Evaluation of (η^5-C_5Me_5)Hf(R)$_2$[N(Et)C(Me)N(*t*-Bu)] (R = Me and *i*-Bu) for the Stereospecific Living and Degenerative Transfer Living Ziegler–Natta Polymerization of α-Olefins

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Dedicated to Professor Richard R. Schrock on the occasion of his 60th birthday.

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Abstract: The dialkyl(monocyclopentadienyl)hafnium acetamidinates, Cp*Hf(R)$_2$[N(Et)C(Me)N(*t*-Bu)] [Cp* = η^5-C_5Me_5, R = Me (**3a**) and *i*-Bu (**3b**)], were prepared through either 'one–pot' carbodiimide insertion or two-step salt elimination protocols starting with commercially available Cp*HfCl$_3$. Protonolysis of **3a** and **3b** with [PhNHMe$_2$][B(C_6F_5)$_4$] in chlorobenzene produced the cationic complexes, {[Cp*Hf(R)[N(Et)C(Me)N(*t*-Bu)]}[B(C_6F_5)$_4$] [R = Me (**4a**) and *i*-Bu (**4b**)], which were characterized in solution. Compounds **4a** and **4b** were evaluated as initiators for the stereospecific living Ziegler–Natta polymerization of 1-hexene. These results reveal that, while an extremely high level of stereoselectivity can be achieved to produce isotactic poly(1-hexene) in a living fashion, the rate constant for polymerization, k_p, using either **4a** or **4b**, is ~60 times less than that of the analogous zirconium initiators. Finally, upon substoichiometric activation of **3a** with [PhNHMe$_2$][B(C_6F_5)$_4$] in a 2:1 ratio, degenerative transfer living Ziegler–Natta polymerization of 1-hexene can be accomplished to produce atactic poly(1-hexene).

Keywords: amidinate complexes; degenerative transfer living polymerization; living polymerization; α-olefins; Ziegler–Natta reaction

Introduction

The past decade has witnessed several important advances in the development of single-site catalysts for the Ziegler–Natta polymerization of α-olefins, including identification of a small number of metal complexes that can serve as initiators for carrying out these polymerizations in a living fashion, and in some cases, with a high degree of stereocontrol.[1] Among early transition metals, the only hafnium-based living Ziegler–Natta polymerization system reported to date is the {[MesNpy]Hf(*i*-Bu)}[B(C_6F_5)$_4$] {[MesNpy]$^{2-}$ = [H_3C(2-C_5H_4N)(CH_2NMesityl)$_2$]$^{2-}$} initiator of Schrock and co-workers[2] that produces atactic poly(1-hexene) of narrow polydispersity and with expected M_n values. Interestingly, these investigators reported that the rate constant, k_p, for 1-hexene polymerization with this hafnium initiator is approximately the same as that obtained with the analogous zirconium initiator.

Since 2000, we have been mapping structure/activity relationships for the family of cationic monocyclopentadienylzirconium amidinates of general structure, {Cp*Zr(R)[N(R^1)C(R^3)N(R^2)]}[B(C_6F_5)$_4$] (**1**), that can function as highly active initiators for the living polymerization of α-olefins and α,ω-non-conjugated dienes.[3] In the case where, R = R^3 = Me, R^1 = Et, and R^2 = *t*-Bu (**1a**), these polymerizations also proceed in a stereospecific fashion to produce an isotactic polyolefin microstructure. We have further identified a novel degenerative transfer (DT) living Ziegler–Natta polymerization process that arises upon substoichiometric 'activation' of the corresponding neutral dimethyl complex, Cp*ZrR$_2$[N(Et)C(Me)N(*t*-Bu)] (R = Me, **2a**), through methyl group protonolysis with the borate, [PhNHMe$_2$][B(C_6F_5)$_4$].[4] In this living DT Ziegler–Natta polymerization, all cationic (active) and neutral (dormant) metal propagating centers effectively appear to propagate at the same rate through fast and reversible transfer of a methyl group between active and dormant species to produce polyolefins of narrow polydispersity and M_n values that are dictated by the ratio of monomer concentration to that of the total concentration of zirconium species (both cationic and neutral). Thus, given the wealth of information now acquired regarding this class of zirconium initiator, it became of interest to explore the properties of the analogous hafnium species. Herein,

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we report the synthesis and characterization of the titled hafnium complexes and comparatively assess their ability to function in the stereoselective living and DT living Ziegler–Natta polymerization of α-olefins.

Results and Discussion

Carbodiimide ($R^1N{=}C{=}NR^2$) insertion into a metal-methyl bond of Cp*MMe_3 has previously been shown to be an effective, high-yielding route to neutral dimethyl(pentamethylcyclopentadienyl)metal acetamidinates, Cp*$MMe_2[N(R^1)C(Me)N(R^2)]$, when M = Ti and Zr.[3a, e,g,5] As shown in Scheme 1, extension of this methodology for the synthesis of the analogous hafnium compounds (M = Hf) could be achieved as demonstrated by the moderate yields (58%) that were obtained for **3a** when R^1 = Et and R^2 = *t*-Bu. As with the corresponding titanium and zirconium complexes, **3a** was found by variable temperature ^{1}H NMR spectroscopy to be configurationally unstable in solution with respect to metal-centered racemization that occurs through a low energy amidinate 'ring–flipping' process ($\Delta G_c^{\ddagger} < 10$ kcal mol^{-1}, $T_c = 253$ K).[5] As determined by single crystal X-ray analysis, in the solid state **3a** adopts the molecular geometry shown in Figure 1 that is reminiscent of its zirconium congener **2a**.[3c] More specifically, both the nitrogen atoms of the acetamidinate fragment in **3a** are nearly trigonal coplanar as determined by the sum of the bond angles about these atoms, *cf.*, $\Sigma\theta_{N(1)} = 356.7°$ and $\Sigma\theta_{N(2)} = 356.3°$. The acetamidinate four-membered ring in this compound is also puckered to the same extent as its zirconium analogue as determined by the angle between the mean planes that are defined by: Hf(1)–N(1)–C(11) and Hf(1)–N(2)–C(11) (*cf.*, 17.7° for **3a** *vs.* 18.3° for **2a**). Regarding bond lengths, a comparison between the structures for **2a** and **3a** reveal that, due to the effect of lanthanide contraction,[6] those involving hafnium are shorter than those for zirconium. For instance, in **3a**, the Hf(1)–N(1) and Hf(1)–N(2) bond lengths are 2.237(3) and 2.247(3) Å, respectively, whereas in **2a**, they are 2.251(3) and 2.265(2) Å, respectively.[3c] One also observes a significant contraction in the Hf–C_{Me} bond lengths of **3a** [2.247(5) and 2.253(4) Å] relative to the Zr–C_{Me} bond lengths of **2a** [2.272(3) and 2.273(3) Å]. Finally, the distance between the metal center and the computed centroid of the Cp* fragment, i.e., Hf(1)–CT(1), is shorter in **3a** than the corresponding distance in the zirconium analogue **2a** [*cf,* 2.2172(18) Å and 2.232(2) Å, respectively].

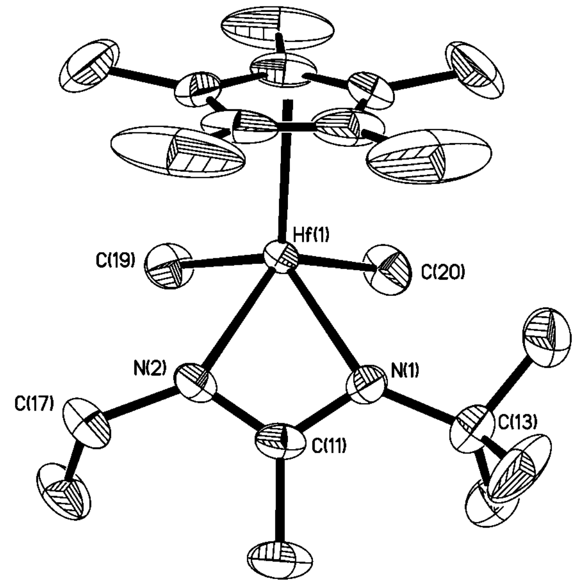
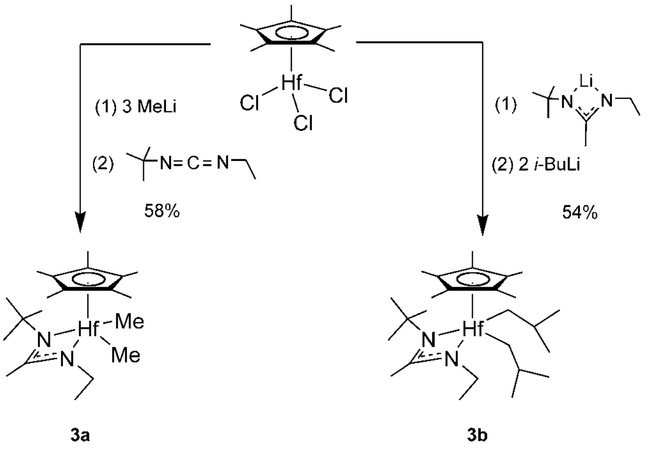


Figure 1. Molecular structure (30% thermal ellipsoids) of **3a** with partial atom labeling. Hydrogen atoms have been removed for the sake of clarity.



Scheme 1.

Schrock and co-workers[7] have previously identified a pronounced "initiator effect" for their zirconium-based living Ziegler–Natta polymerization in which attempts to prepare the cationic zirconium methyl initiator, {[MesNpy]ZrMe}[B(C_6F_5)$_4$], failed due to facile formation of the dinuclear species, {[MesNpy]$_2$Zr$_2$Me$_3$}[B(C_6F_5)$_4$], through coordination with the neutral dimethyl precursor, [MesNpy]ZrMe$_2$. In order to investigate whether a similar initiator effect might be possible in the present system, the diisobutyl derivative **3b** was prepared in two steps using conventional salt-elimination methodology as shown in Scheme 1. Thus, reaction of Cp*HfCl$_3$ with the lithium acetamidinate prepared from addition of MeLi to the carbodiimide, EtN=C=N-Bu-*t*, first provided the dichloride, Cp*HfCl$_2$[N(Et)C(Me)N(*t*-Bu)],[8] which was then alkylated with two equivalents of isobutyllithium to produce, after 48 h at 25 °C, a 61% yield of the desired product **3b**. As with the dimethyl derivative **3a**, variable temperature ^{1}H NMR revealed that **3b** is configurationally unstable in solution with respect to metal-centered racemization that occurs through facile amidinate ring-flipping. Figure 2 further provides the solid-state molecular struc-

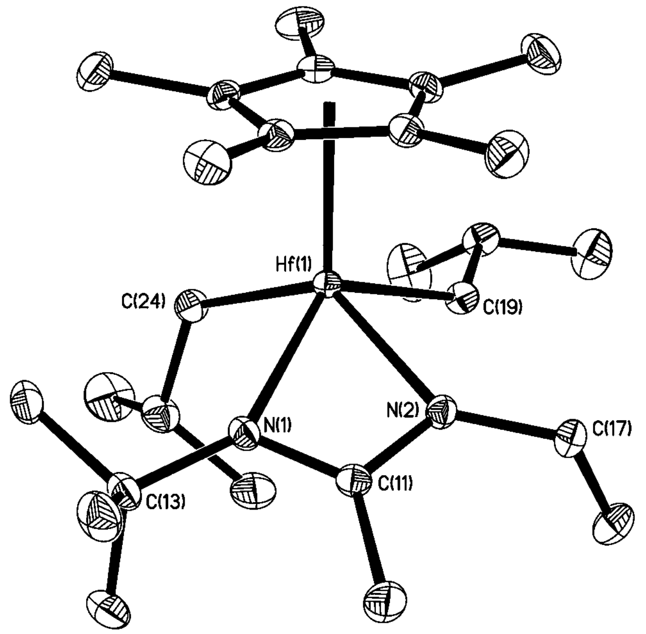
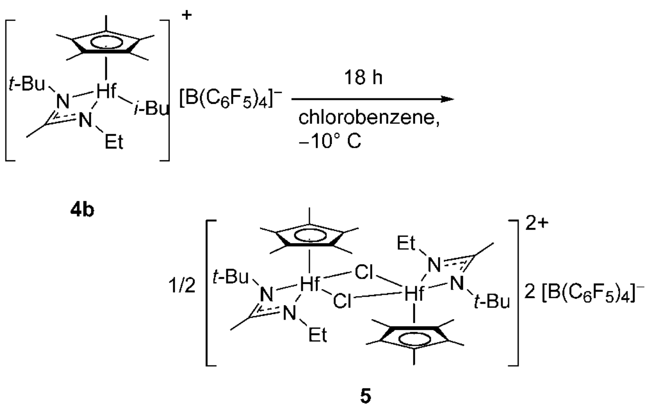


Figure 2. Molecular structure (30% thermal ellipsoids) of **3b** with partial atom labeling. Hydrogen atoms have been removed for the sake of clarity.



Scheme 2.

ture of **3b** as determined by single crystal X-ray analysis, and once again, as with **3a**, the bond lengths involving the hafnium metal center in this complex are shorter than those in the previously reported analogous zirconium complex, $\mathrm{Cp^*Zr(\mathit{i}\text{-}Bu)_2[N(Et)C(Me)N(\mathit{t}\text{-}Bu)]}$ (**2b**).[9] Thus, in **3b**, the hafnium-nitrogen bond lengths are Hf(1)–N(1) 2.3298(1) Å and Hf(1)–N(2) 2.2003(12) Å, whereas in the zirconium complex **2b**, the bond lengths are 2.2471(16) and 2.3113(15) Å, respectively. The Cp* fragment is also closer to the metal center in **3b** *vs.* **2b** as evidenced by the two metal-centroid distances of 2.2301(7) and 2.2508(9) Å, respectively.

Protonolysis of **3a** and **3b** with one equivalent of the borate, $\mathrm{[PhNHMe_2][B(C_6F_5)_4]}$, in chlorobenzene at −10 °C, cleanly provided the corresponding cationic monoalkyl complexes, $\mathrm{\{[Cp^*Hf(R)[N(Et)C(Me)N(\mathit{t}\text{-}Bu)]\}[B(C_6F_5)_4]}$ [R = Me (**4a**) and *i*-Bu (**4b**)], which were not isolated, but rather, characterized in solution by ^1H and ^{13}C NMR techniques using chlorobenzene-d_5. Comparison of the solution structural characteristics of **4a** and **4b** with their known zirconium counterparts, $\mathrm{\{Cp^*Zr(R)[N(Et)C(Me)N(\mathit{t}\text{-}Bu)]\}[B(C_6F_5)_4]}$ [R = Me (**1a**) and *i*-Bu (**1b**)],[3c, d,g,4a,10] revealed some important similarities and differences. To begin, both **4a** and **4b** were found to be configurationally stable on the NMR timeframe at −10 °C with respect to metal-centered racemization, and this is in keeping with similar behavior observed for **1a** and **1b**. On the other hand, whereas the cationic isobutyl zirconium species **1b** possesses a strong β-hydrogen agostic interaction with the metal center[11] in both solution and the solid state,[4a,10] no evidence of a similar solution agostic interaction for the analogous hafnium complex **4b** could be obtained by NMR. At the present time, it is not certain whether chlorobenzene coordination might be interfering with formation of this β-hydrogen agostic interaction in the hafnium complex, but given the known structure of **1b**, it is unlikely that the metal center is engaged in close metal-fluorine interactions with the borate anion. In addition, unlike isotopically labeled **1b**,[10] **4b** that is isotopically labeled within the isobutyl fragment does not undergo label-scrambling within this fragment either over extended periods of time, or at more elevated temperatures.[12] Finally, compound **4b** was found to decompose in solution at 0 °C in a first-order fashion with a half-life of 12.5 h ($k_{obs} = 0.0554\ h^{-1}$), and after extended periods of time, the insoluble dichloro dicationic dimer, $\mathrm{[Cp^*Hf(\mu\text{-}Cl)[N(Et)C(Me)N(\mathit{t}\text{-}Bu)]_2[B(C_6F_5)_4]_2}$ (**5**), shown in Scheme 2 was obtained; the structure of which was confirmed by single crystal X-ray analysis. Similar dihalide dicationic group 4 dinuclear complexes have been obtained in studies of cationic alkyl metal species in halogenated solvents.[3 g,13]

The ability of **4a** and **4b** to function as initiators for the living Ziegler–Natta polymerization of α-olefins was investigated in the standard fashion with chlorobenzene as the solvent at −10 °C using 1-hexene as the monomer.[3] Figure 3 presents a kinetic analysis of monomer consumption *vs.* time using **4a** as the initiator and 200 equivs. of 1-hexene. Importantly, the clear linearity of this plot unequivocally establishes that polymerization of 1-hexene is occurring in a living fashion even after extended periods of time (i.e., 30 h).[14] Further support for this living character was obtained from GPC data for the final poly(1-hexene) material (90% isolated yield) which provided an M_n value of 18,600 (relative to polystyrene standards, calcd. M_n 16,800) and a polydispersity index ($D = M_w/M_n$) of 1.08.[15] Satisfactorily, ^{13}C NMR analysis of this poly(1-hexene) also revealed it to have a strictly isotactic microstructure, thereby confirming that polymerization using **4a** as the initiator proceeds in a stereospecific fashion as well. With respect to the rate of polymerization of 1-hexene initiated by **4a**, however, k_p was

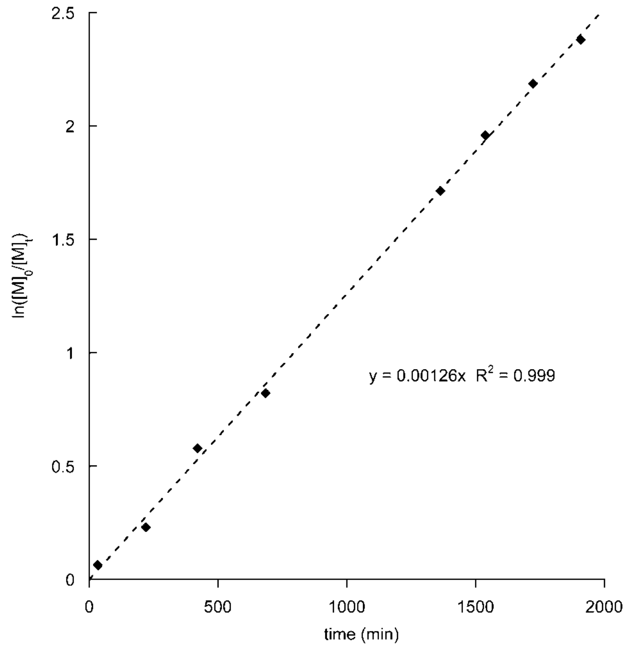
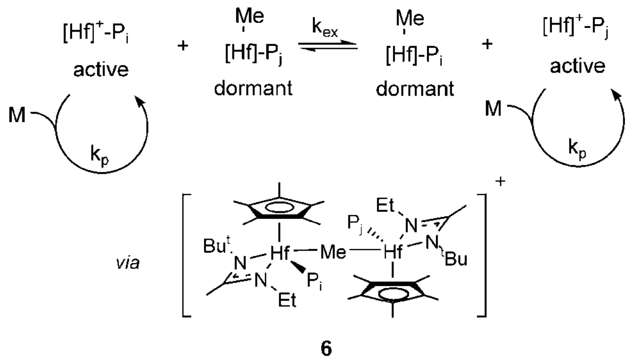


Figure 3. Monomer consumption *vs.* time for 1-hexene polymerization initiated by **4a** in chlorobenzene at $-10\,°C$. $[\mathbf{4a}]_o = 6.0$ mM, $[\text{1-hexene}]_0 = 1.2$ M.



Scheme 3.

determined from the data of Figure 3 to be only 0.0035 $M^{-1}\,s^{-1}$, and this value is ~60 times smaller than that determined for the polymerization of 1-hexene by the zirconium initiator **1a** (i.e., $k_p = 0.212\,M^{-1}\,s^{-1}$). Similar attenuations of rate constants for hafnium *vs.* zirconium have been observed in other systems and it is most likely attributable to a greater hafnium-carbon bond enthalpy. Finally, although a detailed kinetic analysis was not performed, polymerization of 1-hexene using **4b** as the initiator once again provided isotactic poly(1-hexene) with nearly identical M_n and D values to those obtained with **4a**.

The fact that **4a** and **4b** provide poly(1-hexene) materials of similar M_n and D values suggests that no 'initiator effect' similar to that observed by Schrock and coworkers[7a] is operative in the present system. Accordingly, if any formation of a dinuclear species occurs between **3a** and **4a** (i.e., such as compound **6**, *vide infra*) during protonolysis of the former, it must be fast and reversible: a conclusion further supported by ^1H NMR spectra acquired at $-10\,°C$ for a 2:1 mixture of **3a** and $[PhNHMe_2][B(C_6F_5)_4]$ which revealed only a single set of exchanged broadened resonances. With this in mind, it became of interest to determine whether or not DT living Ziegler–Natta polymerization of 1-hexene could be performed upon substoichiometric activation of **3a** in a manner previously demonstrated for the analogous zirconium system.[4a] Scheme 3 depicts the processes that should be involved in a DT living Ziegler–Natta polymerization that occurs through rapid and reversible methyl group transfer between cationic (active) and neutral (dormant) hafnium species *via* the cationic μ-methyl dinuclear species **6**. Importantly, for such a DT living polymerization, it is expected that the degree of polymerization (DP) will be determined by the ratio of monomer concentration to the total concentration of both active and dormant hafnium species as defined by, $DP = [M]/[Hf]_{tot}$, and the polydispersity index, D, will be determined by the relative rate constants for polymerization and exchange through the relationship; $D = 1 + k_p/k_{ex}$.[16] In practice, polymerization of 200 equivs. of 1-hexene under the same conditions as before, but now using only a 0.5 equivs. of $[PhNHMe_2][B(C_6F_5)_4]$ relative to **3a** (i.e., 50% activation), provided, after 64 h, a 71% yield of poly(1-hexene) with an M_n value of 11,600 (calc. M_n 11,928 based on $[Hf]_{total}$ and yield) and a D value of 1.27. The fact that both ^1H and ^{13}C NMR spectra of this material did not provide evidence for any vinylic end-groups arising from termination through either β-hydrogen elimination or β-hydrogen transfer strongly suggests that the larger value for the polydispersity index, D, relative to that previously reported for the analogous zirconium-based DT process[4a] is due to a larger k_p/k_{ex} ratio for the hafnium system.

While we are still investigating this hypothesis further, the linear relationship between monomer consumption *versus* time shown in Figure 4 confirms that the system is still strictly living under DT conditions. Finally, the apparent rate constant for polymerization, k_{app} is essentially the same as that obtained under standard non-degenerative living conditions and this observation is in keeping with a transient lifetime for **6** during DT living polymerization.[4b,17] As a final note, ^{13}C NMR analysis of the poly(1-hexene) formed under DT conditions confirms that this material is essentially atactic, or iso-rich at best, and this microstructure is consistent with a facile epimerization of the neutral dormant hafnium centers (i.e, $k_{epi} > k_p$).

Conclusion

In summary, the present results confirm that cationic monocyclopentadienylhafnium amidinates of the gener-

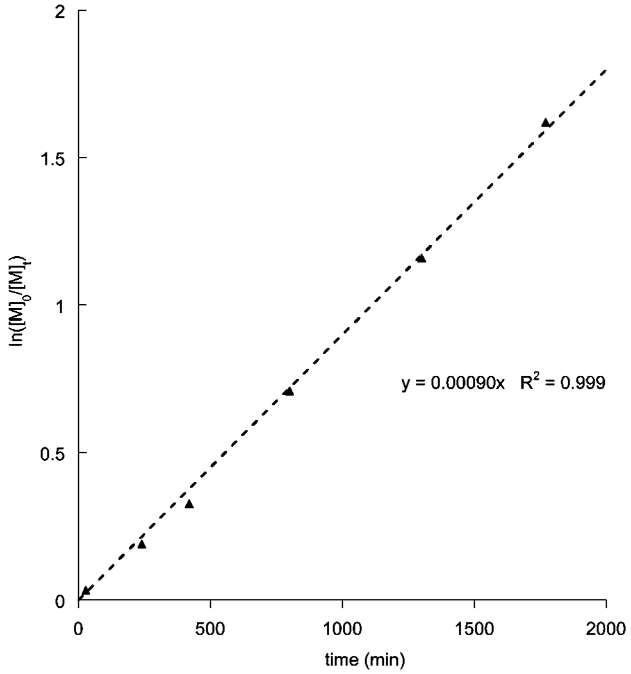


Figure 4. Monomer consumption *vs.* time for 1-hexene polymerization initiated by a 2:1 ratio of **3a** to $[PhNHMe_2][B(C_6F_5)]$ in chlorobenzene at −10 °C. $[\mathbf{3a}]_o$ = 9.0 mM, $[1\text{-hexene}]_0 = 1.8$ M.

al structure, $\{Cp^*Hf(R)[N(R^1)C(R^3)N(R^2)]\}[B(C_6F_5)_4]$, can function as initiators for the stereospecific living Ziegler–Natta polymerization of α-olefins. A reduction in polymerization activity for hafnium relative to the corresponding zirconium system is likely due to a greater metal-carbon bond enthalpy for the former. Solid-state structural investigations of the isobutyl hafnium initiator are currently in progress to identify whether this complex can engage in a β-hydrogen agostic interaction similar to its zirconium congener. Finally, it has been confirmed that DT living Ziegler–Natta polymerization occurring *via* rapid and reversible methyl group transfer between cationic (active) and neutral (dormant) species is possible upon substoichiometric activation of the neutral hafnium precursors.

Experimental Section

General Procedures

All manipulations were performed under an inert atmosphere of dinitrogen using standard Schlenk or glove-box techniques. All solvents were dried [Na/K alloy-benzophenone for diethyl ether (Et_2O), Na/K alloy for toluene and pentane, CaH_2 for chlorobenzene] and distilled under dinitrogen prior to use. *iso*-Butyllithium was prepared according to the procedure described by Gilman and coworkers.[18] 1-Hexene was dried over Na/K alloy and vacuum transferred prior to use. GPC analyses were performed using a Waters GPC system equipped with a column oven and differential refractometer both maintained at 40 °C and four columns (Water Ultrastyragel 500 Å, Waters Stryragel HR3, Waters Styragel HR4, and Shodex K-806M) also maintained at 40 °C. THF was used as the eluate at a flow rate of 1.1 mL/min. M_n and D (M_w/M_n) values were obtained using the Waters GPC software and seven different polystyrene standards (Polymer Laboratories). Elemental analyses were performed by Midwest Microlab laboratory.

Synthesis of $Cp^*HfMe_2[N(Et)C(Me)N(t\text{-}Bu)]$ (3a)

To a suspension of 1.0 g (2.4 mmol) of Cp^*HfCl_3 in 30 mL of Et_2O, 4.54 mL of MeLi (1.6 M in Et_2O) were added at −40 °C. The mixture was allowed to warm gradually to room temperature, stirred for an additional hour and then 370 μL (2.4 mmol) of 1-*tert*-butyl-3-ethylcarbodiimide were added. After stirring the reaction mixture overnight, the volatiles were removed under vacuum, the residue extracted with pentane, the extracts filtered through a pad of Celite and then evaporated to dryness to yield the crude product which was crystallized at −40 °C from pentane (*ca.* 5 mL) to provide **3a** as white crystals; yield: 0.66 g (58%). ^1H NMR (400 MHz, benzene-d_6): δ = −0.04 (s, 6H), 0.84 (t, 3H, J = 8.0 Hz), 1.09 (s, 9H), 1.59 (s, 3H), 1.99 (s, 15H), 2.85 (q, 2H, J = 8.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ = 11.4, 15.3, 17.0, 32.0, 40.7, 51.6, 52.5, 118.4, 172.9; anal. calcd. for $C_{20}H_{38}HfN_2$: C 49.53, H 7.90, N 5.78; found: C 49.21, H 7.72, N 5.48.

Synthesis of $Cp^*HfCl_2[N(Et)C(Me)N(t\text{-}Bu)]$

To a solution of 0.37 ml (2.4 mmol) 1-*tert*-butyl-3-ethylcarbodiimide in 30 mL of Et_2O, 1.49 mL of MeLi (1.6 M in Et_2O) were added at −40 °C. The mixture was allowed to warm gradually to room temperature and stir for 1 h, whereupon, it was cooled once more to −40 °C and 1.0 g (2.4 mmol) of Cp^*HfCl_3 was added. After stirring overnight at room temperature, the volatiles were removed under vacuum, the residue was extracted with toluene, the extracts were filtered through a pad of Celite and evaporated to dryness to provide a crude product. Upon crystallization at −40 °C from a 4:1 toluene/pentane solvent mixture (*ca.* 10 mL) the desired compound could be obtained as white crystals; yield: 1.10 g (88%). ^1H NMR (400 MHz, benzene-d_6): δ = 0.90 (t, 3H, J = 7.2 Hz), 1.17 (s, 9H), 1.48 (s, 3H), 2.07 (s, 15H), 3.06 (br s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, benzene-d_6): δ = 12.2, 15.4, 16.2, 31.7, 42.3, 53.4, 122.9, 173.3; anal. calcd. for $C_{18}H_{32}Cl_2HfN_2$: C 41.11, H 6.13, N 5.33; found: C 41.40, H 6.05, N 5.10.

Synthesis of $Cp^*Hf(i\text{-}Bu)_2[N(Et)C(Me)N(t\text{-}Bu)]$ (3b)

To a solution of 0.49 g (0.9 mmol) of Cp^*HfCl_2-$[N(Et)C(Me)N(t\text{-}Bu)]$) in 30 mL of Et_2O, 9.90 mL of *iso*-butyllithium (0.2 M in pentane) were added at −40 °C. The mixture was allowed to warm gradually to room temperature and stirred for 48 h. After this time, all the volatiles were removed under vacuum, the residue was extracted with pentane, the extracts filtered through a pad of Celite and evaporated to dryness. Upon crystallization at −40 °C from pentane (*ca.* 5 mL), the desired compound **3b** was obtained as white crystals; yield: 0.31 g (61%). ^{1}H NMR (400 MHz, benzene-d_6): $\delta = -0.02$, (br m, 2H), 0.23 (br s, 1H), 0.68 (br s, 1H), 0.86 (t, 3H, $J = 8.0$ Hz), 1.16 (s, 9H), 1.10 (br s, 3H), 1.27 (br s, 3H), 1.62 (s, 3H), 1.97 (s, 15H), 2.36 (m, 1H), 2.88 (br s, 2H); ^{13}C {^{1}H} NMR (100 MHz, benzene-d_6): $\delta = 12.4$, 16.7, 18.1, 27.7, 28.2, 28.6, 29.1, 31.6, 33.0, 42.1, 53.2, 86.4, 88.6, 119.4, 174.0; anal. calcd. for $C_{26}H_{50}HfN_2$: C 54.86, H 8.85, N 4.29; found: C 54.27, H 8.66, N 4.68.

NMR Characterization of *in situ* Generated {Cp*HfR[N(Et)C(Me)N(*t*-Bu)]}[B(C_6F_5)$_4$] (R = Me and *i*-Bu, 4a and 4b, respectively)

To a suspension of 18 mg (20 μmol) of [PhNHMe$_2$][B(C_6F_5)$_4$] in 0.5 mL of chlorobenzene-d_5, a solution of 20 μmol of **3** in 0.2 mL of chlorobenzene-d_5 was added at $-10\,°$C. After 5 min, the clear yellow solution was transferred to an NMR tube and spectra recorded at both $-10\,°$C and room temperature. For **4a**, ^{1}H NMR (400 MHz, chlorobenzene-d_5, 25 °C): $\delta = 0.14$ (s, 3H, Hf*Me*), 0.72 (t, 3H, $J = 7.2$ Hz, CH_2*CH_3*), 0.88 (s, 9H, C*Me_3*), 1.79 (s, 15H, C_5*Me_5*), 1.96 (s, 3H, C*Me*), 3.02 (dq, 1H, $^2J = 12.8$, $^3J = 7.2$ Hz, *CH_2*CH_3), 3.06 (dq, 1H, $^2J = 12.8$, $^3J = 7.2$ Hz, *CH_2*CH_3). For **4b**: ^{1}H NMR (400 MHz, chlorobenzene-d_5, 25 °C): $\delta = 0.45$, 0.495 (dd, 1H, $^2J = 14.4$ Hz, $^3J = 6.4$ Hz, *CH_2*CHMe$_2$), 0.82 (m, 12H, CH_2*CH_3*, CH_2CH*Me_2*), 0.90 (s, 9H, C*Me_3*), 1.33 (m, 1H, CH_2*CH*Me$_2$), 1.78 (s, 15H, C_5*Me_5*), 1.95 (s, 3H, C*Me*), 3.00 (dq, 1H, $^2J = 14.4$, $^3J = 6.8$ Hz, *CH_2*CH_3), 3.05 (dq, 1H, $^2J = 14.4$, $^3J = 6.8$ Hz, *CH_2*CH_3).

Kinetic Analysis of 1-Hexene Polymermization using 4a

To a solution of 120.2 mg (150 μmol) of [PhNHMe$_2$][B(C_6F_5)$_4$] in 16.25 mL of chlorobenzene at $-10\,°$C, was added a solution of 72.8 mg (150 μmol) of **3a** in 5 mL of chlorobenzene at $-10\,°$C. To this mixture, 2.53 g (30 mmol) of 1-hexene were added all at once. Aliquots were quenched with silica gel after different time intervals over the next 31 h. 1-Hexene concentrations were determined by GC using chlorobenzene as the internal standard.

Polymerization of 1-Hexene under Conventional Conditions using 4a

To a solution of 48.0 mg (60 μmol) of [PhNHMe$_2$][B(C_6F_5)$_4$] in 8 mL of chlorobenzene at $-10\,°$C, was added a solution of 29.1 mg (60 μmol) of (η^5-C_5Me_5)HfMe$_2$[*t*-BuNC(Me)NEt] in 2 mL of chlorobenzene at $-10\,°$C. To this mixture, 1.01 g (12 mmol) of **3a** in 1-hexene was added all at once and the resulting mixture was allowed to stir for 31 h at $-10\,°$C, after which time it was rapidly quenched by the addition of acidic methanol. The volatiles were then removed under vacuum, and the crude material was purified through precipitation of a toluene solution into a large volume of acidic methanol. The final pure material was collected and dried overnight at 60 °C/0.01 mmHg. M_n: 18,610, *D*: 1.08, yield: 0.90 g (90%).

Polymerization of 1-Hexene under DT Conditions (50% Activation)

To a solution of 24.0 mg (30 μmol) of [PhNHMe$_2$][B(C_6F_5)$_4$] in 8 mL of chlorobenzene at $-10\,°$C, was added a solution of 29.1 mg (60 μmol) of **3a** in 2 mL of chlorobenzene at $-10\,°$C. To this mixture, 1.01 g (12 mmol) of 1-hexene was added all at once and the resulting mixture was allowed to stir for 64 h at $-10\,°$C, after which time it was rapidly quenched by the addition of acidic methanol. The volatiles were then removed under vacuum, and the crude material was purified through precipitation of a toluene solution into a large volume of acidic methanol. The final pure material was collected and dried overnight at 60 °C/0.01 mmHg. M_n: 11,600, *D* 1.27, yield: 0.72 g (71%).

Kinetic Analysis of 1-Hexene Polymerization under DT Conditions (50% Activation)

To a solution of 36.1 mg (45 μmol) of [PhNHMe$_2$][B(C_6F_5)$_4$] in 5.75 mL of chlorobenzene at $-10\,°$C, was added a solution of 43.7 mg (90 μmol) of **3a** in 2 mL of chlorobenzene at $-10\,°$C. To this mixture, 1.515 g (18 mmol) of 1-hexene was added all at once. Aliquots were quenched with silica gel after different time intervals over the next 30 h. 1-Hexene concentrations were detected by GC using chlorobenzene as the internal standard.

X-Ray Crystallography

The crystallographic studies of **3a** and **3b** are available in the Supporting Information. Crystallographic data (excluding structure factors) for structures **3a** and **3b** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-247035 and CCDC-247036. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; Email: deposit@ccdc.cam.ac.uk].

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