Reinvestigation of the Modes of Chain Transfer during Propene Polymerization by the Cp*$_2$Zr Catalyst System

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Propene polymerization by Cp*$_2$ZrMe(μ-Me)B(C$_6$F$_5$)$_3$ in toluene under 1 atm propene in the temperature range −45 to 25 °C involves β-methyl migration as the primary mode of chain transfer, with β-hydrogen elimination playing a very minor role. Under propene-starved conditions, however, β-hydrogen elimination becomes competitive, and it is concluded that the concentration of free monomer has an effect on the mechanism of chain transfer. To rationalize these findings, it is suggested that β-methyl migration may involve transfer of the methyl group not to the metal, as has been previously thought, but to a coordinated propene.

A perusal of the literature on metallocene-catalyzed Ziegler−Natta polymerization of propene shows that the predominant modes of chain transfer involve either β-hydrogen elimination to metal (eq 1) and thence transfer to monomer, or β-hydrogen migration directly to a molecule of monomer (eq 2).[1]
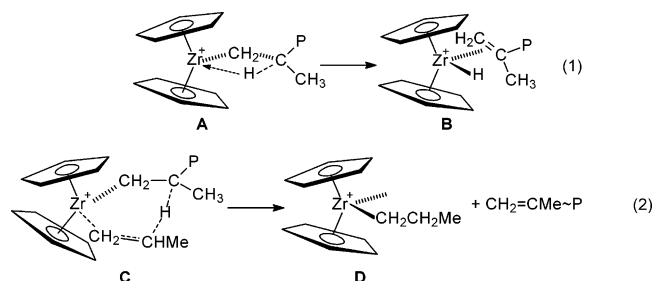

In contrast, β-methyl elimination is dominant during, for example, propene polymerization by sterically crowded catalysts such as bis-η^5-C$_5$Me$_5$-metal (Cp*$_2$M) and other systems (eq 3).[2]

The reasons for the change in behavior are not clear[2l] despite extensive computational[3a−e] and thermochemical studies.[3f] However, it has been suggested that the steric requirements of the bulky Cp* ligands might force
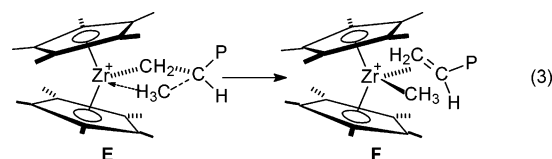
the β-methyl group of a growing polymer chain into the plane perpendicular to the Cp(centroid)−Zr−Cp(centroid), as in **G**.[2c,e−g]
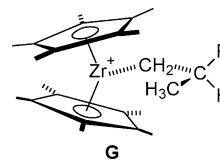
In this conformation, the β-methyl group is in close proximity to the LUMO, an orientation that presumably would facilitate, possibly via a γ-agostic interaction, β-methyl rather than β-hydrogen migration.

A number of stoichiometric β-methyl migration reactions are known,[4] and we have recently reported a kinetics study of β-methyl migration reactions involving the neopentyl ligands in the zirconocene compounds Cp$_2$Zr(CH$_2$CMe$_3$)(μ-Me)B(C$_6$F$_5$)$_3$ and Cp*$_2$Zr(CH$_2$CMe$_3$)-(μ-Me)B(C$_6$F$_5$)$_3$ in various solvents.[4g] Based on this and previous work,[4d−f] it was concluded that β-methyl migration to the metal is a concerted process that involves concomitant loosening of the metal−borate linkages.

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(2) (a) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471. (b) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H. *J. Mol. Catal.* **1990**, *62*, 277. (c) Mise, T.; Kageyama, A.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1991**, 1525. (d) Yang, X.; Stern, C. L.; Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1375. (e) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025. (f) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H.; Renkema, J.; Evens, G. G. *Organometallics* **1992**, *11*, 362. (g) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (h) Repo, T.; Jany, G.; Hakala, K.; Klinga, M.; Polamo, M.; Leskelä, M.; Rieger, B. *J. Organomet. Chem.* **1997**, *549*, 177. (i) Resconi, L.; Camurati, I.; Sudmeijer, O. *Top. Catal.* **1999**, *7*, 145. (j) Weng, W.; Markel, E. J.; Dekmezian, A. H. *Macromol. Rapid Commun.* **2000**, *21*, 1103. (k) Camurati, I.; Fait, A.; Piemontesi, F.; Resconi, L.; Tartarini, S. *ACS Symp. Ser.* **2000**, *760*, 174. (l) Although in principle allyl end groups could result from 2,1-insertions followed by β-hydrogen elimination, this seems unlikely for steric reasons in Cp*$_2$ catalyst systems. Furthermore, 2-butenyl end groups generally result from 2,1-insertions,[2i] and these are not generally observed, either by others or in this work.

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In the course of this study,[4g] we also investigated the analogous isobutyl compounds $Cp_2Zr(CH_2CHMe_2)(\mu\text{-}Me)B(C_6F_5)_3$ and $Cp^*_2Zr(CH_2CHMe_2)(\mu\text{-}Me)B(C_6F_5)_3$, for which there would in principle be competition between β-hydrogen and β-methyl migration reactions. As mentioned above, β-hydrogen migration is generally the preferred mode of chain transfer during metallocene-catalyzed alkene polymerization processes,[1] but β-methyl migration becomes competitive during, for example, propene polymerization by metallocene catalysts containing heavily substituted cyclopentadienyl rings.[2] We hoped to be able to shed light on the factors controlling the mode of migratory β-migration reactions taken by various zirconocene systems.

However we, as have others for a similar reaction,[5] observed solely β-hydrogen migration with both compounds. Thus it seemed that the isobutyl group is not a good model for a growing polypropene chain in Cp^*_2Zr catalyst systems, although molecular mechanics calculations[4g] on the cationic species $[Cp^*_2Zr(isobutyl)]^+$ indicated that the preferred conformation of the isobutyl ligand is indeed as in **E**, with one of the β-methyl groups lying in the plane perpendicular to the Cp(centroid)−Zr−Cp(centroid) plane while the β-hydrogen atom eclipses a Cp* ring. One of the γ-hydrogen atoms on the β-methyl group is situated about 3.08 Å from the zirconium, much closer to the zirconium than is the isobutyl β-hydrogen atom, which is about 3.41 Å from the zirconium. Thus the complex cation appears to prefer the conformation believed[2c,e] to be prerequisite to β-methyl elimination, which does not occur. In this paper, we look more closely at propene polymerization utilizing the Cp^*_2Zr catalyst system, identifying conditions under which predominantly β-hydrogen migration occurs and hence the factors that lead to β-methyl rather than β-hydrogen migration.

Experimental Section

General Comments. Syntheses were carried out under purified argon using standard Schlenk line and glovebox techniques. The deoxygenated solvents toluene, dichloromethane, diethyl ether, hexanes, and tetrahydrofuran were dried by passing through activated Al_2O_3 columns, toluene-d_8 and benzene-d_6 by refluxing over sodium, and dichloromethane-d_2 and chlorobenzene-d_5 by refluxing over calcium hydride. ^{1}H and ^{13}C{^{1}H} NMR spectra were run on Bruker AV300, -400, or -500 spectrometers, chemical shifts being referenced using the residual proton signals of the deuterated solvents. $Cp^*_2ZrCl_2$ was purchased from Strem Chemicals; $[Ph_3C][B(C_6F_5)_4]$ was purchased from Asahi Glass Co. $B(C_6F_5)_3$,[6] $Cp^*_2ZrMe_2$,[7] and $Cp^*_2ZrMe(i\text{-}Bu)$[5] were prepared via published procedures.

Polymerization of Propene by $Cp^*_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$. As a general procedure, 16.8 mg of $Cp^*_2ZrMe_2$ (43 μmol) were dissolved in 18 mL of toluene at the desired polymerization temperature. Propene was bubbled through this solution for 10 min, and then 26.8 mg of $B(C_6F_5)_3$ solution (52 μmol) in 2 mL of toluene was added; a characteristic ion pair orange color developed immediately.[4g] Propene bubbling was continued for another 15 min, the polymerization was quenched by addition of 1 mL of methanol, and the solvent and volatiles were removed under reduced pressure. The
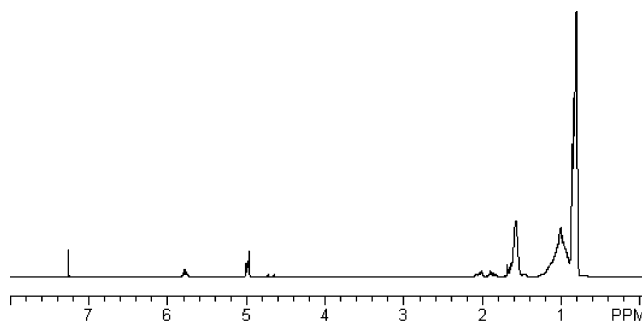

Figure 1. ^{1}H NMR spectrum (CDCl₃) of polypropene obtained by using $Cp^*_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ in toluene at 0 °C.

resulting polymer was dissolved in a minimum of hexanes and eluted through a silica gel column to remove inorganic byproducts. The polypropene obtained was characterized by GPC measurements and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (CDCl₃).

Alternatively, a solution containing 1 mg of $Cp^*_2ZrMe_2$ (2.6 μmol) in 0.2 mL of toluene-d_8 in an NMR tube cooled to −78 °C was treated with 1.6 mg of $B(C_6F_5)_3$ (3.1 μmol) in 0.3 mL of toluene-d_8. The NMR tube was vigorously shaken, an NMR spectrum was obtained at −70 °C, the sample was removed from the probe and recooled to −78 °C, and a known amount of propene was added using a gastight syringe. The reaction mixture was quickly shaken and placed back into the probe, and NMR spectra were obtained at various temperatures. A number of similar NMR studies were carried out.

Polymerization of Propene by $Cp^*_2ZrMe_2$/[Ph₃C][B(C₆F₅)₄]. A solution of 4.1 mg of $Cp^*_2ZrMe_2$ (10.2 μmol) in 0.2 mL of CD₂Cl₂ in a NMR tube was treated with a solution of 12.2 mg of $[Ph_3C][B(C_6F_5)_4]$ (10.8 μmol) in 0.3 mL of CD₂Cl₂ at −78 °C. The orange-yellow sample was then vigorously shaken and put into an NMR probe precooled to −80 °C. A spectrum was acquired, and the sample was removed, placed in a dry ice bath, and treated with 2.5 mL of propene (112 μmol). The solution turned darker orange and was replaced in an NMR probe at −80 °C. Spectra were collected at −80 and −50 °C. A number of similar NMR studies were carried out.

Results and Discussion

As outlined above, we wished to understand why the isobutyl compound $Cp^*_2Zr(CH_2CHMe_2)(\mu\text{-}Me)B(C_6F_5)_3$, presumably the initial propene insertion product of the $Cp^*_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ catalyst system, undergoes solely β-hydrogen elimination,[4g] while analogous polymeryl species of the type $Cp^*_2Zr(CH_2CHMe)_n(CH_2\text{-}CHMe_2)(\mu\text{-}Me)B(C_6F_5)_3$ undergo chain transfer predominantly via β-methyl elimination during propene polymerization.[2] We describe below a series of experiments designed to assess the factors possibly in play.

Propene Polymerization under 1 atm of Propene. To ensure congruence with the polymerization literature,[2b−g,i] we initially carried out a series of propene polymerization reactions in toluene using the zirconium catalyst $Cp^*_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$. Polymerizations were carried out under 1 atm of propene, and the polymeric products were purified, using standard procedures, as described in the Experimental Section. Olefinic end group analyses were carried out using ^{1}H NMR spectroscopy, based on literature precedents.[2i] The ^{1}H NMR spectrum of polypropene formed in toluene at 0 °C is shown in Figure 1, with the olefinic region shown in Figure 2. As can be seen, the spectrum exhibits predominantly the multiplet resonances of allyl (CH_2=

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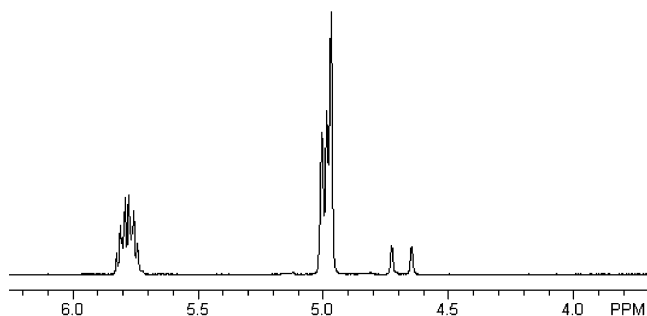
Figure 2. ^{1}H NMR spectrum (CDCl$_3$), in the olefinic end group region, of polypropene obtained using Cp*$_2$ZrMe-(μ-Me)B(C$_6$F$_5$)$_3$ in toluene at 0 °C.

Table 1. Molecular Weight Data for the Polymers Made in Toluene at Different Temperatures Using the Cp*$_2$ZrMe$_2$/B(C$_6$F$_5$)$_3$ Catalyst System

temperature (°C)	M_w	PDI
25	377	1.29
0	720	1.88
−20	6356	1.66
−45	62 417	1.14

CHCH$_2$−P) end groups (δ ~5.75 and ~4.95),[2i] consistent with β-methyl elimination.[2l] There were only very weak resonances at δ 4.6 and 4.7, attributable to the vinylidene (CH$_2$=CMe−P) end groups,[2i] which would result from β-hydrogen migration. This result is consistent with the literature,[2b−g,i] and only these olefinic end groups were obtained in polymerizations carried out at +25, 0, −20, and −45 °C, although the molecular weights varied significantly (Table 1). Interestingly, the allyl:vinylidene ratios varied little and thus the polymerization temperature does not affect the selectivity of the chain transfer processes to a significant extent.

Propene Polymerization under Monomer-Starved Conditions. To gain further information on the polymerization process, we complemented these polymerization experiments with a series of similar experiments carried out in the presence of lower propene:catalyst ratios and monitored in situ via ^{1}H NMR spectroscopy. In view of the great differences in behavior of polymeryl groups Cp*$_2$Zr(CH$_2$CHMe)$_n$(CH$_2$CHMe$_2$)-(μ-Me)B(C$_6$F$_5$)$_3$ and the isobutyl compound Cp*$_2$Zr(CH$_2$-CHMe$_2$)(μ-Me)B(C$_6$F$_5$)$_3$, we wondered if chain length might somehow be the distinguishing factor. We thought this unlikely in view of our previous molecular mechanics calculations, which had suggested that even the isobutyl group prefers the conformation shown as **E**,[4g] believed to be the key feature favoring β-methyl elimination. If, however, very short chain polymeryl groups were to prefer β-hydrogen migration, evidence for the process would in fact generally pass unnoticed since the normal methodologies for isolation and purification of polypropene involve precipitation from solution, washing with pure solvent, and then drying in vacuo at room temperature or above.[2] Thus low-boiling, short-chain olefinic products would be lost, leading to possibly incorrect conclusions concerning the chain transfer processes involved.

To test the importance of chain length, we attempted to prepare short-chain polymeryl compounds, beginning with the model polymeryl compound Cp*$_2$Zr(CH$_2$-CHMeCH$_2$CHMe$_2$)(μ-CH$_3$)B(C$_6$F$_5$)$_3$. This compound would be the second insertion product of propene with Cp*$_2$-
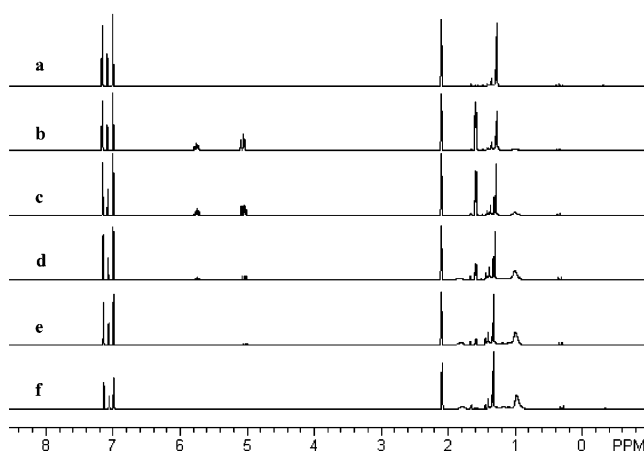

Figure 3. NMR spectra of an in situ propene polymerization reaction in toluene-d_8. Spectrum a is of Cp*$_2$ZrMe-(μ-Me)B(C$_6$F$_5$)$_3$ at −70 °C; spectra b−g are of the reaction of C$_3$H$_6$ with Cp*$_2$ZrMe(μ-Me)B(C$_6$F$_5$)$_3$ at (b) −70 °C, (c) −60 °C, (d) −50 °C, (e) −40 °C, and (f) −30 °C.
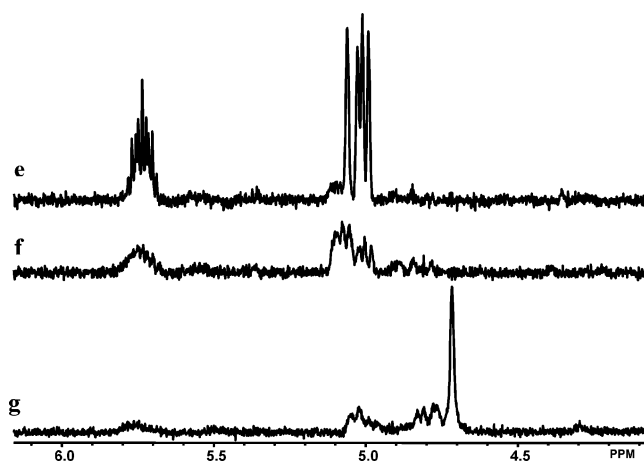
Figure 4. Details of the spectra of Figure 3 in the olefinic region.

ZrMe(μ-CH$_3$)B(C$_6$F$_5$)$_3$, and we endeavored to make it via hydrozirconation of CH$_2$=C(CH$_3$)CH$_2$CH(CH$_3$)$_2$ with Cp*$_2$ZrHCl, a known reaction for the Cp analogue.[8] Unfortunately the reaction did not work, presumably because of steric hindrance by the bulky Cp* ligands.

With a view to perhaps generating short-chain polymeryl compounds in situ, we carried out a series of NMR scale experiments, in toluene-d_8 and using low propene:catalyst ratios and the Cp*$_2$ZrMe(μ-Me)B(C$_6$F$_5$)$_3$ catalyst system. As a typical example, 10 equiv of propene was added to a solution of Cp*$_2$ZrMe(μ-Me)B(C$_6$F$_5$)$_3$ in toluene-d_8 at −78 °C. A ^{1}H NMR spectrum was run, and then the temperature was raised successively to −70, −60, −50, −40, and −30 °C; spectra were run at each temperature after thermal equilibration, which generally took ~15 min. Full-scale ^{1}H NMR spectra are shown in Figure 3, the olefinic resonances of the −40, −30, and 25 °C (run a day later) spectra in Figure 4. As can be seen, although some polypropene (δ ~1.0) had formed at −70 °C, polymerization actually occurred very slowly at the lower temperatures and some free propene (multiplets at δ ~5.75, 5.0) was still present at −30 °C. Interestingly, allyl end group resonances at δ ~5.78 and

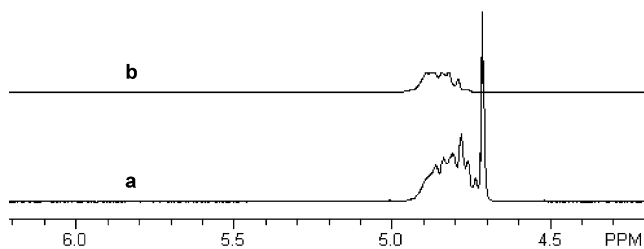(8) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974**, *96*, 8115−8116

Figure 5. Olefinic region of (a) an in situ ^{1}H NMR spectrum of polypropene prepared using Cp*$_2$ZrMe$_2$/B(C$_6$F$_5$)$_3$ in a propene-saturated solution of toluene-d_8 at 25 °C; (b) the same sample after being pumped to dryness and redissolved in toluene-d_8.

~5.02 were observable by −40 °C, but vinylidene resonances (δ 4.7−4.8) did not appear until ~−30 °C. On warming to 25 °C, both allyl and vinylidene resonances were present, although the relative intensities of the olefinic end group resonances were in all cases very low, suggesting in fact that the polymer molecular weights were rather high. However, it seems clear that the preferred mode of chain transfer involved exclusively β-methyl elimination in the presence of the higher concentrations of free propene but that β-hydrogen elimination became competitive as the availability of free monomer decreased. Also present in the final spectrum was a relatively strong singlet at δ 4.72, which was shown (COSY) to couple to another at δ 1.63; these are assigned to free isobutene.

The appearance of considerable amounts of isobutene in the late stages of the polymerization reaction implies, interestingly, the occurrence of β-hydrogen migration from the isobutyl compound Cp*$_2$Zr(i-Bu)(μ-CH$_3$)B-(C$_6$F$_5$)$_3$. The latter was presumably formed via propene insertion into Cp*$_2$ZrMe(μ-Me)B(C$_6$F$_5$)$_3$, left stranded when most or all of the propene had been consumed. This interpretation is reasonable as the Zr-Me, μ-Me, and Cp* resonances of unreacted Cp*$_2$ZrMe(μ-Me)B-(C$_6$F$_5$)$_3$, although somewhat temperature dependent, are evident in the temperature range −70 to −30 °C.

In a complementary experiment, polymerization was initiated in a saturated solution of propene in toluene-d_8 at 25 °C using Cp*$_2$ZrMe(μ-Me)B(C$_6$F$_5$)$_3$ (propene: catalyst ratio ~120:1). Although this experiment involved a much higher concentration of monomer, polymerization was much more rapid when initiated at 25 °C, the free propene disappeared very quickly, and, in fact, the temperature of the orange-red solution increased noticeably. NMR spectra were recorded after 4, 12, 20, and 110 min, and although weak allyl end group resonances were observed at 4 min, they quickly disappeared and we assume that the macromonomers that presumably formed were incorporated into the growing polymer chains. Although macromonomer incorporation did not occur in the above-mentioned low-temperature experiments, we find that 1-hexene is readily polymerized by the Cp*$_2$ZrMe(μ-Me)B(C$_6$F$_5$)$_3$ catalyst system in toluene-d_8 at 25 °C, and thus macromoner incorporation at this temperature seems reasonable.

Since the polymerization was completed very quickly, the NMR spectra at 12, 20, and 110 min were all very similar, and a typical spectrum in the olefinic region is shown in Figure 5a. Again the presence of isobutene and vinylidene groups is apparent, but the allyl end group

resonances that were initially observed have disappeared. Furthermore, the multiplet observed at δ 4.7−4.9 is far too complex to correspond to solely vinylidene end groups, and COSY and HSQC experiments were carried out to facilitate assignments. These experiments showed that resonances at δ 4.76 and 4.82 were coupled to each other and to a carbon resonance at δ 111.5, consistent with a vinylidene end group.[2i] Other resonances in the region δ 4.7−4.9 were shown by COSY and HSQC experiments to be mutually coupled and coupled also to carbon residences at δ 108−112 and, thus, may be attributed to methylidene groups of type **H** (P$_{1,2}$ = different polymeryl groups).[2i]
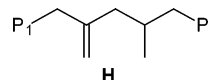
Such groups have been reported previously and are believed to be formed via η^3-allylic intermediates resulting from thermal rearrangements of the growing polymer chain.[2i] In the cases discussed here, it is probably significant that internal methylidene groups form only in the (relatively) high-temperature polymerization reactions (≥25 °C).

Interestingly, by monitoring the polymerization reactions in situ rather than subjecting the resulting polymeric products to workup procedures that would dispose of unidentified, low molecular weight volatile products, we provided ourselves with the opportunity to detect such products. As a test of the above-mentioned hypothesis that normal polymer workup and purification procedures would remove evidence for low molecular weight products, we removed the solvent and all volatile products under reduced pressure and redissolved the oily residue in toluene-d_8. A ^{1}H NMR spectrum is shown in Figure 5b, and it is readily apparent that the resonance of isobutene has disappeared, as have many of the resonances in the region δ 4.7−4.9. Thus the reaction produced considerable low molecular weight, volatile material.

We also attempted to create short-chain polymeryl species by generating the complex [Cp*$_2$ZrMe][B(C$_6$F$_5$)$_4$] in situ in CD$_2$Cl$_2$ at low temperatures in the presence of only a few equivalents of propene. We hoped that use of a limited amount of propene combined with the more weakly coordinating anion [B(C$_6$F$_5$)$_4$]$^-$ instead of [Me-B(C$_6$F$_5$)$_3$]$^-$ and the more polar solvent CD$_2$Cl$_2$ instead of toluene-d_8 might result in a higher proportion of the catalytic sites being active[9] and hence in the formation of a greater proportion of short-chain polymeryl groups. Polymerization of propene in the presence of the Cp*$_2$-ZrMe$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] catalyst system (propene:catalyst ratio ~10:1) was therefore initiated in CD$_2$Cl$_2$ at −78 °C, and a ^{1}H NMR spectrum of the reaction mixture at −78 °C is shown in Figure 6 with the olefinic region shown in the inset. As can be clearly seen, the propene polymerized rapidly and completely, and thus our

(9) It is well known that the [B(C$_6$F$_5$)$_4$]$^-$ anion coordinates much more weakly that does the [BMe(C$_6$F$_5$)$_3$]$^-$ anion,[10] and thus it is to be expected that the Cp*$_2$ZrMe$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] catalyst system will form more active sites than does the Cp*$_2$ZrMe$_2$/B(C$_6$F$_5$)$_3$ catalyst system. Furthermore, since the first insertion of monomer is likely to be much slower than is chain propagation,[11] it follows that the Cp*$_2$ZrMe$_2$/[Ph$_3$C]-[B(C$_6$F$_5$)$_4$] catalyst system will produce lower molecular weight polymers than does the Cp*$_2$ZrMe$_2$/B(C$_6$F$_5$)$_3$ catalyst system.
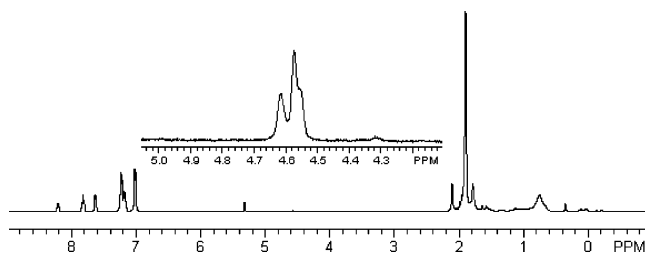
Figure 6. ^{1}H NMR spectra of an in situ propene polymerization utilizing as catalyst $Cp*_2ZrMe_2/[Ph_3C][B(C_6F_5)_4]$ in CD_2Cl_2 at -78 °C; inset shows the olefinic region.

assumption that the system would be more reactive than the $Cp*_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$ catalyst system in toluene is justified.[12]

Interestingly, the ^{1}H NMR spectrum exhibited the resonances of isobutene at δ 4.57 (and 1.63) in addition to vinylidene resonances at δ 4.61 and 4.55, but no resonances in the allyl end group region. A COSY experiment showed that the resonances at δ 4.61 and 4.55 were both correlated to a resonance at δ 1.57, and we assign these to polymeric species with vinylidene end groups of the type $CH_2=CMe(CH_2CHMe)_nCH_2CMe-P$. In support of these assignments, NMR spectra of mixtures of isobutene and $CH_2=CMeCH_2CHMeCH_2$-CH_2Me and of isobutene, $CH_2=CMeCH_2CHMeCH_2CH_2$-Me, and $CH_2=CMeCH_2CHMe_2$ in CD_2Cl_2 were run at -78 °C. The spectra in the olefinic region were essentially identical to that shown in Figure 6, the resonances of the isobutene being observed at δ 4.61 and 1.67 and the vinylidene resonances of the two long-chain olefins overlapping at δ 4.66 and 4.59 and coupled with a resonance at δ 1.61.

It is not clear whether the absence of allyl end group resonances is a result of an absence of β-methyl elimination during chain transfer or of incorporation of β-methyl-eliminated allyl macromonomers into the growing polymer chains, as noted above. This process is very slow when polymerization is carried out using the $Cp*_2$-$ZrMe(\mu\text{-Me})B(C_6F_5)_3$ catalyst system in toluene-d_8 at very low temperatures, but does occur at room temperature in toluene-d_8 and may well be competitive even at -78 °C in the polar CD_2Cl_2 when using the more reactive $Cp*_2ZrMe_2/[Ph_3C][B(C_6F_5)_4]$ catalyst system.

Interestingly, comparison of the integrated intensity of the vinylidene doublet at δ 4.61 and 4.55 with that of the broad polypropene methyl resonance at δ $\sim$0.8 gives an M_n value of 2000 for the material obtained at -50 °C, confirming our expectation of relatively low molecular weights in CD_2Cl_2 using $Cp*_2ZrMe_2/[Ph_3C]$-$[B(C_6F_5)_4]$. However, the M_n value corresponds to an average polymer chain containing over 45 propene units, and the notion that β-hydrogen elimination requires "short" polymeryl chains is clearly untenable. Similar

results (observation solely of isobutene and longer chain vinylidene oligomers) were obtained using the $Cp*_2$-$ZrMe_2/B(C_6F_5)_3$ catalyst system and a propene:catalyst ratio of $\sim$10:1 in CD_2Cl_2, and the polypropene formed had a similar molecular weight.

Mechanisms of Chain Transfer. On the basis of the above evidence, it seems that the only factor correlating at all with the occurrence of β-methyl as opposed to β-hydrogen elimination is the concentration of free propene. During propene polymerizations by the $Cp*_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$ catalyst system in toluene, where propene pressure is maintained at 1 atm or higher, β-methyl elimination to give allyl end groups is the dominant process for chain transfer over a range of temperatures. The presence of relatively weak vinylidene resonances suggests a strangely minor role for β-hydrogen elimination, which is much the preferred mechanism for chain transfer for most metallocene catalyst systems. Similarly, in a low-temperature polymerization reaction utilizing the same $Cp*_2ZrMe(\mu$-Me)$B(C_6F_5)_3$ catalyst system but in which the initial propene:catalyst ratio was 10:1, the initially preferred mode of chain transfer again involved β-methyl elimination, and β-hydrogen elimination became competitive only as the temperature was raised and as the concentration of free propene decreased significantly. Ultimately much of the $Cp*_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$ catalyst was converted via insertion of a single propene to $Cp*_2$-$Zr(i\text{-Bu})(\mu\text{-Me})B(C_6F_5)_3$, which released isobutene via β-hydrogen elimination, just as this compound does when generated from $Cp*_2ZrMe(i\text{-Bu})$ on treatment with $B(C_6F_5)_3$.[4g]

While several other of the experiments reported here, involving low propene:catalyst ratios, the alternative $Cp*_2ZrMe_2/[Ph_3C][B(C_6F_5)_4]$ catalyst system, and/or CD_2-Cl_2 as solvent, seemingly complemented these findings in that polymeric products containing allyl end groups were largely absent, incorporation into growing polypropene chains of macromonomers containing allyl end groups almost certainly provides an alternative for the absence of such end groups in the polymerization products. Thus, these results were ambiguous.

There have been several reports of monomer participation in chain transfer processes during metallocene-catalyzed Ziegler polymerizations, and in all cases the chemistry of eq 2 is involved such that the migrating hydrogen transfers not to the metal but directly to a coordinated monomer molecule.[3a-d,13] The end result in terms of overall chemistry is the same, a polymer containing a terminal olefinic group and initiation of a new polymer chain, but the phenomenon has been detected by the effects of changing monomer concentration on polymer molecular weights. In cases where β-hydrogen migration to coordinated monomer occurs, the rates of chain transfer and chain propagation both increase as the monomer concentration increases, and therefore the latter has little effect on molecular weights.

To our knowledge nothing has been reported concerning the effects of free monomer concentration on molecular weights of polypropene produced by any $Cp*_2Zr$ catalyst system, and the experiments described here do

(10) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

(11) (a) Landis, C. R.; Rosaaen, K. A.; Sillars, D. R. *J. Am. Chem. Soc.* **2003**, *125*, 1710. (b) Liu, Z.; Somsook, E.; White, C. B.; Rosaaen, K. A.; Landis, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 11193.

(12) (a) Since some free trityl ion was present in the reaction mixture (δ 7.64(d), 7.83(t), 8.21(t)), it seemed possible albeit unlikely that propene oligomers had formed via carbocationic oligomerization[12b] induced by the trityl ion. A control experiment involving exposure of propene only to $[Ph_3C][B(C_6F_5)_4]$ in CD_2Cl_2 at -80 °C showed that no reaction occurred, and thus the polypropene formed in the presence of $Cp*_2ZrMe_2/[Ph_3C][B(C_6F_5)_4]$ had indeed formed via a Ziegler polymerization process. (b) Kennedy, J. P.; Maréchal, E. *Carbocationic Polymerization*; John Wiley and Sons: New York, 1982.

(13) (a) Boor, J. *Ziegler-Natta Catalysts and Polymerization*; Academic Press: New York, 1979; pp 258, 259. (b) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Polymer* **1989**, *30*, 428.

not shed light on this issue. However, it seems from the results presented here that β-methyl elimination as a mode of chain transfer during propene polymerization by the Cp*$_2$Zr catalyst system may require the availability of free propene. While the orientation of the polymeryl group shown in **E** may be relevant if there are cases of β-methyl migration directly to metal, it may not in itself be sufficient to induce β-methyl elimination during propene polymerization by the Cp*$_2$ZrMe(μ-Me)B(C$_6$F$_5$)$_3$ catalyst system. Instead a transition state resembling **I** may pertain, possibly for steric and electronic reasons.
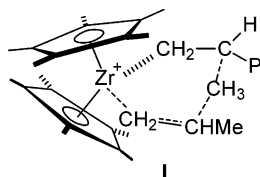
Methyl transfer to propene as in **I** would certainly be more facile sterically and would involve less ring strain in the transition state than the process shown in eq 3. Furthermore, inasmuch as a strong C−C bond would be formed rather than a weaker C−Zr bond, transfer to propene would also be favored enthalpically.

Conclusions. Propene polymerization by Cp*$_2$ZrMe-(μ-Me)B(C$_6$F$_5$)$_3$ in toluene under 1 atm propene in the temperature range −45 to 25 °C involves β-methyl migration as the primary mode of chain transfer, with β-hydrogen elimination playing a very minor role. Under propene-starved conditions, however, chain transfer involving β-hydrogen migration becomes competitive. It is concluded that β-methyl migration may involve transfer of the methyl group not, as has been previously thought, to the metal guided by the orienting effects of the bulky Cp* ligands, but directly to an incoming molecule of propene. Both steric and electronic factors may be important.