

Kinetic Investigation of the Polymerization of 1-Hexene by the $\{[t\text{-BuNON}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ Initiator

Jonathan T. Goodman and Richard R. Schrock*

Department of Chemistry and the Center for Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139

Received August 6, 2001

We have investigated the rates of polymerization of 1-hexene by cationic monoalkyl zirconium catalysts that contain the $[t\text{-BuNON}]^{2-}$ ligand ($[t\text{-BuNON}]^{2-} = \{[(\text{CH}_3)(\text{CD}_3)_2\text{CN}-\text{o}-\text{C}_6\text{H}_4]_2\text{O}\}^{2-}$). Catalysts obtained by activation of $[t\text{-BuNON}]\text{ZrMe}_2$ with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ at 0 °C in mixtures of C_6D_6 and bromobenzene polymerize 1-hexene at a rate that is first order in Zr and first order in 1-hexene with $k_p = 9.2 \pm 0.7 \text{ M}^{-1} \text{ min}^{-1}$ and activation parameters $\Delta H^\ddagger = 7.9 \pm 0.4 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -33.1 \pm 1.1 \text{ cal mol}^{-1} \text{ K}^{-1}$. The rate of polymerization decreases upon addition of dimethylaniline to the initiator and increases upon addition of $[t\text{-BuNON}]\text{ZrMe}_2$ to the initiator. In both circumstances, especially the latter, catalyst decomposition via β hydride elimination compromised the strictly living character of the polymerization.

Introduction

Alkene polymerization by group 4 cationic metallocene-based catalysts has dominated the literature in the last two decades.^{1,2} However, in the last five years especially there has been a search for new types of olefin polymerization catalysts that do not contain a cyclopentadienyl ligand.³ A breakthrough in the development of new early metal systems was made by McConville, who showed that relatively simple titanium catalysts that contain an aryl-substituted, bidentate, propylene-bridged diamido ligand would polymerize 1-hexene in a living fashion, as judged by the polydispersity of the resulting poly(1-hexene), as long as the concentration of 1-hexene was high (neat).^{4–8} At that point we had begun work on zirconium complexes that contain a diamido/donor ligand, $[t\text{-BuNON}]^{2-}$ ($[t\text{-BuNON}]^{2-} = \{[(\text{CH}_3)(\text{CD}_3)_2\text{CN}-\text{o}-\text{C}_6\text{H}_4]_2\text{O}\}^{2-}$). We subsequently found that treatment of $[t\text{-BuNON}]\text{ZrMe}_2$ with $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ in chlorobenzene at 0 °C produced a species that would behave as an initiator for the polymerization of up to ~ 1000 equiv of 1-hexene in an apparently living manner, as judged from the low polydispersities obtained (< 1.05) and a correlation between molecular weight (as determined by a combination of gel permeation chromatography and light scattering) and the number of equivalents of 1-hexene employed.^{9,10} Unlike

the diamido Ti system,⁸ the $\{[t\text{-BuNON}]\text{ZrR}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ system was stable (at 0 °C) after 1-hexene had been consumed. NMR studies revealed that activation of $[t\text{-BuNON}]\text{Zr}(\text{CH}_3)_2$ with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ at -30 °C in $\text{C}_6\text{D}_5\text{Br}$ yielded solutions whose ^{13}C NMR spectra contained a resonance at ~ 54 ppm that was assigned to the zirconium methyl group in $\{[t\text{-BuNON}]\text{Zr}(\text{CH}_3)\}[\text{B}(\text{C}_6\text{F}_5)_4]$. Addition of 1 equiv of 1-hexene to this initiator led to ^{13}C NMR spectra that contained $^{13}\text{CH}_3$ resonances for the first, second, and multiple 1,2-insertion products.¹¹ In another labeling experiment activation of $[t\text{-BuNON}]\text{ZrMe}_2$ at -30 °C in $\text{C}_6\text{D}_5\text{Br}$ by $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ followed by 13 equiv of 1-nonene and 1 equiv of $^{13}\text{CH}_2=\text{CHC}_7\text{H}_{15}$ yielded ^{13}C NMR spectra that contained a broad resonance at 93 ppm. This resonance could be assigned to the methylene carbon atom in the growing polymer chain formed by 1,2-insertion of 1-hexene into the Zr–C bond, i.e., $\{[t\text{-BuNON}]\text{Zr}(\text{CH}_2\text{CH}(\text{C}_7\text{H}_{15}))\}[\text{B}(\text{C}_6\text{F}_5)_4]$. Since $\{[t\text{-BuNON}]\text{ZrR}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ species appear to be relatively stable in bromobenzene at 0 °C, they should be amenable to kinetic studies. In this paper we report the results of our first kinetic investigation of the $\{[t\text{-BuNON}]\text{ZrR}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ living polymerization system.

Results

Addition of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to $[t\text{-BuNON}]\text{ZrMe}_2$ (**1**) in $\text{C}_6\text{D}_5\text{Br}$ at -20 °C produces a bright yellow solution. The ^1H NMR spectrum of this solution contains a broad resonance at 0.72 ppm, which we assign to the ZrMe group in $\{[t\text{-BuNON}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$. Addition of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to $[t\text{-BuNON}]\text{Zr}(\text{CH}_3)_2$ yields a sample in which the methyl resonance is found at 53.5 ppm in the

(1) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(2) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 144.

(3) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 428.

(4) Scollard, J. D.; McConville, D. H.; Payne, N. C.; Vittal, J. J. *Macromolecules* **1996**, *29*, 5241.

(5) Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008–10009.

(6) Scollard, J. D.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 4415.

(7) Scollard, J. D.; McConville, D. H.; Vittal, J. J.; Payne, N. C. *J. Mol. Catal. A* **1998**, *128*, 201–214.

(8) Scollard, J. D.; McConville, D. H.; Rettig, S. J. *Organometallics* **1997**, *16*, 1810–1812.

(9) Baumann, R.; Davis, W. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1997**, *119*, 3830.

(10) Schrock, R. R.; Baumann, R.; Reid, S. M.; Goodman, J. T.; Stumpf, R.; Davis, W. M. *Organometallics* **1999**, *18*, 3649.

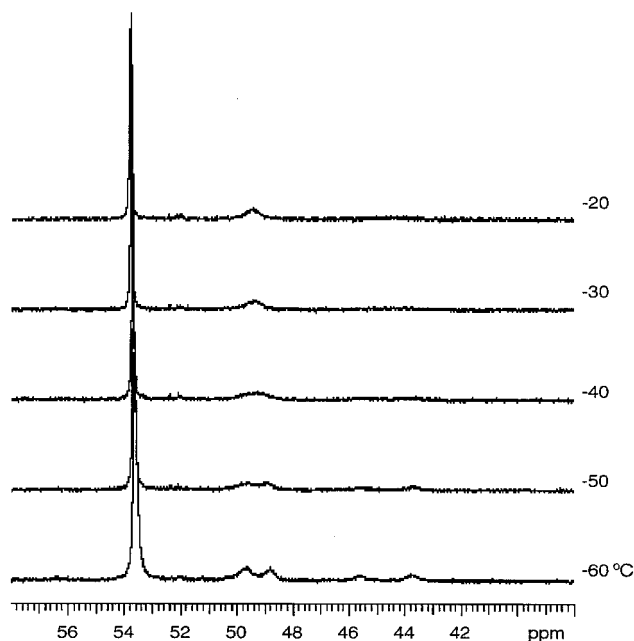


Figure 1. Variable-temperature ^{13}C NMR spectra of $[\text{t-BuNON}]\text{Zr}(\text{}^{13}\text{CH}_3)_2$ activated with 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in $\text{C}_6\text{D}_5\text{Br}$.

^{13}C NMR spectrum, as described previously.¹¹ The yield of $\{[\text{t-BuNON}]\text{Zr}(\text{}^{13}\text{CH}_3)\}[\text{B}(\text{C}_6\text{F}_5)_4]$ is essentially quantitative, relative to $\text{Ph}_3\text{C}^{13}\text{CH}_3$, which is formed in the activation step. However, a typical $-20\text{ }^\circ\text{C}$ spectrum of $\{[\text{t-BuNON}]\text{Zr}(\text{}^{13}\text{CH}_3)\}[\text{B}(\text{C}_6\text{F}_5)_4]$ between 42 and 56 ppm usually reveals another broad resonance near 49 ppm and a weaker and even broader one near 44 ppm (Figure 1). At $-60\text{ }^\circ\text{C}$ these two can be resolved into what appear to be four additional resonances between ~ 44 and 50 ppm (Figure 1). The intensities of these resonances relative to that at 53.5 ppm vary slightly from sample to sample. Addition of only 0.5 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to $[\text{t-BuNON}]\text{Zr}(\text{}^{13}\text{CH}_3)_2$ leads to a somewhat paler yellow solution whose variable-temperature ^{13}C NMR spectra contain only two broad resonances in a 2:1 ratio between -20 and $-30\text{ }^\circ\text{C}$ (Figure 2). The ratio of the total intensity of these two resonances to the methyl resonance in $\text{Ph}_3\text{C}^{13}\text{CH}_3$ is 3:1. At $30\text{ }^\circ\text{C}$ these resonances coalesce to yield a broad weighted average near 48 ppm. Between -50 and $-60\text{ }^\circ\text{C}$ these resonances are further resolved, with that near 44 ppm splitting into two at ~ 43.5 and ~ 45.5 ppm.

We propose that the species being observed in the spectra shown in Figure 2, and the minor species in Figure 1, is the dimeric monocation, $\{[\text{t-BuNON}]_2\text{Zr}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$. A dimeric monocation in this general category of diamido/donor complexes, $\{[\text{MesNMe}]_2\text{Zr}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$ ($[\text{MesNMe}]^{2-} = [(\text{MesNCH}_2\text{CH}_2)_2\text{NMe}]^{2-}$), has been structurally characterized and shown to contain a single bridging methyl group and two terminal methyl groups that are equivalent as a consequence of a C_2 axis passing through the bridging methyl group.¹² The terminal ZrCH_3 resonance is found at 41.23 ppm, while the bridging methyl resonance is found at 40.11 ppm at $-25\text{ }^\circ\text{C}$ in $\text{C}_6\text{H}_5\text{Br}$. We propose that the spectrum

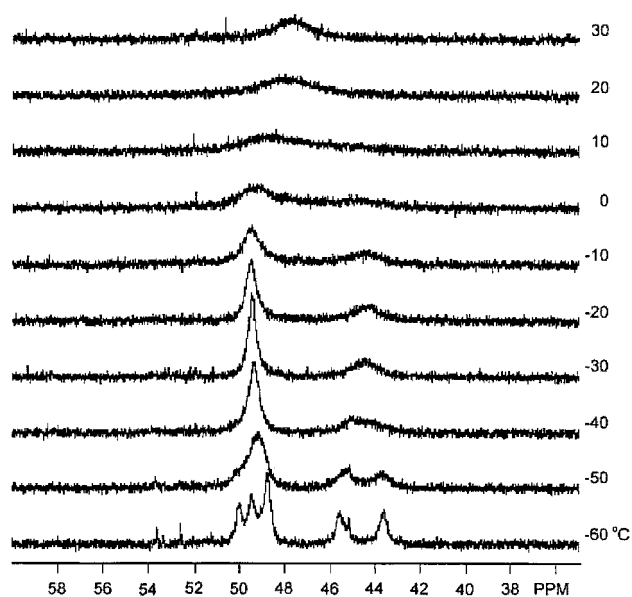


Figure 2. Variable-temperature ^{13}C NMR spectra of the 2:1 d_8 -toluene/ $\text{C}_6\text{H}_5\text{Br}$ solution containing 2 equiv of $[\text{t-BuNON}]\text{Zr}(\text{}^{13}\text{CH}_3)_2$ and 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$.

of $\{[\text{t-BuNON}]_2\text{Zr}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$ at -20 to $-30\text{ }^\circ\text{C}$ reveals resonances for two equivalent terminal methyl groups at ~ 49.5 ppm and one bridging methyl group at ~ 44 ppm. At these temperatures the $[\text{t-BuNON}]^{2-}$ ligand still contains a mirror plane on the NMR time scale. We ascribe the splitting of the terminal and bridging methyl resonances at $-60\text{ }^\circ\text{C}$ to a slowing of the motion that creates a plane of symmetry in a TBP $[\text{t-BuNON}]^{2-}$ complex, i.e., introduction of a chiral twist in the $[\text{t-BuNON}]^{2-}$ ligand on the NMR time scale.¹³ A chiral twist at each five-coordinate metal center in the dimeric dication would result in "rac" and "meso" diastereomers. If no symmetry relates the two metal centers, then the terminal methyl groups in each diastereomer would be inequivalent and potentially have different chemical shifts. Above $0\text{ }^\circ\text{C}$ the terminal and bridging methyl groups begin to interconvert on the NMR time scale and yield a broad weighted average resonance at ~ 48 ppm at $30\text{ }^\circ\text{C}$. It should be noted that the terminal and bridging methyl groups in $\{[\text{MesNMe}]_2\text{Zr}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$ do not interconvert on the NMR time scale rapidly at $30\text{ }^\circ\text{C}$, although they do exchange rapidly on the chemical time scale by dissociation of $[\text{MesNMe}]\text{ZrMe}_2$.¹² All efforts to isolate $\{[\text{t-BuNON}]_2\text{Zr}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$ have failed, perhaps in part because $[\text{t-BuNON}]\text{ZrMe}_2$ dissociates more readily from $\{[\text{t-BuNON}]_2\text{Zr}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (for steric reasons) than $[\text{MesNMe}]\text{ZrMe}_2$ dissociates from $\{[\text{MesNMe}]_2\text{Zr}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$. The resonances in Figure 1 can be ascribed to some $\{[\text{t-BuNON}]_2\text{Zr}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$ "impurity" being formed, because of either inexact stoichiometry or simply incomplete activation of $[\text{MesNMe}]\text{ZrMe}_2$ under these conditions.

(13) The solid-state structures of $[\text{t-BuNON}]\text{MMe}_2$ species ($\text{M} = \text{Ti}$ or Zr) have a twisted, chiral structure analogous to that for the five-coordinate metal center in the dimeric dication proposed here.¹⁰ An example of the consequence of an induced chiral twist in a *tri*amido/donor ligand at low temperatures can be found in a paper devoted to the synthesis of rhenium complexes that contain the $[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_3\text{N}]^{3-}$ ligand: Reid, S. M.; Neuner, B.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 4077.

(11) Baumann, R.; Schrock, R. R. *J. Organomet. Chem.* **1998**, *557*, 69.

(12) Schrock, R. R.; Casado, A. L.; Goodman, J. T.; Liang, L.-C.; Bonitatebus, P. J., Jr.; Davis, W. M. *Organometallics* **2000**, *19*, 5325.

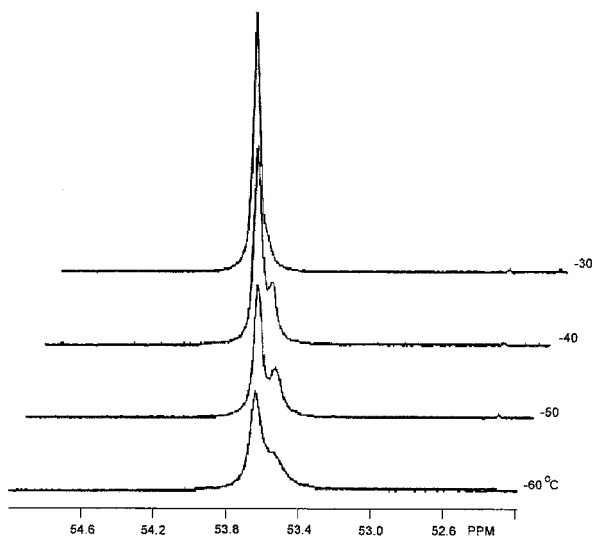


Figure 3. Variable-temperature ^{13}C NMR spectra of the 2:1 d_8 -toluene/ $\text{C}_6\text{H}_5\text{Br}$ solution containing $[\text{t-BuNON}]\text{Zr}-(^{13}\text{CH}_3)_2$ and 2 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$.

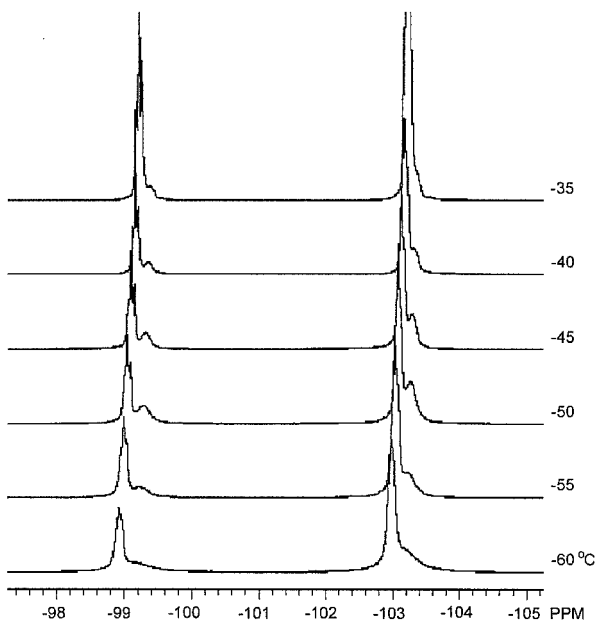


Figure 4. Variable-temperature ^{19}F NMR spectra of the 2:1 d_8 -toluene/ $\text{C}_6\text{H}_5\text{Br}$ solution containing $[\text{t-BuNON}]\text{Zr}-(^{13}\text{CH}_3)_2$ and 2 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. The upfield resonances (-103 ppm) correspond to the *meta*-F atoms in $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, and the resonances at -99 ppm correspond to the *para*-F atoms. The *ortho*-F resonance (not shown) is unaffected by the change in temperature.

Addition of 2 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to $[\text{t-BuNON}]\text{Zr}-(^{13}\text{CH}_3)_2$ in a 1:2 mixture of $\text{C}_6\text{D}_5\text{Br}/\text{C}_6\text{D}_5\text{CD}_3$ produced a yellow solution, the ^{13}C NMR spectrum of which at -30 °C consisted of a ZrMe resonance at 53.6 ppm with evidence of a shoulder at higher field (Figure 3). No resonances ascribable to $\{[\text{t-BuNON}]_2\text{Zr}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$ were observed. Upon lowering the temperature to -50 °C the shoulder became more distinct. Below -50 °C the resonances broadened, most likely as a consequence of an increase in viscosity. (The solution froze at approximately -65 °C.) Variable-temperature ^{19}F NMR spectra of this sample are shown in Figure 4. At approximately -45 °C high-field shoulders on the meta and para fluorine resonances are observable, although

the ortho fluorine resonances remained unchanged at -55 °C. The data in Figures 3 and 4 suggest that the anion is associating with a fraction of some cationic species in solution at low temperature, and/or that more than one phase containing ionic species is present under these conditions. Later we present evidence that polymerization activity slows down significantly in the presence of excess $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, consistent with a cationic zirconium center being less accessible to the olefin.

Samples of $\{[\text{t-BuNON}]\text{Zr}-(^{13}\text{CH}_3)\}[\text{B}(\text{C}_6\text{F}_5)_4]$ decompose over a period of 24 h at room temperature in ambient light. A dark yellow-orange oil separates from solution, leaving a nearly colorless supernatant. A resonance that corresponds to methane is observed at -3.2 ppm, but the insoluble species could not be identified unambiguously. In the absence of light $\{[\text{t-BuNON}]\text{Zr}-(^{13}\text{CH}_3)\}[\text{B}(\text{C}_6\text{F}_5)_4]$ decomposes in what appears to be a different manner that unfortunately also could not be elucidated.

Addition of 1-hexene (1, 3, 5, 10, and 20 equiv) to $\{[\text{t-BuNON}]\text{Zr}-(^{13}\text{CH}_3)\}[\text{B}(\text{C}_6\text{F}_5)_4]$ at 0 °C in $\text{C}_6\text{D}_5\text{Br}$ was monitored by ^{13}C NMR spectroscopy. The resonance associated with the $\text{Zr}-(^{13}\text{CH}_3)$ group in $\{[\text{t-BuNON}]\text{Zr}-(^{13}\text{CH}_3)\}[\text{B}(\text{C}_6\text{F}_5)_4]$ disappeared by the time 5 equiv of 1-hexene had been added, while resonances at ~ 30.8 ppm (assigned to the terminal $^{13}\text{CH}_3$ group in the first insertion product) and at ~ 24.0 ppm (assigned to the terminal $^{13}\text{CH}_3$ group in the second insertion product) were observable, especially in the spectrum in which only 1 equiv of 1-hexene had been added. Eventually only the resonance near 20 ppm, assigned to the terminal $^{13}\text{CH}_3$ group in higher insertion products, was visible, along with natural abundant ^{13}C resonances for atactic poly[1-hexene] at 41.1, 35.4–34.5, 33.2, 29.6–29.2, 24.2, and 15.2 ppm. These observations are entirely analogous to those described previously.¹¹

The consumption of 1-hexene was followed by NMR methods in a 1:1 mixture of C_6D_6 and $\text{C}_6\text{H}_5\text{Br}$ at 0 °C employing catalyst concentrations of ~ 0.0025 M and initial 1-hexene concentrations of ~ 0.24 M. (Concentrations in the final solution were determined by employing hexamethylbenzene as an internal standard. No difference in rate was observed when the internal standard concentration was increased by a factor of 3.) The consumption of 1-hexene was followed by monitoring the resonance for the methylene group next to the double bond at 1.93 ppm. This resonance was chosen because of its proximity to the resonance for the internal standard, the short relaxation time for these methylene protons, and the lack of any overlap of this resonance with any polymer resonances. Plots of $\ln[1\text{-hexene}]$ vs time were linear over greater than four reaction half-lives and yielded an observed rate constant (k_{obs}) of 0.0207 min^{-1} (Figure 5). After ~ 130 min little 1-hexene remained, a fact that gives rise to some scatter in the points beyond this time. This experiment was repeated six times, and an average second-order rate constant of 9.2 ± 0.7 $\text{M}^{-1} \text{min}^{-1}$ was calculated, assuming that $d[1\text{-hexene}] = -k_p[\text{Zr}][1\text{-hexene}]dt$. The first-order dependence on the zirconium concentration was confirmed by doubling the concentration of the catalyst, which yielded the expected 2-fold increase in the observed rate of

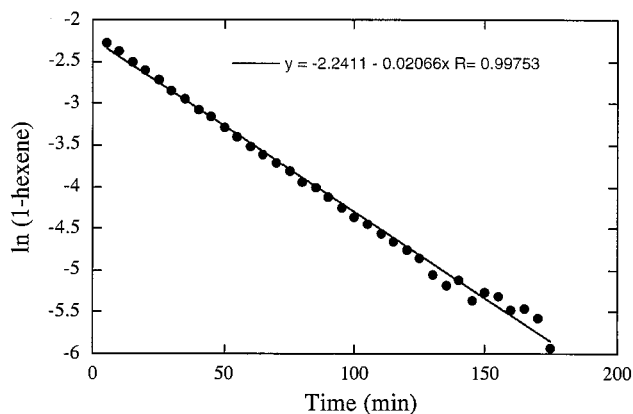


Figure 5. First-order consumption of 1-hexene at 0 °C in 1:1 C₆D₆/C₆H₅Br with [Zr] ≈ 2.5 mM; average $k_p = 9.2 \pm 0.7 \text{ M}^{-1} \text{ min}^{-1}$ (six runs).

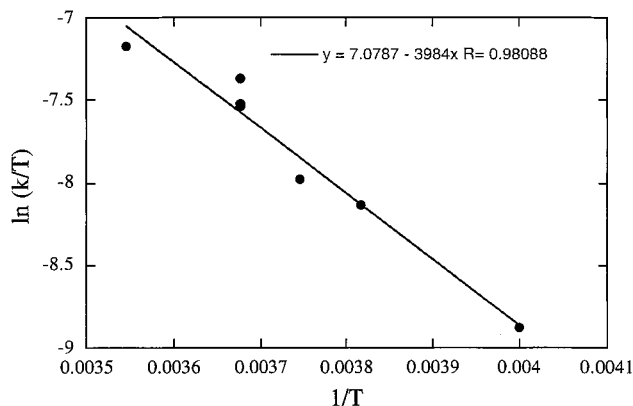


Figure 6. Eyring plot for the polymerization of 1-hexene by {[t-BuNON]ZrMe}[B(C₆F₅)₄] in 1:1 C₆D₆/C₆H₅Br.

polymerization; the rate constant in this experiment was found to be $9.8 \pm 0.8 \text{ M}^{-1} \text{ min}^{-1}$.

The rate of 1-hexene polymerization was similarly well-behaved at -20, -10, -5, and 10 °C. The consumption of 1-hexene was monitored over four half-lives with the exception of the reaction run at -20 °C; in this case data acquisition was terminated after 8 h. Plots of ln[1-hexene] vs time were linear at all temperatures. An Eyring plot (Figure 6) yielded $\Delta H^\ddagger = 7.9 \pm 0.4 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -33.1 \pm 1.1 \text{ cal mol}^{-1} \text{ K}^{-1}$. The large, negative entropy is consistent with a bimolecular reaction between 1-hexene and {[t-BuNON]ZrR}[B(C₆F₅)₄] in the rate-limiting step.

Polymerizations also were carried out in 1:1 mixtures of C₆D₆/C₆H₅X (X = F, Cl) and in 1:9 mixtures of C₆D₆/C₆H₅Br. The polymerization rate constants in C₆D₆/C₆H₅Br ($9.2 \pm 0.7 \text{ M}^{-1}$) and C₆D₆/C₆H₅Cl ($8.6 \pm 1.2 \text{ M}^{-1}$) were statistically indistinguishable, while the rate constant for polymerization in a 1:9 mixture of C₆D₆ and C₆H₅Br was $7.5 \pm 1.0 \text{ M}^{-1} \text{ min}^{-1}$. The polymerization rate constant in C₆D₆/C₆H₅F was $6.7 \pm 0.1 \text{ M}^{-1} \text{ min}^{-1}$. The relatively small variation in k_p in different solvents and solvent mixtures lead us to conclude that none of the halogenated solvents binds so strongly to the cation that {[t-BuNON]ZrR(S)}[B(C₆F₅)₄] (S = halogenated solvent) is a more valid description than the {[t-BuNON]ZrR}[B(C₆F₅)₄] ion pair and that slight differences in rates can be ascribed solely to different dielectric values for the various solvent mixtures, i.e., to slightly different degrees of solvation of that ion pair.

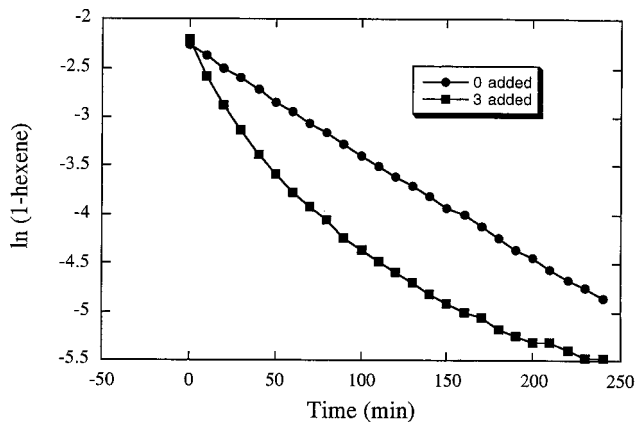


Figure 7. Effect of added [t-BuNON]ZrMe₂ on the rate of consumption of 1-hexene by {[t-BuNON]ZrMe}[B(C₆F₅)₄] at 0 °C in 1:1 C₆D₆/C₆H₅Br.

A standard polymerization also was conducted in the presence of an additional equivalent of [Ph₃C][B(C₆F₅)₄] at 0 °C. The plot of ln[1-hexene] vs time was linear throughout the course of the reaction and the calculated rate constant was found to be $3.8 \pm 0.9 \text{ M}^{-1} \text{ min}^{-1}$ (versus $9.2 \text{ M}^{-1} \text{ min}^{-1}$ in the absence of additional [Ph₃C][B(C₆F₅)₄]). The extra equivalent of [Ph₃C][B(C₆F₅)₄] clearly suppressed the rate of polymerization by a factor of approximately 2. By analogy with living carbanionic polymerization systems,^{14,15} the simplest explanation of this effect is that addition of the [B(C₆F₅)₄]⁻ ion in the form of [Ph₃C][B(C₆F₅)₄] decreases the average degree of dissociation of the {[t-BuNON]ZrR}[B(C₆F₅)₄] ion pair and therefore the rate of polymerization of 1-hexene. The assumptions are that [Ph₃C][B(C₆F₅)₄] is more readily solvated than the {[t-BuNON]ZrR}[B(C₆F₅)₄] ion pair, since *some* bonding interaction beyond a Coulombic interaction is likely to take place between {[t-BuNON]ZrR}⁺ and [B(C₆F₅)₄]⁻,¹⁶ and that an “unsolvated ion pair” reacts with 1-hexene much more slowly than a solvated ion pair.

The effect of conducting the polymerization of 1-hexene after adding [t-BuNON]ZrMe₂ (1) to {[t-BuNON]ZrMe}[B(C₆F₅)₄] (or by employing a deficiency of [Ph₃C][B(C₆F₅)₄]) was more dramatic. For example, a plot of ln[1-hexene] vs time after 3 equiv of [t-BuNON]ZrMe₂ had been added to {[t-BuNON]ZrMe}[B(C₆F₅)₄] showed an initially *accelerated* consumption of 1-hexene relative to the rate at the same concentration of {[t-BuNON]ZrMe}[B(C₆F₅)₄] alone, followed by some slowing of the rate of polymerization, i.e., a significant curvature in the plot (Figure 7). A slowing of the rate of polymerization suggests that some propagating species may have decomposed irreversibly as a consequence of adding 1 to {[t-BuNON]ZrMe}[B(C₆F₅)₄]. Indeed, a broad olefinic resonance is observed at ~5.50 ppm in the ¹H NMR spectrum in reactions in which 1 equiv of 1 has been added to the cation. (This is the stoichiometry that would correspond to formation of the dimeric monocation, {[t-BuNON]₂Zr₂Me₃}[B(C₆F₅)₄].) This decomposi-

(14) Mueller, A. H. E. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: New York, 1989; Vol. 3, Chapter 26.

(15) We thank Dr. Kai Hultzsich for pointing out the extensive studies of carbanionic polymerization systems.

(16) Jia, L.; Yang, X.; Stern, C.; Marks, T. J. *Organometallics* **1994**, *13*, 3755.

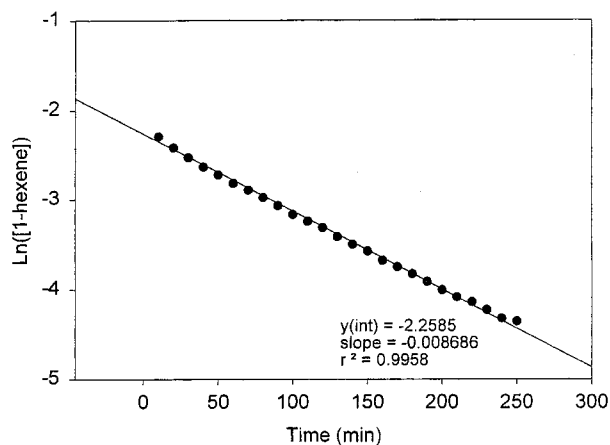


Figure 8. Plot showing the pseudo-first-order consumption of 1-hexene by $[t\text{-BuNON}][\text{ZrMe}(\text{NMe}_2\text{Ph})][\text{B}(\text{C}_6\text{F}_5)_4]$ ($k_p = 3.5 \pm 0.6 \text{ M}^{-1} \text{ min}^{-1}$).

tion product appeared at a rate that is first order and with a rate constant (k_{decomp}) of $(1.18 \pm 0.7) \times 10^{-3} \text{ min}^{-1}$ in the experiment involving an additional 1 equiv of **1**. This is the region where one would expect to find olefinic resonances for an internal olefin formed by decomposition of a 2,1-insertion product.^{17,18} We cannot explain why the rate of polymerization by “[$t\text{-BuNON}$] $_2\text{Zr}_2\text{Me}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ ” is initially greater than by $\{[t\text{-BuNON}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ alone.

Polymerization of 1-hexene at 0 °C by $[t\text{-BuNON}]\text{ZrMe}_2$ activated with $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ was monitored by ^1H NMR spectroscopy under conditions similar to those employed for the $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ activated system. The polymerization was approximately first order in 1-hexene, as shown by the plot of $\ln[1\text{-hexene}]$ vs time, with $k_p = 3.5 \pm 0.6 \text{ M}^{-1} \text{ min}^{-1}$ (Figure 8), a value that is approximately one-third that in the absence of dimethylaniline, i.e., in the $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ activated system. However, there is a slight curvature in this plot also, consistent with irreversible decomposition of polymerization intermediates. During the polymerization a broad olefinic resonance also appeared at 5.4 ppm in the ^1H NMR spectrum characteristic of olefinic protons in a β elimination product formed from a 2,1-insertion product. This β elimination product also was formed in approximately a first-order manner with $k_{\text{decomp}} = 1.57 \times 10^{-3} \text{ min}^{-1}$, a value that is essentially the same as that formed for a catalyst where **1** is added to $\{[t\text{-BuNON}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ instead of dimethylaniline. (Irreversible catalyst decomposition at this rate would imply that $\sim 80\%$ of the original catalyst is present at $t = 200 \text{ min}$.) It should be noted that the system in which $[t\text{-BuNON}]\text{ZrMe}_2$ was activated with $[\text{PhNHMe}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ was said to be living on the basis of measurement of poly(1-hexene) molecular weights and polydispersities.¹⁰ Under the conditions employed here, that apparently is not *strictly* the case.

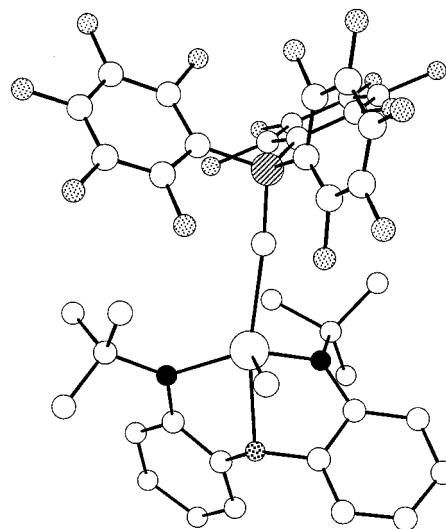


Figure 9. Structure of $[t\text{-BuNON}]\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ (from ref 10).

We have found that active catalysts for polymerization of 100 equiv of 1-hexene at 0 °C are obtained upon addition of other ArNMe_2 species ($\text{Ar} = 4\text{-methylphenyl}$, $4\text{-tert-butylphenyl}$, and 2-naphthyl), triphenylamine, pentafluoropyridine, or diphenyl ether to $\{[t\text{-BuNON}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$. These polymerizations were not investigated in detail. Polymerization activity was effectively quenched upon addition of diethyl ether, trimethylamine, pyridine, 2,4-lutidine, 2,5-lutidine, 2-ethylpyridine, or 2,6-difluoropyridine to $\{[t\text{-BuNON}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$.

Discussion

Activation of $[t\text{-BuNON}]\text{ZrMe}_2$ by $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ can be viewed in what we might call “classical” terms; that is, a methyl group is abstracted by trityl and a dynamic $\{[t\text{-BuNON}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ ion pair is formed, the average degree of solvation of which depends on the dielectric constant of the medium. At present the only model for this ion pair is obtained when $[t\text{-BuNON}]\text{ZrMe}_2$ is activated with $\text{B}(\text{C}_6\text{F}_5)_3$ to yield $[t\text{-BuNON}]\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$,¹¹ a species in which the “incipient $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ ion” is located in the axial position of an approximate TBP structure trans to the oxygen donor in the $[t\text{-BuNON}]^{2-}$ ligand (Figure 9). (This species has not yet been investigated as a catalyst for 1-hexene polymerization.) We propose that the $\{[t\text{-BuNON}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ “tight” ion pair contains the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ion in a similar “axial” position interacting with the metal in a relatively weak, poorly defined, and likely dynamic manner. Any olefin that reacts with the $\{[t\text{-BuNON}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ ion pair presumably must push the anion further away from the metal in the process of binding to the metal and before inserting into the Zr–R bond. Therefore we cannot assume that the activation enthalpy and entropy refer solely to the rate of insertion of the olefin into the Zr–R bond. Recent experimental^{19,20} and theoretical^{21,22} studies of metallocene cations suggest that solvent and/or anion interactions with the cation are approximately as strong as interaction of the incoming olefin with the cationic metal center (probably

(17) Mehrkhodavandi, P.; Bonitatebus, P. J., Jr.; Schrock, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 7841.

(18) (a) Busico, V.; Cipullo, R.; Chadwick, J. C.; Modder, J. F.; Sudmeijer, O. *Macromolecules* **1994**, *27*, 7538. (b) Busico, V.; Cipullo, R.; Talarico, G. *Macromolecules* **1998**, *31*, 2387. (c) Busico, V.; Cipullo, R.; Talarico, G.; Segre, A. L.; Caporaso, L. *Macromolecules* **1998**, *31*, 8720. (d) Resconi, L.; Piemontesi, F.; Balboni, D.; Sironi, A.; Moret, M.; Rychlicki, H.; Zeigler, R. *Organometallics* **1996**, *15*, 5046. (e) Guerra, G.; Longo, P.; Cavallo, L.; Corradini, P.; Resconi, L. *J. Am. Chem. Soc.* **1997**, *119*, 4394.

5–10 kcal/mol²³) and that therefore it is best to regard the catalyst as an ion pair that is solvated to varying degrees. More complex multiion aggregates also have been proposed.^{19,20}

Relatively small, good donors such as dimethoxyethane, THF, or diethyl ether strongly inhibit polymerization of 1-hexene. We know that THF binds to the metal to yield $\{[t\text{-BuNON}]\text{ZrMe}(\text{THF})_2\}[\text{B}(\text{C}_6\text{F}_5)_4]$, while dimethoxyethane binds to yield $\{[t\text{-BuNON}]\text{ZrMe}(\text{MeOCH}_2\text{CH}_2\text{OMe})\}[\text{B}(\text{C}_6\text{F}_5)_4]$;¹⁰ in each X-ray study the anion is well-separated from the cation in the solid state. X-ray diffraction showed $\{[t\text{-BuNON}]\text{ZrMe}(\text{THF})_2\}[\text{B}(\text{C}_6\text{F}_5)_4]$ to be a pseudooctahedral species containing trans THF ligands in which the $[t\text{-BuNON}]^{2-}$ ligand adopts a “twisted *mer*” geometry, while $\{[t\text{-BuNON}]\text{ZrMe}(\text{MeOCH}_2\text{CH}_2\text{OMe})\}[\text{B}(\text{C}_6\text{F}_5)_4]$ was found to be a distorted “twisted *fac*” variety (as shown in Figure 9 for $[t\text{-BuNON}]\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$) in which the dimethoxyethane is bound asymmetrically and the methyl group is found in the apical position. The catalyst prepared by addition of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ to $[t\text{-BuNON}]\text{ZrMe}_2$ has been viewed as an actual solvent adduct, $\{[t\text{-BuNON}]\text{ZrMe}(\text{PhNMe}_2)\}[\text{B}(\text{C}_6\text{F}_5)_4]$, although broad resonances for free and coordinated dimethylaniline were observed in the presence of added dimethylaniline, consistent with ready exchange of coordinated and free dimethylaniline.¹⁰ It is assumed that exchange takes place via dissociation of dimethylaniline to yield $\{[t\text{-BuNON}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$, although exchange via attack by dimethylaniline on $\{[t\text{-BuNON}]\text{ZrMe}(\text{PhNMe}_2)\}[\text{B}(\text{C}_6\text{F}_5)_4]$ cannot be ruled out. Unfortunately no crystals of $\{[t\text{-BuNON}]\text{ZrMe}(\text{PhNMe}_2)\}[\text{B}(\text{C}_6\text{F}_5)_4]$ suitable for X-ray studies have been obtained.

The concept of a neutral dimethyl complex as a base is well-established in metallocenes^{24–29} and other diamido/donor ligand systems.^{12,17,30} Although we find that $\{[t\text{-BuNON}]_2\text{Zr}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$ forms readily upon activation of **1** with 0.5 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, the dimeric monocation cannot be isolated. In contrast, $\{[\text{MesNMe}]_2\text{Zr}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$ ¹² can be isolated, and an X-ray study has been carried out, although this dimeric monocation loses $[\text{MesNMe}]\text{ZrMe}_2$ readily on the chemical time scale, as judged by reaction of the dimeric monocation with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to give $\{[\text{MesNMe}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$. Finally, when $[\text{MesNpy}]\text{ZrMe}_2$ ($[\text{MesNpy}]^{2-} = [(\text{MesNCH}_2)_2\text{C}(\text{CH}_3)(2\text{-C}_5\text{H}_4\text{N})]^{2-}$) is activated

with even 1 equiv of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, largely $\{[\text{MesNpy}]_2\text{Zr}_2\text{Me}_3\}[\text{B}(\text{C}_6\text{F}_5)_4]$ forms readily and does *not* react further with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ or olefins.¹⁷ (The small amount of $\{[\text{MesNpy}]\text{ZrMe}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ that escapes capture by $[\text{MesNpy}]\text{ZrMe}_2$ is the active catalyst for 1-hexene polymerization in this case.) These data suggest that the ease of loss of the dimethyl “base” from the dimeric monocation follows the order $[t\text{-BuNON}]^{2-} > [\text{MesNMe}]^{2-} > [\text{MesNpy}]^{2-}$, which qualitatively is the order of decreasing steric hindrance around the metal. One might conclude that the $[t\text{-BuNON}]^{2-}$ ligand leads to a cation in which the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ion competes with the dimethyl species for the cation most effectively, while $[\text{MesNpy}]^{2-}$ produces a cation in which the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ion competes least effectively with the dimethyl species. This seems sensible, since a dimethyl species is likely to bind to the metal through a bridging methyl group more strongly than $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ binds to the metal through fluoride interactions,¹⁶ if the metal is accessible. If the metal is relatively inaccessible, then the $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ion is the better “base” through purely a Coulombic attraction.

We can now compare directly some k_p values for 1-hexene polymerization in well-behaved or relatively well-behaved cationic systems that contain a diamido/donor ligand. (These values refer to the reaction of 1-hexene with propagating species formed by 1,2-insertion of 1-hexene. The k_i values for reaction of 1-hexene in a 1,2 fashion with the initial cationic methyl species have not been determined.) For $\{[t\text{-BuNON}]\text{ZrR}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ (measured in this work in a mixture of bromobenzene and C_6D_6 at 0 °C) $k_p = 0.15 \text{ M}^{-1} \text{ s}^{-1}$. For $\{[\text{MesNMe}]\text{Zr}(\text{PhNMe}_2)\text{R}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ 1-hexene polymerization is complicated by CH activation in an ortho mesityl methyl group and concomitant rapid catalyst decomposition; k_p was estimated to be $4.8 \text{ M}^{-1} \text{ s}^{-1}$.³¹ For $\{[(2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{ZrR}\}[\text{B}(\text{C}_6\text{F}_5)_4]$, k_p was estimated by interpreting data for polymerization of 1-hexene by $\{[(2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{NCH}_2\text{CH}_2)_2\text{NMe}]\text{Zr}(\text{PhNMe}_2)\text{R}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ in terms of competitive inhibition by dimethylaniline; k_p was found to be $0.80 \text{ M}^{-1} \text{ s}^{-1}$.³² For $\{[\text{MesNpy}]\text{ZrR}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ it is estimated that $k_p = 0.13 \text{ M}^{-1} \text{ s}^{-1}$.¹⁷ (In this case the concentration of the catalyst was estimated on the basis of the resulting molecular weight of the 1-hexene, which is approximately 3–4 times that expected if all metal were active.) Finally, in the well-behaved polymerization of 1-hexene by $\{[\text{MesNpy}]\text{HfR}\}[\text{B}(\text{C}_6\text{F}_5)_4]$, which is not complicated by initiator decomposition, k_p was found to be $0.067 \text{ M}^{-1} \text{ s}^{-1}$, $\Delta H^\ddagger = 10.9(5) \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -23(2) \text{ cal mol}^{-1} \text{ K}^{-1}$.³³ At this stage the k_p values for $\{[t\text{-BuNON}]\text{ZrR}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ ($0.15 \text{ M}^{-1} \text{ s}^{-1}$) and $\{[\text{MesNpy}]\text{HfR}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ ($0.067 \text{ M}^{-1} \text{ s}^{-1}$) are the only entirely reliable numbers, free of assumptions. The possibility that the olefin may not react with the $\{[\text{diamido/donor}]\text{ZrR}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ ion pairs via exactly analogous mechanisms should be kept in mind when comparing rate constants in systems that contain different ligands.

(19) Beck, S.; Geyer, A.; Brintzinger, H.-H. *J. Chem. Soc., Chem. Commun.* **1999**, 2477.

(20) Beck, S.; Lieber, S.; Schaper, F.; Geyer, A.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **2001**, *123*, 1483.

(21) Vanka, K.; Chan, M. S. W.; Pye, C. C.; Ziegler, T. *Organometallics* **2000**, *19*, 1841.

(22) Vanka, K.; Ziegler, T. *Organometallics* **2001**, *20*, 905.

(23) Casey, C. P.; Carpenetti, D. W., II; Sakurai, H. *J. Am. Chem. Soc.* **1999**, *121*, 9483.

(24) Beck, S.; Prosen, M. H.; Brintzinger, H. H.; Goretzki, R.; Herfert, N.; Fink, G. *J. Mol. Catal. A* **1996**, *111*, 67.

(25) Bochmann, M.; Lancaster, S. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634.

(26) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235.

(27) Koehler, K.; Piers, W. E.; Jarvis, A. P.; Xin, S.; Feng, Y.; Bravakis, A. M.; Collins, S.; Clegg, W.; Yap, G. P. A.; Marder, T. B. *Organometallics* **1998**, *17*, 3557.

(28) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842.

(29) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840.

(30) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672.

(31) Schrodi, Y.; Schrock, R. R.; Bonitatebus, P. J., Jr. *Organometallics* **2001**, *20*, 3560.

(32) Schrock, R. R.; Bonitatebus, P. J., Jr.; Schrodi, Y. *Organometallics* **2001**, *20*, 1056.

(33) Mehrkhodavandi, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2001**, *123*, 10746.

We have uncovered some peculiar phenomena in the process of examining these polymerizations in detail. One that stands out is that the initial rate of polymerization of 1-hexene by $\{[t\text{-BuNON}]\text{ZrR}\}[\text{B}(\text{C}_6\text{F}_5)_4]$ increases in the presence of $[t\text{-BuNON}]\text{ZrMe}_2$, although no new cationic metal centers are created. (Methyl groups, if not the growing polymer chain, are likely to transfer between charged and uncharged metal centers,¹² but this phenomenon alone should not result in a dramatic increase in the rate of polymerization.) At the same time the presence of $[t\text{-BuNON}]\text{ZrMe}_2$ results in formation and decomposition of 2,1-insertion products, or regioerrors.¹⁸ Although addition of dimethylaniline slows the rate of polymerization to one-third its normal value, as one would expect for inhibition of polymerization when dimethylaniline binds to the metal, dimethylaniline also allows some competitive 2,1-insertion and subsequent β hydride elimination. We cannot rationalize these results at this time.

We should note that other catalyst systems that contain nitrogen ligands have been published recently that appear to be living.^{34–36} Some of these catalysts also produce isotactic polymers, and unusual species such as relatively stable dimeric dications that contain two bridging methyl groups have been crystallographically characterized. Other types of early^{37–41} and late^{42–44} metal living catalysts have been claimed in the literature in the last several years. Ultimately some of these systems also may prove to be amenable to cation observation and kinetic studies.

It is becoming clear that we have much to learn about the integrity of an ion pair in an olefin polymerization reaction, the role of what would appear to be a simple inhibitor, the role of dimeric monocations or even dications, alkyl exchange reactions, multiion aggregates, etc. Kinetic studies of strictly living systems ultimately should be able to clarify some of these issues, as have kinetic studies of anionic polymerization processes for a number of years.¹⁴ In the future we plan to carry out more elaborate studies of $[t\text{-BuNON}]^{2-}$ and other well-

behaved diamido/donor catalysts that contain zirconium or hafnium.^{10,17,31,33} We hope that generalized patterns of behavior will be forthcoming eventually, although we expect each system to have its own set of characteristics, only a few of which have been hinted at so far.

Experimental Section

General Procedures. All NMR samples were prepared in an N_2 -filled glovebox and transferred to precooled instruments at 10 to 20 deg below the acquisition temperature. $[t\text{-BuNON}]\text{ZrMe}_2$ was synthesized via a previously published procedure¹⁰ and was recrystallized prior to use. The activators, $[\text{PhNHMe}_2]\text{B}(\text{C}_6\text{F}_5)_4$ and $[\text{Ph}_3\text{C}]\text{B}(\text{C}_6\text{F}_5)_4$, were ground to a fine powder in a mortar and pestle and dried in vacuo for 48 h. Solvents were distilled from common drying agents and stored in an N_2 -filled glovebox. All NMR spectra were collected on a Varian-Oxford Unity 500 spectrometer equipped with a variable-temperature unit and operating at 500.247 MHz (^1H) and 125.799 MHz (^{13}C). It should be noted that all kinetic samples were prepared in a dedicated drybox free of diethyl ether and all other potentially coordinating solvents.

Typical Preparation of a Sample for Kinetic Studies. A vial containing 0.020 g (0.045 mmol) of $[t\text{-BuNON}]\text{ZrMe}_2$ was cooled to -20°C , and 1 mL of 1:1 $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{Br}$ was added. A second vial containing 0.040 g (0.043 mmol) of $[\text{Ph}_3\text{C}]\text{B}(\text{C}_6\text{F}_5)_4$ was cooled to -20°C , and 1 mL of 1:1 $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{Br}$ was added. In a third vial was dissolved 0.01 g (0.062 mmol) of $\text{C}_6(\text{CH}_3)_6$ in 1 mL of 1:1 $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{Br}$. A reaction vial with 0.806 mL of 1:1 $\text{C}_6\text{D}_6/\text{C}_6\text{H}_5\text{Br}$ was cooled to -20°C , and 0.05 mL (0.0031 mmol) of the hexamethylbenzene solution was added. To the reaction vial was added 0.056 mL (0.0025 mmol) of the $[t\text{-BuNON}]\text{ZrMe}_2$ solution followed by 0.058 mL (0.0025 mmol) of the $[\text{Ph}_3\text{C}]\text{B}(\text{C}_6\text{F}_5)_4$ solution. The reaction solution slowly turned bright yellow and was maintained at -20°C for 20 min, at which point 0.03 mL (0.24 mmol) of 1-hexene was added. The sample was transferred to a NMR tube, and the reaction was monitored by ^1H NMR spectroscopy.

In the temperature study k_p ($\text{M}^{-1}\text{min}^{-1}$) was found to be 13 (at 10°C), 5.5 (at -5°C), 4.6 (at -10°C), and 2.1 (at -20°C).

Preparation and Examination of Base Adducts. A 20 dram vial containing 0.050 g (0.113 mmol) of $[t\text{-BuNON}]\text{ZrMe}_2$ and 0.104 g (0.113 mmol) of $[\text{Ph}_3\text{C}]\text{B}(\text{C}_6\text{F}_5)_4$ was cooled to -20°C , and 5 mL of cold (-20°C) $\text{C}_6\text{D}_5\text{Br}$ was added. The solution turned golden yellow during a period of ~ 1 min. The base (e.g., NMe_2Ph) was added at this point. One 1 mL sample was removed, 1-hexene 0.28 mL (2.23 mmol) was added, and the consumption of 1-hexene (or lack of consumption) was monitored by NMR spectroscopy.

Acknowledgment. R.R.S. thanks the Department of Energy (DE-FG02-86ER13564) and the MRSEC program of the National Science Foundation (DMR 98-08941) for supporting this research. We also thank ExxonMobil Corporation for samples of $[\text{Ph}_3\text{C}]\text{B}(\text{C}_6\text{F}_5)_4$ and $[\text{PhNHMe}_2]\text{B}(\text{C}_6\text{F}_5)_4$. NMR spectra were acquired with the assistance of Dr. Jeff Simpson and Mark Wall.

OM0107082

(34) Jayaratne, K. C.; Keaton, R. J.; Henningsen, D. A.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 10490.

(35) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958.

(36) Keaton, R. J.; Jayaratne, K. C.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 12909.

(37) Hagihara, H.; Shiono, T.; Ikeda, T. *Macromolecules* **1998**, *31*, 3184–3188.

(38) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Weitman, H.; Goldschmidt, Z. *Chem. Commun.* **2000**, 379.

(39) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706.

(40) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Inorg. Chem. Commun.* **2000**, *3*, 611.

(41) Mashima, K.; Fujikawa, S.; Tanaka, Y.; Urata, H.; Oshiki, T.; Tanaka, E.; Nakamura, A. *Organometallics* **1995**, *14*, 2633–2640.

(42) Killian, C. M.; Tempel, D.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664.

(43) Brookhart, M.; Desimone, J. M.; Grant, B. E.; Tanner, M. J. *Macromolecules* **1995**, *28*, 5378–5380.

(44) Gottfried, A. C.; Brookhart, M. *Macromolecules* **2001**, *34*, 1140.