Kinetics Study of β-Methyl Elimination from a Metallocene Compound of the Type Cp$_2$HfR(μ-Me)B(C$_6$F$_5$)$_3$ (R = Alkyl)

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*Summary: Variable-temperature kinetics studies of the reversible β-methyl elimination reaction of Cp$_2$Hf(CH$_2$-CMe$_3$)(μ-Me)B(C$_6$F$_5$)$_3$ (**I**) to give Cp$_2$Hf(Me)(μ-Me)B-(C$_6$F$_5$)$_3$ and CH$_2$=CMe$_2$ are reported. Activation enthalpies of 21.3(0.5) and 17.0(0.3) kcal/mol in toluene and chlorobenzene, respectively, are shown to represent the energy barrier for β-methyl migration accompanied by concomitant, solvent-assisted dissociation of [BMe(C$_6$F$_5$)$_3$]$^-$ anion from the metal.*

There has in recent years been extensive research into the use of group 4 metallocene compounds as homogeneous catalysts for alkene polymerization. Among the most successful catalysts are the formally 14-electron, cationic complexes [Cp′$_2$MR]$^+$X$^-$ (Cp′ = functionalized cyclopentadienyl, M = Ti, Zr, Hf; R = alkyl, H; X$^-$ = anion), which contain a vacant coordination site and an alkyl ligand and which can therefore readily take part in Ziegler−Natta polymerization processes with a variety of alkenes.[1] Of great relevance here is the importance of incorporating weakly coordinating counteranions X$^-$ into catalyst systems, which has been studied intensively as it is becoming ever more obvious that facile anion displacement by monomer is crucial if a catalyst is to exhibit high activity.[2]

A great deal of progress has also been made in the development of theoretical models of alkene polymerization, with considerable interest being shown not only in the individual steps involved in initiation and chain propagation, termination, and transfer steps but also in the nature of the resting states and the effects of varying the solvent and counteranions.[3] However, while it is clear that good computational models have greatly enhanced our mechanistic understanding of metallocene catalyst systems, 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 of computational results,[3] including activation energies for β-hydrogen[1] and the much rarer β-methyl elimination reactions,[3b,4] important in chain transfer and chain termination processes.

While β-hydrogen elimination is normally the predominant mode of chain transfer during metallocene-catalyzed alkene polymerization processes,[1] β-methyl elimination seems generally dominant during, for example, propene polymerization by sterically crowded catalysts such as bis-η^5-C$_5$Me$_5$−metal systems.[4] The reasons for the variations in behavior are not clear, but β-methyl elimination probably involves orientation of a growing polymer chain to a conformation in which the migrating methyl group lies between rather than eclipses the sterically demanding η^5-C$_5$Me$_5$ rings.[4d,g] The methyl group would then be in a position to migrate to the LUMO of the metal, while a β-hydrogen atom would not. Both computational and experimental data for β-elimination processes are in short supply; we report here experimental data for β-methyl elimination reactions in a hafnocene system.

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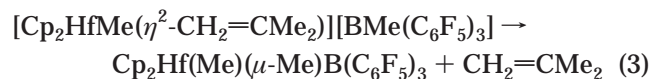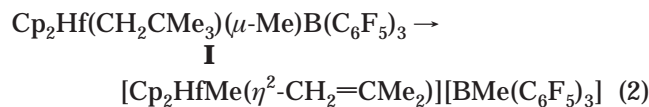
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While investigating the methyl abstraction chemistry in toluene of compounds of the type Cp_2HfMeR (R = alkyl) with various electrophiles, as shown in eq 1, we

$$Cp_2HfMeR + B(C_6F_5)_3 \rightarrow Cp_2HfR(\mu\text{-Me})B(C_6F_5)_3 \quad (1)$$
$$\mathbf{I}$$
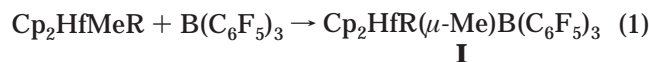
found that the new compound $Cp_2HfMe(CH_2CMe_3)$[5] undergoes methyl abstraction to form $Cp_2Hf(CH_2CMe_3)$-$(\mu\text{-Me})B(C_6F_5)_3$ (**I**).[5] The latter is stable at −30 °C but undergoes β-methyl elimination at higher temperatures to form $Cp_2HfMe(\mu\text{-Me})B(C_6F_5)_3$, presumably via an undetected η^2-isobutene intermediate (eqs 2 and 3).

$$Cp_2Hf(CH_2CMe_3)(\mu\text{-Me})B(C_6F_5)_3 \rightarrow$$
$$\mathbf{I}$$
$$[Cp_2HfMe(\eta^2\text{-CH}_2{=}CMe_2)][BMe(C_6F_5)_3] \quad (2)$$

$$[Cp_2HfMe(\eta^2\text{-CH}_2{=}CMe_2)][BMe(C_6F_5)_3] \rightarrow$$
$$Cp_2Hf(Me)(\mu\text{-Me})B(C_6F_5)_3 + CH_2{=}CMe_2 \quad (3)$$

Similar β-methyl elimination reactions from neopentylzirconium compounds have been noted previously[4h] and are of growing interest in general.[4] Thus when the β-methyl elimination process here was found to proceed at a convenient rate in toluene in the temperature range 0−20 °C, a kinetics study was undertaken with a view to obtaining reliable activation data. While this work was in progress, Beswick and Marks reported a similar kinetics study for the complexes $(1,2\text{-Me}_2Cp)_2M(CH_2\text{-}CMe_3)(\mu\text{-Me})B(C_6F_5)_3$ (M = Zr, Hf), also in toluene.[2k]

Kinetics studies of β-methyl elimination from **I** were carried out in toluene-d_8 by careful monitoring of the decay of the Cp resonance of **I** using ^1H NMR spectroscopy.[5] At 0 °C, the formation of isobutene (IB) resulting from β-methyl elimination from **I** (eqs 2 and 3) was indicated by growth of the resonances of $Cp_2HfMe(\mu\text{-}Me)B(C_6F_5)_3$[5] and IB ($\delta$ 4.74 (CH_2), 1.61 (Me)), accompanied by diminution of the resonances of **I**. Although the chemical shifts are all somewhat temperature dependent, the reaction is quite clean in the temperature range 0−20 °C and kinetics data were obtained at 0, 5, 10, 15, and 20 °C. Interestingly, the β-methyl elimination reactions all reached equilibrium within 4 half-lives, an unexpected difference between this system and $(1,2\text{-Me}_2Cp)_2M(CH_2CMe_3)(\mu\text{-Me})B(C_6F_5)_3$.[2k] Unfortunately, addition of excess IB to an equilibrated reaction mixture in an effort to measure the equilibrium constant resulted in polymerization, presumably via a carbocationic process.[6]

Linear plots of $\ln(A_0 - A_e)/(A_t - A_e)$ vs time[7] (Figure 1) indicate that the β-methyl elimination process is reversible and first order in **I** in the temperature range 0−20 °C; on the basis of the temperature dependence of k_{obs}, an activation energy E_a of 21.9(0.6) kcal/mol was calculated. In Figure 2 is shown a plot of $\ln(k/T)$ vs $1/T$, from which $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ (0 °C) were found to be 21.3(0.5) kcal/mol, 9.0(0.8) cal/mol, and 18.9(0.3) kcal/mol, respectively. These data may be compared with 17.3(0.9) kcal/mol, −11.9(3.4) cal/mol and 20.7(0.2) kcal/
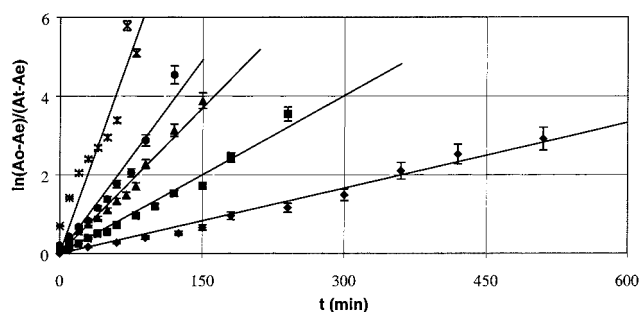

Figure 1. Plot of $\ln(A_0 - A_e)/(A_t - A_e)$ vs time for the β-methyl migration reaction in toluene-d_8.
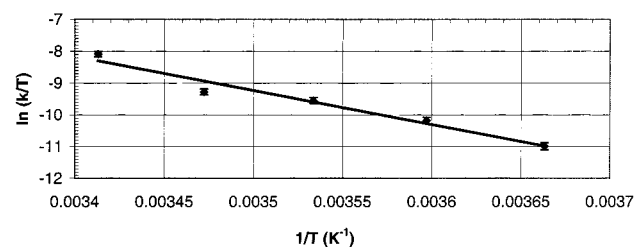

Figure 2. Plot of $\ln(k/T)$ vs $1/T$ based on observed reaction rates in toluene-d_8.

mol, respectively, for the irreversible β-methyl elimination reaction of $(1,2\text{-Me}_2Cp)_2M(CH_2CMe_3)(\mu\text{-Me})B(C_6F_5)_3$ in toluene,[2k] and the activation enthalpy may be compared with calculated values of ΔE of 16−26 kcal/mol, depending on the methodology used, for methyl migration involving the complex $[(H_2SiCp_2)HfCH_2CH_2Me]^+$.[3a] However, it does not seem likely that we are measuring specifically the intrinsic barrier to methyl migration in **I**.

The 1,2-migration under consideration is strongly inhibited if the borane-induced methyl abstraction reaction of $Cp_2HfMe(CH_2CMe_3)$ is carried out in the presence of Lewis bases as weak as ethyl ether. Similar results have been reported for zirconium analogues,[4h] and clearly complexes of the type $[Cp_2M(L)CH_2CMe_3]^+$ (L = ligand) are stabilized with respect to methyl migration by blockage by a ligand L of the migrating methyl terminus. Presumably, therefore, the migration step involves at least a degree of prior or concomitant dissociation of the $[BMe(C_6F_5)_3]^-$ anion from the metal en route to the presumed intermediate $[Cp_2Hf(Me)(\eta^2\text{-}CH_2{=}CMe_2)][BMe(C_6F_5)_3]$, and it seemed in fact possible that the activation parameters measured were to be attributed *primarily* to the requirements of anion dissociation. Indeed, enthalpy requirements for complete dissociation of the borate anion $[BMe(C_6F_5)_3]^-$ from metallocene cations $[Cp_2MR]^+$ have been estimated as 40−50 kcal/mol in the gas phase, <20 kcal/mol in toluene, and <10 kcal/mol in chorobenzene, depending on the theoretical model chosen.[3a,c,d,g] Thus, solvent effects are expected to be important and might be expected to shed light on the issue.

Therefore, on the premise that ion separation should be more facile in polar solvents, a similar kinetics study of the β-methyl elimination reaction of **I** was conducted in the more polar C_6D_5Cl over the temperature range −5 to +10 °C. The resulting linear plots of $\ln(A_0 - A_e)/(A_t - A_e)$ vs time (Figure 3) again indicated that the reaction is reversible and first order in **I**, this time with

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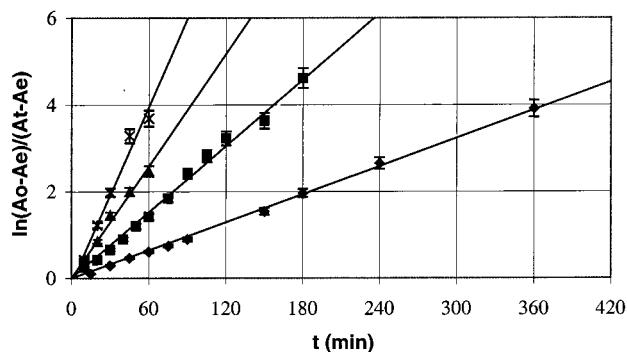
Figure 3. Plot of $\ln(A_o - A_e)/(A_t - A_e)$ vs time for the β-methyl migration reaction in C_6D_5Cl.
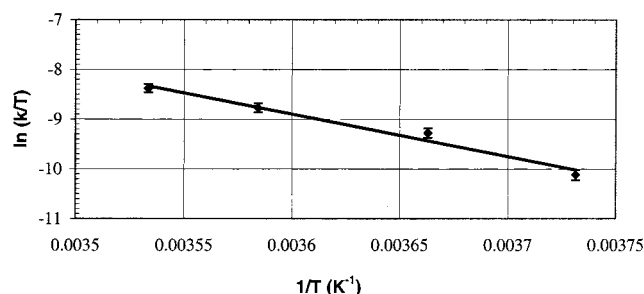

Figure 4. Plot of $\ln(k/T)$ vs $1/T$ based on observed reaction rates in C_6D_5Cl.

an activation energy E_a of 17.5(0.4) kcal/mol. Figure 4 shows plots of $\ln(k/T)$ vs $1/T$, from which $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ (0 °C) were found to be 17.0(0.3) kcal/mol, $-3.9(0.2)$ cal/mol, and 18.0(0.3) kcal/mol, respectively. Comparison with theoretical findings[3a,c,d,g] suggests that the values of $\Delta H^{\ddagger}$ in both toluene and chlorobenzene are too high for pure borate dissociation to be rate determining.

Highly relevant to the issue of anion dissociation are two complementary experimental investigations which have appeared recently. Marks et al.[2b,d–g,j–l] have utilized elegant NMR studies to determine enthalpies of activation for apparent unimolecular dissociation-recombination reactions of $[BMe(C_6F_5)_3]^-$ in the complexes $(1,2-Me_2C_5H_3)_2MR(\mu-Me)B(C_6F_5)_3$ (M = Zr, Hf; R = Me, CH_2CMe_3, CH_2SiMe_3, $CH(SiMe_3)_2$). While their measured values of $\Delta H^{\ddagger}$ in toluene are comparable to the activation enthalpy observed here when R = Me ($\sim$22 kcal/mol when M = Zr, >22 kcal/mol when M = Hf),[2k] $\Delta H^{\ddagger}$ for dissociation–recombination of $(1,2-Me_2C_5H_3)_2Hf(CH_2CMe_3)(\mu-Me)B(C_6F_5)_3$ is only $\sim$12 kcal/mol in toluene,[2k] apparently because the sterically very demanding neopentyl ligand weakens considerably the Hf–borate interaction. This value of $\Delta H^{\ddagger}$ for dissociation–recombination is considerably less than the values of $\Delta H^{\ddagger}$ observed for methyl migration here for $Cp_2Hf(CH_2CMe_3)(\mu-Me)B(C_6F_5)_3$ and elsewhere[2k] for the very similar $(1,2-Me_2C_5H_3)_2Hf(CH_2CMe_3)(\mu-Me)B(C_6F_5)_3$, and it seems very unlikely that the processes of dissociation–recombination[2b,d–g,j–l] and methyl migration involve $[BMe(C_6F_5)_3]^-$ dissociation as a common rate-determining step. Activation data for dissociation–recombination reactions of the neopentyl compound $(1,2-Me_2C_5H_3)_2Hf(CH_2CMe_3)(\mu-Me)B(C_6F_5)_3$ in solvents other than toluene are unfortunately not available, although $\Delta H^{\ddagger}$ for the very similar compound $(1,2-Me_2C_5H_3)_2Hf(CH_2SiMe_3)(\mu-Me)B(C_6F_5)_3$ decreases from $\sim$15 kcal/mol in toluene-d_8

to $\sim$11 kcal/mol in CD_2Cl_2.[2k] Thus, these dissociation–recombination processes are also strongly solvent-assisted, consistent with theoretical considerations.[3a,d,g]

In work which bears an apparent relationship to that reported here, Brintzinger et al. have reported thermodynamic and kinetics data for reactions involving displacement in benzene of the $[BMe(C_6F_5)_3]^-$ anion by Lewis bases from a series of methylzirconocene cations (as in eq 4).[8] Interestingly, the reactions are associative,

$$Cp'_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3 + L \rightarrow$$
$$[Cp'_2ZrMe(L)][BMe(C_6F_5)_3] \quad (4)$$
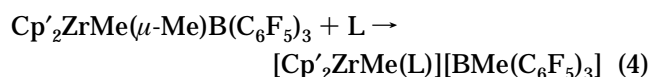
proceeding via five-coordinate intermediates, and most exhibit $\Delta H^{\ddagger}$ values in the range $\sim$13–20 kcal/mol. If one considers the intramolecular methyl migration reaction of eq 2 to be a quintessential example of an associative displacement of the $[BMe(C_6F_5)_3]^-$ anion (by the methide anion), as in **A**, then the similarities in activation

A
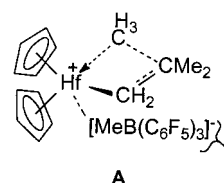
parameters may well be significant. Unfortunately, no hafnium complexes were examined, and thus direct comparisons with our results cannot be made.

Examination of borane abstraction from the analogous isobutyl compound $Cp_2HfMe(CH_2CHMe_2)$ has also been initiated in toluene and chlorobenzene, and a previous report[4f] that only β-hydrogen elimination occurs in this type of system was confirmed. To this point, unfortunately, we have been unable to obtain reliable kinetics data; however, we are pursuing similar experiments with $Cp-C_5Me_5$ and $(C_5Me_5)_2$ hafnium and zirconium systems.

In summary, the activation parameters obtained here and elsewhere[2k] for β-methyl migration reactions of neopentylhafnocene complexes apparently provide information pertinent to the migration step of eq 2, albeit influenced by solvent effects during the concomitant loosening of the hafnium–borate linkage. Activation data of the types discussed and compared above for all three processes, methyl migration, borate dissociation–recombination and borate substitution, can be expected to provide useful benchmarks for future theoretical research.

Supporting Information Available: Text giving information concerning the synthesis and characterization of the new compound $Cp_2HfMe(CH_2CMe_3)$, in addition to procedures for the kinetics studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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