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Metal-Alkyl Group Effects on the Thermodynamic Stability and Stereochemical Mobility of $B(C_6F_5)_3$-Derived Zr and Hf Metallocenium Ion-Pairs

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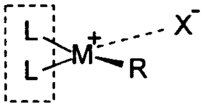
Abstract: This paper reports significant dependence of ion-pair formation energetics and stereomutation rates upon the metal-bound alkyl substituent (R) and the solvent dielectric constant in the metallocenium series $(1,2\text{-}Me_2Cp)_2MR^+\ MeB(C_6F_5)_3^-$ where R = Me, $CH_2{}^tBu$, CH_2TMS, $CH(TMS)_2$, and M = Zr and Hf, as determined by reaction titration calorimetry and dynamic NMR spectroscopy. For the ion-pair forming reaction, $(1,2\text{-}Me_2Cp)_2M(R)Me + B(C_6F_5)_3 \rightarrow (1,2\text{-}Me_2Cp)_2MR^+\ MeB(C_6F_5)_3^-$, enthalpies in toluene solution at 25 °C for M = Zr and R = Me, CH_2TMS, and $CH(TMS)_2$ are −24.6(0.8), −22.6(1.0), and −59.2(1.4) kcal/mol, respectively. Corresponding values for M = Hf and R = Me and CH_2TMS are −20.8(0.5) and −31.1(1.6) kcal/mol, respectively. $\Delta H^\ddagger_{\text{reorg}}$ values for the reorganization process that interchanges the ion-pair enantiotopic sites for M = Zr and R = Me, $CH_2{}^tBu$, CH_2TMS, and $CH(TMS)_2$ are 22(1), 18(1), 17(1), and 9(2) kcal/mol, respectively. Corresponding $\Delta H^\ddagger_{\text{reorg}}$ values for M = Hf and R = Me, $CH_2{}^tBu$, and CH_2TMS are >24, 12(3), and 15(2) kcal/mol, respectively. $\Delta H^\ddagger_{\text{reorg}}$ values are highest in low dielectric constant solvents such as C_6D_{12}. Activation parameters for β-Me elimination in the complexes $(1,2\text{-}Me_2Cp)_2MCH_2{}^tBu^+\ MeB(C_6F_5)_3^-$ for M = Zr and Hf are found to be $\Delta H^\ddagger_{\beta-\text{Me}} = 22.5(0.9)$ and 17.3(0.9) kcal/mol, and $\Delta S^\ddagger_{\beta-\text{Me}} = 4.3(3.3)$ and −11.9(3.4) cal/mol·K, respectively.

Introduction

Metal-mediated olefin polymerization catalysis has experienced vast growth since pioneering discoveries were made in the 1950s which showed that systems such as $TiCl_4/AlClEt_2$ promote the polymerization of ethylene to high-density polyethylene[1] and propylene to stereoregular polypropylene.[2] More recently, homogeneous "single-site" systems that provide high activity, narrow product polydispersities, and control over macromolecular architecture, and lend themselves to experimental characterization have fueled intense basic and applied research efforts.[3] Homogeneous group 4 catalyst systems represented by **I** embody many of the elements required for an active olefin polymerization catalyst, including an appropriate ancillary ligand framework (L_2), an electron-deficient and coordinatively unsaturated metal center (M), an effective cocatalyst/weakly coordinating counteranion (X^-), and appropriate conditions of temperature, pressure, and solvent.[3,4]

I



The versatility of metallocene ligation and a counteranion offers access to structures providing a wide range of symmetries, activities, and enchainment stereocontrol mechanisms.[3−5] Recent advances in nonmetallocene ligation for late and early transition metals are also promising.[3c,6] The role of the central metal has also been investigated, and although the Ziegler−Natta termi-

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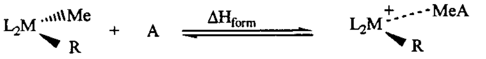
nology has traditionally referred to Ti, Zr, and Hf catalysts, some characteristics of these systems are also observable in later transition metal,[3c,6] lanthanide,[7] and actinide catalysts.[4d,8] Finally, in the past decade, cocatalyst research, building upon the initial discovery of methylalumoxane (MAO),[9] has blossomed with the introduction of fluoroaryl boron,[4,10] aluminum,[4c] and other cation−anion reagents[11] capable of stoichiometric precatalyst activation.

Previous work in our laboratory focused on acquiring and quantitatively analyzing energetic information describing the stability and structural dynamics of **I** as a function of ancillary ligation, borane Lewis acidity, metal identity, and solvent dielectric constant in such a manner as to vary only one component while other variables were held constant.[4]



(1)

(2)

Ion-pair formation exothermicity as in eq 1, ion pair reorganization rates as were quantified in eq 2, and where applicable, olefin polymerization activities were found to be promoted by sterically encumbered, electron-donating ancillary ligation such as $(Me_5Cp)_2$, strongly Lewis acidic boranes such as $B(C_6F_5)_3$, and Zr complexes over Hf analogues. Ion-pair reorganization barriers were found to be lower in higher dielectric constant solvents such as CH_2Cl_2, in comparison with less polar media such as toluene. Furthermore, catalyst formation energetics were found to be highly sensitive to small changes in the structural components enumerated above. For instance, modification of a *single* aryl ring in $B(C_6F_5)_2Ar$ can alter $(1,2\text{-}Me_2Cp)_2ZrMe_2$ methide abstraction enthalpies by as much as 14 kcal/mol.[4b] Armed with quantitative thermodynamic and kinetic information, the rational design of more reactive, selective, and thermodynamically stable catalyst systems becomes more realistic. To this point in our investigation, the metal-hydrocarbyl substituent (R) of the metallocenium ion pair has remained fixed with R = Me in all systems studied. However, the R influence on ion-pair formation/reorganization processes is potentially sizable in view of the close spacial proximity of R to the catalytic center. Considering that the R metal substituent is a growing polymer chain at most times during the olefin polymerization process, the influence of this substituent is expected to be of great relevance to catalyst performance.[5,12,13]

In this paper, we present a full discussion of the influence of the metallocenium metal alkyl substituent on ion-pair formation (eq 1) and ion-pair reorganization (eq 2) processes in solvents of varying dielectric constant for a series of complexes of the formula $(1,2\text{-}Me_2Cp)_2MR^+\ MeB(C_6F_5)_3^-$ where R = Me, $CH_2{}^t$-Bu, CH_2TMS, and $CH(TMS)_2$, and M = Zr and Hf. It will be seen that these processes are highly sensitive to the exact structure of the alkyl substituent, suggesting that the thermodynamic and structural dynamic behavior of “real world” single-site catalysts will be equally sensitive to the nature of a propagating polymer chain. We also report the first kinetic study of metallocenium β-methyl elimination for the system where R = $CH_2{}^tBu$.

Experimental Section

General Considerations. All organometallic complexes were prepared and handled under air- and moisture-free conditions using a circulating nitrogen-filled glovebox operating at <0.1 ppm oxygen (Vacuum Atmospheres) or a vacuum line operating at $<10^{-5}$ Torr with argon purified by passing through supported MnO and molecular sieve columns, or by standard Schlenk line techniques. Routine NMR characterization experiments were carried out on Varian Gemini 300, VXRS 300, Unity 400, or Unity 500 Plus instruments. Notations for describing NMR features are s = singlet, d = doublet, t = triplet, q = quartet, br = broad; the notation “” refers to the appearance to the eye of what may be a more complex multiplet. Variable-temperature ^1H NMR experiments were carried out on the VXR 300 instrument using a 5-mm detection probe calibrated with methanol or ethylene glycol temperature standards. NMR line shape analyses followed standard methods.[14] NMR tubes fitted with Teflon valves were loaded with precisely known quantities of solid samples in the glovebox and then interfaced to a high vacuum line where dry, deoxygenated solvent (~0.6 mL) was vacuum-transferred in, resulting in concentrations of approximately 5−10 mM. All solvents were dried over appropriate drying agents. Elemental analyses were performed by Midwest Microlab (Indianapolis, IN).

Starting Materials and Reagents. Tris(pentafluorophenyl)borane was obtained as a gift from the Dow Chemical Company (Freeport, TX) or was synthesized according to literature procedures.[15] The borane was purified by recrystallization from pentane at −30 °C followed by high vacuum sublimation (80 °C/10^{-5} Torr). LiNp was prepared by a procedure similar to that of Schrock[16,17] except Li powder (Aldrich, <0.5% Na) was used to shorten the reaction time to 1 day. The

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preparation of [(1,2-Me$_2$Cp)$_2$ZrMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (**5a**)[4b] and the analogous Hf complex (**6a**) have been previously described.[4b]

Reaction Calorimetry. Enthalpies of reaction between metallocenes and B(C$_6$F$_5$)$_3$ were determined at 25.0 °C in toluene solution. B(C$_6$F$_5$)$_3$ solutions were prepared by vacuum transferring sufficient toluene from Na/K onto the pure solute to prepare 100 mL (nominal) of solution, while solutions of organometallic complexes having precisely known concentrations were prepared with Na/K-dried toluene in the glovebox. The organometallic titrant was metered into the stirred excess Lewis acid solution using a calibrated buret controlled by a clutched synchronous motor, and temperature changes were recorded using a precision thermistor amplified by a Wheatstone bridge interfaced to an analogue recorder. The calorimeter heat capacity was determined by monitoring temperature changes when heat was introduced with a calibrated resistive heater. Each run consisted of several sequential titrations carried out for each reaction; the mean average deviation is reported for each value. Overall instrument calibrations using established methods[18] ruled out significant sources of systematic error. Other details of the techniques and apparatus for carrying out the calorimetric measurements have been described elsewhere.[19] Data analysis followed standard published methods.[20]

Chlorobis(1,2-dimethylcyclopentadienyl)methylzirconium(IV) (1). Bis(1,2-dimethylcyclopentadienyl)dimethylzirconium(IV)[4b,17] (480 mg, 1.6 mmol) and toluene (100 mL) were added to a vacuum reaction flask. While stirring at 25 °C, HCl gas (1.6 mmol) was slowly introduced over the course of 2 days. Volatile components were then removed under vacuum. The residual crude solid was recrystallized from toluene, resulting in colorless, analytically pure product (351 mg). Yield, 73%. ^{1}H NMR (C$_6$D$_6$): δ 5.62 ("t", 2 H), 5.41 ("t", 2 H), 5.18 ("t", 2 H), 1.99 (s, 6 H), 1.93 (s, 9 H), 0.26 (s, 3 H). ^{13}C NMR (C$_6$D$_6$): δ 125.1 (**C**CH$_3$), 124.3 (**C**CH$_3$), 114.6 (**C**H), 108.8 (**C**H), 104.7 (**C**H), 31.5 (Zr**C**H$_3$), 13.6 (C**C**H$_3$), 13.2 (C**C**H$_3$). Anal. Calcd for C$_{15}$H$_{21}$ClZr: C, 54.92; H, 6.47. Found: C, 54.36; H, 6.39; and C, 54.30; H, 6.44.

Chlorobis(1,2-dimethylcyclopentadienyl)methylhafnium(IV) (2). The following preparation is analogous to that of **1**. Bis(1,2-dimethylcyclopentadienyl)dimethylhafnium(IV) (2.37 g, 6.0 mmol) and toluene (150 mL) were added to a vacuum reaction flask. While stirring at 25 °C, HCl gas (6.0 mmol) was slowly introduced over the course of six days. Volatile components were then removed under vacuum. The residual crude solid was recrystallized from toluene, resulting in colorless, analytically pure product (2.08 g). Yield, 83%. ^{1}H NMR (C$_6$D$_6$): δ 5.54 ("t", 2 H), 5.38 ("t", 2 H), 5.14 ("t", 2 H), 2.00 (s, 6 H), 1.95 (s, 9 H), 0.08 (s, 3 H). ^{13}C NMR (C$_6$D$_6$): δ 123.6 (**C**CH$_3$), 122.8 (**C**CH$_3$), 113.8 (**C**H), 108.5 (**C**H), 103.7 (**C**H), 33.2 (Hf**C**H$_3$), 13.5 (C**C**H$_3$), 13.1 (C**C**H$_3$). Anal. Calcd for C$_{15}$H$_{21}$ClHf: C, 43.38; H, 5.11. Found: C, 43.28; H, 5.21; and C, 43.20; H, 5.12.

Bis(1,2-dimethylcyclopentadienyl)methyl(neopentyl)zirconium(IV) (3b). Pentane (50 mL) was slowly added with stirring to chlorobis(1,2-dimethylcyclopentadienyl)(methyl)-zirconium(IV) (0.80 g, 2.45 mmol) and lithium neopentyl (0.20 g, 2.45 mmol) in a Schlenk flask cooled to −78 °C. The solution was then allowed to warm to 0 °C and stirred for 5 h. The solvent was then removed under vacuum. The resulting crude solid was recrystallized from pentane, resulting in the pale yellow, crystalline product (0.49 g, 1.34 mmol). Yield, 55%. ^{1}H NMR (C$_6$D$_6$): δ 6.40 ("t", 2 H), 5.50 ("t", 2 H), 4.90 ("t", 2 H), 1.99 (s, 6 H), 1.64 (s, 6 H), 1.11 (s, 9 H), 0.35 (s, 2 H), −0.39 (s, 3 H). ^{13}C NMR (C$_6$D$_6$): δ 122.2 (**C**CH$_3$), 121.0 (**C**CH$_3$), 113.6 (**C**H), 106.2 (**C**H), 103.2 (**C**H), 73.0 (Zr**C**H$_2$), 37.5 (Zr**C**H$_3$), 35.9 (**C**H$_3$), 35.6 (**C**CH$_3$), 13.3 (C**C**H$_3$), 12.9 (C**C**H$_3$). Anal. Calcd for C$_{20}$H$_{32}$Zr: C, 66.04; H, 8.89. Found: C, 64.47; H, 8.71; and C, 64.68; H, 8.75.

Bis(1,2-dimethylcyclopentadienyl)methyl(neopentyl)hafnium(IV) (4b). Chlorobis-(1,2-dimethylcyclopentadienyl)(methyl)hafnium(IV) (**2**) (0.81 g, 1.96 mmol) and lithium neopentyl (0.17 g, 2.17 mmol) were added to a Schlenk flask along with pentane (50 mL) at 25 °C. The solution was stirred for 2 days after which time the solution was separated from a small amount of precipitated solid by filtration. The clear solution was cooled to obtain a white crystalline solid which was later sublimed (90 °C/10^{-5} Torr) to afford the analytically pure product (0.63 g, 1.41 mmol). Yield, 72%. ^{1}H NMR (C$_6$D$_6$): δ 6.23 ("t", 2 H), 5.45 ("t", 2 H), 4.93 ("t", 2 H), 2.00 (s, 6 H), 1.65 (s, 6 H), 1.10 (s, 9 H), 0.10 (s, 2 H), −0.54 (s, 3 H). ^{13}C NMR (C$_6$D$_6$): δ 121.2 (s, **C**CH$_3$), 120.4 (s, **C**CH$_3$), 113.5 (d, 170 Hz, **C**H), 106.5 (d, 168 Hz, **C**H), 102.7 (d, 171 Hz, **C**H), 74.9 (t, 106 Hz, Hf**C**H$_2$), 38.3 (q, 115 Hz, Zr**C**H$_3$), 36.4 (q, 122 Hz, **C**H$_3$), 36.2 (s, **C**CH$_3$), 13.2 (q, 126 Hz, C**C**H$_3$), 12.8 (q, 126 Hz, C**C**H$_3$). Anal. Calcd for C$_{20}$H$_{32}$Hf: C, 53.26; H, 7.17. Found: C, 53.05; H, 7.16; and C, 52.78; H, 6.99.

Bis(1,2-dimethylcyclopentadienyl)(neopentyl)zirconium(IV) Methyltrispentafluoro-phenylborate (5b). This complex was prepared in situ at low temperature due to the propensity for β-methyl elimination, resulting in complex **5a** and isobutene. Bis(1,2-dimethylcyclopentadienyl)methyl(neopentyl)zirconium(IV) (**3b**) (3.6 mg, 0.010 mmol) and tris(pentafluorophenyl)borane (6.6 mg, 0.012 mmol) were loaded into a Teflon valved NMR tube in the glovebox. Toluene-*d*$_8$ (dried over Na/K alloy) was next transferred in at −78 °C. The clear yellow solution was then used for variable-temperature NMR experiments. Above 0 °C, the solution turns to a faint yellow and the ^{1}H NMR is indicative of β-elimination. ^{1}H NMR (C$_7$D$_8$, −40 °C): δ 5.96 ("t", 2.59 Hz, 2 H), 5.31 ("t", 3.09 Hz, 2 H), 5.11 ("t", 2.15 Hz, 2 H), 1.50 (s, 6 H), 1.27 (s, 6 H), 1.22 (s, 2 H), 0.89 (s, 9 H), 0.06 (br, 3 H). The β-methyl elimination products appear as follows: **5a**: ^{1}H NMR (C$_6$D$_6$, RT): δ 5.51 ("t", 2.86 Hz, 2 H), 5.27 ("t", 3.06 Hz, 2 H), 4.83 ("t", 2.77 Hz, 2 H), 1.53 (s, 6 H), 1.23 (s, 6 H), 0.10 (s, 3 H), 0.03 (br, 3 H). ^{19}F NMR (C$_6$D$_6$, RT): δ −126.0 (d, $^3J_{FF}$ = 21.26 Hz), −150.1 (t, $^3J_{FF}$ = 20.51 Hz), −155.0 ("t", 19.26 Hz). Isobutene: ^{1}H NMR (C$_6$D$_6$, RT) δ 4.74 (m, 2 H), 1.59 ("t", 6 H).

Bis(1,2-dimethylcyclopentadienyl)(neopentyl)hafnium(IV) Methyltrispentafluoro-phenylborate (6b). The in situ preparation is analogous to that for the related Zr complex **5b** with a similar excess of B(C$_6$F$_5$)$_3$. The hafnium complex also undergoes β-methyl elimination to form **6a** and one equivalent of isobutene near 0 °C. ^{1}H NMR (C$_7$D$_8$, −36 °C): δ 5.65 ("t", 2.54 Hz, 2 H), 5.33 ("t", 2.89 Hz, 2 H), 5.19 ("t", 2.31 Hz, 2 H), 1.48 (s, 6 H), 1.32 (s, 6 H), 1.01 (s, 2 H), 0.90 (s, 9 H), 0.30 (br, 3 H).

Chlorobis(1,2-dimethylcyclopentadienyl)(trimethylsilylmethyl)zirconium(IV). A solution of trimethylsilylmethylmagnesium chloride (Aldrich, 1.0 M in Et$_2$O, 8.0 mL, 8.0 mmol) diluted with Et$_2$O (20 mL) was added dropwise over a period of 1 h to a stirred solution of dichlorobis(1,2-dimethylcyclopentadienyl)zirconium(IV)[17] (2.81 g, 8.1 mmol), in a mixture of CH$_2$Cl$_2$ (30 mL) and Et$_2$O (30 mL) at 0 °C. After stirring for 12 h, the solvent was removed under reduced pressure and the remaining solid was triturated with a pentane-toluene solution (1:2). The crude solid recovered after removing the solvent was recrystallized (2×) from toluene. The product was recovered as fine, colorless needlelike crystals (0.77 g). Yield, 24%. ^{1}H NMR (C$_6$D$_6$): δ 6.33 ("t", 2 H), 5.22 ("t", 2 H), 5.14 ("t", 2 H), 2.08 (s, 6 H), 1.80 (s, 6 H), 0.74 (s, 2 H), 0.09 (s, 9 H). ^{13}C NMR (C$_6$D$_6$): δ 125.8 (**C**CH$_3$), 125.1 (**C**CH$_3$), 116.7 (**C**H), 106.8 (**C**H), 104.4 (**C**H), 46.2 (**C**H$_2$), 13.7 (C**C**H$_3$), 13.5 (C**C**H$_3$), 3.6 (Si**C**H$_3$). Anal. Calcd for C$_{18}$H$_{29}$ClSiZr: C, 54.01; H, 7.32. Found: C, 53.33; H, 7.20; and C, 53.37; H, 7.21.

Chlorobis(1,2-dimethylcyclopentadienyl)(trimethylsilylmethyl)hafnium(IV). A solution of trimethylsilylmethyllithium (Aldrich, 6.0 mL, 1.0 M in pentane, 6.0 mmol) was added dropwise to a stirred solution of dichlorobis(1,2-dimethylcyclopentadienyl)hafnium(IV)[4b] (2.52 g, 5.79 mmol) in Et$_2$O (80 mL) at −78 °C. The mixture was then allowed to warm to 25 °C. After stirring overnight, the solvent was removed under vacuum. Toluene (3 × 15 mL) was added to the remaining solid residue, the resulting solution was filtered to remove

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solid byproducts, and then the solvent was removed under vacuum. The remaining crude solid was recrystallized from toluene. The analytically pure product was recovered as a colorless crystalline solid (1.97 g, 4.05 mmol). Yield, 70%. ^{1}H NMR (C$_6$D$_6$): δ 6.25 ("t", 2 H), 5.18 ("t", 2 H), 5.17 ("t", 2 H), 2.13 (s, 6 H), 1.84 (s, 2 H), 0.34 (s, 2H), 0.15 (s, 9 H). ^{13}C NMR (C$_6$D$_6$): δ 123.2 (**C**CH$_3$), 124.3 (**C**CH$_3$), 116.7 (d, 170.8 Hz, **C**H), 106.7 (d, 169.5 Hz, **C**H), 105.8 (d, 172.0 Hz, **C**H), 43.39 (t, 105.4 Hz, **C**H$_2$), 13.6 (q, 127.1 Hz, C**C**H$_3$), 13.3 (q, 127.3 Hz, C**C**H$_3$), 3.9 (q, 117.2 Hz, Si**C**H$_3$). Anal. Calcd for C$_{18}$H$_{29}$ClSiHf: C, 44.35; H, 6.00. Found: C, 44.53; H, 5.98; and C, 44.66; H, 6.06.

Bis(1,2-dimethylcyclopentadienyl)methyl(trimethylsilylmethyl)zirconium(IV) (3c). Method A. A solution of methyllithium (Aldrich, 1.4 M in Et$_2$O, 2.5 mL, 3.5 mmol) diluted with Et$_2$O (10 mL) was added dropwise to a stirred solution of chlorobis(1,2-dimethylcyclopentadienyl)(trimethylsilylmethyl)zirconium(IV) (0.80 g, 2.0 mmol) in toluene (30 mL) at 0 °C. After stirring for 5 h, the solvent was removed under reduced pressure and the remaining solid was triturated with pentane (4 × 10 mL). The analytically pure colorless powder (0.64 g) was recovered after removing the pentane under reduced pressure. Yield, 85%. ^{1}H NMR (C$_6$D$_6$): δ 6.17 ("t", 2 H), 5.41 ("t", 2 H), 4.94 ("t", 2 H), 1.99 (s, 6 H), 1.67 (s, 6 H), 0.16 (s, 9 H), −0.03 (s, 2 H), −0.43 (s, 3 H). ^{13}C NMR (C$_6$D$_6$): δ 122.0 (**C**CH$_3$), 121.4 (**C**CH$_3$), 113.4 (**C**H), 106.2 (**C**H), 103.2 (**C**H), 44.5 (**C**H$_2$), 32.3 (Zr**C**H$_3$), 13.3 (C**C**H$_3$), 13.0 (C**C**H$_3$), 3.9 (Si**C**H$_3$). Anal. Calcd for C$_{19}$H$_{32}$SiZr: C, 60.08; H, 8.51. Found: C, 59.92; H, 8.16; and C, 59.87; H, 8.00.

Method B. Chlorobis(1,2-dimethylcyclopentadienyl)methylzirconium(IV) (**1**) (0.97 g, 3.0 mmol), toluene (30 mL), and pentane (25 mL) were charged into a reaction flask and cooled to 0 °C. Under constant stirring, a solution of trimethylsilylmethyllithium (Aldrich, 4.0 mL, 1.0 M in pentane) diluted with pentane (20 mL) was added dropwise over 0.5 h. The resulting solution was stirred for an additional 3 h. Precipitated solid byproducts were removed by filtration, and volatiles were removed from the filtrate under reduced pressure. After recrystallization from pentane, a colorless solid (0.56 g, 1.5 mmol) was obtained with spectral characteristics identical to those reported in method A. Yield, 50%.

Methylbis(1,2-dimethylcyclopentadienyl)(trimethylsilylmethyl)hafnium(IV) (4c). A solution of methyllithium in Et$_2$O (1.8 mL, 1.4 M in Et$_2$O, 2.5 mmol) was added dropwise to a stirred Et$_2$O/toluene solution (15 mL/20 mL) of chlorobis(1,2-dimethylcyclopentadienyl)−(trimethylsilylmethyl)hafnium(IV) (0.78 g, 1.60 mmol) at 0 °C. The mixture was then allowed to warm to 25 °C. After stirring overnight, the solvent was removed under vacuum. Pentane (3 × 15 mL) was then added to the remaining solid residue, the mixture filtered to remove solid byproducts, and solvent subsequently removed from the filtrate under vacuum, leaving the crude colorless solid. Purification was achieved by preferentially crystallizing the impurities from a pentane solution, obtaining the supernatant solution by filtration, and removing the pentane under vacuum. The analytically pure product was recovered as a white solid (1.97 g, 4.05 mmol). Yield, 69%. ^{1}H NMR (C$_6$D$_6$): δ 6.05 ("t", 2 H), 5.36 ("t", 2 H), 4.93 ("t", 2 H), 2.00 (s, 6 H), 1.69 (s, 6 H), 0.16 (s, 9 H), −0.40 (s, 2H), −0.58 (s, 3H). ^{13}C NMR (C$_6$D$_6$): δ 120.7 (**C**CH$_3$), 117.3 (**C**CH$_3$), 113.2 (d, 169.3 Hz, **C**H), 106.0 (d, 169.2 Hz, **C**H), 102.4 (d, 107.7 Hz, **C**H), 46.3 (t, 104.4 Hz, **C**H$_2$), 37.4 (q, 114.9 Hz, Hf**C**H$_3$), 13.2 (q, 126.2 Hz, C**C**H$_3$), 12.9 (q, 126.7 Hz, C**C**H$_3$), 4.2 (q, 117.1 Hz, Si**C**H$_3$). Anal. Calcd for C$_{19}$H$_{32}$SiHf: C, 48.86; H, 6.91. Found: C, 48.99; H, 6.89; and C, 49.06; H, 6.92.

Bis(1,2-dimethylcyclopentadienyl)(trimethylsilylmethyl)zirconium(IV) Methyl-trispentafluorophenylborate (5c). Bis(1,2-dimethylcyclopentadienyl)methyl(trimethylsilyl-methyl)zirconium(IV) (0.15 g, 0.40 mmol) and tris(pentafluorophenyl)borane (0.21 g, 0.42 mmol) were loaded into a fritted reaction apparatus. Pentane (20 mL) was vacuum transferred in at −78 °C, and the mixture was allowed to warm to 25 °C while stirring. After 30 min, the solution was cooled to −78 °C, filtered, and the solvent removed under reduced pressure. The solid was then redissolved in pentane at 0 °C and filtered. Removal of the solvent and pumping under vacuum (6 h) left the pale yellow, analytically pure product (0.12 g). Yield, 30%. ^{1}H NMR (C$_7$D$_8$, −40 °C): δ 5.74 ("t", 2.54 Hz, 2 H), 5.22 ("t", 3.12 Hz, 2 H), 5.01 ("t", 2.42 Hz, 2 H), 1.53 (s, 6 H), 1.30 (s, 2 H), 1.21 (s, 6 H), −0.03 (br, 3 H), −0.06 (s, 9 H). ^{13}C NMR (C$_7$D$_8$, −40 °C): δ 148.5 (**C**F, d, $^1J_{CF}$ = 233 Hz), 139.5 (**C**F, d, $^1J_{CF}$ = 249 Hz), 137.35 (**C**F, d, $^1J_{CF}$ = 249 Hz), 127.4 (**C**CH$_3$), 126.7 (**C**CH$_3$), 116.9 (**C**H), 111.0 (**C**H), 110.2 (**C**H), 64.6 (Zr**C**H$_2$), 17.1 (B**C**H$_3$, br), 12.6 (C**C**H$_3$), 12.5 (C**C**H$_3$), −3.11 (Si**C**H$_3$). ^{19}F NMR (C$_7$D$_8$, RT): δ −125.4 (d, $^3J_{FF}$ = 22.19 Hz), −150.1 (t, $^3J_{FF}$ = 19.71 Hz), −154.8 ("t", 20.52 Hz). Anal. Calcd for C$_{37}$H$_{32}$BF$_{15}$SiZr: C, 49.77; H, 3.62. Found: C, 49.23; H, 3.92; and C, 49.37; H, 3.82.

Bis(1,2-dimethylcyclopentadienyl)(trimethylsilylmethyl)hafnium(IV) Methyl-trispentafluorophenylborate (6c). Bis(1,2-dimethylcyclopentadienyl)methyl(trimethylsilyl-methyl)hafnium(IV) (0.21 g, 0.44 mmol) and tris(pentafluorophenyl)borane (0.24 g, 0.47 mmol) were loaded into a flip-frit vacuum apparatus. Toluene (25 mL) was vacuum transferred in at −78 °C, and the mixture was allowed to warm to 25 °C while stirring. After 45 min, the solvent was removed under reduced pressure after which pentane (30 mL) was vacuum transferred in. The solution was filtered and then cooled to afford a colorless solid. Removal of pentane by filtration and pumping under vacuum left the beige, analytically pure product (0.21 g). Yield, 48%. ^{1}H NMR (C$_7$D$_8$, −42 °C): δ 5.58 ("t", 2 H), 5.21 ("t", 2 H), 5.01 ("t", 2 H), 1.57 (s, 6 H), 1.22 (s, 6 H), 0.75 (s, 2 H), −0.24 (br, 3 H), −0.04 (s, 9 H). ^{19}F NMR (C$_7$D$_8$, RT): δ −133.5 (6 F), −159.4 (3 F), −164.8 (6 F). Anal. Calcd for C$_{37}$H$_{32}$BF$_{15}$SiHf: C, 45.34; H, 3.30. Found: C, 45.14; H, 3.41; and C, 45.19; H, 3.55.

Bis(trimethylsilyl)methyllithium. The following procedure is modified from that of Lappert[21] and is carried out under an argon atmosphere. A solution of bis(trimethylsilyl)methyl chloride (Aldrich, 10.0 g, 51.3 mmol) in Et$_2$O (20 mL) was added dropwise to a refluxing suspension of Li powder (Aldrich, ~3 g, ~430 mmol) in Et$_2$O (50 mL). The mixture was stirred for 12 h, cooled, and then filtered through Celite. The solvent was removed from the filtrate under reduced pressure and the resulting solid sublimed (140 °C/10^{-5} Torr). The product was obtained as a colorless solid (6.62 g). Yield, 87%. ^{1}H NMR (C$_6$D$_6$): δ 0.14 (s, 18 H), −2.55 (s, 1 H).

Chlorobis(1,2-dimethylcyclopentadienyl)[bis(trimethylsilyl)methyl]zirconium(IV). Dichlorobis(1,2-dimethylcyclopentadienyl)zirconium(IV)[4b,17] (3.18 g, 9.16 mmol) and bis(trimethylsilyl)methyllithium (1.95 g, 11.7 mmol) were added to a Schlenk flask, cooled to −78 °C, and then Et$_2$O (100 mL) was added. The mixture was slowly warmed to 25 °C and was then stirred for 7 days. The solution was next filtered, and the solvent was removed under reduced pressure. The crude solid was recrystallized from pentane, resulting in analytically pure, tan crystals of the product (3.51 g). Yield, 81%. ^{1}H NMR (C$_6$D$_6$): δ 6.59 ("t", 1 H), 6.18 ("t", 1 H), 6.08 ("t", 1 H), 5.33 ("t", 1 H), 5.19 ("t", 1 H), 5.03 ("t", 1 H), 2.09 (s, 3 H), 1.99 (s, 1 H), 1.96 (s, 3 H), 1.88 (s, 3 H), 1.51 (s, 3 H), 0.34 (s, 9 H), 0.21 (s, 9 H). ^{13}C NMR (CDCl$_3$): δ 130.7 (**C**CH$_3$), 127.5 (**C**CH$_3$), 124.2 (**C**CH$_3$), 122.3 (**C**H), 120.8 (**C**CH$_3$), 117.0 (**C**H), 108.6 (**C**H), 108.2 (**C**H), 107.1 (**C**H), 104.2 (**C**H), 46.5 (Zr**C**H), 14.0 (C**C**H$_3$), 13.9 (C**C**H$_3$), 13.7 (C**C**H$_3$), 13.2 (C**C**H$_3$), 5.7 (Si**C**H$_3$), 4.7 (Si**C**H$_3$). Anal. Calcd for C$_{21}$H$_{37}$ClSi$_2$Zr: C, 53.39; H, 7.91. Found: C, 53.06; H, 7.89; and C, 53.10; H, 7.97.

Methylbis(1,2-dimethylcyclopentadienyl)[bis(trimethylsilyl)methyl]zirconium(IV) (3d). Chlorobis(1,2-dimethylcyclopentadienyl)[bis(trimethylsilyl)methyl]zirconium(IV) (2.69 g, 5.71 mmol) and Et$_2$O (35 mL) were added to a Schlenk flask and cooled to −78 °C. MeLi (Aldrich, 1.4 M in Et$_2$O, 4.9 mL, 6.9 mmol) was then injected with stirring. After warming to 25 °C and stirring for 24 h, the solution was filtered and the solvent was removed from the filtrate under reduced pressure. The resulting solid was recrystallized twice from pentane, resulting in colorless, analytically pure crystals of the product (1.82 g). Yield, 71%. ^{1}H NMR (C$_6$D$_6$): δ 6.49 ("t", 1 H), 6.46 ("t", 1 H), 5.96 ("t", 1 H), 5.27 ("t", 1 H), 5.19 ("t", 1 H), 4.58 ("t", 1 H), 2.08 (s, 3 H), 1.70 (s, 3 H), 1.67 (s, 3 H), 1.40 (s, 3 H), 1.32 (s, 1 H), 0.21 (s, 9 H), 0.20 (s, 9 H), −0.29 (s, 3 H). ^{13}C NMR (C$_6$D$_6$): δ 125.0 (**C**CH$_3$), 122.3 (**C**CH$_3$), 122.2 (**C**CH$_3$), 119.0 (**C**H), 118.2 (**C**CH$_3$), 115.5 (**C**H), 107.3 (**C**H), 107.2 (**C**H), 107.0 (**C**H), 102.1 (**C**H), 42.9 (Zr**C**H), 40.7 (Zr**C**H$_3$), 13.2 (C**C**H$_3$), 13.1 (C**C**H$_3$), 13.0 (C**C**H$_3$), 12.8

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(C**C**H_3), 6.0 (Si**C**H_3), 5.3 (Si**C**H_3). Anal. Calcd for $C_{22}H_{40}Si_2Zr$: C, 58.45; H, 8.94. Found: C, 58.28; H, 8.83; and C, 58.22; H, 8.77.

Bis(1,2-dimethylcyclopentadienyl)[bis(trimethylsilyl)methyl]-zirconium(IV) Methyl-trispentafluorophenylborate (5d). Methylbis(1,2-dimethylcyclopentadienyl)-[bis(trimethylsilyl)methyl]zirconium(IV) (0.21 g, 0.46 mmol) and tris(pentafluorophenyl)borane (0.24 g, 0.48 mmol) were added to a vacuum reaction/filtration flask. Toluene (25 mL) was vacuum transferred in at −78 °C, and the resulting solution was warmed to 25 °C and stirred for 30 min. The solvent was then removed under reduced pressure leaving a viscous orange oil. Pentane (20 mL) was then vacuum transferred in, and after stirring, the oil solidified. The solid was collected by filtration and the solvent removed. The solid product was washed a second time with pentane after which bright yellow, analytically pure product (0.39 g, 0.41 mmol) was recovered. Yield, 92%. ^1H NMR (C_7D_8): δ 5.80 (t, 3.18 Hz, 1 H), 5.55 (d, 3.22 Hz, 2 H), 5.38 (d, 3.13 Hz, 2 H), 5.30 (t, 3.12 Hz, 1 H), 3.09 (s, 1 H), 1.53 (s, 6 H), 1.43 (s, 6 H), 1.24 (br, 3 H), −0.30 (s, 18 H). ^1H NMR (CD_2Cl_2): δ 6.43 (t, 3.12 Hz, 1 H), 6.26 (d, 3.12 Hz, 2 H), 6.16 (d, 3.12 Hz, 2 H), 5.96 (t, 3.12 Hz, 1 H), 3.72 (s, 1 H), 2.15 (s, 6 H), 2.05 (s, 6 H), 0.40 (br, 3 H), 0.07 (s, 18 H). ^{13}C NMR (CD_2Cl_2): δ 147.2 (d, $^1J_{CF}$ = 241 Hz), 137.1 (d, $^1J_{CF}$ = 244 Hz), 136.0 (d, $^1J_{CF}$ = 249 Hz), 129.8 (**C**CH_3), 127.1 (**C**CH_3), 116.2 (**C**H), 114.0 (**C**H), 113.1 (**C**H), 110.3 (**C**H), 80.7 (Zr**C**H), 13.7 (C**C**H_3), 13.4 (C**C**H_3), 3.8 (Si**C**H_3). ^{19}F NMR (C_7D_8): −124.17 (d, $^3J_{FF}$ = 23.1 Hz), −154.78 (t, $^3J_{FF}$ = 20.6 Hz), −157.12 (“t”, $^3J_{FF}$ = 21.5 Hz). Anal. Calcd for $C_{40}H_{40}BF_{15}Si_2Zr$: C, 49.83; H, 4.19. Found: C, 49.39; H, 4.19; and C, 49.31; H, 4.05.

Results

The following sections first describe the synthesis and characterization of the $(1,2\text{-}Me_2Cp)_2M(R)Me$ precursor complexes as well as the corresponding metallocenium ion pairs. Calorimetrically determined enthalpies of methide abstraction from the $(1,2\text{-}Me_2Cp)_2M(R)Me$ series by $B(C_6F_5)_3$ are then discussed along with a kinetic study of β-methyl elimination for the metallocenium complexes containing the R = $CH_2{}^tBu$ substituent. The rates of ion-pair structural reorganization processes are then measured and related to the type of substituent and the nature of the solvent, with close attention to substituent rotational barriers about the M−R bonds which in this case can be an index of intramolecular nonbonded interactions.

Synthetic Methodology. To examine metal-alkyl substituent effects on metallocenium ion-pair formation and structural dynamics, a series of new Zr and Hf complexes was prepared as shown in Scheme 1. One metal-bound methyl substituent on each of the $(1,2\text{-}Me_2Cp)_2MMe_2$ complexes **3a** and **4a** was replaced with chloride using 1.0 equivalent of $HCl_{(g)}$. Alkylation of the resulting mixed methyl-chloro metallocenes **1** and **2** was accomplished with either lithium or Grignard reagents to obtain the methyl-alkyl Zr complexes **3b**−**d** and Hf complexes **4b**,**c**. An alternate route to complexes **3c** and **4c** is to add 1.0 equivalent of trimethylsilylmethyllithium to $(1,2\text{-}Me_2Cp)_2MCl_2$, and to then use MeLi for alkylation of the second chloride. Methide abstraction to obtain the ion-pair complexes **5** and **6** was accomplished with the strongly Lewis acidic borane, $B(C_6F_5)_3$.[10c] For most cases, abstraction is completely selective for the methide functionality within ^1H NMR detection limits.[22] The steric demands of the alkyl substituent R = $CH(TMS)_2$ apparently preclude the formation of what would have been Hf complex **4d**, even starting from $(1,2\text{-}Me_2Cp)_2HfCl_2$. Lappert[23] reported similar experimental difficulties with less sterically encumbered Cp_2HfCl_2. In contrast, formation of the related Zr complex **3d** proceeds smoothly. Of significant interest in the present study is the properties of neopentyl ion-pair complexes **5b** and **6b**. While methide abstraction proceeds cleanly at low temperatures, as judged by ^1H NMR, β-methyl elimination is observed at room temperature leading to quantitative formation of **3a** and **4a** in the case of Zr and Hf, respectively, along with an accompanying equivalent of isobutene. Complexes **5** and **6** are all colorless or light-beige solids with the exception of **5d** which is bright yellow both in solution and as a solid. The new complexes were characterized by standard spectroscopic and analytical methodologies (see Experimental Section for data).

Scheme 1. Synthetic Pathways to Substituted Metallocenium Ion-Pair Complexes

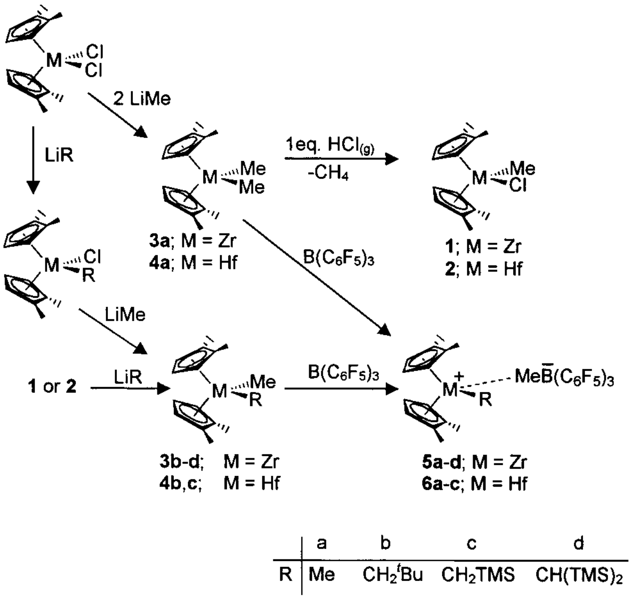

Table 1. Formation Enthalpies in Toluene Solution at 25 °C for $(1,2\text{-}Me_2Cp)_2MR^+\ MeB(C_6F_5)_3^-$ Complexes

complex	M	R	$\Delta H_{form}{}^a$ (kcal/mol)
5a	Zr	Me	−24.6(0.8)[b]
5b	Zr	$CH_2{}^tBu$	[c]
5c	Zr	CH_2TMS	−22.6(1.0)
5d	Zr	$CHTMS_2$	−59.2(1.4)
6a	Hf	Me	−20.8(0.5)[b]
6b	Hf	$CH_2{}^tBu$	[c]
6c	Hf	CH_2TMS	−31.1(1.6)

[a] Values are determined by titration calorimetry. See eq 3 for reaction details. [b] From ref 4b. [c] β-Me elimination precludes determination at 25 °C.

Ion-Pair Formation Enthalpies (ΔH_{form}). Metallocenium ion-pair enthalpies of formation (ΔH_{form}) as shown in eq 3 were measured in toluene solution by isoperibol titration calorimetry, and results are presented in Table 1. In all cases, ^1H NMR experiments under the same conditions as the calorimetric experiments show that methide abstraction from the neutral metallocene by $B(C_6F_5)_3$ is clean, fast, and quantitative at 25 °C. Multiple alkyl substituent abstraction from a single metallocene is not observed, even with a stoichiometric excess of borane, and at no time are binuclear complexes,[4c,24] such as **II**, detectable by features such as a characteristically high-field M-(μ-Me)-M$^+$ ^1H NMR signal. As noted above, ^1H NMR experiments show that metallocene−Me substituent abstraction is exclusive over abstraction of other R groups, to the accuracy

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(22) In the case of R = CH_2Ph, abstraction chemistry is not clean as a result of competitive benzyl abstraction.

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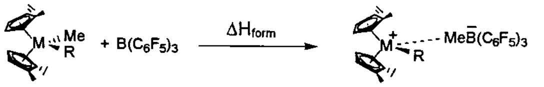
(24) (a) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Orgnometallics* **1997**, *16*, 842−857. (b) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235−2243.

of ^{1}H NMR spectroscopic detection limits.



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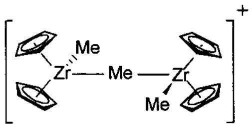
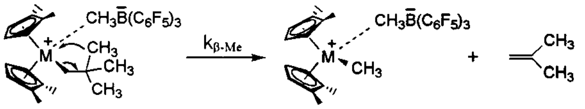


II

Table 1 indicates that abstraction enthalpies (ΔH_{form}) for zirconocene complexes **5a** and **5c** are similar for R = Me and R = CH_2TMS. In contrast, Zr complex **5d** having the R = $CH(TMS)_2$ alkyl substituent exhibits a significantly greater abstraction exothermicity, in excess of twice that of the other Zr entries in Table 1. The physical properties of **5d**, such as a bright yellow color and limited solubility in relatively nonpolar hydrocarbon solvents such as toluene, suggest looser ion-pairing characteristics.[24a,25] This hypothesis is corraborated by NMR spectroscopic observables such as the upfield shift of the boron-bound CH_3 ($\delta = 0.40$ ppm) in toluene solution, which is characteristic of free $MeB(C_6F_5)_3$,$^-$ [4a–c,25a] as is the modest $\Delta\delta$(*m*-, *p*-F)[25b] value of 2.34 ppm. Hafnium complex **6a** (R = Me) exhibits an abstraction enthalpy 2–4 kcal/mol less exothermic than the analogous Zr complex; however, ΔH_{form} for Hf complex **6c** where R = CH_2TMS is significantly more exothermic than for the Zr analogue.

***β*-Methyl Elimination Kinetics in Metallocenium Neopentyl Complexes.** In the case of neopentyl complexes **5b** and **6b**, methide abstraction enthalpies could not be obtained by calorimetry because the complexes begin to undergo β-Me elimination near −15 °C. This result is not completely surprising as ample evidence exists for metallocenium β-Me elimination in the literature.[4d,26] However, the present transformation is unique in being clean and quantitative, affording an opportunity to directly observe and *quantitatively* measure and compare rates and barriers for β-Me elimination in Zr and Hf metallocenium complexes. Rates of eq 4 were measured at 4–5 different temperatures over a 30 °C range in toluene-d_8 solution. The progress of the reactions was monitored by integration of at least one ^{1}H NMR signal from the reactant (**5b** for M = Zr and **6b** for M = Hf) and product (**5a** for M = Zr and **6a** for M = Hf). The ^{1}H NMR signals for the coproduct isobutene are identical to those for the free olefin, arguing against significant olefin coordination to the metal center[26d] in the ground state. Furthermore, the reaction proceeds to completion, and no detectable back reaction is observed as reported in other zirconocenium systems where β-Me elimination has been analyzed in a more qualitative fashion.[26c] The present data can be fit to first-order kinetic plots as shown in Figure 1.



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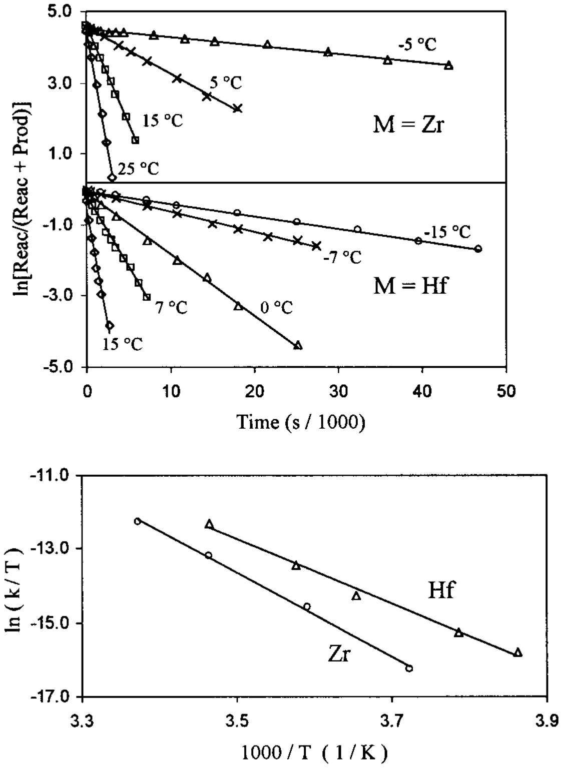

Figure 1. First-order kinetic plots (top) and corresponding Eyring plots (bottom) for the β-Me elimination processes depicted in eq 4 for $(1,2\text{-}Me_2Cp)_2MCH_2{}^tBu^+$ $MeB(C_6F_5)_3{}^-$ in toluene-d_8 where M = Zr (**5b**) and M = Hf (**6b**).

Table 2. Activation Parameters for β-Me Elimination in the Complexes $(1,2\text{-}Me_2Cp)_2MCH_2{}^tBu^+$ $CH_3B(C_6F_5)_3{}^-$ Where M = Zr and Hf

complex	M	$\Delta G^\ddagger_{\beta\text{-Me}}$ (0 °C) (kcal/mol)	$\Delta H^\ddagger_{\beta\text{-Me}}$ (kcal/mol)	$\Delta S^\ddagger_{\beta\text{-Me}}$ (cal/mol•K)
5b	Zr	21.2(0.2)	22.5(0.9)	4.3(3.3)
6b	Hf	20.7(0.2)	17.3(0.9)	−11.9(3.4)

Eyring plots of the β-methyl elimination kinetic data are also shown in Figure 1, and derived β-Me elimination barriers compiled in Table 2. Activation parameters for Zr complex **5b** are $\Delta H^\ddagger_{\beta\text{-Me}} = 22.5(0.9)$ kcal/mol and $\Delta S^\ddagger_{\beta\text{-Me}} = 4.3(3.3)$ cal/mol•K. Corresponding values for the Hf complex **6b** are $\Delta H^\ddagger_{\beta\text{-Me}} = 17.3(0.9)$ kcal/mol and $\Delta S^\ddagger_{\beta\text{-Me}} = -11.9(3.4)$ cal/mol•K. The enthalpic barrier for the zirconium complex is ~5 kcal/mol greater than that in the Hf complex, which is partially offset by the entropic contribution which is ~16 cal/mol•K greater for the Zr complex.

Ion-Pair Reorganization Processes. Increasing amounts of data argue that metallocene olefin polymerization activity and enchainment stereochemistry are correlated with, among other factors, the ability to form structurally mobile ion pairs containing an electrophilic, coordinatively unsaturated metal center.[3,4,10,24a] Strongly Lewis acidic $B(C_6F_5)_3$ induces a high degree of cationic polarization at the metal center via methide abstraction to form a metallocenium cation–methyl borate anion ion pair.[4,10,24a,27] Separation and subsequent recombination of the ion pair exchanges diastereotopic ring Me groups via the reorganization process shown in eq 5 and Figure 2A. This effectively permutes the coordination sites of the $MeB(C_6F_5)_3{}^-$

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(25) (a) Lee, R. A.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 6037–6047. (b) Horton, A. D.; deWith, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672–2674.

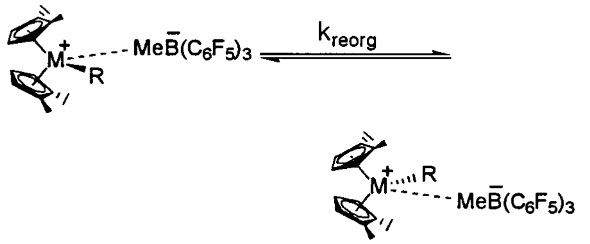
(26) (a) Resconi, L.; Camurati, I.; Sudmeijer, O. *Top. Catal.* **1999**, *7*, 145–163. (b) Shaffer, T. D.; Cannich, J. M.; Squire, K. R. *Macromolecules* **1998**, *31*, 5145–5147. (c) Horton, A. D. *Organometallics* **1996**, *15*, 2675–2677. (d) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424–1432. (e) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025–1032. (f) Eshuis, J. J. W.; Tan, Y. Y.; Meetsma, A.; Teuben, J. H. *Organometallics* **1992**, *11*, 362–369. (g) Kesti, M. R.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 3565–3567. (h) Mise, T.; Kageyama, A.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1991**, 1525–1528. (i) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H. *J. Mol. Catal.* **1990**, *62*, 277–287.

Table 3. Ion-Pair Reorganization Activation Parameters for $(1,2\text{-}Me_2Cp)_2MR^+$ $MeB(C_6F_5)_3^-$ Complexes as Determined by ^1H NMR Line Shape Analysis

complex	M	R	solvent	ϵ^a	$\Delta G^{\ddagger}_{reorg}{}^f$ (kcal/mol)	$\Delta H^{\ddagger}_{reorg}{}^i$ (kcal/mol)	$\Delta S^{\ddagger}_{reorg}{}^i$ (cal/K•mol)	coalescence (°C)
5a	Zr	Me	toluene-d_8	2.37	17.6(2)^b	22(1)^b	13(2)^b	110^b
			C_6D_5Cl	5.71	15.5^c	11(2)^b	−15(8)^b	
			1,2-$C_6D_4Cl_2$	9.93	15.0^c	12(2)^b	−10(4)^b	
5b	Zr	$CH_2{}^tBu$	toluene-d_8	2.37	13.8(2)^g	18(1)^g	15(2)^g	> −6
5c	Zr	CH_2TMS	C_6D_{12}	2.02	*d*	*d*	*d*	35
			$C_6D_{11}CD_3$	2.07	14.8(2)	19(1)	15(2)	35
			toluene-d_8	2.37	13.8(2)	17(1)	10(3)	20
			CCl_2DF		12.2(2)	14(3)	17(4)	−8
			CD_2Cl_2	9.08	10.0(2)	17(1)	23(2)	−25
5d	Zr	$CH(TMS)_2$	toluene-d_8	2.37	*d*	*d*	*d*	< −60^h
			CCl_2DF		8.0(4)	9(2)	7(4)	−100^h
			CD_2Cl_2	9.08	*d*	*d*	*d*	< −78^h
6a	Hf	Me	toluene-d_8	2.37	*e*	*e*	*e*	*e*
			C_6D_5Cl	5.71	15.7^c	13(4)^b	−9(1)^b	
			CD_2Cl_2	9.08	15.8^c	11(1)^b	−16(2)^b	
			1,2-$C_6D_4Cl_2$	9.93	13.5^c	12(3)^b	−5(8)^b	
6b	Hf	$CH_2{}^tBu$	toluene-d_8	2.37	13.8(2)^g	12(3)	−6(13)	10
6c	Hf	CH_2TMS	C_6D_{12}	2.02	15.5(2)	19(2)	12(5)	55
			$C_6D_{11}CD_3$	2.07	15.2(2)	15(1)	0(3)	50
			toluene-d_8	2.37	14.0(2)	15(2)	3(5)	20
			CD_2Cl_2	9.08	13.1(2)	11(2)	−5(4)	0

[a] Dielectric constant from ref 28. [b] Also see ref 4b. [c] Calculated at 25 °C from $\Delta H^{\ddagger}_{ips}$ and $\Delta S^{\ddagger}_{ips}$ values. [d] Solvent froze before the slow exchange limit was reached. [e] Barrier too high to be determined by this method. [f] At the indicted coalescence temperature unless otherwise noted. [g] At 0 °C. [h] Coalescence of diastereotopic TMS signals. [i] Estimated uncertainties are obtained from standard regression analysis. Also see ref 14a.

and R substituents. The rate of such processes provides one measure of the "tightness" of the ion pairing.[4b,10c,24a]



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Equilibration rates (k_{reorg}) for eq 5 were measured as a function of R and solvent via spectral line broadening[14] in variable-temperature ^1H NMR experiments and were used to calculate the activation parameters shown in Table 3. Line shapes in typical experiments were found to be independent of metallocenium complex concentration over a 7-fold range and independent of borane concentration over a 3-fold range, arguing against the significance of intermolecular processes such as "S_E2 like" mechanisms under these conditions. Rather, it is proposed that the principal dynamic process observed involves the borate anion passing between symmetrically disposed sites in the metallocenium coordination sphere (Figure 2). Representative NMR spectra are shown for **5c** in Figure 3. For Zr and Hf complexes **5a**−**c** and **6a**−**c**, analysis of the exchange-broadened, diastereotopic (see Figure 2A) ring methyl signals was carried out. As shown in Figure 2B, the inferred orientation of the R = $CH(TMS)_2$ substituent in Zr complex **5d** removes the horizontal symmetry plane bisecting the metallocene wedge which is present in the other complexes. In this case, four ring Me and two TMS ^1H NMR signals are observed in the slow-exchange limit. Broadening of the TMS proton signals was used to quantitate rates of ion-pair reorganization because of the complicated pattern of four MeCp signals at low temperature, as shown in Figure 4. However, from a limited data set, reorganization activation barriers determined from one pair of broadened MeCp signals agree well with those determined from TMS signal broadening, as expected if the process depicted in Figure 2B is correct. Respective activation parameters determined from ring methyl exchange and related TMS exchange in **5d** are $\Delta H^{\ddagger}_{reorg} = 9$ and 9(2) kcal/mol; $\Delta S^{\ddagger}_{reorg} = 5$ and 7(4) cal/mol·K; and $\Delta G^{\ddagger}_{reorg}$ (−100 °C) = 8.0 and 8.0(0.4) kcal/mol. Rotation about the Zr−$CH(TMS)_2$ bond is found to be slow up to and exceeding 40 °C, as judged by variable-temperature ^1H NMR experiments on neutral precursor complex **3d** (vide infra).

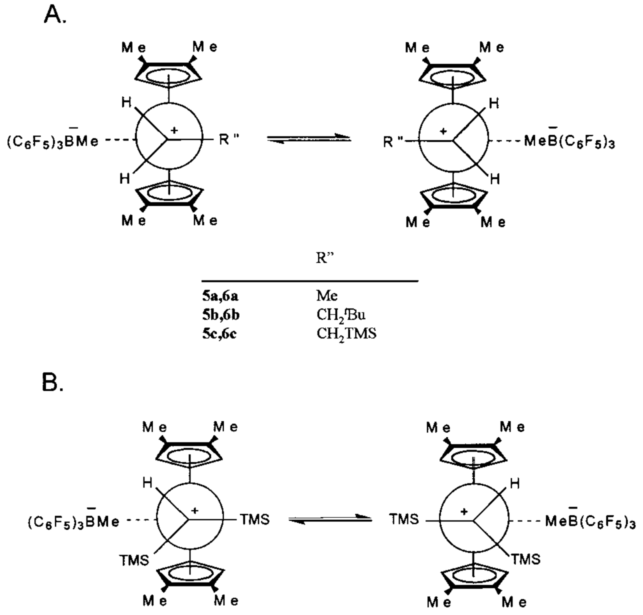

Figure 2. Newman projections illustrating dynamic reorganization processes in various $(1,2\text{-}Me_2Cp)_2MR^+$ $MeB(C_6F_5)_3^-$ metallocenium complexes. The methylborate anion detaches from the cationic metal center and reattaches to the opposite side. In A, two ring-methyl signals are observed at slow exchange, and simultaneous rotation about the M-CH_2R'' bond is postulated. In B, four ring-methyl signals are observed at slow exchange.

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(27) (a) Lanza, G.; Fragala, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 8257−8258. (b) Lanza, G.; Fragala, I. L. in ref 3b, pp 45−60. (c) Lanza, G.; Fragala, I. L.; Marks, T. J., submitted for publication.

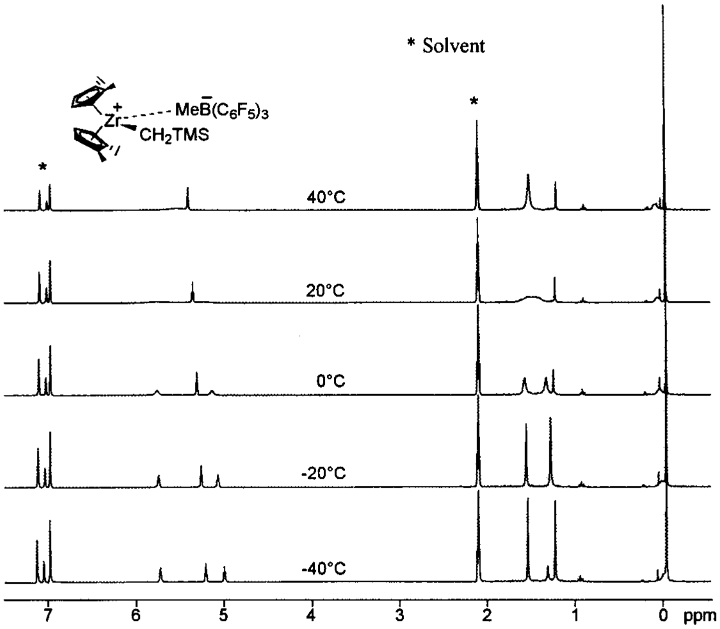

Figure 3. Variable-temperature ^{1}H NMR spectra for $(1,2\text{-}Me_2Cp)_2ZrCH_2TMS^+$ $MeB(C_6F_5)_3^-$ in toluene-d_8 solution from −40 to +40 °C. Dynamic processes are shown in Figure 2A (R = CH_2TMS).

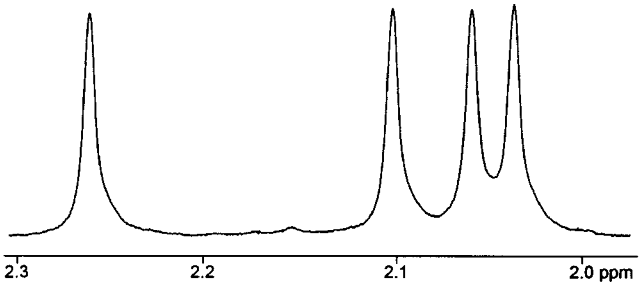

Figure 4. ^{1}H NMR ring-Me signal region at −126 °C for the complex $(1,2\text{-}Me_2Cp)_2ZrCHTMS_2$+ $MeB(C_6F_5)^-_3$ (**5d**) in $CDCl_2F$ solution.

The kinetic data collected in Table 3 reveal a number of interesting trends concerning how the ion-pair separation/reorganization barrier is related to the identity of R, the metal, and the solvent dielectric constant.[28] In regard to R effects, the barriers for M = Zr ion-pair reorganization decrease in the order Me > $CH_2{}^tBu$ ∼ CH_2TMS > $CH(TMS)_2$ with reorganization rates spanning over 8 orders of magnitude. As noted above, the low solubility of **5d** in toluene is suggestive of significant ionic character,[24a,25] and the $CH_3B(C_6F_5)_3^-$ ^{1}H chemical shift (δ = 0.40 in CD_2Cl_2, 1.24 in toluene-d_8) at 25 °C is also indicative of a free anion rather than one tightly ion-paired with the cation.[4a−c,25,29] A similar ordering of $\Delta H^{\ddagger}_{\mathrm{reorg}}$ parameters is observed in the M = Hf series. For R = Me in toluene solution, the reorganization barrier is too large to measure by line-broadening (>24 kcal/mol), while for R = $CH_2{}^tBu$ and R = CH_2TMS, $\Delta H^{\ddagger}_{\mathrm{reorg}}$ is significantly lower (12(3) and 15(2) kcal/mol, respectively). The free energies of activation ($\Delta G^{\ddagger}_{\mathrm{reorg}}$) at the indicated temperatures (Table 3) are somewhat larger for the Hf complexes than for the corresponding Zr complexes with the same R substituent and measurement solvent, even though the corresponding $\Delta H^{\ddagger}_{\mathrm{reorg}}$ parameters for the Hf complexes are 2−6 kcal/mol *smaller* in each case except for R = Me. The reorganization enthalpies are offset by somewhat less favorable (less positive) $\Delta S^{\ddagger}_{\mathrm{reorg}}$ values in the case of the Hf complexes, suggestive of more highly organized transition states.

The data in Table 3 also indicate that higher polarity solvents significantly reduce the barriers to ion-pair reorganization. Solvent polarity, as indexed by dielectric constant, influences $\Delta H^{\ddagger}_{\mathrm{reorg}}$ by as much as 7−8 kcal/mol in the case of **6c** in C_6D_{12} (ϵ = 2.02), versus toluene-d_8 (ϵ = 2.37), versus CD_2Cl_2 (ϵ = 9.08) where the $\Delta H^{\ddagger}_{\mathrm{reorg}}$ values are 19(2), 15(2), and 11(2) kcal/mol, respectively. In the case of R = Me, it was previously observed[4b] that activation entropies ($\Delta S^{\ddagger}_{\mathrm{reorg}}$) are somewhat less favorable (more negative) in solvents with larger dielectric constants. However, for the larger substituents R = $CH_2{}^tBu$ and R = CH_2TMS, the activation entropies are considerably more positive (suggestive of less organized transition states) although values for Hf complexes are not as large as for the Zr complexes.

The enhanced solubility of R = CH_2TMS complexes **5c** and **6c** in aliphatic hydrocarbons versus the corresponding R = Me complexes **5a** and **6a** allows ion-pair reorganization barriers to be measured for the first time in a minimally coordinating saturated hydrocarbon solvent (the medium in which most large-scale polymerizations are carried out). In cyclohexane-d_{12}, $\Delta H^{\ddagger}_{\mathrm{reorg}}$ for **6c** (M = Hf) is 19(2) kcal/mol— slightly higher than the 15(2) kcal/mol barrier in toluene-d_8 solution. The high freezing point of cyclohexane-d_{12} precludes a similar determination for the analogous Zr complex **5c**. However, in methylcylohexane-d_{14}, $\Delta H^{\ddagger}_{\mathrm{reorg}}$ values for **5c** and **6c** are found to be 19(1) and 15(1) kcal/mol, respectively, both of which are slightly larger than the corresponding values in toluene solution. It is interesting to note that in these low dielectric constant solvents, reorganization barriers still do not approach the magnitudes of barriers for complete ion-pair separation calculated for the gas phase.[27c]

Alkyl Substituent Rotational Barriers. Steric congestion engendered by the R substituent bulk was also evaluated by variable-temperature ^{1}H NMR spectroscopy. The experiments

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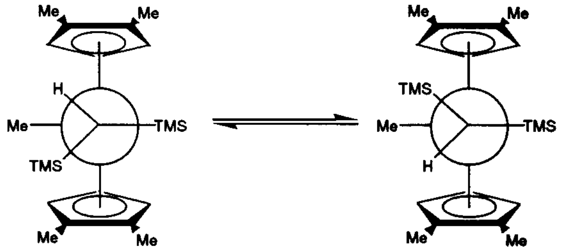
[28] Solvent dielectric constants (ϵ) are taken from the following: (a) *CRC Handbook of Chemistry and Physics*, 77th ed.; CRC Press: New York, 1996; p G-161 and (b) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier Publishing: New York, 1950 (Vol. I) and 1965 (Vol. II).

[29] (a) Beck, S.; Prosenc, M. H.; Brintzinger, H. H. *J. Mol. Catal. A: Chem.* **1998**, 41−52. (b) Horton, A. D.; de With, J. *Organometallics* **1997**, *16*, 5424−5436. (c) Wang, Q.; Gillis, D. J.; Quyoum, R.; Jeremic, D.; Tudoret, M.-J.; Baird, M. C. *J. Organomet. Chem.* **1997**, *527*, 7−14. (d) Bochmann, M.; Lancaster, S. J.; Hursthouse, M. B.; Malik, K. M. A. *Organometallics* **1994**, *13*, 2235−2243.

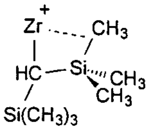
reveal that the rotational barrier about the Zr—CH(TMS)$_2$ bond in neutral precursor complex **3d** is rather large ($\Delta G^{\ddagger} = 17.4(2)$ kcal/mol at 85 °C). At 25 °C, four Cp-Me signals and two TMS ^{1}H NMR signals are observed, as expected, for the proposed static structure shown in eq 6. Upon heating to 110 °C, the TMS signals broaden, coalesce, and form one signal, as



(6)

expected for fast exchange between rotamers. Solvent and instrumental constraints preclude observation of the expected pair of Cp-Me signals at high rotation rates, and only a broad, coalesced signal is observed at 110 °C. NOE measurements on **5d**, the metallocenium derivative of **3d**, at 25 °C indicate that the C*H*(TMS)$_2$ methine proton is in close proximity to one of the 1,2-Me$_2$Cp rings (cf. Figure 2B). Furthermore, low-temperature ^{1}H NMR spectra of **5d** at −126 °C in CDCl$_2$F reveal four magnetically nonequivalent ring-methyl group signals (Figure 4) and four TMS signals (integration: 3:1:1:1), indicative of two magnetically distinct TMS groups. The pattern where three distinct Me resonances are observed for one TMS group is consistent with the instantaneous structure in Figure 2B, having the added feature of restricted rotation about one CH—TMS bond and suggestive of an agostic interaction[12] as shown in structure **III** or severe steric interactions or some combination of both. Interactions of this type have been observed in isoelectronic, neutrally charged lanthanide complexes.[7a,b,30] Further support for the **5d** rotomer configuration shown in Figure 2B is the large downfield shift of the C*H*(TMS)$_2$ methine ^{1}H NMR signal (δ 3.09 ppm), presumably reflecting proximity to the electrophilic Zr center and Cp ring currents. A similar downfield methine shift is observed in neutral precursor **3d**.

III



Discussion

A long-term goal of our single-site polymerization catalyst research has been to investigate and better understand those factors governing catalyst thermodynamic stability and ion-pair structural dynamics in metallocenium systems. Key energetic components of $\Delta H_{\rm form}$ can be described by an approximate Born−Haber cycle (Figure 5). The capacity of ancillary ligand framework modifications such as L_2 = Cp$_2$ → (1,2-Me$_2$Cp)$_2$ → (Me$_5$Cp)$_2$ to lower metallocene ionization potentials (IPs) was shown previously to correlate with thermodynamic stabilization of the corresponding $L_2MMe^+MeB(C_6F_5)_2Ar^-$ ion pairs (M = Zr, Hf).[4b] Electron-donating and sterically sizeable (Me$_5$-Cp)$_2$ ancillary ligation was found to be especially effective in promoting ion-pair formation. Metal identity influences IP and D[L$_2$M(Me)-Me] in the cycle in that both values are slightly lower for M = Zr than for Hf. It was found[4b] that Zr−Me$^+$ ion pairs are more thermodynamically stable with respect to neutral precursors ($\Delta H_{\rm form}$ is more exothermic), have somewhat lower ion-pair reorganization barriers (eq 5; $\Delta H^{\ddagger}_{\rm reorg}$), and exhibit somewhat higher rates of ethylene polymerization than isostructural Hf complexes. In the B(C$_6$F$_5$)$_2$Ar series,[4b] higher borane Lewis acidity leads to more exothermic $\Delta H_{\rm form}$ values, presumably via the borane methide affinity ($\Delta H_{\rm B-Me}$) in the cycle (Figure 5).[4b,10c] Finally, increasing solvent dielectric constant was found to decrease $\Delta H^{\ddagger}_{\rm reorg}$, presumably because polar solvents stabilize the charge separation in the transition state.[4b]

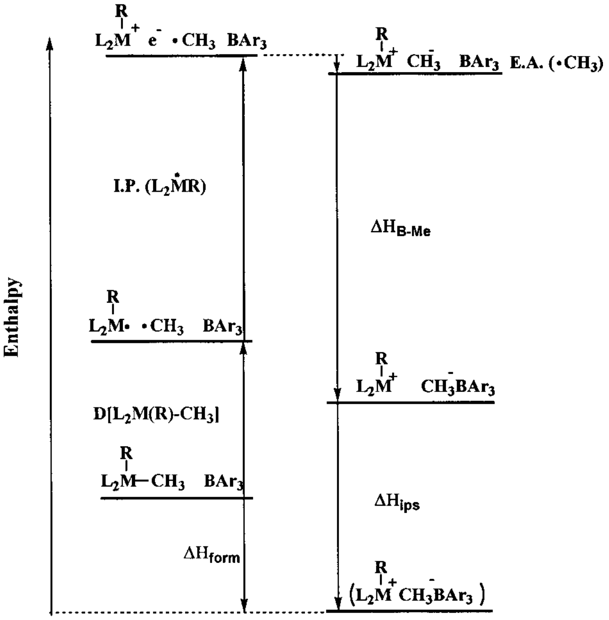


Figure 5. Born−Haber cycle for formation of L$_2$MR$^+$ MeB(C$_6$F$_5$)$_3^-$ ion pairs from neutral metallocene and borane precursors.

The present discussion focuses on how alkyl group (R) electronic and steric properties influence metallocenium ion-pair thermodynamic stability and structural dynamics and, by inference, the efficiency of catalyst activation, polymerization activity, and possibly some aspects of stereoregulation. Thermodynamic and kinetic parameters of the ion-pair chemistry are shown to be highly sensitive to the nature of the alkyl substituent. Important relationships to polymerization chemistry are also addressed including metal effects on β-methyl elimination.

Thermodynamics of Ion-Pair Formation/Catalyst Activation. R-dependent ion-pair formation thermodynamic parameters, as described by eqs 1 and 3 and reported in Table 1, can be interpreted in terms of the aforementioned Born−Haber cycle, making the pragmatic and physically reasonable assumption that solvation effects in hydrocarbon solvents are small and constant for a homologous series.[4b,10c] The component parameters of $\Delta H_{\rm form}$ include the metal−methyl homolytic bond dissociation enthalpy, D[L$_2$M(R)-Me]; the ionization potential of the trivalent metallocene fragment, IP (L$_2$MR•); the electron affinity of the methyl radical, EA(Me•);[31] the methide affinity of the borane, $\Delta H_{\rm B-Me}$; and the ion-pair separation enthalpy, $\Delta H_{\rm ips}$. For the present series with B(C$_6$F$_5$)$_3$ as the sole methide

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[30] (a) Klooster, W. T.; Brammer, L.; Schaverien, C. J.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **1999**, *121*, 1381−1382. (b) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 108−112. (c) Di Bella, S.; Lanza, G.; Fragalà, I. L.; Marks, T. J. *Organometallics* **1996**, *15*, 205−208. (d) Haar, C. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1996**, *15*, 1765−1784. (e) Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C. L. *J. Am. Chem. Soc.* **1994**, *116*, 10212−10240. (f) Di Bella, S.; Gulino, A.; Lanza, G.; Fragalà, I. L.; Stern, D.; Marks, T. J. *Organometallics*, **1994**, *13*, 3810−3815.

[31] Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2556−2558.

Table 4. Literature Ionization Potential Values for Metal Complexes

complex	ionization potential (eV)[a,b]	ref
$GeCl_4$	11.88	36
$Ge(Me)_4$	9.33	36
$Ge(CH_2{}^tBu)_4$	9.01	36
$Ge(CH[TMS]_2)_2$	7.75	39
$SnCl_4$	11.5	42
$Sn(Me)_4$	8.89	37
$Sn(CH_2{}^tBu)_4$	8.67	38
$Sn(CH_2TMS)_4$	8.71	39
$SnCl_2$	10.4	41
$Sn(CH[TMS]_2)_2$	7.42	41
$Ti(CH_2{}^tBu)_4$	8.33	36
$Ti(CH_2TMS)_4$	8.58	36
$Zr(CH_2{}^tBu)_4$	8.33	36
$Zr(CH_2TMS)_4$	8.64	36
Cp_2ZrCl_2	8.60	37
$(Me_5Cp)_2ZrCl_2$	7.55	38
$(Me_5Cp)_2ZrMe_2$	7.18	38
Cp_2HfCl_2	8.89	37
$Hf(CH_2{}^tBu)_4$	8.51	36
$Hf(CH_2TMS)_4$	8.58	36
$(1,3\text{-}{}^tBu_2Cp)_2ZrI$	5.72	33
$Hg(Me)_2$	9.3	40
$Hg(CH[TMS]_2)_2$	8.12	41
$Cd(Me)_2$	8.8	40
$Cd(CH_2TMS)_2$	8.8	40

[a] 1.00 eV = 23.1 kcal/mol. [b] Uncertainties are typically reported as ±0.1 eV or less.

abstractor, both the methyl radical electron affinity and the borane methide affinity are invariant. Therefore, parameters describing methide abstraction enthalpy differences between two different metallocene dialkyls differing in R group can be described by eq 7 where $L_2 = (1,2\text{-}Me_2Cp)_2$

$$\Delta\Delta H_{form} = \{D[L_2M(R)\text{-}Me] - \mathit{D}[\mathit{L_2M(R)\text{-}Me}]\} + \{IP - \mathit{IP}\} - \{\Delta H_{ips} - \Delta \mathit{H}_{ips}\} \quad (7)$$

Bond dissociation enthalpy values for $D[(Me_5Cp)_2Zr(Me)\text{-}Me]$, $D[Cp_2Zr(Me)\text{-}Me]$, and $D[(Me_5Cp)_2Hf(Me)\text{-}Me]$ of 67.2(1.0), 67.0(1.0), and 72.0(3.7) kcal/mol, respectively,[32] argue that M−Me bond enthalpies are relatively insensitive to cyclopentadienyl ancillary ligand substitution (excepting cases with extreme steric congestion[33]) and metal identity. The limited thermochemical data available for $Cp_2M(X)R/Cp^*M(X)R$ complexes[32] suggest that X = alkyl effects on $D[L_2M(R)\text{-}Me]$ should be relatively small. Ionization potentials for trivalent Zr and Hf metallocenes as a function of σ-alkyl substituent such as those addressed here (R = Me, $CH_2{}^tBu$, CH_2TMS, and $CH[TMS]_2$) are not readily available (only a single IP value is available for a trivalent zirconocene, $[1,3\text{-}{}^tBu_2Cp]_2ZrI$, 5.72 eV[33]). Table 4 collects available IP values for homoleptic and Zr and Hf metallocene complexes as well as for main group elements with similar alkyl substituents. It can be seen that Zr vs Hf IP data differ only modestly for identical ligation,[34−37] while Cp methylation reduces the IP substantially.[38] The trend of decreasing IP values from $GeMe_4$[36] to $Ge(CH_2{}^tBu)_4$[36] (ΔIP = −0.29 eV), from $SnMe_4$[37] to $Sn(CH_2{}^tBu)_4$[38] and $Sn(CH_2TMS)_4$[39] (ΔIP = −0.22 and −0.18 eV, respectively), and from $CdMe_2$[40] to $Cd(CH_2TMS)_2$[40] (ΔIP = 0.0 eV), indicates the progression R = Me → $CH_2{}^tBu$ and CH_2TMS transfers increasing electron density to the metal center (more effectively stabilizes positive charge). Furthermore, the diminution of IP values from $HgMe_2$[40] to $Hg[CH(TMS)_2]_2$[41] (ΔIP = −1.2 eV) argues that $CH(TMS)_2$ substitution can depress IPs by ~28 kcal/mol vs R = Me. Lowering of IP values for R = $CH(TMS)_2$ is also observed from $SnMe_4$[42] to $Sn[CH(TMS)_2]_2$[41] (ΔIP = −1.5 eV), which exceeds the depression expected for a reduction in Sn oxidation state as estimated from $SnCl_4$[42] vs $SnCl_2$[41] (ΔIP = −1.1 eV). Taken in total, the above data argue that the progression R = Me → $CH_2{}^tBu$, CH_2TMS → $CHTMS_2$, will have a similar effect in depressing the group 4 L_2MR IP values in Figure 5.

The thermochemical data indicate that ΔH_{form} values for the present metallocenium systems are strongly influenced both by metal alkyl and cyclopentadienyl substituents. Versus $(1,2\text{-}Me_2Cp_2)ZrMe_2$, $-CH(TMS)_2$ substitution at the zirconocene center increases the exothermicity of CH_3^- abstraction by 34.6 kcal/mol, while permethylation of the Cp ligands increases ΔH_{form} by somewhat less, 12.1 kcal/mol. The aforementioned IP data and the Born−Haber analysis are consistent with the observed large alkyl group electronic effects on ΔH_{form}. However, note that stabilization via release of steric congestion upon CH_3^- abstraction is also likely operative in $(1,2\text{-}Me_2Cp)_2Zr(Me)CH(TMS)_2$ and $(Me_5Cp)_2ZrMe_2$. Within the Born−Haber cycle description, such strain would most likely be manifested in diminished $D(L_2MR-CH_3)$ values, although IP may be influenced as well. For $(1,2\text{-}Me_2Cp)_2ZrCH(TMS)_2^+$, it is likely that agostic interaction **III** (vide supra), identified in the low-temperature ^1H NMR, imparts additional stabilization.[43]

ΔH_{ips}, the Coulombic and covalent stabilization accrued by joining the metallocenium cation and the methylborate anion (Figure 5),[27] is the other major parameter defining ΔH_{form}. While we know of no way to measure this parameter directly, ring or R steric bulk which enforced greater cation−anion separation would doubtless be electrostatically destabilizing. This qualitative contention is supported by recent ab initio computational studies on the $R_2Si(R'_4C_5)(R''N)TiR'''\cdot H_3CB(C_6F_5)_3$ system to be discussed elsewhere.[27c] To the extent that the magnitudes of the present measured kinetic $\Delta H^{\ddagger}_{reorg}$ parameters of Table 3 index the "tightness" of ion pairing and hence would qualitatively track ΔH_{ips}, then the decline in $\Delta H^{\ddagger}_{reorg}$ values from R = Me to R = $CH_2{}^tBu$ ~ CH_2TMS by ~4−5 kcal/mol and from R = Me to R = $CH(TMS)_2$ by ~13 kcal/mol argues that the

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[33] For an example where extreme metallocene intramolecular nonbonded repulsion can affect bonding energetics, see: King, W. A.; DiBella, S.; Gulino, A.; Lanza, G.; Fragalà, I. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 355−366.

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[42] Bancroft, G. M.; Pellach, E.; Tse, J. S. *Inorg. Chem.* **1982**, *21*, 2950−2955.

[43] There is a literature precedent for electronic stabilization effects by this substituent: (a) Bassindale, A. R.; Taylor, P. G. in *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 14, pp 893−956. (b) Fleming, I. in *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon Press: Oxford, U.K., 1979; Chapter 13, pp 541−671.

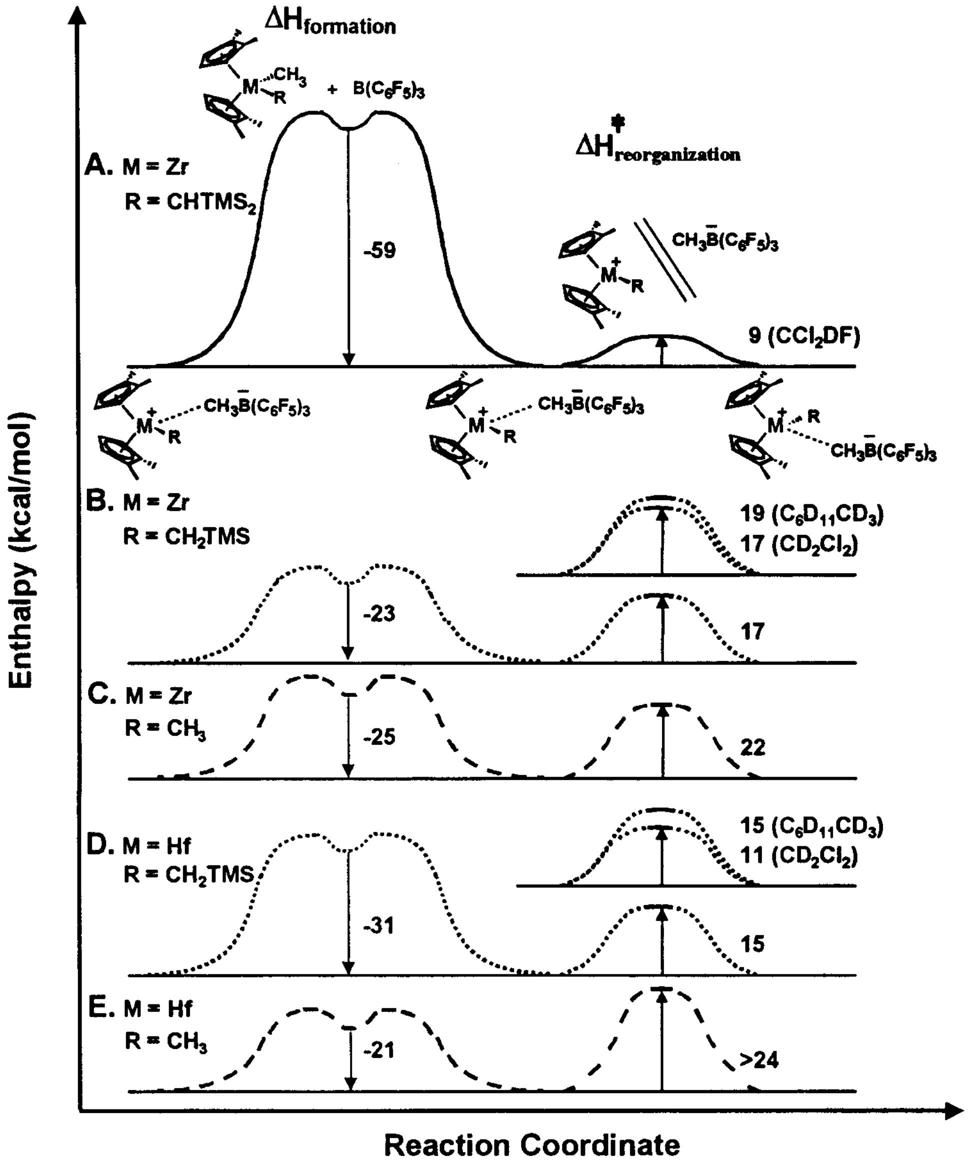


Figure 6. Reaction coordinate for formation and structural reorganization of (1,2-$Me_2Cp)_2M(R)^+$ $MeB(C_6F_5)_3^-$ ion-pairs where R = Me, CH_2TMS, and CH(TMS)$_2$ in toluene solution unless otherwise noted. Features representative of $\Delta H^\ddagger_{form}$ processes are shown as a "double hump", in accord with ref 4b. No information is available on ΔH_{reorg}.

ion-pairing interactions are significantly greater and hence enhance ΔH_{form} for smaller, less-electron-donating alkyl substituents, which allow closer cation−anion approach/interaction.

Ion-Pair Formation and Reorganization Reaction Coordinates. The schematic potential surfaces in Figure 6 illustrate the relative energetics of ion-pair formation from the neutral precursors and reorganization symmetrization as a function of R and solvent. Combined with earlier data for (1,2-Me_2-$Cp)_2MMe^+MeB(C_6F_5)^-_3$ and other $L_2MMe^+MeB(C_6F_5)_3^-$ systems,[4b] these results and those in Tables 1 and 3 lead to the following generalizations:

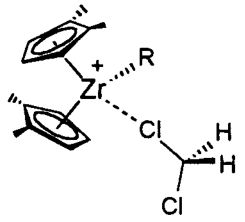
1. Sterically encumbered alkyl groups can greatly stabilize metallocenium ion-pairs with respect to the neutral precursors.

2. For alkyl groups more closely approximating growing poly-(α-olefin) chains, the stabilization versus R = Me is less (~0 kcal/mol for M = Zr, R = CH_2TMS; ~10 kcal/mol for M = Hf, R = CH_2TMS).

3. All alkyl groups examined depress the barrier to ion-pair reorganization (eq 5; $\Delta H^\ddagger_{reorg}$) versus R = Me. The effect is largest for sterically encumbered R groups.

4. Polar solvents lower the barrier to ion-pair reorganization; however, the effect is greatest for sterically unencumbered R = Me. This may reflect inhibition of cation solvation or specific solvent complexes (e.g., **IV**) in the case of larger R. The present results include the first measurements of $\Delta H^\ddagger_{reorg}$ in a saturated hydrocarbon solution. The barrier is increased slightly (2−4 kcal/mol) versus that in toluene (Table 3, complexes **5c** and **6c**).

IV



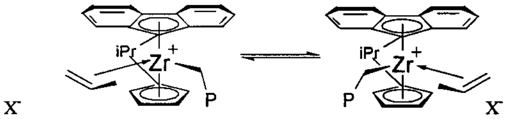
5. In the (1,2-$Me_2Cp)_2MMe^+MeB(C_6F_5)_3^-$ series,[4b] $\Delta H^\ddagger_{reorg}$ is only less than $|\Delta H_{form}|$ and $|-\Delta H_{form} + \Delta H^\ddagger_{form}|$ (estimated formation barriers from the neutrals are small[4b]) for M = Zr.

However, for the larger R substituents of the present series, $\Delta H^{\ddagger}_{\mathrm{reorg}}$ is invariably less than $|\Delta H_{\mathrm{form}}|$. Hence, reorganization of the ion pair is substantially more rapid under the present conditions than borane dissociation−reassociation.

***β*-Methyl Elimination Kinetics.** β-Alkyl elimination is an important chain-transfer mechanism in single-site α-olefin polymerization/oligomerization and can be the predominant mechanism under conditions such as low monomer concentrations or for specific catalysts.[26e,f,h] β-Me elimination can be kinetically favored over β-H elimination in cases of specific steric interactions, even though β-H elimination is thermodynamically favored by ~10 kcal/mol.[26f,32] In the present complexes, β-Me elimination is only realistically possible for $(1,2\text{-}Me_2Cp)_2ZrCH_2{}^tBu^+\ MeB(C_6F_5)_3^-$ (**5c**) and $(1,2\text{-}Me_2Cp)_2HfCH_2{}^tBu^+\ MeB(C_6F_5)_3^-$ (**6c**). In this case, the process obeys first-order kinetics, and the enthalpy of activation for Zr is higher than that for Hf, $\Delta H^{\ddagger}_{\beta-\mathrm{Me}} = 22.5(0.9)$ kcal/mol vs 17.3(0.9) kcal/mol, respectively. However, this difference is partly offset by the corresponding entropies of activation, $\Delta S^{\ddagger}_{\beta-\mathrm{Me}} = 4.3(3.3)$ cal/mol·K vs −11.9(3.4) cal/mol·K, respectively (Table 2). Thus, the β-Me elimination rates for Zr and Hf are comparable near 0 °C as indicated by $\Delta G^{\ddagger}_{\beta-\mathrm{Me}}$ values (Table 2), while at higher temperatures β-Me elimination in the Hf complex becomes less favored versus the Zr complex. There is also a strong dependence on ancillary ligation. For example, the analogous complex $(Me_5Cp)_2ZrCH_2{}^tBu^+\ MeB(C_6F_5)_3^-$ cannot be observed by in situ NMR at temperatures as low as −75 °C because of the facile β-Me elimination (the complex can be stabilized as THF or RCN adducts).[26c] In contrast, significantly less hindered $Cp_2ZrCH_2{}^tBu^+\ MeB(C_6F_5)_3^-$ is reported to be stable at 0 °C in toluene solution.[26c]

Kinetic Comparison of Ion-Pair Reorganization and Olefin Enchainment Rates. Potentially, structural reorganization of the metallocenium ion-pair is intimately connected with olefin enchainment. A relevant example is the methylalumoxane (MAO) activated form of Ewen's $^{i}Pr[Cp\text{-}1\text{-}Flu]ZrCl_2$ propylene polymerization catalyst (**V**, eq 8; X⁻ = "MAO⁻").[5,44,45]

V



(8)

The high syndiospecificity in propylene polymerization is thought to result from (1) alternating olefin insertions at the enantiomeric "left" and "right" catalyst coordination sites and (2) enantiofacial orientation of each inserting propylene unit as a result of steric constraints imposed by the ancillary ligand and propagating chain structure. This mechanism requires that the growing polymer chain "swing" from side to side concurrent with each insertion, analogous to the ion pair reorganization depicted in eq 5. If this is the case, then it may be expected that the MAO-based counteranion[9,46] undergoes concurrent repositioning with each insertion. Rates in toluene solution for methylborate anion/R repositioning in the present $(1,2\text{-}Me_2Cp)_2ZrR^+\ MeB(C_6F_5)_3^-$ complexes range at 25 °C from ~0.2 s^{-1} for R = Me to 2.6×10^7 s^{-1} for R = CH(TMS)$_2$; however, R = CH$_2$TMS (rate = 160 s^{-1}) is likely a more realistic approximation of a growing polypropylene chain.[47] Rates of propylene enchainment in these and related complexes vary depending upon conditions. As an example, the rate of monomer enchainment is ~130 s^{-1} for Ewen's catalyst at 25 °C in neat polypropylene.[44b,48] Propylene polymerization turnover frequencies for a number of borane-activated metallocenes are compiled in Table 5 and range from 4 to 126 s^{-1}.[4c] If measured rates of ion-pair reorganization (if synonymous with "chain swinging") were vastly lower than measured enchainment rates, it is difficult to envision how this process could be coupled to the stereoselective enchainment mechanisms discussed for such systems.[49] On the other hand, if ion-pair reorganization rates were far in excess of enchainment rates, then coupling of chain swinging to enchainment at the observed rates is not implausible; however, site isomerization prior to enchainment could lead to stereoerrors. In either case, the present data indicate that the rates of the two processes are not vastly different. This issue is being explored further in ongoing experimental and theoretical studies.

Table 5. Propylene Polymerization Rates for Selected Metallocenium Catalysts[a]

catalyst	T(°C)	turnover frequency (s^{-1})
$Me_2C(Cp)(Flu)ZrMe_{2,} + B(C_6F_5)_3$	24	2
$Me_2C(Cp)(Flu)ZrMe_{2,} + B(C_{12}F_9)_3$	24	2
rac-$Me_2Si(Ind)_2ZrMe_{2,} + B(C_6F_5)_3$	24	12
rac-$Me_2Si(Ind)_2ZrMe_{2,} + Ph_3C^+B(C_6F_5)_4^-$	24	38
rac-$Me_2Si(Ind)_2ZrMe_{2,} + B(C_{12}F_9)_3$	24	62
rac-$Me_2Si(Ind)_2ZrMe_{2,} + B(C_6F_5)_3$	60	15
rac-$Me_2Si(Ind)_2ZrMe_{2,} + Ph_3C^+B(C_6F_5)_4^-$	60	126
rac-$Me_2Si(Ind)_2ZrMe_{2,} + B(C_{12}F_9)_3$	60	106

[a] Polymerizations carried out in toluene solution at 1 atm of propylene under conditions designed to minimize mass-transfer effects. See ref 4c.

Conclusions

The dependence of methide abstraction thermodynamics and catalyst ion-pair structural reorganization dynamics on the size and electronic structure of the metal-bound R substituent has been shown to be substantial for the series of complexes having the formula $(1,2\text{-}Me_2Cp)_2MR^+\ MeB(C_6F_5)_3^-$. The sterically encumbered R = CH(TMS)$_2$ group strongly promotes ion-pair formation by stabilization of the metal cationic charge and by release of steric strain from the neutral metallocene precursor. Ion-pair reorganization barriers generally decrease as the alkyl substituent increases in size, and barriers are further lowered by solvents of higher dielectric constant, able to stabilize charge-separated intermediates. β-Me elimination activation parameters for R = CH$_2{}^t$Bu complexes are higher for Zr than for Hf; however, higher temperatures enhance elimination in Zr as a result of entropic contributions. Finally, rates of ion-pair

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(46) MAO solutions are complex oligomeric mixtures; however, recent evidence suggests that a major role is anionic stabilization of the cationic metal center. See refs 9a,c,d.

(47) R = CH$_2{}^t$Bu is equally representative of a polymer chain as R = CH$_2$TMS. Both exhibit similar $\Delta H^{\ddagger}_{\mathrm{reorg}}$ and $\Delta G^{\ddagger}_{\mathrm{reorg}}$ parameters (Table 3).

(48) Olefin polymerization rates are sensitive to the reaction conditions. For comparison, the same catalyst activated with MAO at 50 °C, 100 psi of propylene, and in toluene solution exhibits a turnover frequency of ~1600 s^{-1} (Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bott, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1999**, *48*/*49*, 253−295). For comparison, a reasonably active metallocene ethylene polymerization catalyst activated with $B(C_6F_5)_3$ at 25 °C, 1 atm of ethylene in toluene solution exhibits a turnover frequency of 50 s^{-1} (See ref 4b).

(49) We cannot exclude the possibility that the presence of olefin might "loosen" the ion pairing in some noncoordinative (i.e., without embarking on the enchainment reaction coordinate) or coordinative but nonpreinsertive manner. However, it is difficult to envision how this type of mobilization could be more effective than neat aromatic solvents.
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stereomutation and propylene polymerization are not vastly different, suggesting that chain-swinging/anion motion may be closely coupled in some stereoselective chain propagation mechanisms.

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