Mechanistic Study of β-Methyl and β-Hydrogen Elimination in the Zirconocene Compounds $Cp'_2ZrR(\mu\text{-}CH_3)B(C_6F_5)_3$ ($Cp' = Cp$, Cp^*; $R = CH_2CMe_3$, CH_2CHMe_2)

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A kinetics study of β-methyl elimination reactions of the compounds $Cp_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ (in various solvents) and $Cp^*_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ (in CD_2Cl_2) shows that the reactions are accelerated by polar solvents and by steric crowding in the Cp* system, results consistent with previous findings and conclusions that the methyl migrations are accompanied in a concerted process by borate anion departure from the inner coordination sphere of the metal ion. Surprisingly, however, the isobutyl compound $Cp^*_2Zr(i\text{-}Bu)(\mu\text{-}Me)B(C_6F_5)_3$, which is expected to undergo β-methyl elimination by analogy with an extensive literature on chain transfer processes during propylene polymerization, undergoes very rapid β-hydrogen elimination only.

There has in recent years been explosive growth in the use of zirconocene compounds as homogeneous catalysts for coordination (Ziegler−Natta) polymerization of alkenes. Among the most successful catalysts are the formally 14-electron, cationic complexes $[Cp'_2ZrR]^+X^-$ (Cp' = functionalized cyclopentadienyl, R = alkyl, H; X^- = weakly coordinating anion), which contain a very labile anionic ligand and an alkyl group.[1] A great deal of progress has also been made in the development of theoretical models of alkene polymerization, with considerable interest being shown in the individual steps involved in the initiation, chain propagation, termination, and chain transfer steps.[2] However, while it is clear that good computational models have greatly enhanced our mechanistic understanding of metallocene-induced polymerization reactions, there remains a need to gain clearer insight into the complex solution equilibria and processes which are often involved. There is therefore also a very great need for more extensive experimental thermodynamic and kinetic data for purposes of calibration and confirmation of computational models,[2] including activation energies for β-hydrogen[1] and the much rarer β-methyl elimination reactions,[2h,3,4] important in chain transfer and chain termination processes.

While β-hydrogen migration to metal (β-elimination) or directly to incoming monomer molecule is normally the predominant mode of chain transfer during metallocene-catalyzed alkene polymerization processes,[1] β-methyl elimination is generally dominant during, for example, propylene polymerization by sterically crowded catalysts such as the bis-η^5-C_5Me_5-metal (Cp^*_2M) system.[3] The reasons for the variations in behavior are not clear, as β-hydrogen elimination seems clearly to be significantly preferred thermodynamically.[5] However,

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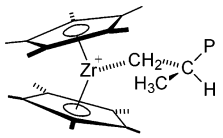
suggestions[3c,e] that steric interactions of the bulky Cp* ligands with the β-methyl group of a growing polymer chain might force the β-methyl group of the polymeryl chain into the plane perpendicular to the Cp(centroid)−Zr−Cp(centroid), as in **A**, seem generally to have found acceptance.[3f,g,4a]



A

In this conformation, the β-methyl group is in close proximity to the LUMO, an orientation that presumably would facilitate, via a γ-agostic interaction, β-methyl rather than β-hydrogen migration. However, both computational and experimental data for such processes are in short supply. Indeed, while there have been reported numerous experimental and computed activation energy data for reversible migratory insertion reactions involving, for example, metallocene hydrides and alkenes,[1] there has been reported very little information about the analogous reactions involving alkyl groups.[2h]

A number of stoichiometric β-methyl elimination reactions from neopentyl (Np) groups have been described,[4] and we[4e] and Beswick and Marks[4d] have reported kinetics studies of a small number of β-methyl elimination reactions of related zirconocene and hafnocene systems in toluene and chlorobenzene. In both cases the net chemistry, of a type originally observed by Horton,[4c] is illustrated in eq 1.

$$Cp'_2MMe(Np) + B(C_6F_5)_3 \rightarrow Cp'_2M(Me)(\mu\text{-}Me)B(C_6F_5)_3 + CH_2{=}CMe_2 \quad (1)$$

The reactions involve initial methyl abstraction from the compounds $Cp_2HfMe(Np)$ and $(1,2\text{-}Me_2C_5H_3)_2MMe(Np)$ (M = Zr, Hf) by $B(C_6F_5)_3$ to give the zwitterionic intermediates $Cp_2M(Np)(\mu\text{-}Me)B(C_6F_5)_3$ and $(1,2\text{-}Me_2C_5H_3)_2M(Np)(\mu\text{-}Me)B(C_6F_5)_3$, and these exhibit varying degrees of thermal stability depending on the metal, the nature of the cyclopentadienyl ligand, and the solvent. All are, however, readily induced to undergo β-methyl elimination to form $Cp_2MMe(\mu\text{-}Me)B(C_6F_5)_3$ or $(1,2\text{-}Me_2C_5H_3)_2MMe(\mu\text{-}Me)B(C_6F_5)_3$, presumably via an undetected η^2-isobutene intermediate as in eqs 2 and 3.

$$Cp_2M(Np)(\mu\text{-}Me)B(C_6F_5)_3 \rightarrow [Cp_2MMe(\eta^2\text{-}CH_2{=}CMe_2)][BMe(C_6F_5)_3] \quad (2)$$

$$[Cp_2MMe(\eta^2\text{-}CH_2{=}CMe_2)][BMe(C_6F_5)_3] \rightarrow Cp_2MMe(\mu\text{-}Me)B(C_6F_5)_3 + CH_2{=}CMe_2 \quad (3)$$

The kinetics studies indicated that the chemistry summed in eqs 2 and 3 is first order in the product of eq 1 and is reversible for $Cp_2HfMe(\mu\text{-}Me)B(C_6F_5)_3$ but not for the $1,2\text{-}Me_2C_5H_3$−Zr and $1,2\text{-}Me_2C_5H_3$−Hf compounds. In addition, the reaction of $Cp_2Hf(Np)(\mu\text{-}Me)B(C_6F_5)_3$, at least, is seriously inhibited by ligands L, which can coordinate preferentially to give complexes of the type $[Cp_2M(L)Np][BMe(C_6F_5)_3]$; similar results had been observed previously.[4a,c] The activation parameters for all three compounds are similar in toluene, although $\Delta H^{\ddagger}$ for $Cp_2Hf(Np)(\mu\text{-}Me)B(C_6F_5)_3$ is lower in the more polar chlorobenzene. It was tentatively concluded that the β-methyl migration reactions involve concomitant loosening of the metal−borate linkages, but clearly more information is needed. While the current work was being completed, Chirik et al. reported kinetic isotope effects in the range 1.28−1.49 for β-methyl elimination reactions of a series of deuterated neopentyl compounds, including $Cp_2Zr\{CH_2C(CD_3)(CH_3)_2\}(\mu\text{-}CH_3)B(C_6F_5)_3$ and $Cp^*_2Zr\{CH_2C(CD_3)(CH_3)_2\}(\mu\text{-}CH_3)B(C_6F_5)_3$.[4f] On the basis of these results, they deduced a transition state γ-agostic interaction during the methyl migration reaction, as might be anticipated in the orientation shown in **A**, above. Interestingly, for all compounds studied evidence was found of reversibility in the deinsertion process.

We have expanded our earlier kinetics study of the hafnium neopentyl compound $Cp_2Hf(Np)(\mu\text{-}Me)B(C_6F_5)_3$, opting to utilize zirconium compounds in this study because of the extensive literature on the synthesis of relevant zirconocene-type compounds,[6] and because of the preeminent position of zirconocene systems in propylene polymerization.[1] We wished to carry out a broader study in which we would vary the substituents on the cyclopentadienyl ring and also substitute the neopentyl group with iso- and *sec*-butyl groups, in which there would be a competition between β-hydrogen and β-methyl elimination reactions. As mentioned above, β-hydrogen elimination is generally the preferred mode of chain transfer during metallocene-catalyzed alkene polymerization processes,[1] but β-methyl elimination becomes dominant during, for example, propylene polymerization by metallocene catalysts containing heavily substituted cyclopentadienyl rings.[3] We hoped to be able to shed light on the factors controlling the mode of migratory β-elimination reaction taken by various zirconocene systems, and although we were not completely successful in our endeavors, we have extended the work of refs 4d and 4e and have gained a clearer picture of the activation barriers to β-methyl elimination. Interestingly, we have also found conditions under which chain transfer processes during propylene polymerization by the $Cp^*_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ catalyst system preferentially involves β-hydrogen elimination rather than the often-reported β-methyl elimination. This aspect of our study is addressed separately.[3l]

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. ^1H NMR spectra were run on Bruker AV400 or AV500 spectrometers, chemical shifts being referenced using the residual

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proton signals of the deuterated solvents. Molecular mechanics calculations were carried out using PCModel V. 8.0 (Serena Software, Bloomington, IN). Cp_2ZrCl_2 and $Cp^*_2ZrCl_2$ were purchased from Strem Chemicals; $[Ph_3C][B(C_6F_5)_4]$ was purchased from Asahi Glass Co. $(Cp_2ZrCl)_2O$,[7a] $Cp_2ZrMeCl$,[7b] neopentyllithium (NpLi),[8] $B(C_6F_5)_3$,[9] $Cp^*_2ZrMe_2$,[10] and $Cp^*_2ZrMe(i\text{-}Bu)$[11] were prepared via published procedures.

Synthesis of $Cp_2ZrMe(Np)$. To a mixture of 583 mg of $Cp_2ZrClMe$ (2 mmol) and 156 mg of NpLi (2 mmol) at −78 °C was added 20 mL of THF. The solution was stirred at −78 °C for a few minutes and allowed to warm to room temperature, and then the solvent was removed. The resulting solid was recrystallized from hexanes to give 385 mg of pale yellow, crystalline product. Yield: 62%. ^1H NMR (C_6D_6): δ 5.78 (s, 10H, Cp), 1.07 (s, 9H, $CH_2C(CH_3)_3$), 0.48 (s, 2H, $CH_2C(CH_3)_3$), −0.06 (s, 3H, $ZrCH_3$). Lit.[4c] (C_6D_6Br): δ 5.92 (Cp), 0.98 ($CH_2C(CH_3)_3$), 0.42 ($CH_2C(CH_3)_3$), −0.17 ($Zr-CH_3$).

Synthesis of $Cp^*_2ZrMe(Np)$. To a mixture of 1 g of $Cp^*_2ZrCl_2$ (2.3 mmol) and 0.45 g of NpLi (5.7 mmol) in a Schlenk flask at −78 °C was added 40 mL of ethyl ether. The resulting brownish suspension was allowed to slowly warm to room temperature and turned yellow after stirring overnight. The solvent was then removed under reduced pressure, and the resulting solid material was extracted with 40 mL of hexanes and filtered. The filtrate was pumped to dryness to give $Cp^*_2ZrClNp$ as a yellow powder. A solution of the latter was dissolved in 25 mL of THF at −78 °C, and 1 mL of a 3 M solution of MeMgBr in ethyl ether (3 mmol) was added. The solution was slowly warmed to room temperature and was stirred overnight, the solvent was removed under reduced pressure, and the resulting material was extracted with hexanes and filtered. The volume of the filtrate was reduced and the solution was cooled to −78 °C to give 0.89 g of yellow product, which contained (NMR) $Cp^*_2Zr(Np)_2$ and $Cp^*_2ZrMe(Np)$ in a 56:43 ratio. ^1H NMR of $Cp^*_2ZrMe(Np)$ (CD_2Cl_2): δ 1.89 (s, 30H, Cp*), 0.77 (s, 9H, $CH_2C(CH_3)_3$), −0.13 (s, 2H, $CH_2C(CH_3)_3$), −0.74 (s, 3H, $Zr-CH_3$). Lit.[4c] (C_6D_6): δ 1.80 (Cp*), 1.12 ($CH_2C(CH_3)_3$), 0.03 ($CH_2C(CH_3)_3$), −0.39 ($Zr-CH_3$). ^1H NMR of $Cp^*_2ZrNp_2$ (CD_2Cl_2): δ 1.96 (s, 30H, Cp*), 1.02 (s, 18H, $CH_2C(CH_3)_3$), −0.13 (s, 4H, $CH_2C(CH_3)_3$). Attempts to separate these two compounds failed because of close similarities in solubilities.

Synthesis of $Cp_2ZrMe(i\text{-}Bu)$. This compound has been previously reported but with little information included,[6a] and we have used a modified synthetic procedure. A solution of 1.2 mL of *i*-BuMgBr (2 M in Et_2O, 2.4 mmol) was added to a stirred and cooled (−78 °C) solution of 0.67 g of $Cp_2ZrMeCl$ (2.4 mmol) in 25 mL of Et_2O. The solution was then stirred for 1 h as it warmed to room temperature, and the solvent was removed under reduced pressure. The resulting sticky solid was washed with hexanes and filtered, and the solvent was removed from the filtrate under reduced pressure to give $Cp_2ZrMe(i\text{-}Bu)$ as a thick yellow oily material. ^1H NMR (C_6D_6): δ 5.72 (s, 10H, Cp), 2.14 (m, 1H, $CH_2CH(CH_3)_2$), 0.96 (d, 6H, $CH_2CH(CH_3)_2$), 0.30 (d, 2H, $CH_2CH(CH_3)_2$), −0.14 (s, 3H, $Zr-CH_3$). The product could not be purified because of thermal instability and contained up to ~20% Cp_2ZrMe_2.

Synthesis of $Cp^*_2ZrMe(i\text{-}Bu)$. This compound was prepared as in the literature.[11] ^1H NMR (CD_2Cl_2): δ 1.86 (s, 30H, Cp*), 1.67 (m, 1H, $CH_2CH(CH_3)_2$), 0.60 (d, 6H, $CH_2CH(CH_3)_2$), −0.34 (d, 2H, $CH_2CH(CH_3)_2$), −0.85 (s, 3H, $Zr-CH_3$). Lit.[11] (CD_2Cl_2): δ 1.89 (Cp*), 0.61 ($CH_2CH(CH_3)_2$), −0.33 ($CH_2CH(CH_3)_2$), −0.83 ($Zr-CH_3$).

Formation of the Complexes $[Cp'_2ZrR(\mu\text{-}CH_3)B(C_6F_5)_3]$ (Cp′ = *Cp, Cp*; R = Np,* *i*-Bu) and Studies of Their Thermal Degradation. These compounds were typically formed in situ by treating Cp'_2ZrMeR with a slight excess of $B(C_6F_5)_3$ in a deuterated solvent at low temperature and were characterized and their chemistry studied by VT NMR spectroscopy. As an example, an NMR tube containing 14 mg of $B(C_6F_5)_3$ (0.027 mmol) in 0.25 mL of C_6D_5Cl was cooled to −40 °C. A solution of $Cp_2ZrMe(Np)$ (7.7 mg, 0.025 mmol) in 0.25 mL of C_6D_5Cl was added slowly to the above solution, which turned pale yellow during the addition. The sample was quickly placed in an NMR probe precooled to −40 °C, and ^1H NMR spectra (500 MHz) of $Cp_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ were obtained at various temperatures. ^1H NMR (C_6D_5Cl, −10 °C): δ 5.95 (s, 10H, Cp), 0.87 (s, 9H, $Zr-CH_2C(CH_3)_3$), 1.30 (s, 2H, $Zr-CH_2C(CH_3)_3$), 0.30 (br, 3H, CH_3B). Lit.[4c] (toluene-d_8, −25 °C): δ 5.50 (Cp), 1.08 ($Zr-CH_2C(CH_3)_3$), 0.80 ($ZrCH_2C(CH_3)_3$), 0.16 (CH_3B). $[Cp_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3]$ is thermally unstable above −10 °C, giving $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$[4c] and isobutene.

The compound $Cp^*_2ZrNp(\mu\text{-}CH_3)B(C_6F_5)_3$ was prepared similarly. ^1H NMR (CD_2Cl_2, −70 °C): δ 1.99 (s, 30H, Cp*), 1.11 (s, 9H, $Zr-CH_2C(CH_3)_3$), 1.04 (s, 2H, $Zr-CH_2C(CH_3)_3$), 0.38 (br, 3H, CH_3B). $Cp^*_2ZrNp(\mu\text{-}CH_3)B(C_6F_5)_3$ was found to be thermally unstable above −70 °C, giving $[Cp^*_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3]$[4c] and isobutene.

The compounds $Cp_2Zr(i\text{-}Bu)(\mu\text{-}CH_3)B(C_6F_5)_3$ and $Cp^*_2Zr(i\text{-}Bu)(\mu\text{-}CH_3)B(C_6F_5)_3$ were prepared similarly, from $Cp_2ZrMe(i\text{-}Bu)$ or $Cp^*_2ZrMe(i\text{-}Bu)$, with $B(C_6F_5)_3$ in CD_2Cl_2 at −78 °C. ^1H NMR for $Cp_2Zr(i\text{-}Bu)(\mu\text{-}CH_3)B(C_6F_5)_3$ (CD_2Cl_2, −40 °C): δ 6.35 (s, 10H, Cp), 2.29 (m, 1H, $CH_2CH(CH_3)_2$), 1.23 (d, 2H, $CH_2CH(CH_3)_2$), 0.75 (d, 6H, $CH_2CH(CH_3)_2$), 0.19(br, 3H, B*Me*). ^1H NMR for $[Cp^*_2Zr(i\text{-}Bu)(\mu\text{-}CH_3)B(C_6F_5)_3]$ (CD_2Cl_2, −80 °C): δ 1.90 (s, 30H, Cp*), 2.00 (m, 1H, $CH_2CH(CH_3)_2$), 1.16 (d, 2H, $CH_2CH(CH_3)_2$), 0.62 (d, 6H, $CH_2CH(CH_3)_2$), 0.30(br, 3H, B*Me*). $[Cp_2Zr(i\text{-}Bu)(\mu\text{-}CH_3)B(C_6F_5)_3]$ was found to be unstable above −40 °C, giving isobutylene and, presumably, $[Cp_2ZrH(\mu\text{-}CH_3)B(C_6F_5)_3]$ (δ_{Zr-H} δ 7.31 in methylene chloride-d_2), and $[Cp^*_2Zr(i\text{-}Bu)(\mu\text{-}CH_3)B(C_6F_5)_3]$ was found to be unstable above −60 °C, giving isobutylene and $[Cp^*_2ZrH(\mu\text{-}CH_3)B(C_6F_5)_3]$[3d] ($\delta_{Zr-H}$ δ 7.30 in CD_2Cl_2; lit. 7.70 in benzene-d_6).

Results and Discussion

Syntheses and Attempted Syntheses of $Cp'_2ZrMe(R)$ (Cp′ = Cp, Cp*; R = CH_2CMe_3, CH_2CHMe_2, CHMeEt). The compounds $Cp_2ZrMe(Np)$ and $Cp^*_2ZrMe(Np)$ have been prepared previously,[4c] but we have utilized somewhat modified synthetic procedures; both exhibit ^1H NMR spectra consistent with the literature values, although the synthesis of $Cp^*_2ZrMe(Np)$ was accompanied by the formation also of $Cp^*_2Zr(Np)_2$, presumably because of a redistribution reaction. The compound $Cp^*_2ZrMe(i\text{-}Bu)$ has also been prepared previously,[11] and the ^1H NMR spectrum confirmed its identity. The compound $Cp_2ZrMe(i\text{-}Bu)$ was prepared similarly and identified unambiguously by ^1H NMR spectroscopy, but it is thermally labile and as well could not be separated from the byproduct Cp_2ZrMe_2. All attempts to prepare the *sec*-butyl compounds $Cp_2ZrMe(sec\text{-}Bu)$ and $Cp^*_2ZrMe(sec\text{-}Bu)$ and mixed Cp−Cp* compounds of any kind resulted in mixtures that could not be utilized.

Kinetics Studies of β-Methyl Elimination Reactions of $Cp'_2ZrNp(\mu\text{-}CH_3)B(C_6F_5)_3$. Horton has previously shown that the compounds $Cp_2ZrNp(\mu\text{-}CH_3)B(C_6F_5)_3$ and $Cp^*_2ZrNp(\mu\text{-}CH_3)B(C_6F_5)_3$ undergo β-methyl elimination in toluene-d_8 as in eqs 1−3, the former

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(8) Feldman, D.; Barbalata, A. *Synthetic Polymers Technology, Properties, Applications*; Chapman and Hall: New York, 1996.
(9) Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245.
(10) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 2716.
(11) Casey, C. P.; Carpenetti, D. W. *J. Organomet. Chem.* **2002**, *642*, 120.

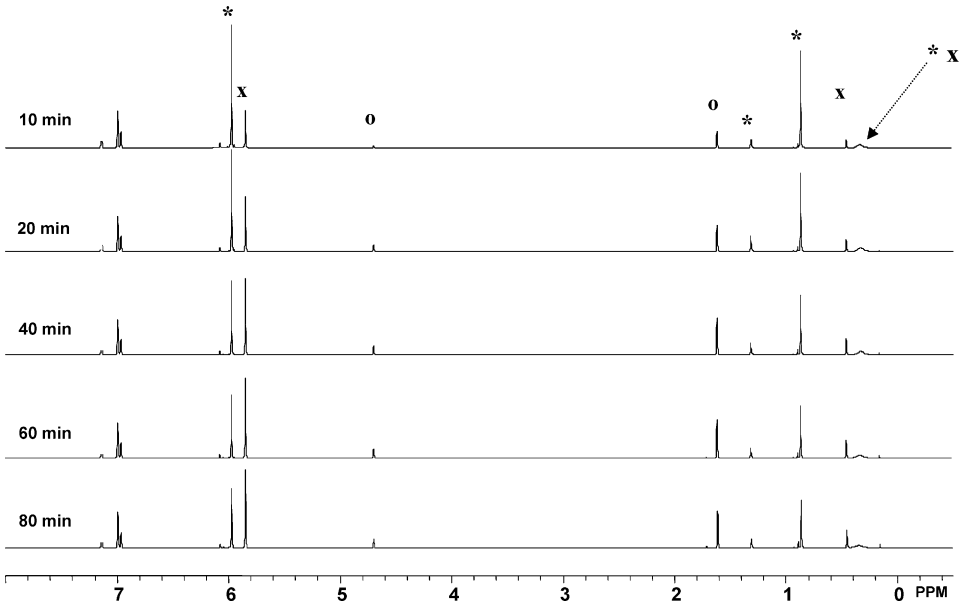


Figure 1. Decay of $Cp_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$ in C_6D_5Cl at 10 °C. *: $Cp_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$, **x**: $Cp_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$, **o**: isobutylene.

reversibly at temperatures above 0 °C, the latter instantaneously and apparently completely at −78 °C.[4c] Somewhat surprisingly, perhaps, we were able to obtain for the first time the ^{1}H NMR spectrum of the intermediate, $Cp^*_2ZrNp(\mu\text{-}CH_3)B(C_6F_5)_3$, in CD_2Cl_2 at −70 °C; the previous study of the reaction of $Cp^*_2ZrMe(Np)$ with $B(C_6F_5)_3$ resulted in the observation only of $Cp^*_2ZrMe(\mu\text{-}CH_3)B(C_6F_5)_3$ (toluene-d_8 at −75 °C).[4c] For purposes of comparison, we note that the earlier kinetics study on $(1,2\text{-}Me_2C_5H_3)_2Zr(Np)(\mu\text{-Me})B(C_6F_5)_3$ and $(1,2\text{-}Me_2C_5H_3)_2Hf(Np)(\mu\text{-Me})B(C_6F_5)_3$ was carried out[4d] in toluene-d_8 in the temperature ranges −5 to 25 °C and −15 to 15 °C, respectively, while $Cp_2Hf(Np)(\mu\text{-Me})B(C_6F_5)_3$ was studied in the temperature range 0 to 20 °C in toluene-d_8 and in the temperature range −5 to 10 °C in C_6D_5Cl.[4e,h]

The kinetics studies carried out here all involved NMR scale reactions in C_6D_5Cl, toluene-d_8, or CD_2Cl_2, depending on solubilities and the temperature range required. As outlined in the Experimental Section, the general procedure involved reacting solutions of each of the compounds $Cp'_2ZrMe(R)$ (Cp′ = Cp, Cp*; R = CH_2CMe_3, CH_2CHMe_2) with 1 equiv of $B(C_6F_5)_3$ to give the compounds $Cp'_2Zr(R)(\mu\text{-Me})B(C_6F_5)_3$, which were identified by NMR spectroscopy. Decay of the μ-Me compounds was then monitored by ^{1}H NMR spectroscopy at four different temperatures. The temperature ranges studied were unfortunately rather narrow, in all cases only about 15 degrees, but formation of other decomposition products became a factor during the longer times required at lower temperatures and the reactions were too rapid to be monitored satisfactorily at higher temperatures.

The zwitterionic complex $Cp_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$ formed cleanly and instantly when $Cp_2ZrMeNp$ was reacted with a slight excess of $B(C_6F_5)_3$ in C_6D_5Cl at −10 °C, at which temperature $Cp_2ZrNp(\mu\text{-}CH_3)B(C_6F_5)_3$ is stable. Above −10 °C, however, $Cp_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$ decomposed via β-Me elimination to form $Cp_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$, as indicated at, for example, 10 °C by weakening of the resonances of $Cp_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$ at δ 5.97 (Cp), 1.31 (CH_2), and 0.86 (CMe) and the appearance of the resonances of $Cp_2ZrMe(\mu\text{-Me})B(C_6F_5)_3$ at δ 5.85 (Cp) and 0.45 ($Zr-CH_3$) and isobutene at δ 4.73 (CH_2) and 1.60 (Me); the broad resonance of the μ-Me group remained constant at δ 0.33. A rate study of the β-Me elimination reaction was carried out in C_6D_5Cl by carefully monitoring the decay of the Cp signals in the ^{1}H NMR spectrum at the temperatures 5, 10, 15, and 20 °C. Although the chemical shifts are slightly temperature dependent, the reactions were quite clean, as shown in Figure 1.

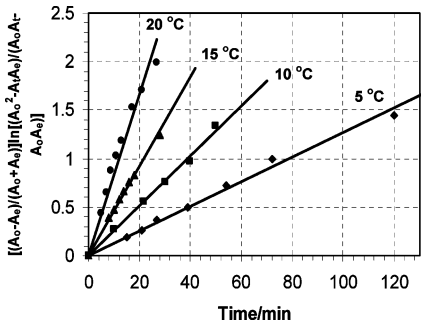


Figure 2. Plots of $[(A_o - A_e)/(A_o + A_e)]\ \ln[(A_o^2 - A_tA_e)/(A_oA_t - A_oA_e)]$ vs time for the decomposition of $Cp_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$ in C_6D_5Cl.

Interestingly, we found that at all temperatures the β-Me elimination reactions in C_6D_5Cl appeared to eventually reach equilibrium, linear plots of $[(A_o - A_e)/(A_o + A_e)]\ \ln[(A_o^2 - A_tA_e)/(A_oA_t - A_oA_e)]$ vs time (Figure 2)[12] confirming that the reactions are reversible and first-order with respect to the concentration of $Cp_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$. The slopes give k_1 for the β-Me elimination reaction, and rate constant data are provided in Table 1. On the basis of the temperature dependence of k_1, an activation energy E_a of 19.4(0.9) kcal/mol was calculated. Activation parameters for the β-Me elimination reaction were determined utilizing an Eyring plot, shown in Figure 3; values for $\Delta H^‡$, $\Delta S^‡$, and $\Delta G^‡$ (0 °C)

(12) Capellos, C.; Bielski; B. H. J. *Kinetic Systems*; Wiley-Interscience: New York, 1972; pp 41−43.

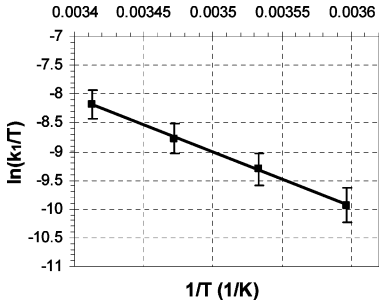


Figure 3. Eyring plot for the decomposition of $Cp_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ in C_6D_5Cl.

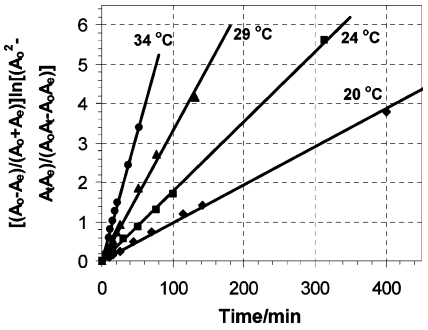


Figure 4. Plots of $[(A_o - A_e)/(A_o + A_e)]\ \ln[(A_o^2 - A_tA_e)/(A_oA_t - A_oA_e)]$ vs time for the decomposition of $Cp_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ in toluene-d_8.

Table 1. First-Order Rate Constants k_1 for the β-Me Elimination of $Cp_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ in C_6D_5Cl and Toluene-d_8, and of $Cp^*_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ in CD_2Cl_2

compound (solvent)	temperature (°C)	$k_1 \times 10^2$ (min^{-1})
$Cp_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ (C_6D_5Cl)	5	1.35 ± 0.02
	10	2.57 ± 0.05
	15	4.46 ± 0.12
	20	8.25 ± 0.28
$Cp_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ (toluene-d_8)	20	1.10 ± 0.02
	24	1.71 ± 0.03
	29	3.32 ± 0.07
	34	6.55 ± 0.10
$Cp^*_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ (CD_2Cl_2)	−68	0.83 ± 0.01
	−63	1.73 ± 0.02
	−58	3.38 ± 0.06
	−53	5.74 ± 0.22

were found to be 18.8(0.9) kcal/mol, 0.6(3.2) cal/mol·deg, and 18.6(0.9) kcal/mol, respectively.

The zwitterionic complex $Cp_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ also formed cleanly and instantly when $Cp_2ZrMeNp$ was reacted with a slight excess of $B(C_6F_5)_3$ in toluene-d_8 at −10 °C, although concentrations had to be kept lower than in C_6D_5Cl in order to prevent precipitation. The room-temperature resonances of $Cp_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ in toluene-d_8 were δ 5.74 (s, 10H) 0.78 (s, 9H), 1.11 (s, 2H), and 0.19 (s, 3H), assigned to the Cp, neopentyl methyl, Zr−CH_2, and B−Me groups, respectively. This compound was stable below 10 °C in toluene-d_8, but decomposed above 10 °C to give $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ (δ 5.44 (Cp), 0.26 (Zr-Me), 0.10 (B-Me)) and isobutene (δ 4.72 (CH_2), 1.60 (Me)).

A kinetics study of β-Me elimination in toluene-d_8 was carried out as above at 20, 25, 30, and 35 °C, and linear plots of $[(A_o - A_e)/(A_o + A_e)]\ \ln[(A_o^2 - A_tA_e)/(A_oA_t - A_oA_e)]$ vs time (Figure 4)[12] again showed that the β-Me elimination was reversible and first-order with respect

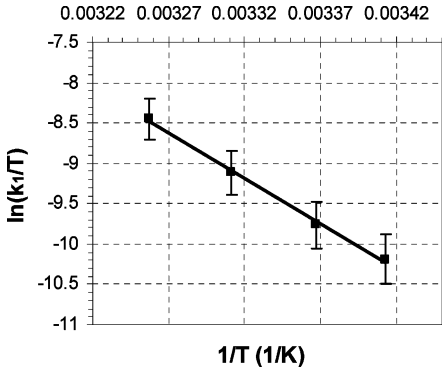


Figure 5. Eyring plot for the decomposition of $Cp_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$ in toluene-d_8.

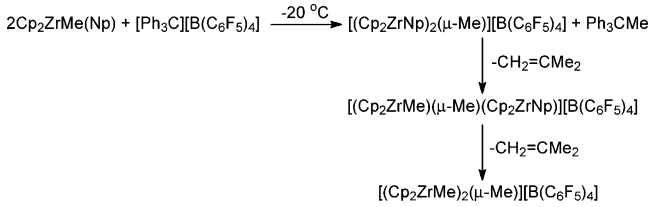
to the concentration of $Cp_2ZrNp(\mu\text{-}Me)B(C_6F_5)_3$. Rate constant data are presented in Table 1. On the basis of the temperature dependence of k_1, an activation energy E_a of 22.9(0.9) kcal/mol was calculated. Activation parameters for the β-Me elimination reaction were determined utilizing an Eyring plot, shown in Figure 5; $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ (0 °C) were found to be 22.3(0.9) kcal/mol, 8.5(3.0) cal/mol·deg, and 20.0(0.9) kcal/mol, respectively. Similar chemistry was observed when $Cp_2ZrNp(\mu\text{-}CH_3)B(C_6F_5)_3$ was treated with 1 equiv of $B(C_6F_5)_3$ in CD_2Cl_2, but side reactions precluded further work.

As mentioned above, the kinetics runs in both toluene-d_8 and C_6D_5Cl appeared to reach equilibrium such that reasonable values of the equilibrium concentrations could be obtained in order to utilize the rate law for the processes. However, we did not attempt to determine the equilibrium constants precisely by, for example, adding excess isobutene at the end of each kinetics run, as this approach with $Cp_2HfNp(\mu\text{-}Me)B(C_6F_5)_3$ resulted in the formation of polyisobutene,[4e] presumably via carbocationic initiation by the cationic hafnium species $[Cp_2HfNp]^+$ or $[Cp_2HfMe]^+$. Either could be a good initiator of isobutene polymerization,[13a] and we had good reason to anticipate that the analogous zirconium compounds would be also.[13b−f] That said, assuming that reasonable values of K_{eq} could be obtained at least approximately from plots of the kinetics data, K_{eq} in C_6D_5Cl increased from ∼0.5 mol·L^{-1} at 5 °C to ∼1.8 mol·L^{-1} at 20 °C in C_6D_5Cl, and from ∼4.1 mol·L^{-1} at 24 °C to ∼17.3 mol·L^{-1} at 34 °C in toluene-d_8. We hesitate to calculate thermodynamic parameters, given the possible uncertainties in values of K_{eq}, but the β-Me elimination process summed in eqs 2 and 3 appears to be moderately endothermic. We are unaware of analogous conclusions being reached elsewhere for this type of reaction.

An attempt to study the kinetics of the β-Me elimination process in the presence of the more weakly coordinating anion $[B(C_6F_5)_4]^-$, utilizing the reaction of $Cp_2ZrMeNp$ and $[Ph_3C][B(C_6F_5)_4]$ in C_6D_5Cl, failed

(13) (a) Baird, M. C. *Chem. Rev.* **2000**, *100*, 1471. For examples of cationic zirconium complexes as isobutene polymerization initiators, see: (b) Carr, A. G.; Dawson, D. M.; Bochmann, M. *Macromolecules* **1998**, *31*, 2035. (c) Carr, A. G.; Dawson, D. M.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1999**, *18*, 2933. (d) Song, X.; Thornton-Pett, M.; Bochmann, M. *Organometallics* **1998**, *17*, 1004. (e) Carr, A. G.; Dawson, D. M.; Bochmann, M. *Macromol. Rapid Commun.* **1998**, *19*, 205. (f) Garrat, S.; Carr, A. G.; Langstein, G.; Bochmann, M. *Macromolecules* **2003**, *36*, 4276.

Scheme 1



because of the preferential formation of the bridged, dinuclear species $[(Cp_2ZrNp)_2(\mu\text{-Me}][B(C_6F_5)_4]$ (δ 6.22 (Cp), 1.15 (C-Me), 0.96 (CH_2), −0.59 (μ-Me)) even in the presence of an excess of $[Ph_3C][B(C_6F_5)_4]$. $\{[Cp_2ZrNp]_2\text{-}CH_3\}\{B(C_6F_5)_4\}$ was found to undergo β-Me elimination to give first $[(Cp_2ZrMe)(\mu\text{-Me})(Cp_2ZrNp)][B(C_6F_5)_4]$ (δ 6.16 (Cp), 1.15 (C-Me), 0.98 (CH_2), −0.64 (μ-Me)) and then $[(Cp_2ZrMe)_2(\mu\text{-Me})][B(C_6F_5)_4]$ (δ 6.05 (Cp), 0.33 (Zr-Me), −0.77 (μ-Me)), as observed previously for the analogous reaction of $Cp_2HfMeNp$.[4g] While the various intermediates could not be isolated, the changes in the NMR spectra were consistent with this sequence of events, and the presence of three resonances at negative chemical shifts shows unequivocally that three distinct μ-Me species are present (see Scheme 1).[14] In view of the complications, our attempt to study this system was abandoned.

In contrast to $Cp_2ZrNp(\mu\text{-}CH_3)B(C_6F_5)_3$ but in general agreement with a previous report,[4c] we find $Cp^*_2ZrNp(\mu\text{-}CH_3)B(C_6F_5)_3$ to be extremely unstable when generated in C_6D_5Cl, toluene-d_8, and CD_2Cl_2. Indeed, it was found that β-Me elimination occurred in CD_2Cl_2 even at −70 °C, below the freezing point of C_6D_5Cl and a temperature at which solubility in toluene-d_8 was minimal. A possibly complicating factor was the presence of a noticeable amount of $Cp^*_2ZrNp_2$ in the material used, but this compound was found to be inert to $B(C_6F_5)_3$ at the temperatures used, and thus its presence was not a problem.

A kinetics study of β-Me elimination from $[Cp^*_2ZrNp(\mu\text{-Me})B(C_6F_5)_3]$ was successfully carried out in CD_2Cl_2 at the temperatures −68, −63, −58, and −53 °C. However, in contrast to the situation with $Cp_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$, establishment of an equilibrium was not observed during β-methyl elimination of $Cp^*_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$, and linear plots of ln A_t vs time (Figure 6) confirmed that the β-Me elimination reaction of this compound is irreversible and first-order with respect to the concentration of $Cp^*_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$. Rate constant data are given in Table 1; on the basis of the temperature dependence of k_{obs}, an activation energy E_a of 11.6(0.4) kcal/mol was calculated. An Eyring plot (Figure 7) resulted in $\Delta H^‡$, $\Delta S^‡$, and $\Delta G^‡$ (0 °C) values of 11.2(0.4) kcal/mol, −12.7(2.0) cal/mol·deg, and 14.7(0.7) kcal/mol, respectively.

The activation parameters for all of the β-methyl elimination reactions studied here and reported in refs 4d and 4e are listed in Table 2. The data for $Cp_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$ in toluene-d_8 compare gratifyingly well with Marks' data for $(1,2\text{-}Me_2Cp)_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$.[4d] Where comparisons are possible, hafnium complexes seem somewhat more labile than their zirconium analogies, but the interplay between $\Delta H^‡$ and $\Delta S^‡$ is clearly

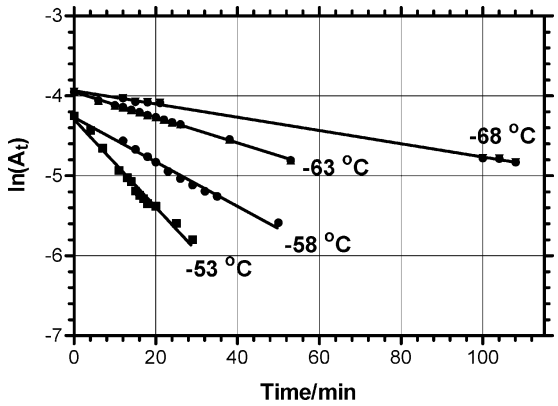


Figure 6. Plot of ln A_t vs T for the decomposition of $Cp^*_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$ in CD_2Cl_2.

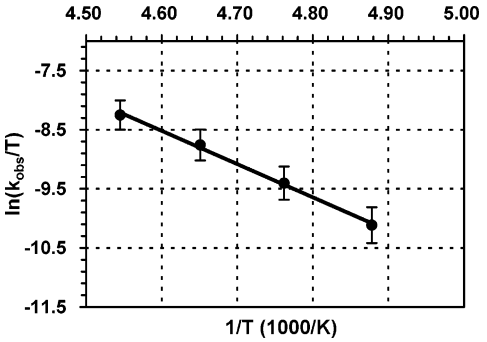
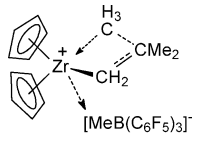


Figure 7. Eyring plot for the decomposition of $Cp^*_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$ in CD_2Cl_2.

complex and, in addition, solvent polarity clearly plays an important role. We have previously suggested that the β-methyl migration reactions under consideration here are accompanied by concomitant, solvent-assisted dissociation of $[BMe(C_6F_5)_3]^-$ anion from the metal, in essence an intramolecular, nucleophilic displacement process as in **B**.[4e] The data in Table 2 are certainly consistent with this proposal since, where comparisons are possible, the values of $\Delta H^‡$ are lower in the more polar solvent C_6D_5Cl than they are in toluene-d_8.



B

This proposal is also clearly consistent with the recent results of Chirik et al.,[4f] who have interpreted significant kinetic isotope effects for β-methyl elimination reactions of a series of deuterated neopentyl zirconocenium compounds in terms of a transition state γ-agostic interaction during the methyl migration reaction. Interestingly, the β-methyl elimination reactions studied by Chirik et al. were all found to be reversible,[4f] as are the analogous reactions of the compounds $Cp_2ZrNp(\mu\text{-Me})B(C_6F_5)_3$ (this work) and $Cp_2HfNp(\mu\text{-Me})B(C_6F_5)_3$.[4e] In contrast the compounds $(1,2\text{-}Me_2Cp)_2MNp(\mu\text{-Me})B(C_6F_5)_3$ (M = Zr, Hf) are reported to undergo irreversible β-methyl elimination reactions, possibly because of steric effects resulting from the presence of the four methyl groups on the rings, although this rationale does not seem overly convincing.[4d]

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

Table 2. Activation Parameters for β-Methyl Elimination Reactions

complex[a]	solvent	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol·K)	$\Delta G^{\ddagger}$ (0 °C) (kcal/mol)	ref
[1,2-Me$_2$Cp$_2$ZrNp]$^+$	toluene-d_8	22.5 ± 0.9	4.3 ± 3.3	21.2 ± 0.2	4d
[1,2-Me$_2$Cp$_2$HfNp]$^+$	toluene-d_8	17.3 ± 0.9	−11.9 ± 3.4	20.7 ± 0.2	4d
[Cp$_2$HfNp]$^+$	toluene-d_8	21.4 ± 1.1	8.0 ± 4.0	19.2 ± 1.1	4e
[Cp$_2$HfNp]$^+$	C$_6$D$_5$Cl	16.5 ± 5	−7.0 ± 18	18.4 ± 5	4e
[Cp$_2$ZrNp]$^+$	toluene-d_8	22.3 ± 0.9	8.5 ± 3.0	20.0 ± 0.9	this work
[Cp$_2$ZrNp]$^+$	C$_6$D$_5$Cl	18.8 ± 0.9	0.6 ± 3.2	18.6 ± 0.9	this work
[Cp*$_2$ZrNp]$^+$	CD$_2$Cl$_2$	11.2 ± 0.4	−12.7 ± 2.0	14.7 ± 0.7	this work

[a] All with [μ-MeB(C$_6$F$_5$)$_3$]$^-$ as counteranion.

Steric factors do appear to be important with the compound Cp*$_2$ZrNp(μ-Me)B(C$_6$F$_5$)$_3$, which exhibits the lowest activation energy, 11.6 kcal/mol in CD$_2$Cl$_2$, of all complexes studied. It may be that the presence of the bulky Cp* ligands helps ease the [BMe(C$_6$F$_5$)$_3$]$^-$ ligand from the inner coordination sphere, thus leading to a lowered value of the activation energy. Consistent with the above rationalization of irreversibility of the β-methyl elimination reactions of the compounds (1,2-Me$_2$Cp)$_2$MNp(μ-Me)B(C$_6$F$_5$)$_3$ (M = Zr, Hf), β-methyl elimination from Cp*$_2$ZrNp(μ-Me)B(C$_6$F$_5$)$_3$ is also irreversible.

In an effort to extend our kinetics studies, we synthesized the isobutyl compounds Cp$_2$Zr(*i*-Bu)Me and Cp*$_2$Zr(*i*-Bu)Me as precursors to Cp$_2$Zr(*i*-Bu)(μ-Me)B(C$_6$F$_5$)$_3$ and Cp*$_2$Zr(*i*-Bu)(μ-Me)B(C$_6$F$_5$)$_3$. The compounds are of interest because of the possibility of a competition between β-hydrogen and β-methyl elimination from Cp$_2$Zr(*i*-Bu)(μ-Me)B(C$_6$F$_5$)$_3$ and Cp*$_2$Zr(*i*-Bu)(μ-Me)B(C$_6$F$_5$)$_3$ and because these compounds provide the simplest models of zirconocenium ions containing polypropylene chains. On the basis of the known modes of chain transfer during propylene polymerizations by the Cp$_2$Zr[1b,i,k] and Cp$_2$*Zr[3] catalyst systems, one might anticipate predominantly β-hydrogen elimination from Cp$_2$Zr(*i*-Bu)(μ-Me)B(C$_6$F$_5$)$_3$ and β-methyl elimination from Cp*$_2$Zr(*i*-Bu)(μ-Me)B(C$_6$F$_5$)$_3$.

Although Cp$_2$Zr(*i*-Bu)Me is a thermally unstable oil at room temperature and could not be purified, reactions of both Cp$_2$Zr(*i*-Bu)Me and Cp*$_2$Zr(*i*-Bu)Me could be carried out with B(C$_6$F$_5$)$_3$ in CD$_2$Cl$_2$ and satisfactorily monitored at −40 and −60 °C, respectively; in both cases the only olefinic product was isobutene. Careful inspection of the NMR spectra indicated that neither free propylene (multiplets at δ ∼5.75, 5.0) nor polypropylene (δ ∼1.75, ∼0.75) were formed, and thus the compounds Cp$_2$Zr(*i*-Bu)(μ-Me)B(C$_6$F$_5$)$_3$ and Cp*$_2$Zr(*i*-Bu)(μ-Me)B(C$_6$F$_5$)$_3$ both undergo only β-hydrogen elimination. This result for Cp*$_2$Zr(*i*-Bu)(μ-Me)B(C$_6$F$_5$)$_3$ is consistent with reports of similar chemistry elsewhere.[11] Unfortunately, kinetics studies could not be carried out because the β-hydrogen elimination reactions of both compounds were too rapid in CD$_2$Cl$_2$ and both compounds oiled out in the less polar solvent toluene-d_8. However, isobutene is nonetheless the only olefinic product formed when Cp*$_2$Zr(*i*-Bu)(μ-Me)B(C$_6$F$_5$)$_3$ is generated in toluene-d_8 at temperatures ranging from −35 to +10 °C, and thus β-hydrogen elimination is a general result with this compound and not an artifact derived from the nature of the solvent.

The fact that no propylene was detected in these experiments, only isobutene, led us to reconsider the mechanism of chain transfer during propylene polymerization by the Cp$_2$*Zr catalyst system. Why is it that β-methyl elimination is the dominant mechanism of chain transfer during propylene polymerization while only β-hydrogen elimination is observed during the thermal degradation of Cp*$_2$Zr(*i*-Bu)(μ-Me)B(C$_6$F$_5$)$_3$? Is it that the steric factors implicit in **A** do not apply when the polymeryl chain is very short?

To assess the latter possibility, molecular mechanics calculations were carried out on the cationic species [Cp*$_2$Zr(isobutyl)]$^+$, and the minimized structure is shown in Figure 8. As is indicated, the preferred conformation is indeed that in which one of the β-methyl groups lies in the plane perpendicular to the Cp(centroid)−Zr−Cp(centroid), while the β-hydrogen atom eclipses a Cp* ring, as depicted above in **A**. One of the hydrogen atoms on the β-methyl group, pictured in red, is situated about 3.08 Å from the zirconium, more than the 2.24 Å calculated for full γ-agostic interactions[2h] but less than the sum of the zirconium and hydrogen van der Waals radii (∼3.5 Å).[15] Interestingly, this γ-hydrogen atom is much closer to the zirconium than is the isobutyl β-hydrogen atom (deep blue), which is about 3.41 Å from the zirconium. Thus the complex cation appears to prefer the conformation believed[3c,e] to be prerequisite to β-methyl elimination, which does not occur.

Conclusions. Our kinetics study on β-methyl elimination reactions of the compounds Cp$_2$ZrNp(μ-Me)B(C$_6$F$_5$)$_3$ (in various solvents) and Cp*$_2$ZrNp(μ-Me)B(C$_6$F$_5$)$_3$ (in CD$_2$Cl$_2$) shows that the reactions are accelerated by polar solvents and by steric crowding in the Cp* system. These results are consistent with previous findings and conclusions and strengthen the case for methyl migration being accompanied in a concerted process by borate anion departure from the inner coordination sphere of the metal cation. Of some

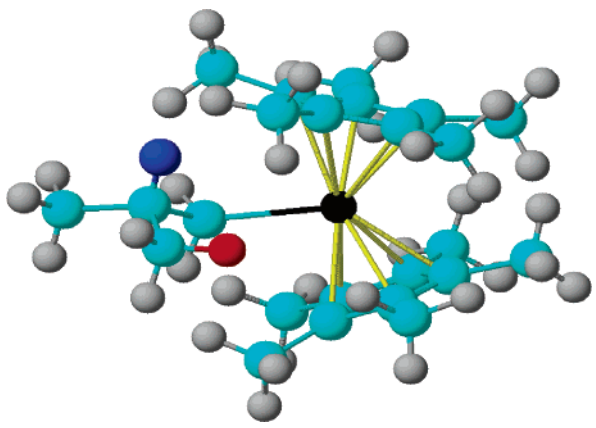


Figure 8. Optimized structure of [Cp*$_2$Zr(isobutyl)]$^+$.

surprise, however, is the finding that the isobutyl compound $Cp^*_2Zr(i\text{-}Bu)(\mu\text{-}Me)B(C_6F_5)_3$, which is expected to undergo β-methyl elimination by analogy with an extensive literature on chain transfer processes during propylene polymerization, in fact undergoes only β-hydrogen elimination. This apparent conundrum will be addressed in the following paper in this issue.[31]

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