm*, and *rrrm*) of the ten possible pentad stereoerrors.[13,15] Most significantly, at 100% activation, all three bimetallic initiators, **3–5**, are highly isoselective, with the nature and integrated intensities of the pentad stereoerrors observed being consistent with exclusive enantiomorphic site control during propagation (i.e., *mmmr*:*mmrr*:*mrrm* ≈ 2:2:1, see Figure 2).[15] Additionally, as Figure 3 reveals, the degree of stereocontrol that was achieved during propagation at 100% activation revealed no appreciable quantitative difference in the % *mmmm* pentad content for PP prepared using mononuclear **1** and C_8-linked bimetallic **3**, whereas, a slight decrease in this high degree of stereoselectivity is observed as the tether length decreases (*cf.* insertion selectivity, $\sigma = 0.92$ for **1**, 0.92 for **3**; 0.91 for **4** and 0.89 for **5**). These results provide strong support for the important conclusion that with $[Zr]_{tot}/[\mathbf{2}]_o = 1.0$ (100% activation), *both metal centers within the neutral bimetallic complexes, **3–5**, have undergone successful methyl group protonolysis to produce a bifunctional initiator possessing two cationic metal centers that are each identically competent with the same degree of stereoselectivity for polypropene propagation*. Based on the extensive structure/activity/microstructure relationship database that has now been developed for this specific family of initiators to which **1** belongs,[16] it is reasonable to conclude that the observed tether length reduction in propene enantioface discrimination in going from **3** to **5** most likely arises from an increase in non-bonded steric interactions as the two cationic active propagating centers are brought into closer proximity. Here, it is important to note that if only partial activation of either both or one of the metal centers had occurred, the resulting microstructure of the PP material obtained should present evidence of increased *mr* triad stereoerror incorporation, which is the hallmark of reversible methyl group transfer between active and dormant states, followed by metal-centered epimerization of the dormant state.[3] Indeed, the ability of the bimetallic species derived from substoichiometric activation of **3–5** to engage in these dynamic processes under SDTL conditions at rates that are competitive with propagation is substantiated by the data presented in both Figure 2 and Figure 3 for which some intriguing trends can be further noted. Thus, by focusing first on the chart in Figure 3 that presents % *mmmm* as a function of both the level of activation and initiator type, it can be seen that while isotactic content drops off rapidly at 70% and 50% activation for the mononuclear system derived from **1**, a much less precipitous drop in *mmmm* content is observed for all of the bimetallic systems, with a steady increase in this parameter being observed as tether length between the two metal centers decreases. Furthermore, from similar charts for % *rmrm* and % *rrrm* shown in Figure 3, it can be readily corroborated that the main factor responsible for the erosion of *mmmm* content is an increased frequency of *mr* triad stereoerror incorporation as the level of activation decreases. While this observation is in keeping with expectations based on the previously noted behaviour of **1** under SDTL conditions, as the data in Figure 3 clearly demonstrate, as tether length decreases within the series of bimetallic initiators **3–5**, the frequency of *mr* triad stereoerror incorporation, as tracked by % *rmrm* and % *rrrm*, also decreases. Indeed, it is readily obvious from this data that even with a fairly long (C_8) *n*-alkyl tether between the two metal centers, bimetallic **3** *is not* a good model for two independently acting mononuclear species derived from **1**.

From a first level analysis, we presently believe that the best likely origin of the proximity effects that appear in the PP polymerization data for **3–5** is steric in nature.[17] More specifically, when one considers the steric bulk of a propagating PP chain attached to each of the two metal centers, as well as, possibly that of one borate counterion, it is hardly surprising that, as tether length decreases, the barrier height for metal-centered epimerization increases, thereby, reducing the frequency of *mr* triad stereoerror incorporation. These same steric constraints might also be responsible for degenerative methyl group transfer occurring primarily, if not exclusively, through intermolecular exchange between 'open' forms of the bimetallic catalysts that are prevented from adopting conformations that can support Zr(μ-Me)Zr interactions required for facile intramolecular methyl group exchange. Routine production of PP materials possessing narrow polydispersities strongly suggests, however, that in spite of these increasing steric constraints, intermolecular methyl group transfer is still rapid and reversible for all three bimetallic systems under SDTL conditions. We are presently pursuing experimental means by which to quantify the kinetic and thermodynamic parameters associated with these different intra- and intermolecular dynamic processes.

Conclusions

In summary, the present report documents the first demonstration of highly stereoselective and living Ziegler–Natta polymerization within a family of bifunctional bimetallic initiators under both standard and SDTL conditions. Building further upon the picture of sterically interacting polymeryl groups held in close proximity within a tethered bimetallic system, we are now investigating the design and synthesis of new bimetallic initiators through which novel polyolefin microstructural and copolymer compositions might be envisioned and obtained. Finally, while the present results are of interest in the context of efforts to expand the present range of polyolefin-based materials through use of bimetallic catalysts, they also further serve to highlight the possible benefit or deleterious role(s) that dimers or higher-order aggregates of propagating centers can have in dictating the stereochemical microstructure of polyolefins.[17]

Experimental Section

General Procedures

All manipulations were performed under an inert atmosphere of dinitrogen using standard Schlenk or glove-box techniques. Dry, oxygen-free solvents were employed throughout. Diethyl ether (Et_2O) and pentane were distilled from sodium/benzophenone (with a few milliliters of triglyme being added to the pot in the case of pentane), toluene and chlorobenzene were refluxed over sodium metal and calcium hydride, respectively, and distilled under dinitrogen prior to use. Benzene-d_6 for NMR spectroscopy was vacuum transferred from NaK prior to use. Polymer grade propene was purchased from Matheson Trigas, and passed through Q5 and molecular sieves (4 Å).

(η^5-C_5Me_5)$ZrMe_2$[N(Et)C(Me)N(*t*-Bu)] (**1**) was prepared as previously reported.[3a] (η^5-C_5Me_5)$ZrCl_3$ was obtained from Strem Inc and [$PhNHMe_2$] [$B(C_6F_5)_4$] (**2**) was purchased from Boulder Scientific and used without further purification. GPC analyses were performed using a Viscotek GPC system equipped with a column oven and differential refractometer, both maintained at 45 °C, and four columns also maintained at 45 °C. THF was used as the eluant at a flow rate of 1.0 mL min^{-1}. M_n, M_w and M_w/M_n values were obtained using the Viscotek OmniSEC software and seven polystyrene standards (Polymer Laboratories). ^{1}H NMR spectra were recorded at 400 MHz at ambient temperature while ^{13}C {^{1}H} NMR spectra were recorded at 125 MHz, using 1,1,2,2-tetrachloroethane-d_2 as the solvent at 70 °C.

Preparation of *t*-Bu−NH−CO−NH−(CH_2)$_8$−NH−CO−NH-*t*-Bu (6)

To a solution of 4.96 g (50.0 mmol) *tert*-butyl isocyanate in 125 mL $CHCl_3$ at 0 °C was added a solution of 3.61 g (25.0 mmol) 1,8-diaminooctane in 125 mL $CHCl_3$ over 30 min. The resulting solution was stirred for 30 min before being concentrated under vacuum and then precipitated into 500 mL pentane. The product was isolated as a white powder *via* filtration and washed with several portions of pentane before being dried under vacuum; yield of **6**: 8.51 g (95.1%); ^{1}H NMR (400 MHz, $CDCl_3$, 293 K): $\delta = 4.25$ (2H, br s), 4.18 (2H, br t), 3.10 (4H, dt, $J = 6.0$, $J = 6.8$ Hz), 1.46 (4H, br p), 1.33 (18H, s), 1.30 (8H, br s).

Preparation of *t*-Bu-N=C=N−(CH_2)$_8$−N=C=N-*t*-Bu (7)

To a solution of 14.8 g (56.3 mmol) triphenylphosphine in 225 mL CH_2Cl_2 under a nitrogen atmosphere and at 0 °C was added dropwise, a solution of 8.99 g (56.3 mmol) bromine in 25 mL CH_2Cl_2 *via* a pressure-equalizing addition funnel over a period of 30 min. After stirring for an additional 15 min, 11.4 g (113 mmol) triethylamine was added dropwise in similar fashion into the reaction mixture over 15 min. During the next hour, 7.71 g (22.5 mmol) **6** were added in four equal portions. The solution was stirred overnight, washed with 125 mL of distilled water, and the organic layer separated and dried with anhydrous sodium sulfate. After being concentrated under vacuum, the solution was slowly added into 700 mL pentane, filtered, and the volatiles were removed under vacuum to provide the crude product as an orange liquid, which was then vacuum distilled from calcium hydride; yield of **7**: 4.82 g (70.0%); bp 158 °C/0.40 torr; ^{1}H NMR (400 MHz, C_6D_6, 293 K): $\delta = 3.05$ (4H, t, $J = 6.8$ Hz), 1.44 (4H, br p), 1.20 (18H, s), 1.26–1.16 (4H, m), 1.14–1.06 (4H, m).

Preparation of [(η^5-C_5Me_5)$ZrMe_2$]$_2$[N(*t*-Bu)C(Me)N(CH_2)$_8$NC(Me)N(*t*-Bu)] (3)

To a solution of 0.33 g (1.0 mmol) (η^5-C_5Me_5)$ZrCl_3$ in 50 mL Et_2O at −65 °C was added a solution of 1.9 mL of MeLi (1.68 M in Et_2O) *via* syringe over 10 min. The mixture was stirred for 3 h at −30 °C and then quenched with the addition of 0.05 mL Me_3SiCl *via* syringe. A solution of 0.15 g

(0.50 mmol) **7** in 10 mL of Et_2O was then added *via* cannula at −30 °C over 45 min. The mixture was stirred for 1 h at −30 °C and then was allowed to warm up to room temperature overnight, after which time, the volatiles were removed under vacuum. The resulting white residue was extracted with toluene and filtered through a pad of Celite in a glass frit. The volatiles were removed under vacuum and the yellow crude product was washed with 10 mL cold pentane to provide the final product as a white powder; yield: 0.31 g (73% yield). Single-crystals of **3** suitable for X-ray analysis were obtained by slow evaporation of a pentane solution at room temperature. ^1H NMR (400 MHz, C_6D_6, 293 K): $\delta =$ 2.97–2.90 (4H, m), 2.06 (30H, s), 1.80 (6H, s), 1.50–1.39 (4H, m), 1.35–1.27 (4H, m), 1.26–1.21 (4H, m), 1.20 (18H, s), 0.29 (12H, s); anal. calcd. for $C_{44}H_{82}N_4Zr_2$: C 62.20, H 9.73, N 6.59; found:C 61.90, H 9.77, N 6.59%.

Preparation of *t*-Bu−NH−CO−NH−$(CH_2)_6$−NH−CO−NH-*t*-Bu (8)

To a solution of 4.96 g (50.0 mmol) *tert*-butyl isocyanate in 125 mL $CHCl_3$ at 0 °C was added a solution of 2.91 g (25.0 mmol) 1,6-diaminohexane in 125 mL $CHCl_3$ over 30 min. The resulting solution was stirred for 30 min before being concentrated under vacuum and then precipitated into 700 mL pentane. The product was isolated as a white powder *via* filtration and washed with several portions of pentane before being dried under vacuum; yield of **8**: 7.79 g (99%); ^1H NMR (400 MHz, $CDCl_3$, 293 K): $\delta = 4.34$ (2H, br t), 4.28 (2H, br s), 3.14 (4H, q, $J = 6.4$ Hz), 1.51–1.42 (4H, m), 1.36–1.31 (4H, m), 1.33 (18H, s).

Preparation of *t*-Bu-N=C=N−$(CH_2)_6$−N=C=N-*t*-Bu (9)

To a solution of 14.8 g (56.3 mmol) triphenylphosphine in 225 mL CH_2Cl_2 under a dinitrogen atmosphere and at 0 °C was added dropwise a solution of 8.99 g (56.3 mmol) bromine in 25 mL CH_2Cl_2 *via* a pressure-equalizing addition funnel over 30 min. After stirring for an additional 15 min, 11.4 g (113 mmol) triethylamine was added dropwise into the reaction mixture over 15 min. During the next hour, 7.08 g (22.5 mmol) **8** was added in four equal portions. The solution was stirred overnight, washed with 125 mL of distilled water, and the organic layer separated and dried with anhydrous sodium sulfate. After being concentrated under vacuum, the solution was slowly added into 800 mL pentane, filtered, and the volatiles were removed under vacuum to provide the crude product as an orange liquid, which was then vacuum distilled; yield of **9**: 4.27 g (68.2); bp 114 °C/0.02 torr; ^1H NMR (400 MHz, C_6D_6, 293 K): $\delta = 3.01$ (4H, t, $J = 6.8$ Hz), 1.43–1.34 (4H, m), 1.20 (18H, s), 1.13–1.19 (4H, m).

Preparation of $[(\eta^5\text{-}C_5Me_5)ZrMe_2]_2$[N(*t*-Bu)C(Me)N$(CH_2)_6$NC(Me)N(*t*-Bu)] (4)

To a solution of 0.33 g (1.0 mmol) $(\eta^5\text{-}C_5Me_5)ZrCl_3$ in 50 mL Et_2O at −65 °C was added a solution of 1.8 mL of MeLi (1.77 M in Et_2O) *via* syringe over 10 min. The mixture was stirred for 3 h at −30 °C and then quenched with the addition of 0.05 mL Me_3SiCl *via* syringe. A solution of 0.14 g (0.50 mmol) **9** in 10 mL of Et_2O was then added *via* cannula at −30 °C over 55 min. The mixture was stirred for 1 h at −30 °C and then was allowed to warm up to room temperature overnight, after which time, the volatiles were removed under vacuum. The resulting white residue was extracted with toluene and filtered through a pad of Celite in a glass frit. The volatiles were removed under vacuum and the yellow crude product was washed with 10 mL cold pentane to provide the final product as a white powder; yield of **4**: 0.24 g (58%). Single-crystals suitable for X-ray analysis were obtained by slow evaporation of a pentane solution at room temperature. ^1H NMR (400 MHz, C_6D_6, 293 K): $\delta = 2.96$–2.91 (4H, m), 2.05 (30H, s), 1.81 (6H, s), 1.50–1.40 (4H, m), 1.28–1.22 (4H, m), 1.19 (18H, s), 0.28 (12H, s); anal. calcd. for $C_{42}H_{78}N_4Zr_2$: C 61.40, H 9.57, N 6.82; found C 61.69, H 9.59, N 6.73%.

Preparation of *t*-Bu-NH−CO−NH−$(CH_2)_4$−NH−CO−NH-*t*-Bu (11)

To a solution of 4.96 g (50.0 mmol) *tert*-butyl isocyanate in 200 mL $CHCl_3$ at 0 °C was added a solution of 2.20 g (25.0 mmol) 1,4-diaminobutane in 20 mL $CHCl_3$ *via* cannula over 25 min. The resulting solution was stirred for 20 min before being concentrated under vacuum and then precipitated into 500 mL pentane. The product was isolated as a white powder *via* filtration and washed with several portions of pentane before being dried under vacuum; yield of **11**: 6.97 g (97.3%); ^1H NMR (400 MHz, $CDCl_3$, 293 K): $\delta = 4.60$ (2H, br t), 4.37 (2H, br s), 3.16 (4H, br q), 1.54–1.48 (4H, m), 1.33 (18H, s).

Preparation of *t*-Bu-N=C=N−$(CH_2)_4$−N=C=N-*t*-Bu (12)

To a solution of 16.4 g (62.5 mmol) triphenylphosphine in 250 mL CH_2Cl_2 under a dinitrogen atmosphere and at 0 °C was added a solution of 10.0 g (62.5 mmol) bromine in 30 mL CH_2Cl_2 *via* a pressure-equalizing addition funnel over 30 min. After stirring for an additional 15 min, 12.8 g (126 mmol) triethylamine was added dropwise into the reaction mixture over 10 min. During the next hour, 6.92 g (24.2 mmol) **11** was added in four equal portions. The reaction mixture was stirred overnight, washed with 100 mL of distilled water, and the organic layer separated and dried with anhydrous sodium sulfate. After being concentrated under vacuum, the solution was slowly added into 500 mL pentane, filtered, and the volatiles were removed under vacuum to provide the crude product as an orange liquid, which was then vacuum distilled from calcium hydride; yield of **12**: 2.96 g (48.9%); bp 85 °C/0.01 torr; ^1H NMR (400 MHz, C_6D_6, 293 K): $\delta = 2.99$–2.93 (4H, m), 1.49–1.41 (4H, m), 1.18 (18H, s).

Preparation of $[(\eta^5\text{-}C_5Me_5)ZrMe_2]_2$[N(*t*-Bu)C(Me)N$(CH_2)_4$NC(Me)N(*t*-Bu)] (5)

To a solution of 0.66 g (2.0 mmol) $(\eta^5\text{-}C_5Me_5)ZrCl_3$ in 100 mL Et_2O at −65 °C was added a solution of 3.7 mLmmol of MeLi (1.68M in Et_2O) *via* syringe over 10 min. The mixture was stirred for 3 h at −30 °C and then quenched with the addition of 0.1 mL Me_3SiCl *via* syringe. A solution of 0.25 g (1.0 mmol) **12** in 10 mL of Et_2O was then added *via* cannula at −30 °C over 35 min. The mixture was stirred for 1 h at −30 °C and then was allowed to warm up to room temperature overnight, after which time, the volatiles were removed under vacuum. The resulting white residue was extracted with toluene and filtered through a pad of Celite in a glass frit. The volatiles were removed under vacuum and the yellow crude product was washed with several ~2 mL portions of cold pentane to provide the final product as a white powder; yield of **5**: 0.63 g (79%). Single-crystals suitable for X-ray analysis were obtained by slow evaporation of a toluene solution at room temperature. ^{1}H NMR (400 MHz, C_6D_6, 293 K): $\delta = 2.97–2.89$ (4H, m), 2.05 (30H, s), 1.77 (6H, s), 1.39–1.32 (4H, m), 1.18 (18H, s), 0.27 (12H, s); anal. calcd. for $C_{40}H_{74}N_4Zr_2$: C 60.55, H 9.40, N 7.06; found: C 60.54, H 9.37, N 7.11%.

Propene Polymerization

The following description provides a typical procedure for polymerization reactions. This procedure was performed exactly unless otherwise noted.

To a solution of 0.0125 mmol **3**, **4**, or **5** or 0.025 mmol **1** in 0.5 mL of chlorobenzene at −10 °C was added a desired amount of co-catalyst **2** in 0.5 mL of chlorobenzene. This solution was then rapidly added to a 250-mL Schlenk flask charged with 19 mL of chlorobenzene at −10 °C, which was previously pressurized to 5 psi with propene and stirred for at least 10 min. The flask was then repressurized and the pressure maintained for the desired reaction time while stirring before quenching with 0.5 mL of methanol. The volatiles were then removed under vacuum and the crude polymeric material was purified through precipitation of a hot toluene solution into a large volume of acidic methanol. The final pure polypropene was collected and dried overnight at 60 °C (0.01 torr).

Kinetic Experiment under SDTL Conditions for 5 at 50% Activation

Polymerization of propene was carried out in the same manner as the procedure described above, using 29.8 mg (0.0375 mmol) of **5**, 30.1 mg (0.0375 mmol) of **2** and 30 mL chlorobenzene. The reaction was allowed to proceed for 3 h before aliquots were quenched every 45 min with methanol over the next 4.5 h. Polypropene samples were filtered through silica gel prior to GPC analysis.[14]

Kinetic Experiment under SDTL Conditions for 5 at 75% Activation

The same kinetic experiment was carried out in the same manner as above, except 45.1 mg (0.0563 mmol) of **2** were used and the reaction was allowed to proceed for 1.5 h before aliquots were quenched every 30 min over the next 3 h. Polypropene samples were filtered through silica gel prior to GPC analysis.[14]

X-Ray Crystallography

The crystallographic studies of **3**–**5** are available in the Supporting Information. Crystallographic data (excluding structure factors) for structures **3**–**5** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC-664645, CCDC-664646, and CCDC-664647, respectively.

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