

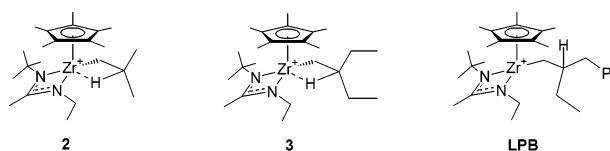
End-Group-Confined Chain Walking within a Group 4 Living Polyolefin and Well-Defined Cationic Zirconium Alkyl Complexes for Modeling This Behavior

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One of the last remaining mysteries associated with the Ziegler–Natta polymerization of propene by zirconocene-based catalysts is the mechanism by which chain-end epimerization of the last generated stereocenter occurs under conditions of low monomer concentration.¹ In this regard, Landis and co-workers^{1f} recently reported the direct observation of chain-end epimerization of living zirconocene polypropylene by low-temperature NMR spectroscopy. Simple model complexes for this process are still required, however, as they should greatly facilitate mechanistic studies. Unfortunately, given the low kinetic stability of alkyl substituents bearing β -hydrogens within neutral and cationic zirconocene complexes,² such model systems do not exist, and they may prove extremely difficult to come by.³ Herein, we now report our direct observation of end-group-confined chain walking, which is an integral part of the proposed Busico mechanism for chain-end epimerization,^{1a} within living polyolefins derived from higher α -olefins and the cyclopentadienyl zirconium acetamidinate initiator, $\{\text{Cp}^*\text{ZrMe}[\text{N}(\text{Et})\text{C}(\text{Me})\text{N}(\text{tBu})]\}[\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) (**1**).^{4,5} We further report that the well-defined cationic zirconium complexes, **2** and **3**, bearing alkyl groups with strong β -hydrogen agostic interactions, can serve as models for chain walking; however, these complexes are surprisingly more stable toward β -hydride elimination/chain release than the living system derived from 1-butene polymerization (LPB) where such β -agostic interactions appear to be absent. These results should prove useful in better defining the steric and electronic factors that govern chain walking and chain-end epimerization within early transition-metal propagating species.



$[\text{B}(\text{C}_6\text{F}_5)_4]$ counterions not shown
P = isotactic poly(1-butene)

Polymerizations of 1-butene and 1-hexene proceed in a living and highly stereoselective manner when **1** is used as the initiator at -10°C in chlorobenzene, with propagation occurring in a strict 1,2-fashion.^{5,6} Further, if living polymers with a degree of polymerization (DP) ≥ 100 are acid quenched at -10°C immediately after formation, virtually no alkene ^1H NMR resonances resulting from termination by β -hydride elimination are discernible using standard acquisition parameters. However, as the two selected ^1H NMR spectra in Figure 1 reveal, when a low-molecular weight isotactic poly(1-butene) living polymer ($\text{DP} \approx 20$) is allowed to incubate at -10°C for varying periods of time before quenching, alkene resonances for end groups resulting from β -hydride elimination do grow in at a steady rate.⁶ Unexpectedly, however, in addition to the ^1H NMR resonances at δ 4.69 and 4.76 ppm for the vinylidene moiety **I** that originates from direct β -hydride elimination of the initially formed living polymer, those for a *cis,trans* mixture

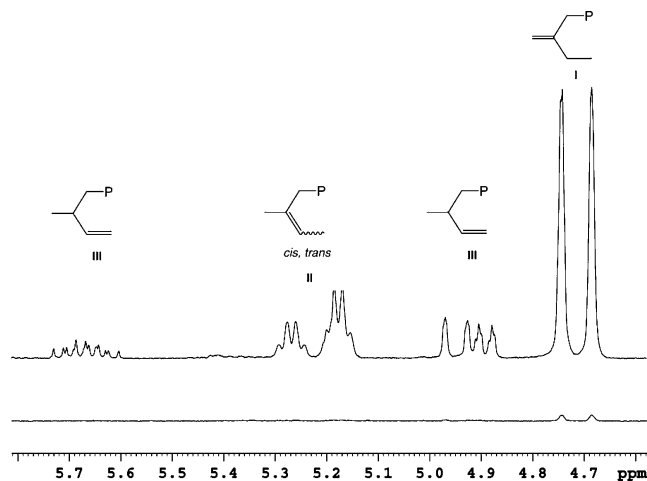
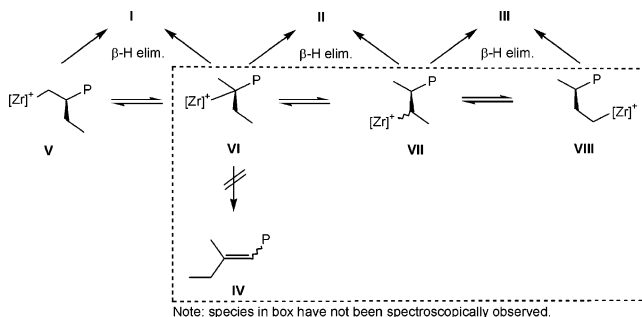


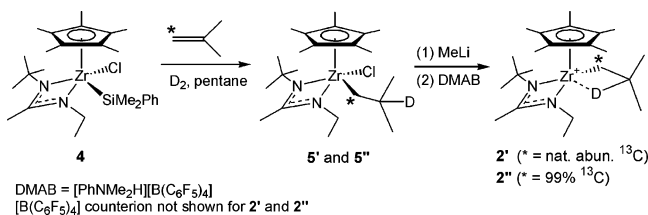
Figure 1. ^1H NMR (400 MHz) spectra of olefinic region for living polymer of isotactic poly(1-butene) ($\text{DP} \approx 20$) kept at -10°C and (bottom) immediately quenched after formation and (top) quenched after 72 h.⁶

Scheme 1



of the terminal trisubstituted alkene **II** (δ 5.18 and 5.27 ppm) and for the vinyl end group **III** (δ 4.90, 4.96, and 5.68 ppm) also appear at later time intervals (see Figure 1). Noticeably absent within the detection limits of NMR, however, are resonances for the trisubstituted olefin **IV** (see Scheme 1). As shown in Scheme 1, it is reasonable to assume that **II** and **III** are derived from the intermediates **VI**–**VIII** that arise from **V** through end-group-confined chain walking involving a series of successive β -hydride elimination/olefin rotation/reinsertion steps.^{1,3} Importantly, this chain walking, which is assumed to be intramolecular in nature, must be competitive with chain release after each β -hydride elimination step. It is further assumed that **IV** is inaccessible from the tertiary intermediate **VI** for steric reasons. Unfortunately, attempts to spectroscopically observe ^{13}C NMR resonances for the α -carbons of either **VI** or of the secondary and primary species, **VII** and **VIII**, respectively, have not yet been productive due to either low abundance or transient lifetimes. By employing the isobutyl initiator **2**⁵ and (1- ^{13}C , 50%) 1-decene, however, it could be established that chain-end epimerization of the resulting living polymer does not

Scheme 2



appear to occur in the present system as evidenced by a single diastereomeric ¹³C-labeled methyl end group being observed at 20.4 ppm by ¹³C NMR analysis after acid quenching at various times [cf., the two methyl end group resonances observed at 20.4 and 19.9 ppm that arise from the first insertion of 1-hexene into **1** that occurs with 95% diastereoselectivity in the formation of isotactic poly(1-hexene)].⁶

Well-defined model complexes that can mimic the chain walking behavior of living polymers derived from **1** should lead to a better understanding of the factors governing this process. Accordingly, in addition to complexes **2** and **3** that were prepared through previously reported procedures,^{5–7} the isotopic single- and double-labeled derivatives, **2'** and **2''**, respectively, were prepared according to Scheme 2 using a recently reported hydrozirconation procedure that provides products that are kinetically stable toward alkyl group isomerizations, thus preserving the location of the isotopic label prior to formation of **2'** and **2''** through chemoselective demethylation as shown.^{6,8}

As previously reported,⁵ a series of ¹H and ¹³C 1- and 2D (COSY, J-resolved HSQC) NMR experiments revealed that, at 25 °C and below, the β-hydrogen of **2** is engaged in a strong agostic interaction⁹ with the metal center, and this was once again found to be true for **3** as well [cf., δ_{BH} −0.27 ppm, ¹J(¹³C_β–¹H_β) 92 Hz for **2** and 0.06 ppm, 86 Hz for **3**]. Additional support for this agostic interaction was obtained in the case of **2** through single-crystal X-ray analysis that provided a molecular structure in which the crystallographically located β-hydrogen is clearly bound to the metal in an agostic fashion [Zr–H_β distance of 2.25(3) Å].¹⁰ In contrast, a similar NMR search involving a living isotactic poly(1-butene) polymer (DP ≈ 10) failed to detect any β-hydrogen agostic interactions in solution.

At 0 °C, ¹H NMR studies with 9 mM solutions in chlorobenzene-*d*₅ revealed that **2** and **3** disappear in a strictly first-order fashion, with the rate constant for the latter being approximately twice as large [cf. 0.0335(3) h^{−1} (t_{1/2} = 21.0 h) vs 0.0668(2) h^{−1} (10.2 h), respectively]. More surprisingly, however, was the observation that the first-order rate constant for disappearance of the ¹³C NMR resonance at δ 83 ppm for the α-carbon of the living polymer (6 mM in chlorobenzene-*d*₅), prepared using 1-¹³C-1-decene,⁵ was the largest of all, being 6 times greater than that of **2** at 0.22(1) h^{−1} (t_{1/2} = 3.2 h). Similarly, both **2** and **3** appear to be indefinitely stable toward decomposition at −10 °C while the chain end of the living polymer **LPB** undergoes a slow rate of overall decomposition with t_{1/2} ≈ 40 h (see Figure 1).

With respect to chain walking, at 0 °C, compound **2'** was found to undergo complete scrambling of the deuterium label within the isobutyl group over 11 h in a process that is concomitant with decomposition.⁶ A similar study of the double-labeled complex **2''** revealed that, upon scrambling, the deuterium label is always located on a ¹³C-labeled position, and this observation is consistent with the Busico mechanism for chain-end epimerization rather than that proposed by Resconi.^{1a,d,e} Finally, for **3**, ¹H NMR analysis of the vacuum-transferred volatiles obtained after complete decomposition revealed the olefinic component to be a mixture of 2-ethyl-1-butene,

3-methyl-2-pentene (*cis* and *trans*), and 3-methyl-1-pentene which is in agreement with a chain-walking process that is competitive with chain release. Unfortunately, for both **2** and **3**, it has not yet proven possible to detect any zirconium tertiary alkyl intermediates that are presumed to be part of the isomerization mechanism, nor has it been possible to observe zirconium secondary alkyl products derived from chain walking of **3**. Finally, it should be mentioned that as with decomposition, at −10 °C, structural isomerizations involving **2** and **3** appear to be significantly retarded relative to the chain-walking process observed for the living polymer **LPB**.

The unexpected result that decomposition through chain release and chain walking appear to be accelerated by an increase in the steric bulk of the alkyl substituent bound to zirconium (i.e., **2** < **3** < **LPB**) can be reconciled by assuming a ground-state destabilization by steric effects. It is also possible that, as originally proposed by Bercaw and co-workers,¹¹ the strong β-agostic interactions observed for both **2** and **3** increase the barrier for β-hydride elimination through stabilization of the ground state relative to that of the living polymer in which such a strong interaction is absent. Clearly, these observed differences between model compounds and the living polymer, which are likely the cause of subtle steric and electronic factors, suggest that caution should be exercised in extrapolating the properties of the latter from those of the former. Additional mechanistic studies are now in progress to define further the factors controlling β-hydride elimination and chain walking in the present system, including the potential observation or trapping of zirconium tertiary alkyl species that are proposed as intermediates in the latter process.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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