Highly Electrophilic Olefin Polymerization Catalysts. Quantitative Reaction Coordinates for Fluoroarylborane/Alumoxane Methide Abstraction and Ion-Pair Reorganization in Group 4 Metallocene and "Constrained Geometry" Catalysts

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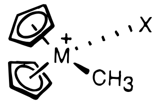
Abstract: Reaction enthalpies of group 4 metallocenes having the general formula $L_2M(CH_3)_2$ (L = Cp, 1,2-Me_2Cp, Me_5Cp; L_2 = $Me_2Si(Me_4Cp)(^tBuN)$; M = Ti, Zr, and Hf) with the strong organo-Lewis acid $B(C_6F_5)_3$ were measured using batch titration calorimetry in toluene. Methide abstraction to form the corresponding $L_2MCH_3^+CH_3B(C_6F_5)_3^-$ contact ion pairs is highly exothermic in all cases. Exothermicity increases with increasing Cp methyl substitution: for M = Zr, $\Delta H = -23.1(3)$, $-24.3(4)$, and $-36.7(5)$ kcal mol^{-1} for L = Cp, Me_2Cp, and Me_5Cp, respectively. For M = Hf and L = 1,2-Me_2Cp, $\Delta H = -20.8(5)$ kcal mol^{-1}. "Constrained geometry" complexes (L_2 = $Me_2Si(Me_4Cp)(^tBuN)$) exhibit similar exothermicities, with $\Delta H = -22.6(2)$, $-23.9(4)$, and $-19.3(6)$ kcal mol^{-1} for M = Ti, Zr, and Hf, respectively. In contrast, analogous reactions with methylalumoxane (M:Al = 1:50) are less exothermic, with $\Delta H = -10.9(3)$ and $-8.9(4)$ kcal mol^{-1} for L = 1,2-Me_2Cp and M = Zr and Hf, respectively. Under identical conditions, $(1,2\text{-}Me_2Cp)_2M(CH_3)_2$ (M = Zr, Hf) complexes also undergo methide abstraction with the less Lewis-acidic triarylboranes $(C_6F_5)_2$BAr (Ar = 3,5-$C_6H_3F_2$, Ph, and 3,5-$C_6H_3Me_2$); however, conversions to the corresponding $(Me_2Cp)_2MCH_3^+$ $CH_3B(C_6F_5)_2Ar^-$ ion pairs are incomplete. Variable-temperature NMR measurements yield thermodynamic parameters for partial methide abstraction by these less Lewis-acidic boranes. For Ar = 3,5-$C_6H_3F_2$, $\Delta H = -18.7(7)$ and $-15.2(8)$ kcal mol^{-1} with $\Delta S = -42(2)$ and $-35(3)$ e.u.; for Ar = Ph, $\Delta H = -14.8(8)$ and $-13.3(6)$ kcal mol^{-1} with $\Delta S = -31(2)$ and $-39(2)$ e.u.; for Ar = 3,5-$C_6H_3Me_2$, $\Delta H = -10.8(6)$ and $-12.7(5)$ with $\Delta S = -19(2)$ and $-36(4)$ e.u., in each case for M = Zr and Hf, respectively. Dynamic NMR analyses reveal that the *activation* barriers for methide abstraction from the neutral metallocene dialkyls are small and relatively insensitive to the borane identity ($\Delta H^\ddagger = 2-6$ kcal mol^{-1}) while ion-pair separation/recombination processes are greatly facilitated by polar solvents. Ethylene polymerization activities for eight $(Me_2Cp)_2MCH_3^+$ $CH_3B(C_6F_5)_2Ar^-$ complexes measured in toluene solution (25 °C, 1 atm) follow a trend in metal (Zr > Hf) as well as a substantial trend in triarylborane (Ar = C_6F_5 > 3,5-$C_6H_3F_2$ > Ph ∼ 3,5-$C_6H_3Me_2$). Polymerization activities correlate roughly with MCH_3^+ ^{13}C NMR chemical shifts and enthalpies of methide abstraction.

Introduction

Transformations attending alkyl or hydride anion abstraction from group 4 complexes by strong Brønsted or Lewis acids are currently of great interest owing to their central significance in the activation and function of homogeneous "single-site" Ziegler−Natta catalysts[1] based on metallocene[1] and quasi-metallocene[1,2] frameworks. Synthetic studies have shown that with carefully selected metallocenes, Lewis acidic reagents, and reaction conditions, this abstraction process yields highly electrophilic, mononuclear ion pairs (e.g., **A**), which exhibit unprecedented olefin polymerization activity and selectivity. A number of these species have now been structurally characterized.[2a,3]

A



In reality, "simple" functional models for homogeneous Ziegler−Natta catalysts remain scarce. Surprisingly few Lewis

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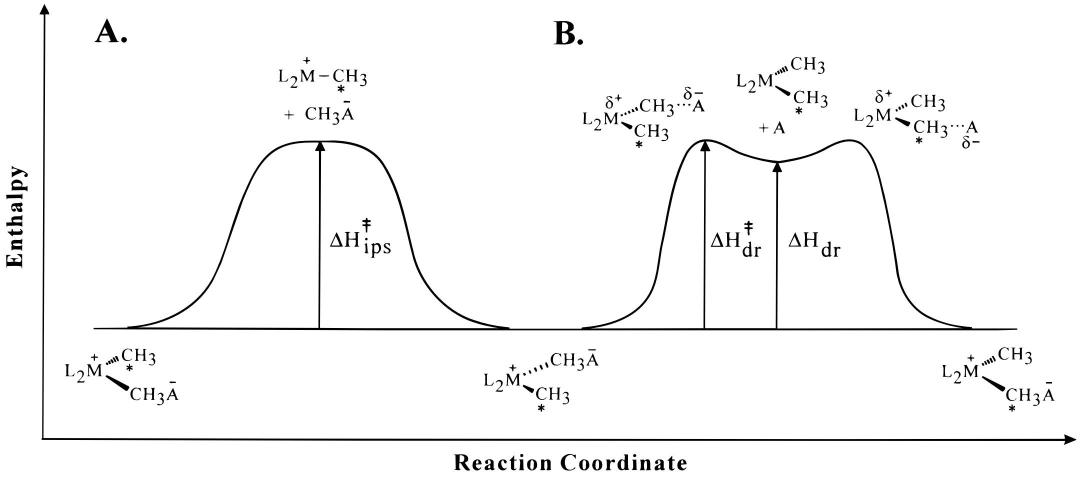
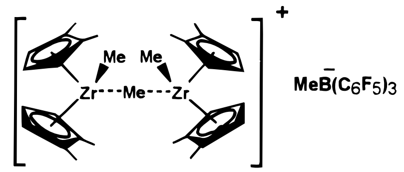


Figure 1. Schematic enthalpic reaction coordinates for metallocenium ion pair reorganization processes: (A) ion pair separation/recombination (ips), (B) Lewis acid methide abstraction/recombination (dr).

acids react with metallocenes to cleanly afford soluble complexes with desirable catalytic activities, and still fewer afford rigorously characterized active species. Effective cocatalysts include Ph_3C^+ (with appropriate weakly coordinating counteranions),[4] perfluoroarylboranes,[4,5] and MAO (methylalumoxane).[1,6] The most important common features appear to be: (1) high native acidity of the electron-deficient centers and (2) lack of labile nucleophilic substituents that might serve as catalyst poisons. For example, simple trihaloboranes (BF_3, BCl_3) irreversibly transfer F^- or Cl^- to the metal center affording inactive metallocene halides,[1] while alkylaluminum halides lead to M(μ-Cl)Al structures, which have generally proven challenging to characterize and exhibit only modest catalytic activity.[7] Even in the absence of halogens and other donors, “base-free” cationic metallocenes can form μ-Me dinuclear species (**B**)[1,3d,f,4a] which likely stabilize the highly electrophilic metal fragments.[3d,4a,8] In contrast to these qualitative observations, quantitative aspects of this chemistry remain virtually undocumented.

B



Complex temperature-dependent chemical/structural equilibria are ubiquitous in metallocenium chemistry. The simplest of these is the *reversible* abstraction of alkide or hydride ligands by a Lewis acid (A, eq 1; R = alkyl, H). With A = Ph_3C^+,

$$L_2MR_2 + A \rightleftarrows L_2MR^+RA^- \tag{1}$$

this equilibrium likely lies far to the right, while with A = MAO and $B(C_6F_5)_3$, those factors affecting the position of this equilibrium are presently unclear, however the relative acidities of A and the metallocenium cation, as well as the energetics of contact ion-pairing, must certainly be chief among them. While studies of ligand steric and electronic effects,[1] solvent effects,[9] and anion effects[3b,d,4,10] offer important incremental improvement in understanding these ion pairs, the kinetic and thermodynamic constraints under which neutral dialkylmetallocenes are converted to metallocenium species remain largely unquantified. Such information is crucial to understanding catalyst stability, activity, and stereoselectivity.

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In the present contribution, we quantify metallocenium ion-pair formation/reorganization thermodynamics and kinetics as represented in Figure 1 for a series of variously substituted Ti, Zr, and Hf metallocene and quasi-metallocene dialkyls with a series of triarylborane and methylalumoxane organo-Lewis acids.[11] We show that enthalpies and entropies of methide abstraction (eq 1; R = CH_3) can be determined by titration calorimetry or by ^1H NMR equilibration measurements, while kinetic aspects can be assessed by dynamic NMR line shape analysis or by 2D EXSY techniques.[12] Furthermore, because triarylboranes can serve as precursors to discrete, well-defined metallocenium catalysts, we have synthesized and characterized three new arylbis(pentafluorophenyl)boranes as well as the corresponding ion-paired adducts with $(1,2\text{-}Me_2Cp)_2M(CH_3)_2$ (M = Zr, Hf) to obtain complete thermodynamic and kinetic methide abstraction profiles as a function of borane Lewis acidity. The effects of metallocene ligation and triarylborane substitution on the thermodynamic and kinetic parameters of methide abstraction are quantified. The electrophilicity of the metallocenium species is additionally examined by measuring metal-bound $^{13}CH_3$ NMR parameters. Finally, possible correlations with ethylene polymerization activities are examined.

Experimental Section

General Considerations. All organometallic complexes were manipulated under rigorously anaerobic conditions using a Vacuum Atmospheres nitrogen-filled glovebox with an efficient recirculator (≤ 1 ppm O_2) or in glassware sealed with Viton O-rings and interfaced to a high-vacuum manifold bearing valved inlets for argon purified by passage through a supported MnO bed.[3e,4a] Other reactions were carried out using standard Schlenk techniques. Solvents were freshly distilled from appropriate drying agents.[3e,4a] Elemental analyses were performed by Oneida Research Services (Whitesboro, NY).

Starting Materials and Reagents. The preparation of the pentafluorophenyllithium used in several of the following procedures followed a published method.[13] Reactions of trihaloboranes with arylsilanes were modifications (solvent, temperature) of published procedures.[14] Methylalumoxane (MAO, obtained as a toluene solution from Aldrich) was dried under high vacuum for 15 h to remove excess volatile aluminum alkyls and to produce a solid which could be easily weighed.[6c,15] Tris(pentafluorophenyl)borane (**5a**) was a gift from the Dow Chemical Co. (Freeport, TX). It was purified by crystallization from pentane at −30 °C followed by high vacuum sublimation (80 °C/10^{-5} Torr). Purity was verified by ^{19}F NMR. The complexes $Cp_2Zr(CH_3)_2$,[16a] $(Me_5Cp)_2Zr(CH_3)_2$,[16b] and $(1,2\text{-}Me_2Cp)_2Zr(CH_3)_2$[16c] and the constrained-geometry complexes $Me_2Si(Me_4Cp)(^tBuN)M(CH_3)_2$ (M = Ti, Zr, Hf)[17] were prepared by published methods. $PhBCl_2$ and 1-bromo-3,5-dimethylbenzene (Aldrich) and 1-bromo-3,5-difluorobenzene (PCR) were used as received. Toluene-d_8 was purchased from Isotec and was freshly vacuum-transferred from Na/K. Dimethylcyclopentadiene was synthesized by the method of Skattebøl[18] and converted to the corresponding lithium salt by treatment with *n*-BuLi in hexanes.

NMR Measurements. Routine characterization data were obtained using Varian GEM-300, VXRS-300, and Unity 400-Plus instruments. Variable-temperature ^1H NMR experiments for line-shape analysis and equilbrium constant determinations were carried out on the U400+ instrument using a 5-mm inverse detection probe calibrated with ethylene glycol and methanol temperature standards. Samples were contained in Teflon-valved NMR tubes which were loaded in the glovebox with scrupulously dry, deoxygenated solvent distilled on the high vacuum line. Equilibrium studies were carried out at low concentrations (each precisely known, but nominally 1−4 mM) in order that at least one integrable signal for each important species could be independently measured at four or five temperatures (10 °C intervals) in the slow-exchange regime. Pulse delays of 5 s were found to be adequate for obtaining reliable integration of ^1H NMR signals. Exchange-broadening phenomena were found to be independent of concentration over a 20-fold range. EXSY experiments were carried out according to the methods of Perrin and Dwyer using nominal analytic concentrations of 10 mM.[12]

Due to the limited solubility of a number of the metallocene−borane adducts in toluene at temperatures in the regime of slow exchange, metallocene methyl ligands for ^{13}C chemical shift measurements were isotopically enriched in order to enhance ^{13}C NMR spectral sensitivity. Alkylation of the corresponding dichlorides was carried out using toluene suspensions of fully enriched $^{13}CH_3Li$ prepared from $^{13}CH_3I$ (Cambridge Isotope Laboratories) and lithium in ether followed by recrystallization of the crude product from pentane at −30 °C. Mixtures of isotopically enriched metallocene (nominally 9 mmol) and a slight stoichiometric excess of triarylborane in toluene-d_8 were examined at −60 °C using the Varian VXRS-300 instrument. Chemical shifts (δ_C) and coupling constants ($^1J_{CH}$) for the slightly exchanged-broadened metal methyl ($M{-}CH_3$) and quadrupolar-broadened boron−methyl ($M{\cdots}CH_3{-}B$) signals are provided in Table 6.

Reaction Calorimetry. Enthaplies of reaction between metallocenes and Lewis acids were determined at 25.0 °C in toluene solution. $B(C_6F_5)_3$ and MAO solutions were prepared by vacuum-transferring sufficient toluene from Na/K onto the pure solutes to prepare 100 mL (nominal) of solution, while solutions of organometallic complexes having precisely known concentrations were prepared from Na/K-dried toluene in the glovebox. The organometallic titrant was metered into the stirred excess Lewis acid solution[19] 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 analog recorder. The calorimeter heat capacity was determined by monitoring temperature changes when heat was introduced by a calibrated resistive heater. Each run consisted of several (10−20) sequential titrations carried out for each reaction; average reported deviations are from the mean between these. Overall instrument calibrations using established methods[20] ruled out significant sources of systematic error. Other details of the techniques and

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(19) ^1H NMR experiments indicated that the reactions of the metallocene dimethyl complexes with excess $B(C_6F_5)_3$ quantitatively form mononuclear metallocenium species of the formula $L_2MCH_3^+\ CH_3B(C_6F_5)_3^-$. Further reactions were not observed within 1 h at 25 °C. With the less Lewis acidic triarylboranes described in the text, the methide abstraction process was incomplete; under these conditions, reaction enthalpies are not conveniently determined by titration calorimetry.

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apparatus for carrying out the calorimetric measurements have been described elsewhere.[21] Data analysis followed standard published methods.[22]

Ethylene Polymerization Experiments.[3e,4a] For each polymerization, a precise amount of metallocenium catalyst (**7a**−**d** or **8a**−**d**, nominally 7 mmol) was dissolved in 2.0 mL of Na/K-dried toluene in the glovebox. The catalyst solution was quickly injected with a gastight syringe into a rapidly stirred, ethylene-saturated toluene solution (50 mL) immersed in a room-temperature water bath. The mixture was maintained under 1 atm of ethylene (passed through an activated MnO/SiO_2 column). The temperatures of selected runs were monitored in situ as a function of time using an inserted digital thermometer/thermocouple (OMEGA Engineering, model HH21). For the most active catalysts studied, exotherms were never greater than 8 °C over the reaction periods employed (typically 90 s). After a measured time interval, the reaction was quenched by injecting 10 mL of methanol into the mixture. Reaction times were dictated by the activity of the catalyst (as short as 30 s for Table 6, entry 1; as long as 30 min for Table 6, entry 8). The resulting polymeric solid was collected by filtration. Evaporation of the filtrate afforded an insignificant amount of residue. Several runs with each catalyst were performed to derive standard uncertainties in the activities. These data are collected in Table 6.

Representative Propylene Polymerization Experiment. An O-ring-sealed Pyrex reactor fitted with a magnetic stirring bar, a well-sealed septum inlet, and a vacuum line interface, was flamed out under high vacuum and then charged with 30 mmol of dimethylmetallocene precatalyst (**6a**) in the glovebox. Toluene (50 mL) was vacuum-transferred into the reactor from Na/K, and the reactor was back-filled with an atmosphere of propylene (passed through a MnO/SiO_2 column) and equilibrated at 25 °C. A solution of phenylbis(pentafluorophenyl)-borane (**5c**, 45 mmol in 2 mL of toluene) was then injected in a single portion using a gastight syringe. The mixture was rapidly stirred at room temperature for 1.0 h under an atmosphere of propylene. The reaction was then quenched with methanol (1 mL), and the mixture was washed with aqueous sodium bicarbonate. A portion of the organic layer was subjected to GC/MS analysis to determine the production of dimers and lower oligomers, but none were detected. The remaining toluene solution was evaporated and dried under high vacuum to leave only a small residue (<50 mg) of a dark liquid, which had an appearance and ^{1}H NMR spectrum consistent with atactic polypropylene.

Trimethyl(3,5-difluorophenyl)silane (3b).[23a] To a solution of 1-bromo-3,5-difluorobenzene (19 g, 0.10 mol) in ether (300 mL) maintained at −78 °C was added *n*-butyllithium (45 mL, 2.5 M in hexanes, 0.11 mol), and the resulting mixture was stirred at −78 °C for 2 h. Chlorotrimethylsilane (16 g, 0.15 mol) was then added in one portion. The resulting mixture was warmed to 25 °C with stirring. Aqueous workup and distillation of the crude oil afforded trimethyl-(3,5-difluorophenyl)silane as a colorless liquid (14 g, 0.075 mol, 75%): bp 69−72 °C (20 Torr); ^{1}H NMR ($CDCl_3$): δ 6.99 (m, 2 H), 6.76 (tt, $^{3}J_{HF} = 8.6$ Hz, $^{4}J_{HH} = 2.4$ Hz, 1 H), 0.28 (s, 9 H); ^{13}C NMR ($CDCl_3$): δ 162.8 (**C**F, dd, $^{1}J_{CF} = 262$ Hz, $^{3}J_{CF} = 14$ Hz), 115.3 (**C**Si, d, $^{3}J_{CF} = 9$ Hz), 115.3, (**C**H, $^{2}J_{CF} = 22$ Hz), 104.0 (**C**H, t, $^{2}J_{CF} = 25$ Hz), 1.4 (**C**H_3, s).

Dibromo(3,5-difluorophenyl)borane (4b). A solution of trimethyl-(3,5-difluorophenyl)silane (4.35 g, 23.4 mmol) and boron tribromide (13.0 g, 50.0 mmol) in heptane (50 mL) was stirred under reflux for 24 h. After cooling the reaction mixture, the volatile components were removed under vacuum to leave a dark residue, which contained about 10% of the starting silane according to ^{19}F NMR analysis. Two crystallizations from pentane afforded 2.06 g (7.25 mmol, 31%) of colorless, highly deliquescent crystals of the desired dibromoarylborane: ^{1}H NMR (C_6D_6): δ 7.36 (m, 1 H), 6.54 (m, 2 H); ^{13}C NMR (C_6D_6): δ 162.8 (dd, $^{3}J_{CF} = 252$ Hz, $^{4}J_{CF} = 11$ Hz, **C**F), 140.8 (br s, **C**B), 119.6 (dd, $^{3}J_{CF} = 18$ Hz, $^{4}J_{CF} = 7$ Hz, **C**H), 110.2 (t, $^{3}J_{CF} = 25$ Hz, **C**H).

3,5-Difluorophenylbis(pentafluorophenyl)borane (5b). A solution of dibromo(3,5-difluorophenyl)borane (2.1 g, 7.4 mmol) in pentane (20 mL) was added by cannula to a stirred pentane suspension of pentafluorophenyllithium (prepared from C_6F_5Br and *n*-BuLi in rapidly stirred pentane at − 78 °C). The resulting mixture was stirred for 12 h while slowly warming from − 78 to 25 °C. A fine white precipitate of LiBr was then separated by filtration. Evaporation of the filtrate and recrystallization of the residue from 40 mL of pentane at −30 °C afforded the crude triarylborane in two crops of off-white, feathery crystals. Sublimation (90 °C, 1 × 10^{-5} Torr) afforded a colorless solid (1.0 g, 2.2 mmol, 30%); ^{1}H NMR (toluene-d_8): δ 7.12 (m, 2 H), 6.62 (m, tt, $^{3}J_{HF} = 8.7$ Hz, $^{4}J_{HH} = 2.4$ Hz, 1 H); ^{13}C NMR (CD_2Cl_2): δ 163.4 (**C**F, dd, $^{1}J_{CF} = 250$ Hz, $^{3}J_{CF} = 11$ Hz), 147.6 (**C**F, d, $^{1}J_{CF} = 242$ Hz), 144.3 (**C**F, d, $^{1}J_{CF} = 252$ Hz), 138.0 (**C**F, d, $^{1}J_{CF} = 254$ Hz), 120.5 (**C**H, dd, $^{2}J_{CF} = 23$ Hz, $^{4}J_{CF} = 9$ Hz), 113.8 (**C**, m), 111.2 (**C**H, t, $^{2}J_{CF} = 25$ Hz) (the signal for the boron-attached carbon of the $C_6H_3F_2$ ring was not observed); ^{19}F (C_6D_6): δ −109.8 (t, $^{3}J_{FH} = 7.1$ Hz, 2 F), −129.8 (complex d, $^{3}J_{FF} = 23$ Hz, 4 H), −146.3 (t, $^{3}J_{FF} = 21$ Hz, 2 F), −161.0 (complex t, $^{3}J_{FF} = 21$ Hz, 4 F). Anal. Calcd for $C_{18}H_3BF_{12}$: C, 47.20; H, 0.66. Found: C, 46.92; H, 0.59; and C, 46.99; H, 0.56.

Phenylbis(pentafluorophenyl)borane (5c). To a suspension of C_6F_5Li in pentane at − 78 °C, prepared from C_6F_5Br (34 g, 0.14 mol) and *n*-butyllithium (90 mL, 1.6 M in hexanes, 0.14 mol) in rapidly stirred pentane at − 78 °C, was added dichlorophenylborane (10 g, 0.063 mol) using a syringe. The mixture was stirred while warming to 25 °C over a period of 12 h and then filtered to remove LiCl. The filtrate was evaporated, and the resulting tan residue was recrystallized from 25 mL pentane to afford an off-white solid, which was sublimed at 100 °C (1 × 10^{-5} Torr) to afford the desired triarylborane as a colorless solid (8.5 g, 0.020 mol, 32%): ^{1}H NMR (toluene-d_8): δ 7.78 (d, $^{3}J = 7.4$ Hz, 2 H), d 7.49 (tt, $^{3}J = 6.9$ Hz, $^{4}J = 2.1$ Hz, 1 H), 7.36 (t, $^{3}J = 7.1$ Hz); ^{13}C NMR (toluene-d_8): δ 146.7 (CF, d, $^{1}J_{CF} = 247$ Hz), 143.2 (CF, d, $^{1}J_{CF} = 256$ Hz), 139.6 (CH), 138.7 (C, br), 137.7 (CF, d, $^{1}J_{CF} = 253$ Hz), 136.8 (CH), 128.6 (CH), 114.1 (C, br m); ^{19}F NMR (C_6D_6): δ −130.6, (d, $^{3}J_{FF} = 26$ Hz, 4 F), −149.3 (t, $^{3}J_{FF} = -21$ Hz, 2 F), −161.9 (complex t, $^{3}J_{FF} = 22$ Hz, 4 F). Anal. Calcd for $C_{18}H_5BF_{10}$: C, 51.23; H, 1.19. Found: C, 51.11; H, 1.01; and C, 51.03; H, 1.00.

Trimethyl(3,5-dimethylphenyl)silane (3d).[23b] To a solution of 3,5-dimethyl-1-bromobenzene (28 g, 0.15 mol) in diethyl ether was added *n*-BuLi (80 mL, 2.5 M in hexanes, 0.20 mol); LiBr began to precipitate immediately. The mixture was stirred under reflux for 1 h and then cooled to 25 °C. Chlorotrimethylsilane (27 g, 0.25 mol) was added via syringe, resulting in the precipitation of LiCl, and the solution was stirred under reflux for an additional 1 h. The solution was then cooled to 25 °C, and the solvents were removed under reduced pressure. Aqueous workup afforded a pale yellow oil, which was distilled under reduced pressure (88−90 °C, 11 Torr) to afford a colorless oil (24 g, 0.13 mol, 87%) of trimethyl(3,5-dimethylphenyl)silane. ^{1}H NMR ($CDCl_3$): δ 7.19 (s, 2 H), 7.04 (s, 1 H), 2.38 (s, 6 H), 0.31 (s, 9 H); ^{13}C NMR ($CDCl_3$): δ 140.2 (**C**CH_3), 137.0 (**C**Si), 131.0 (**C**H), 130.5 (**C**H), 21.4 (Ar**C**H_3), 1.1 (**C**H_3Si).

Dichloro(3,5-dimethylphenyl)borane (4d). Trimethyl(3,5-dimethylphenyl)silane (18 g, 0.10 mol) was added to a solution of boron trichloride (120 mL, 1.0 M in dichloromethane, 0.12 mol) maintained at − 78 °C in a 200-mL Schlenk flask. A dry ice condenser was fitted, and the mixture was warmed to 25 °C and then stirred under gentle reflux for 2 h. The solution was next cooled to 25 °C, and the volatile components were transferred to a trap under vacuum. The resulting oil was distilled under reduced pressure (94−97 °C at 9 mmHg) to afford 15 g (0.080 mol, 80%) of dichloro(3,5-dimethylphenyl)borane as a colorless, exceedingly moisture-sensitive liquid: ^{1}H NMR (C_6D_6): δ 7.79 (s, 2 H), 6.91 (s, 1 H), 2.03 (s, 6 H); ^{13}C NMR (C_6D_6): δ 137.6 (**C**CH_3), 136.9 (**C**H), 134.6 (**C**H), 134.0 (**C**B), 21.2 (Ar**C**H_3).

3,5-Dimethylphenylbis(pentafluorophenyl)borane (5d). A solution of dichloro(3,5-dimethylphenyl)borane (9.4 g, 0.050 mol) in pentane (50 mL) was added via cannula to a stirred suspension of pentafluorophenyllithium (prepared from C_6F_5Br and *n*-BuLi in rapidly

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(22) Hansen, L. D.; Lewis, E. A.; Eatough, D. J. In *Analytical Solution Calorimetry*; Grime, K. J., Ed.; Chemical Analysis Monograph 79; Wiley: New York, 1985; Chapter 3.

(23) (a) Effenberger, F.; Haebich, D. *Liebigs Ann. Chem.* **1979**, *6*, 842−867. (b) Laquerre, M.; Dunogues, J.; Calas, R., Duffalt, N. *J. Organomet. Chem.* **1976**, *112*, 49−59.

stirred pentane at −78 °C). The resulting mixture was stirred for 6 h while slowly warming from −78 to 25 °C. A fine white precipitate of LiCl was separated by filtration, and the filtrate was evaporated under vacuum. The residue was recrystallized from 50 mL of pentane at −30 °C to afford 8.1 g (0.018 mol, 36%) of the desired borane. A portion (2.0 g) of the crude borane was sublimed (100 °C, 1 × 10^{-5} Torr) to afford 1.75 g of a highly moisture-sensitive colorless solid: ^{1}H NMR (C_6D_6): δ 7.35 (s, 2 H), 6.90 (s, 1 H), 2.01 (s, 6 H); ^{13}C NMR (toluene-d_8): δ 146.7 (**C**F, d, $^1J_{CF}$ = 244 Hz), 143.2 (**C**F, d, $^1J_{CF}$ = 256 Hz), 139.2 (**C**), 138.2 (**C**), 137.8 (**C**F, d, $^1J_{CF}$ = 251 Hz), 137.5 (**C**H), 137.4 (**C**H), 114.2 (**C**, m), 21.0 (**C**H$_3$); ^{19}F NMR (C_6D_6): δ −131.0 (d, $^3J_{FF}$ = 24 Hz, 4 F), −149.6 (t, $^3J_{FF}$ = 20 Hz, 2 F), −161.8 (complex t, $^3J_{FF}$ = 21 Hz, 4 F). Anal. Calcd for $C_{20}H_9BF_{10}$: C, 53.37; H, 2.02. Found: C, 53.26; H, 1.93; and C, 53.49; H, 1.81.

Bis(1,2-dimethylcyclopentadienyl)hafnium(IV) Dichloride. A solution of $HfCl_4(THF)_2$ (15 g, 32 mmol) and lithium 1,2-dimethylcyclopentadienide (7.0 g, 70 mmol) in tetrahydrofuran (500 mL) was stirred at 25 °C for 2 d. The solvent was then removed under vacuum, and the resulting solid was extracted with chloroform. Concentration of the chloroform solution and recrystallization at −30 °C afforded the desired complex (8.4 g, 19 mmol, 60%) in three crops of colorless needles: ^{1}H NMR ($CDCl_3$): δ 6.01 (t, ^3J = 3.4 Hz, 2 H), 5.95 (d, ^3J = 3.5 Hz, 4 H), 2.14 (s, 12 H); ^{13}C NMR (^{1}H coupled): δ 126.7 (s, **C**CH$_3$), 113.8 (d, $^1J_{CH}$ = 171 Hz, **C**H), 105.3 (dt, $^1J_{CH}$ = 172 Hz, **C**H, $^2J_{CH}$ = 6 Hz), 13.4 (q, $^1J_{CH}$ = 125 Hz, **C**H$_3$). Anal. Calcd for $C_{14}H_{18}Cl_2Hf$: C, 38.59; H, 4.16. Found: C 38.87; H, 3.99; and C, 38.74; H, 3.96.

Bis(1,2-dimethylcyclopentadienyl)hafnium(IV) Dimethyl (6b). A slurry of bis(1,2-dimethylcyclopentadienyl)hafnium(IV) dichloride (4.0 g, 9.2 mmol) and methyllithium (800 mg, 0.037 mmol) in toluene was stirred at 25 °C for 3 d. The mixture was then filtered through Celite to remove lithium chloride and unreacted methyllithium. Evaporation of the colorless filtrate afforded a white solid (3.0 g, 7.8 mmol, 85%), which was shown to be >95% pure by NMR. Recrystallization from toluene gave an analytically pure sample as colorless needles: ^{1}H NMR (C_6D_6): δ 5.37 (d, ^3J = 3.2 Hz, 4 H), 5.18 (t, ^3J = 3.2 Hz, 2 H), 1.92 (s, 6 H), −0.48 (s, 3 H); ^{13}C NMR (proton-coupled, C_6D_6): δ 120.6 (s, **C**CH$_3$) 109.4 (d, $^1J_{CH}$ = 169 Hz, **C**H), 102.9 (d, $^1J_{CH}$ = 171 Hz, **C**H), 37.0 (q, $^1J_{CH}$ = 114 Hz, Zr**C**H$_3$), 13.0 (q, $^1J_{CH}$ = 126 Hz, Cp**C**H$_3$). Anal. Calcd for $C_{16}H_{24}Hf$: C, 48.67; H, 6.13. Found: C, 48.84; H, 5.95; and C, 48.53; H, 5.95.

Bis(1,2-dimethylcyclopentadienyl)hafnium(IV)methyl Methyltris(pentafluorophenyl)borate (8a). A swivel-frit reaction apparatus was charged with bis(1,2-dimethylcyclopentadienyl)hafnium(IV) dimethyl (160 mg, 0.40 mmol) and tris(pentafluorophenyl)borane (210 mg, 0.41 mmol) in the glovebox. The reactor was connected to the vacuum line, and pentane (25 mL) was condensed onto the solids at −78 °C from Na/K. The mixture was warmed with stirring to 25 °C, stirred for 2 h, and then filtered. The precipitate was washed with pentane to afford a colorless solid (330 mg, 0.37 mmol, 92%); ^{1}H NMR (C_6D_6): δ 5.37 (t, ^3J = ^4J = 3.0 Hz, 2 H), 5.22 (t, ^3J = 3.0 Hz, 2 H), 4.72 (t, ^3J = ^4J = 2.7 Hz, 2 H), 1.55 (s, 6 H), 1.26 (s, 6 H), 0.29 (br s, 3 H), −0.10 (s, 3 H); ^{13}C NMR (C_6D_6): δ 148.6 (d, $^1J_{CF}$ = 244 Hz, **C**F), 139.5 (d, $^1J_{CF}$ = 253 Hz, **C**F), 137.6 (d, $^1J_{CF}$ = 242 Hz, **C**F). 114.5 (**C**), 110.9 (**C**H), 105.6 (**C**H), ring **C**CH$_3$ signals not observed (obscured by solvent), C_6F_5 ipso signal not observed, 42.8 (Zr**C**H$_3$), 21.5 (br, B**C**H$_3$), 12.5 (Cp**C**H$_3$), 12.3 (Cp**C**H$_3$); ^{19}F NMR (C_6D_6): δ −133.3 (d, ^3J = 23 Hz, 6 F), −159.2 (t, ^3J = 21 Hz, 3 F), −164.4 (t, ^3J = 21 Hz, 6 F). Anal. Calcd for $C_{34}H_{24}BF_{15}Hf$: C, 45.03; H, 2.67. Found: C, 45.37; H, 2.49; and C, 45.31; H, 2.56.

General Synthetic Procedure for Bis(1,2-dimethylcyclopentadienyl)metal(IV)methyl (Metal = Zirconium or Hafnium) Methyl(aryl)bis(pentafluorophenyl)borates. A swivel-frit reaction apparatus, fitted with two 50-mL (or 100-mL) flasks and a vacuum-line interface, was charged in the glovebox with bis(1,2-dimethylcyclopentadienyl)metal(IV) dimethyl (metal = zirconium (**6a**) or hafnium **(6b),** nominally 0.1 to 0.5 mmol and a slight (10%) excess of the triarylborane (**5b**−**d**). The frit assembly was then mounted on the high vacuum line, and pentane (10−25 mL) was transferred from Na/K onto the solids at −78 °C with stirring. The mixture was then warmed to 25 °C and stirred for an additional 1 h, to afford either a clear solution or a suspension of fine precipitate. Cooling the mixture to −78 °C induced complete precipitation of the product, which was quickly filtered while cold and dried under vacuum. Yields of **7b**−**d** (M = Zr) and **8b**−**d** (M = Hf) are collected in Table 1 along with combustion analytical data. Product yields may be significantly reduced if the mixture is filtered at room temperature or if the precipitates are washed with pentane. ^{1}H NMR data for the new metallocenium complexes are collected in Table 2. Bis(1,2-dimethylcyclopentadienyl)zirconium(IV)methyl methyltris(pentafluorophenyl)borate (**7a**) was prepared by the literature procedure.[3e]

Table 1. Synthetic Yields and Analytical Data for $(1,2\text{-}Me_2Cp)_2MCH_3^+$ $CH_3BAr(C_6F_5)_2^-$ Complexes

				analytical data			
				calcd		found	
entry	M	Ar	% yield	% C	% H	% C	% H
7b	Zr	3,5-$C_6H_3F_2$	83	53.34	3.55	53.54	4.28
7c	Zr	C_6H_5	85	55.97	4.01	56.02	3.91
7d	Zr	3,5-$C_6H_3(CH_3)_2$	72	57.07	4.39	57.11	4.16
8b	Hf	3,5-$C_6H_3F_2$	95	47.88	3.19	48.06	3.48
8c	Hf	C_6H_5	86	49.99	3.58	49.55	3.50
8d	Hf	3,5-$C_6H_3(CH_3)_2$	66	51.18	3.94	51.11	3.92

Results

In this section, the synthesis and characterization of several families of metallocenium ion pairs formed from triarylboranes of varying Lewis acidity are described. Then, thermodynamic parameters obtained by solution calorimetry and ^{1}H NMR equilibrium measurements are reported for methide abstraction from the various metallocenes and quasi-metallocenes by a series of organo-Lewis acids. These thermochemical data are subsequently combined with kinetic parameters obtained from ^{1}H NMR line shape analyses to derive enthalpic and entropic reaction coordinates for methide abstraction/transfer and ion-pair reorganization processes. Trends in the effects of ancillary ligation and abstraction reagent Lewis acidity on methide transfer thermodynamic and kinetic parameters are then discussed. Finally, these data are correlated with NMR ^{13}C chemical shift and coupling constant data as well as with ethylene polymerization activities.

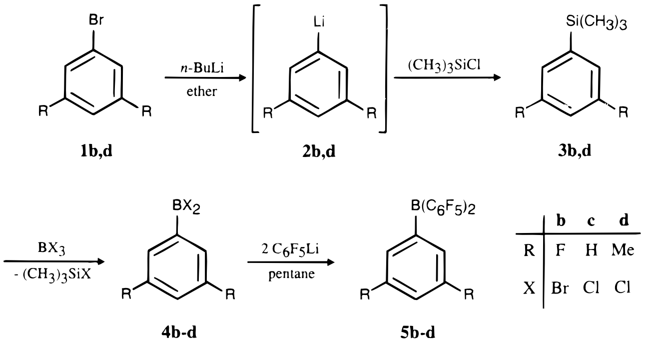
Synthesis and Characterization of $(1,2\text{-}Me_2Cp)_2MCH_3^+$ $CH_3BAr(C_6F_5)_2^-$ Complexes. To examine the effects of varying triarylborane Lewis acidity on the metallocene catalyst activation process, a series of metallocenium salts was prepared in which a methide group is transferred from the group 4 metal center to a triarylborane in which two of the aryl groups are pentafluorophenyl and the third is varied. This overall approach was chosen for the efficiency with which metallocenium borates can be synthesized and rigorously characterized as discreet, monometallic contact ion pairs, and in which ligands and Cp substituents provide convenient spectroscopic probes in ^{1}H NMR spectral line-shape analytical and integration measurements. The triarylborane substituents were chosen in order to incrementally modulate the Lewis acidity of the triarylborane as compared to $B(C_6F_5)_3$; the substantially less Lewis acidic BPh_3 exhibits no detectable reaction with the present metallocene dimethyls at room temperature.[3e] With the metallocene starting materials already in hand, triarylboranes were synthesized via organosilane intermediates as outlined in Scheme 1. Metal−halogen exchange of bromoarenes (**1**) with *n*-butyllithium afforded intermediate lithioarenes (**2**), which were quenched with chlorotrimethylsilane to afford the corresponding arylsilanes (**3**). The arylsilanes were then treated with trihaloboranes[4a,14] to afford intermediate dihaloarylboranes (**4**), which were isolated either as a waxy solid (**4b**) or as an exceedingly moisture-sensitive liquid (**4d**). Treatment of the crude dihaloarylboranes (**4b** and **4d**) and the commercially available phenyl derivative (**4c**) with pentafluorophenyllithium in pentane afforded the respective

Table 2. ^{1}H NMR Data for $(1,2\text{-}Me_2Cp)_2MCH_3^+$ $CH_3BAr(C_6F_5)_2^-$ Complexes

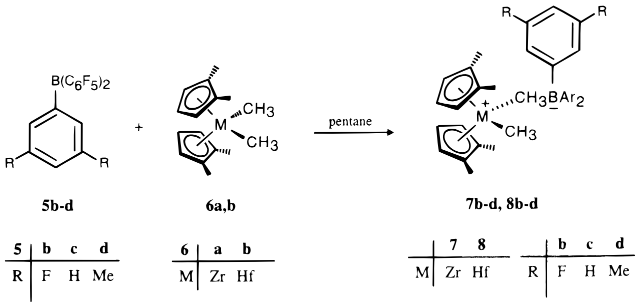
entry	M	Ar	^{1}H NMR data in toluene-d_8 (chemical shifts, ppm)
7b	Zr	3,5-$C_6H_3(CH_3)_2$	7.11 (s^a), 6.82 (s, 1 H), 5.31 (t,^{b} 2 H), 5.11 (t, $^3J = 3.0$ Hz, 2 H), 4.67 (t,^{b} 2 H), 1.49 (s, 6 H), 1.22 (s, 6 H), 0.02 (s, 3 H), −0.07 (br s, 3 H)
7c	Zr	C_6H_5	7.42 (d, $^3J = 6.8$ Hz, 2 H), 7.38 (t, $^3J = 7.0$ Hz, 2 H), 7.23 (t, $^3J = 6.9$ Hz, 1 H), 5.35 (t,^{b} 2 H), 5.10 (t, $^3J = 3.0$ Hz, 2 H), 4.61 (t,^{b} 2 H), 1.51 (s, 6 H), 1.20 (s, 6 H), 0.04 (s, 3 H), −0.07 (br s, 3 H)
7d	Zr	3,5-$C_6H_3F_2$	7.00 (m^a), 6.56 (t, $^3J_{HF} = 8$ Hz, 1 H), 5.36 (t,^{b} 2 H), 5.12 (t, $^3J = 3.0$ Hz, 2 H), 4.64 (t,^{b} 2 H), 1.53 (s, 6 H), 1.23 (s, 6 H), 0.07 (s, 3 H), −0.06 (br s, 3 H)
8b	Hf	3,5-$C_6H_3(CH_3)_2$	7.1 (s^a), 6.79 (s, 1 H), 5.23 (t,^{b} 2 H), 5.15 (t, $^3J = 2.7$ Hz, 2 H), 4.55 (t,^{b} 2 H), 1.52 (s, 6 H), 1.21 (s, 6 H), 0.15 (br s, 3 H), −0.11 (s, 3 H)
8c	Hf	C_6H_5	7.46 (d, $^3J = 7.2$ Hz, 2 H), 7.39 (t, $^3J = 7.4$ Hz, 2 H), 7.27 (t, $^3J = 7.2$ Hz, 1 H), 5.17 (t,^{b} 2 H), 5.01 (t, $^3J = 2.7$ Hz, 2 H), 4.48 (t,^{b} 2 H), 1.52 (s, 6 H), 1.22 (s, 6 H), 0.18 (br s, 3 H), −0.13 (s, 3 H)
8d	Hf	3,5-$C_6H_3F_2$	7.02 (m^a), 6.58 (t, $^3J_{HF} = 9$ Hz, 1 H), 5.26 (t,^{b} 2 H), 5.14 (t, $^3J = 2.5$ Hz, 2 H), 4.60 (t,^{b} 2 H), 1.55 (s, 6 H), 1.23 (s, 6 H), 0.11 (br s, 3 H), −0.14 (s, 3 H)

[a] Signal partially obscured by solvent residual proton resonances. [b] Exchange-broadening prevented accurate determination of coupling constant.

Scheme 1



Scheme 2



triarylboranes (**5**) in moderate yields. Metallocenium methyltriarylborates (**7**, M = Zr and **8**, M = Hf) were then prepared by reacting the triarylboranes (**5**) with metallocene dimethyl complexes (**6**) in pentane, and cooling the mixtures to −78 °C to precipitate the desired products (Scheme 2); synthetic yields and analytical data are provided in Table 1, and NMR data in Table 2.

Thermodynamics of Metallocene Methide Abstraction by Organo-Lewis Acids. Enthalpies of reaction for the forward reactions shown in eq 1 where **A** is $B(C_6F_5)_3$ or a representative MAO sample (see Experimental Section for details) and R = CH_3 were measured by incrementally titrating approximately 0.04 M metallocene solutions in toluene into Lewis acid−toluene solutions (total nominal B:M ratios of 10:1 and Al:M ratios of 50:1 were used). Under these conditions, ^{1}H NMR studies indicate that the reactions with $B(C_6F_5)_3$ are rapid, clean, and complete. We have previously shown by solid-state CPMAS ^{13}C NMR that methylalumoxane (MAO) Al:M ratios of ∼12:1 are adequate to effect complete conversion to metallocenium species.[6c] Since the metallocene solutions are titrated into the MAO or borane solutions in these experiments, *initial* Al:M and B:M ratios are rather large (∼1000:1 Al:M for MAO) and decline through the course of the titration. In no case is the derived heat of reaction dependent upon the stage of the titration.[24] Calorimetric data are presented in Table 3, in which reported uncertainties correspond to 95% confidence limits.

Table 3. Enthalpies of Methide Abstraction from Group 4 Metallocenes and Related Compounds by Organo-Lewis Acids $B(C_6F_5)_3$ and MAO According to $L_2M(CH_3)_2 + A \rightleftarrows L_2MCH_3^+$ CH_3A^-

entry	complex	Lewis acid (A)	$-\Delta H_{dr}{}^a$ (kcal mol^{-1})
1	$Me_2Si(Me_4Cp)(^tBuN)Ti(CH_3)_2$	$B(C_6F_5)_3$	−22.6 (2)
2	$Cp_2Zr(CH_3)_2$	$B(C_6F_5)_3$	−23.1 (3)
3	$(1,2\text{-}Me_2Cp)_2Zr(CH_3)_2$	$B(C_6F_5)_3$	−24.3 (4)
4	$(Me_5Cp)_2Zr(CH_3)_2$	$B(C_6F_5)_3$	−36.7 (5)
5	$Me_2Si(Me_4Cp)(^tBuN)Zr(CH_3)_2$	$B(C_6F_5)_3$	−23.9 (4)
6	$(1,2\text{-}Me_2Cp)_2Hf(CH_3)_2$	$B(C_6F_5)_3$	−20.8 (5)
7	$Me_2Si(Me_2Cp)(^tBuN)Hf(CH_3)_2$	$B(C_6F_5)_3$	−19.3 (6)
8	$(1,2\text{-}Me_2Cp)_2Zr(CH_3)_2$	MAO	−10.9 (3)
9	$(1,2\text{-}Me_2Cp)_2Hf(CH_3)_2$	MAO	−8.9 (4)

[a] See Figure 1 for definition. Errors are average deviations from the mean for two experiments, each of which comprises approximately 20 sequential batch titrations.

In contrast to the metallocene dimethyl behavior with $B(C_6F_5)_3$ and MAO, analogous ^{1}H NMR studies using the less acidic boranes **5b−d** reveal *incomplete* methide abstraction from metallocenes at concentrations and temperatures comparable to the calorimetric conditions. We were unable to detect signals in the ^{1}H NMR spectra assignable to ligand-bridged or dinuclear μ-CH_3 complexes.[3d,f] Rather, the spectra are consistent with a dynamic equilibrium between the neutral metallocene, borane, and the corresponding metallocenium salt (eq 2), as determined by comparisons with published chemical shift data for analogous compounds.[1,3]

$$(1,2\text{-}Me_2Cp)_2M(CH_3)_2 + ArB(C_6F_5)_2 \rightleftarrows (1,2\text{-}Me_2Cp)_2MCH_3^+\ CH_3BAr(C_6F_5)_2^- \quad (2)$$

These observations present a unique opportunity to measure the thermodynamic aspects of eq 2 as a quantitative assessment of the effectiveness of differently substituted organo-Lewis acids in creating "cation-like" metallocene species. When metallocenium salts **7** and **8** are dissolved in toluene-d_8, integration of well-resolved ^{1}H NMR spectral signals (slow-exchange regime) allows the equilibrium constants for eq 2 to be evaluated

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(24) In principle, "breaks" in the MAO−zirconocene thermochemical titration curves might indicate the formation of discrete species of discrete stoichiometry. Such evidence was not observed in these and other thermochemical measurements to be discussed elsewhere (Luo, L.; Marks, T. J. Manuscript in preparation).

(25) (a) Diogo, H. R.; de Alencar Simoni, J.; Minas de Piedade, M. E.; Dias, A. R.; Martinho-Simoes, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 2764−2774. (b) Martinho Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629−688 and references therein.

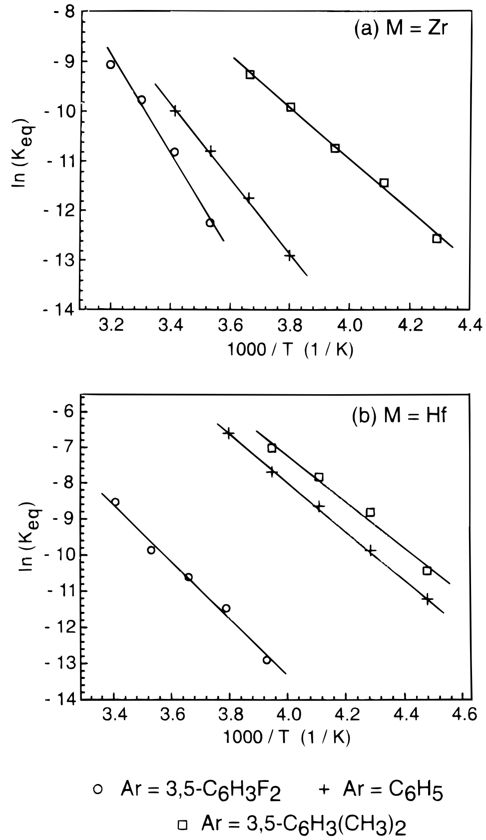

Figure 2. Van't Hoff plots for metallocenium ion pair formation/dissociation (eq 2).

according to eq 3, where [N], [B], and [C] are the concentrations

$$K_{eq} = \frac{[C]}{[N][B]} = \frac{[C]}{[N]^2} \quad (3)$$

of neutral metallocene, free borane, and metallocenium cation, respectively. The equilibrium constants defined in eq 3 were determined for all six metallocenium salts (**7b**–**d**, **8b**–**d**) at four or more temperatures over a 30 °C temperature range, and least-squares analyses of the resulting van't Hoff plots for M = Zr and M = Hf are given in Figure 2. ΔH_{dr} and ΔS_{dr} parameters (Figure 1) are readily obtained from the slope and intercept of each plot, respectively. The ΔH_{dr} values so obtained may be compared directly with the calorimetric $-\Delta H_{dr}$ values shown for methide abstraction in Table 3, eq 1; these data are collected in Table 4. The van't Hoff plots also allow estimation of K_{eq} at a single temperature (298 K), and these values are also compared in Table 4.

The data in Tables 3 and 4 show that the abstraction of methide from a metallocene using ArB(C_6F_5)$_2$ or MAO reagents is rather exothermic, even though enthalpies of homolytic bond disruption for M–CH_3 (M = Zr or Hf) in these systems are substantial.[21d,25] The strengths of methide–Lewis acid bonds formed in the abstraction process and the ability of ring substituents to stabilize the cationic charge are doubtless dominant (but highly variable) contributors to the observed exothermicities (see Discussion section).

From the data in Tables 3 and 4, several noteworthy trends may readily be inferred from the enthalpies of reaction corresponding to variation in ancillary ligation (L_2), metal (M), and Lewis acid (A). First, methide abstraction from Hf is less exothermic than from Zr (Table 3: entry 3 vs 6, entry 5 vs 7; Table 4: entry 2 vs 6; entry 3 vs 7; entry 4 vs 8) by 2–4 kcal mol^{-1}. Abstraction from Ti (Table 3, entry 1) proceeds with an exothermicity between that of Zr (entry 5) and Hf (entry 6) for identical ancillary ligation. Second, increased methyl substitution of the bis-cyclopentadienyl ancillary ligation results in consistent but nonlinear changes in enthalpies of reaction for eq 1. Table 3 entries 2 and 3 evidence a modest increase in exothermicity when four methyl substituents are appended to the Cp ancillary ligands, while (Me_5Cp)$_2$ZrMe_2 evidences an increase of 12 kcal mol^{-1}. A priori, it might be predicted that Cp electronic substituent effects might have an approximately linear influence on cation stabilization,[26] and, therefore, the present data suggest that steric effects may also contribute to the observed large increase in the magnitude of ΔH observed for (Me_5Cp)$_2$ZrMe_2 (see Discussion for further comments). A third noteworthy observation is that methide abstraction by MAO is considerably *less exothermic* than the corresponding abstraction by B(C_6F_5)$_3$ (Table 3: (entries 3 vs 8, 6 vs 9). The observed difference would appear to argue for a higher relative Lewis acidity of B(C_6F_5)$_3$ versus MAO. Finally, methide abstraction enthalpies involving "constrained-geometry" complexes (Table 3, entries 5 and 7)[17,27] are similar to those observed for the conventional metallocenes (entries 3 and 6).

The data in Table 4 reveal several additional noteworthy trends in methide abstraction thermochemical parameters as a function of metal (Zr or Hf) and triarylborane substituents. First, large but orderly decreases in abstraction exothermicity are observed for methide transfer to triarylboranes having the formula ArB(C_6F_5)$_2$ for the progression Ar = C_6F_5 → 3,5-$C_6H_3F_2$ → C_6H_5 → 3,5-C_6H_3(CH_3)$_2$. This result shows that variations in the substituents on a *single* aryl group in these organoborane Lewis acids have a profound effect on the ability to generate electrophilic "cation-like" species. The progression in K_{eq} (estimated at 298 K) is consistent with this conclusion, while the significantly negative values of ΔS_{eq} are consistent with the associative nature of the ion-pair formation process. Also noteworthy is the roughly 9 kcal mol^{-1} difference in ΔH_{dr} for Ar = C_6F_5 vs Ar = C_6H_5 (entries 1 vs 3 and entries 5 vs 7). In qualitative agreement with these results, HF/3-21G-level quantum chemical calculations show B(C_6F_5)$_3$ to be more acidic than B(C_6H_5)(C_6F_5)$_2$ by about 17.8 kcal mol^{-1} with respect to methide as the base.[28]

Ion-Pair Dissociation/Reorganization Kinetics. As is apparent in Figure 1, the construction of quantitative enthalpic surfaces for methide abstraction requires not only thermodynamic but also kinetic information in order to fix the relative positions of enthalpic minima and maxima, respectively, and ultimately to understand the driving force for cationic catalyst formation as well as the ion-pairing dynamics likely operative in stereoregulation processes. In this regard, the molecular structure of the (1,2-Me_2Cp)$_2$MCH_3^+ cation offers unique dynamic NMR spectroscopic probes of ion-pair reorganization dynamics and how those dynamics depend upon M, Lewis acid abstractor, and solvent. Cation–anion dissociation–recombination processes which invert the symmetry of the dissymmetric ion pair structure (Scheme 3, k_{ips}) permute diastereotopic Cp–Me and ring C–H groups. Processes which involve B–CH_3

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[26] Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130–35 and references therein.

[27] (a) Woo, T. K.; Margl, P. M.; Lohrenz, J. C. W.; Blochl, P. E.; Ziegler, T. *J. Am. Chem. Soc.* **1996**, *118*, 13021–13030. (b) Carpenetti, D. W.; Kloppenbrug, L.; Kupec, J. T.; Petersen, J. L. *Organometallics* **1996**, *15*, 1572–1581. (c) Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A.; Stern, C. L. *Organometallics* **1995**, *14*, 3132–3134.

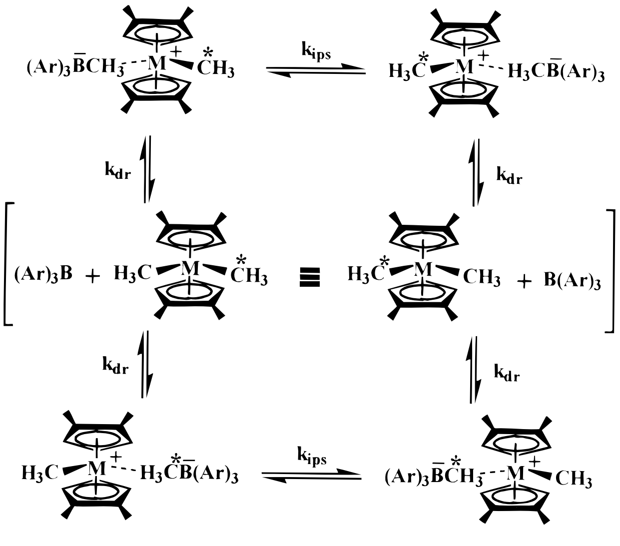
[28] LaPointe, R. E.; Stevens, J. C.; Nickias, P. N.; McAdon, M. H. *Eur. Pat. Appl.* 92305730.1, 1992.

Table 4. Thermochemical and Kinetic Data for Methide Abstraction from $(Me_2Cp)_2M(CH_3)_2$ Complexes in Toluene Solution as a Function of Triarylborane As Depicted in $(1,2\text{-}Me_2Cp)_2M(CH_3)_2 + ArB(C_6F_5)_2 \rightleftarrows (1,2\text{-}Me_2Cp)_2MCH_3^+CH_3BAr(C_6F_5)_2^-$

				thermodynamic data from Van't Hoff Analysis			kinetic data from Eyring analysis[d]		
entry	M	Ar	ion pair	$-\Delta H_{dr}$ (kcal/mol)	$-\Delta S_{dr}$ (eu)	K_{eq} at 298 K[c]	$\Delta H^‡_{dr}$ (kcal/mol)	$\Delta S^‡_{dr}$ (eu)	k_{dr} (s^{-1}) (298 K)
1	Zr	C_6F_5	**7a**	−24.2(5)[a]		3×10^8 [b]	27(2)	22(3)	0.003
2	Zr	$3,5\text{-}C_6H_3F_2$	**7b**	−18.7(7)	−42(2)	3×10^4	23(2)	20(5)	2.2
3	Zr	C_6H_5	**7c**	−14.8(8)	−31(2)	1×10^4	19(2)	14(2)	55
4	Zr	$3,5\text{-}C_6H_3(CH_3)_2$	**7d**	−10.8(6)	−19(2)	2×10^3	17(2)	9(4)	110
5	Hf	C_6F_5	**8a**	−21.4(3)[a]		5×10^7 [b]	22(1)	16(1)	1.3
6	Hf	$3,5\text{-}C_6H_3F_2$	**8b**	−15.2(8)	−35(3)	3×10^3	16(1)	4(4)	160
7	Hf	C_6F_5	**8c**	−13.3(6)	−39(2)	1×10^2	15(1)	10(3)	4600
8	Hf	$3,5\text{-}C_6H_3(CH_3)_2$	**8d**	−12.7(5)	−36(4)	3×10^1	15(1)	10(3)	9800

[a] Obtained by titration calorimetry. [b] K_{eq} too large to determine by the NMR equilibration methods described in the text. Values were estimated assuming $\Delta S_{dr} = 42$ eu (M = Zr) and $\Delta S_{dr} = 35$ eu (M = HF), as these are the experimental ΔS_{dr} values for Zr = $3,5\text{-}C_6H_3F_2$. These values should be considered rough estimates (within two orders of magnitude), since K_{eq} is quite sensitive to ΔS_{dr}, in which there is substantial variability. [c] Defined by eqs 1 and 2 in the text. [d] Activation parameters for the reverse of eq 1 (see Figure 1) in the text determined by NMR line-shape analysis.

Scheme 3



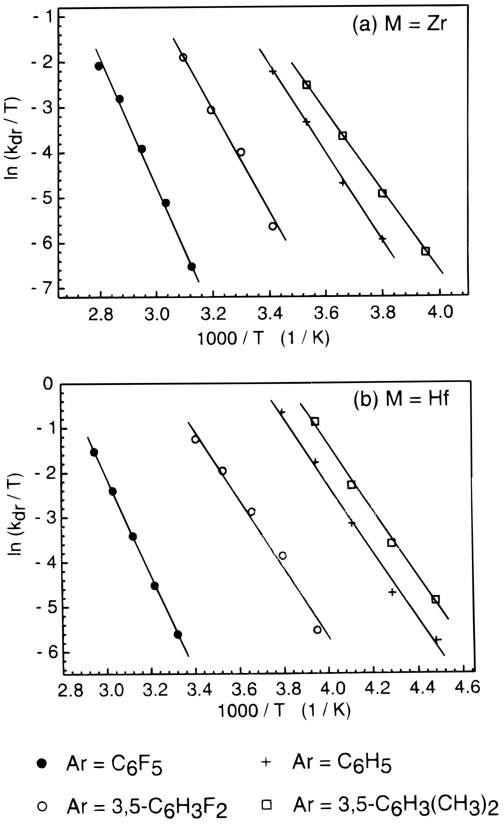


Figure 3. Eyring plots for the kinetics of metallocenium ion pair dissociation/recombination (Figure 1B).

dissociation and subsequent recombination (k_{dr}) also permute Cp−Me and ring C−H groups but additionally permute both $B-CH_3$ and $M-CH_3$ substituents, all at identical rates. Intramolecular versus intermolecular processes can be probed by examining the concentration dependence of the site permutation processes as well as the influence of added BAr_3.

The series **7a**−**d** and **8a**−**d** were studied by variable-temperature NMR techniques in toluene solution (see Experimental Section for details), and rates of Cp−Me (k_{ips}) and M−Me/B−Me (k_{dr}) exchange were determined using standard modified Bloch equation line-shape analysis techniques.[29] In several cases, dilution experiments revealed the line-broadening effects to be independent of concentration over a 20-fold range. The rates of site exchange were furthermore examined over 30−50 °C temperature ranges, and least-squares fits to Eyring plots (Figure 3) yielded the activation parameters set out in Table 4. Several observations are noteworthy. Mechanistically, the rate of ion-pair symmetrization in toluene is undetectably small in comparison to borane dissociation−recombination (the scenario of Figure 1B; the rate of Cp−Me exchange is identical with that of M−Me/B−Me exchange within experimental error). The only exception is complex **7a**, the $(1,2\text{-}Me_2Cp)MCH_3^+$ ion pair with the most strongly bound borane ($B(C_6F_5)_3$) as judged from the calorimetry data (Table 3). In this case, ion-pair symmetrization (ion-pair separation−recombination, the scenario of Figure 1A) is more rapid than borane dissociation/recombination at all temperatures where line-broadening measurements are possible (e.g., $k_{ips} = 30\ s^{-1}$ and $k_{dr} = 3\ s^{-1}$ at 298 K). In regard to the mechanism of the process associated with k_{dr}, the following lines of evidence argue that it is dissociative in character. First, line shapes are insensitive to the addition of a 10-fold molar excess of borane, arguing against an associative S_E-2-like interchange process. Second, the large positive entropies of activation observed for k_{dr} (Table 4) are consistent with a dissociative process. Third, to exclude the possibility that k_{dr} represents purely *intramolecular* repositioning of borane between $M-CH_3$ groups (eq 4), ^{19}F EXSY experiments on

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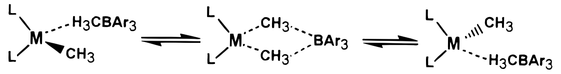
[29] (a) Sandstrøm, J. *Dynamic NMR Spectroscopy;* Academic Press: New York, 1982; pp 77−92. (b) Ham, N. S.; Mole, T. *Prog. Nucl. Magn. Reson. Spectrosc.* **1969**, *4*, 91−192. (c) Kaplan, J. I.; Fraenkel, G. *NMR of Chemically Exhanging Systems*; Academic Press: New York, 1980; pp 71−128.

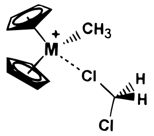


(4)

7a with 1.0 equiv of added $B(C_6F_5)_3$ were carried out. The EXSY experiments reveal that B−Me/M−Me and bound $B(C_6F_5)_3$/free $B(C_6F_5)_3$ exchange rates are indistinguishable.

Since solvent is known to have a significant effect on metallocenium polymerization activity and stereoregulation,[9] the dynamics of $(1,2\text{-}Me_2Cp)_2MMe^+$ $MeB(C_6F_5)_4^-$ ion-pair reorganization were also examined as a function of solvent polarity/coordinating ability using ^1H NMR line-shape analysis techniques. Data are compiled in Table 5. For M = Zr, the only case where the rate of ion-pair symmetrization (Scheme 3, k_{ips}) is detectable in toluene ($\epsilon = 2.37$) solution, the effect of C_6D_5Cl ($\epsilon = 5.71$) and 1,2-$C_6D_4Cl_2$ ($\epsilon = 9.93$) solvation is a *very large enhancement* (∼2000x) in the rate of ion-pair symmetrization (k_{ips}) and a more modest increase in the rate of borane dissociation/recombination (k_{dr}). In the case of M = Hf, where k_{ips} is not detectable in toluene solution, dissolution in more polar solvents has several effects. In the case of C_6F_6 ($\epsilon = 2.03$) and $CCl_2FCF_2Cl_2$ ($\epsilon = 2.41$), small increases in k_{dr} are detected; however, ion-pair symmetrization remains relatively slow. However, in the case of higher dielectric solvents such as C_6D_5Cl, 1,2-$C_6D_4Cl_2$, and CD_2Cl_2 ($\epsilon = 9.08$), k_{ips} becomes nearly as large as in the case of M = Zr. At the first level of analysis, solvent effects on the ion-pair separation process can be related to more facile separation of charged species in higher dielectric media. Any depression in rates of borane dissociation (cf. Table 5, entries 7−9) could then be ascribed to stabilization of the charge-separated ground-state versus the neutral dissociation products (cf. Figure 1). The possibility that the charge-separated metallocene cation might be stabilized by complex formation with the halocarbon solvent[30] (e.g., **C**) was investigated by a variety of low-temperature NMR experiments (e.g., incremental halocarbon addition to the metallocenium salt in toluene-d_8 at low temperatures). In no case was a halocarbon complex detected. The $\Delta S^{\ddagger}$ parameters in Table 5 suggest that the transition states for both borane dissociation and ion-pair separation are more highly organized in the higher dielectric solvents, possibly reflecting reorganization of the solvation sphere.

C



Metallocenium Methyltriarylborate NMR Parameters. In an effort to further probe $(1,2\text{-}Me_2{-}Cp)_2MMe^+$ $MeBAr(C_6F_5)_2^-$ electronic structure in the **7a**−**d** and **8a**−**d** series, $\delta(M{-}^{13}CH_3)$ and $^1J_{C-H}(M{-}CH_3$ and $B{-}CH_3)$ values were measured. Within a homologous series, the former parameter should provide a qualitative measure of metallocenium electron deficiency/electrophilicity.[1,3d,e,4a,b] From the data in Tables 4 and 6, it can be seen that δ $(M{-}^{13}CH_3)$ scales qualitatively with the electron-withdrawing tendencies of the Ar substituents in the $ArB(C_6F_5)_2$ series. Further correlations will be examined in the Discussion section.

An alternative probe of $M{-}CH_3^+$ electrophilicity is the magnitude of $^1J_{C-H}$, with a relevant example being the correlation of $^1J_{C-H}$ $(Ti{-}CH_3)$ in a series of $L_2Ti(Cl)CH_3$ complexes with increasing electron-withdrawing character of the L = Cp-type ligand substituents.[31] Qualitatively, the effect is associated with CH_3 rehybridization leading to greater C 2s character in the C−H bonds; for the above Ti series, the full variation of J_{C-H} coupling constants is ≤ 3.5 Hz. In the present **7a**−**d** and **8a**−**d** series, any consistent variation in $J_{C-H}(M{-}CH_3)$ with borane identity/Lewis acidity/ΔH (complex formation) is below the experimental uncertainty in the −60 °C measurement. The same is true for the $J_{C-H}(B{-}CH_3)$ parameters, where quadrupolar broadening further increases the uncertainty in the measurement.

Polymerization Studies. Ethylene and propylene polymerization experiments with complexes **7a**−**d** and **8a**−**d** were carried out at 25 °C using methodology designed to minimize mass-transfer effects.[3e,4a] With the exception of complex **7a**, propylene polymerization activity under these conditions was too low to warrant further investigation. Ethylene polymerization activity results are presented in Table 6 along with estimations (from K_{eq} data in Table 4) of the percentage of the metallocene methyl complex in the cation-like form under typical polymerization conditions in toluene at 25 °C. It can be seen for M = Zr that there is a qualitative correlation between $\delta(Zr{-}^{13}CH_3)$ and ethylene polymerization activity. For entries 1−4, an approximate correction for the percentage of metallocene in the cation-like form suggests that **7a** is intrinsically more reactive. In the case of M = Hf, there is again a qualitative correlation between $\delta(Hf{-}^{13}CH_3)$ and ethylene polymerization activity. However, factoring in the percentages of metallocene in the cation-like form renders the correlation less montonic. Further comparisons will be made in the following section.

Discussion

The present study provides the first quantitative information on the energetics of forming, dissociating, and reorganizing organo-Lewis acid-derived metallocenium and quasi-metallocenium ion pairs (**A**) active to varying degrees in homogeneous catalytic olefin polymerization. In the discussion which follows, we focus first on the chemical origins of the measured thermodynamic parameters, then on the reaction coordinates for ion-pair formation, dissociation, and rearrangement, and finally, on possible correlations between physicochemical observables and olefin polymerization activity.

Thermochemistry of Ion-Pair Formation. The magnitudes of the thermodynamic parameters describing eqs 1 and 2, Figure 1, and reported in Tables 3 and 4, represent a subtle interplay of several molecular parameters as illustrated by the approximate thermodynamic cycle of Figure 4. It can be seen that metal/ligand sensitivity of the measured methide abstraction enthalpy ($-\Delta H_{dr}$) is sensitive to the $M{-}CH_3$ homolytic bond dissociation enthalpy, the L_2MCH_3 ionization potential, and the ion-pair binding energetics, the latter of which likely contain nonelectrostatic components (e.g., covalent and repulsive nonbonded interactions) judging from crystal structure data[3e] and qualitative orderings of anion coordinating tendencies.[4a,8] The electron affinity of the methyl radical is invariant (180 kcal/mol),[32] while the borane methide affinity will be invariant for a metallocene series with constant BAr_3 (but is presently unknown). Making the pragmatic assumption that the effects of solvation by

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(30) (a) Peng, T.-S.; Winter, C. H.; Gladysz, J. A. *Inorg. Chem.* **1994**, *33*, 2534−2542 and references therein. (b) Igau, A.; Gladysz, J. A. *Organometallics* **1991**, *10*, 2327−2334. (c) Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfsberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.*, **1990**, *112*, 2349−2362 and references therein. (d) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev*, **1990**, *99*, 89−115 and references therein.

(31) Finch, W. C.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2406−2413.

(32) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins: New York, 1993; pp 40−43.

Table 5. Kinetic Data for Ion-Pair Reorganization Processes in $(1,2\text{-}Me_2Cp)_2MCH_3{}^+CH_3B(C_6F_5)_3{}^-$ Complexes as a Function of Solvent and Solvent Dielectric Constant

entry	M	solvent (ϵ)[a]	k_{ips}[b] (10^{-3}/s)	k_{dr}[b] (10^{-3}/s)	$\Delta H^{\ddagger}_{ips}$[c] (kcal/mol)	$\Delta S^{\ddagger}_{dr}$[c] (eu)	$\Delta H^{\ddagger}_{ips}$[c] (kcal/mol)	$\Delta S^{\ddagger}_{dr}$[c] (eu)
1	Zr	toluene-d_8 (2.37)	30 (10)	3 (2)	24 (1)	17 (2)	27 (2)	22 (3)
2	Zr	C_6D_5Cl (5.71)	60 000 (20 000)	20 (8)	11 (2)	−15 (8)	19 (1)	0 (2)
3	Zr	1,2-$C_6D_4Cl_2$ (9.93)	70 000 (20 000)	<1	12 (2)	−10 (4)		
4	Hf	toluene-d_8 (2.37)	*d*	1300 (400)			22 (1)	16 (1)
5	Hf	C_6F_6 (2.03)	*d*	5600 (200)			16 (1)	−2 (4)
6	Hf	CCl_2FCF_2Cl (2.41)	*d*	8000 (4000)			15 (2)	−2 (4)
7	Hf	C_6D_5Cl (5.71)	15 000 (9 000)	600 (300)	13 (4)	−9 (1)	20 (1)	9 (3)
8	Hf	1,2-$C_6D_4Cl_2$ (9.93)	9 000 (4 000)	5 (2)	12 (3)	−5 (8)	23 (1)	7 (1)
9	Hf	CD_2Cl_2 (9.08)	20 000 (10 000)	<1	11 (1)	−16 (2)		

[a] Dielectric constant from *CRC Handbook of Chemistry and Physics*, 77th ed.; CRC Press: New York, 1996; p G-161. [b] Rate constant at 298 K derived from least-squares fitting of Eyring plot. [c] Eyring parameters derived from line-shape analysis. [d] Rate too slow to determine; $k_{ips} << k_{dr}$.

Table 6. $M-{}^{13}CH_3$ Chemical Shifts (δC), $M-{}^{13}CH_3$ and $B-{}^{13}CH_3$ ${}^1J_{CH}$ Coupling Constants, and Ethylene Polymerization Activities for $(1,2\text{-}Me_2Cp)_2MCH_3{}^+$ $CH_3BAr(C_6F_5)_2{}^-$ Complexes in Toluene Solution

entry	catalyst	M	Ar	δC(M**C**H$_3$)[a] (±0.02 ppm)	${}^1J_{CH}$ (M**C**H$_3$)[a] (±0.5 Hz)	${}^1J_{CH}$ (B**C**H$_3$)[a] (±1.0 Hz)	% cation[b]	activity[c]
1	**7a**	Zr	C_6F_5	44.07	120.8	116.6	>99	$5.2(4) \times 10^6$
2	**7b**	Zr	3,6-$C_6H_3F_2$	43.85	120.2	116.3	62	$5.0(4) \times 10^6$
3	**7c**	Zr	C_6H_5	43.17	120.7	115.8	44	$1.3(11) \times 10^5$
4	**7d**	Zr	3,5-$C_6H_3(CH_3)_2$	43.12	120.8	115.6	19	$3.4(15) \times 10^5$
5	**8a**	Hf	C_6F_5	42.33	117.5	116.4	>99	$1.3(10) \times 10^5$
6	**8b**	Hf	3,5-$C_6H_3F_2$	42.23	117.1	115.3	24	$5.8(12) \times 10^4$
7	**8c**	Hf	C_6H_5	41.71	117.1	115.3	2	$6.5(28) \times 10^3$
8	**8d**	Hf	3,5-$C_6H_3(CH_3)_2$	41.71	117.6	115.4	<1	$1.6(30) \times 10^3$

[a] NMR parameters measured at −60 °C. [b] Mole percentage in the cation-like form, estimated from the equilibrium constants in Table 4 for a toluene solution initially 0.140 mM in catalyst at 25 °C. [c] Activities measured in toluene solution at 25 °C and expressed in (g polyethylene) (mol catalyst)$^{-1}$ (atm C_2H_4)$^{-1}$ h^{-1}. Uncertainties in parentheses are standard deviations from several independent runs.

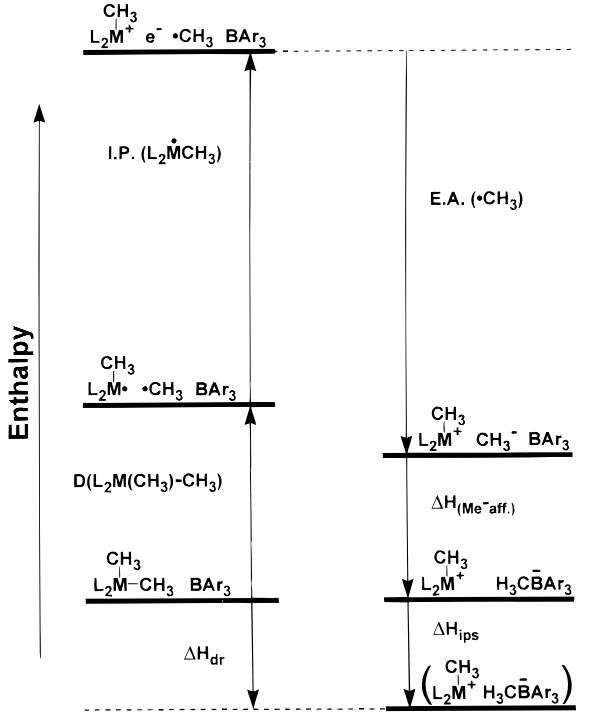


Figure 4. Qualitative thermodynamic cycle for metallocenium ion pair formation from the neutral precursors.

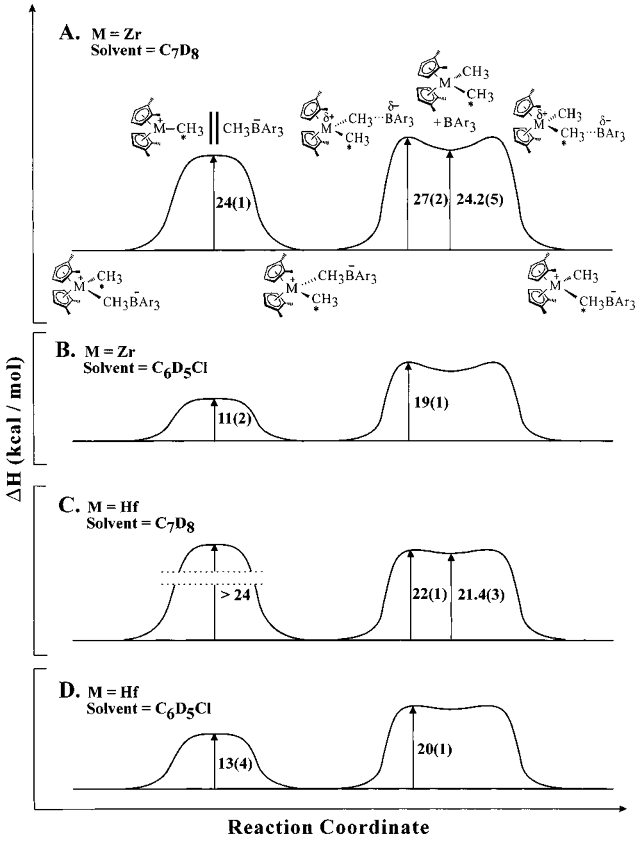


Figure 5. Experimental enthalpic profiles for $(1,2\text{-}Me_2Cp)_2MCH_3{}^+$-$CH_3B(C_6F_5)_3{}^-$ ion pair formation and reorganization for M = Zr or Hf in toluene-d_8 and chlorobenzene-d_5 solutions.

hydrocarbon solvents are relatively small and constant for a homologous series,[33] then the difference in methide abstraction enthalpies for two different metallocene dimethyls, L_2MMe_2 and L_2MMe_2', can be expressed as in eq 5.

$$\Delta\Delta H = [D(M-Me) - D(M-Me')] + (IP - IP') - (\Delta H_{ips} - \Delta H_{ips}') \quad (5)$$

In the case of Cp_2ZrMe_2 versus $(Me_5Cp)_2ZrMe_2$ versus Cp_2HfMe_2, as an example, $D(Cp_2Zr(Me)-Me)$ and $D((Me_5Cp)_2Zr(Me)-Me)$ are virtually identical at 67.2(1.0) and 67.0(1.0) kcal/mol,[21d] respectively,

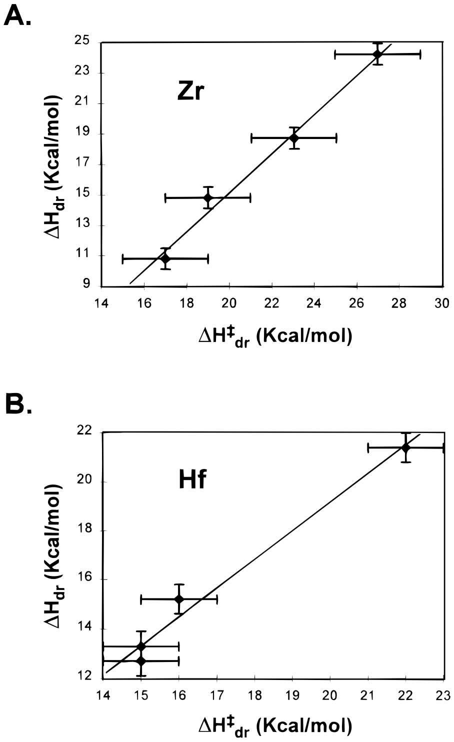


Figure 6. Relation of $\Delta H^{\ddagger}_{\text{dr}}$ for $(1,2\text{-Me}_2\text{Cp})_2\text{MCH}_3^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$/$\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_2\text{Ar}^-$ dissociation to neutral reactants and the corresponding enthalpy of the same process for M = Zr or Hf. The boranes are those of Table 4.

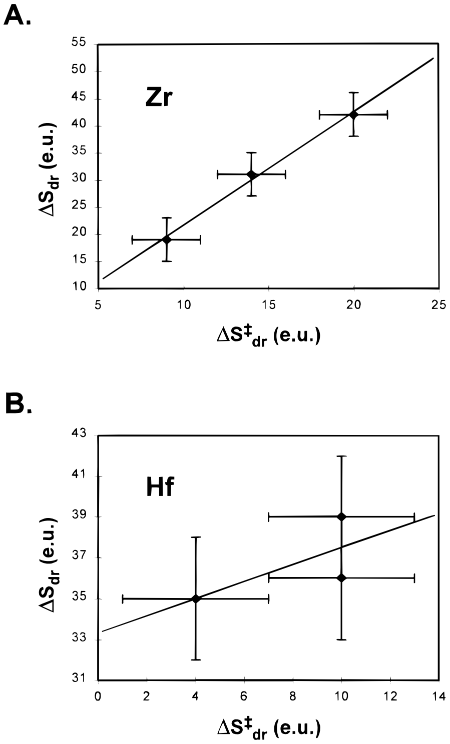
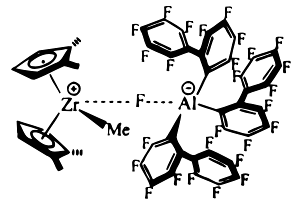


Figure 7. Relation of $\Delta S^{\ddagger}_{\text{dr}}$ for $(1,2\text{-Me}_2\text{Cp})_2\text{MCH}_3^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$/$\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_2\text{Ar}^-$ dissociation to neutral reactants and the corresponding entropy of the same process for M = Zr or Hf. The boranes are those of Table 4.

while $D((\text{Me}_5\text{Cp})_2\text{Hf(Me)}-\text{Me})$ is probably slightly larger (72.0(3.7) kcal/mol).[21d] While few ionization potentials have been recorded for trivalent group 4 metallocenes (for 1,3-$(^t\text{Bu}_2\text{Cp})_2\text{ZrI}$, IP = 5.72 eV),[34] gas-phase photoelectron spectroscopic (PES) data for Cp_2ZrCl_2 (IP = 8.60 eV)[35] and $(\text{Me}_5\text{Cp})_2\text{ZrCl}_2$ (IP = 7.55 eV)[36] indicate that ring methylation should have a substantial effect on the energetic ordering in Figure 4 (ΔIP = 24.2 kcal/mol for this tetravalent pair). PES data for Cp_2HfCl_2 (IP = 8.89 eV)[35] indicate that group 4 metal identity will have a smaller effect (ΔIP = 6.7 kcal/mol).[35] Although ΔH_{ips} data have not been measured, they would appear to be reasonably approximated by $\Delta H^{\ddagger}_{\text{ips}}$ (Table 5; i.e., assuming $\Delta H^{\ddagger}$ for ion-pair recombination is small) and seem unlikely to vary greatly for constant $\text{CH}_3\text{BAr}_3^-$ from one L_2MCH_3^+ $\text{CH}_3\text{BAr}_3^-$ system to another as judged by dynamic NMR results for $(1,2\text{-Me}_2\text{Cp})_2\text{ZrCH}_3^+$ $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ ($\Delta H^{\ddagger}_{\text{ips}} = 24(1)$ kcal/mol in toluene-d_8) and $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(^t\text{BuN})\text{ZrCH}_3^+$ $\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3^-$ ($\Delta H^{\ddagger}_{\text{ips}} = 19(1)$ kcal/mol in toluene-d_8).[37] On the other hand, a greater dispersion in ΔH_{ips} and $\Delta H^{\ddagger}_{\text{ips}}$ values is likely in anions with greater coordinative tendencies (e.g., tris(2,2′,2″-nonafluorobiphenyl)fluoroaluminate, **D**).[3b]

D



From the above analysis, the results in Tables 3 and 4 are not difficult to understand. For the types of group 4 metallocenes and quasi-metallocenes studied here, ancillary ligation as expressed in cation stabilizing ability (e.g., IP) appears to have the greatest influence on ΔH_{dr} for constant borane, while $D(\text{M}-\text{CH}_3)$ and ΔH_{ips} are somewhat less important. It is likely that differences between Zr and Hf reside in a combination of ΔIP and $\Delta D(\text{M}-\text{CH}_3)$ effects.

Reaction Coordinates for Ion-Pair Formation and Reorganization. The topographies of the schematic potential surfaces such as in Figure 1 describe how rapidly the metallocenium catalyst is formed from the neutral precursors, how stable it is thermodynamically with respect to the neutral precursors, how rapidly it reverts to the neutral precursors, and how labile the ion pairing is with respect to separation of cation and anion. The nature of the ion pairing is known to influence catalytic activity, stereoselectivity, and chain transfer characteristics, while the migration of the anion in concert with reorientation of the M^+-polymer vector may facilitate stereo-

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(33) (a) This is most reasonable within homologous L_2MCH_3^+ systems where L = a cyclopentadienyl ligand. For less coordinatively saturated/sterically encumbered structures, such as $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(^t\text{BuN})\text{MCH}_3^+$, arene complexes have been detected in cases of minimally coordinating anions.[4a,8] (b) Solvation energies in nonpolar solvents have been estimated to be on the order of 15−30 kcal/mol.[33c] They should differ negligibly in a homologous series.[21] (c) Richardson, D. E.; Alameddin, N. G.; Ryan, M. F.; Hayes, T.; Eyler, J. R.; Siedle, A. R. *J. Am. Chem. Soc.* **1996**, *118*, 11244−11253 and references therein. (d) Corrections in gas-phase homolytic bond dissociation enthalpies for nonpolar solvents should be minor: Castelhano, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655−3659. (e) Differences in heats of sublimation should be minor in a homologous series.[33f,g] (f) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; Saied, N. I.; Suradi, S.; Carson, R.; Takhin, G. A.; Skinner, H. A. *Organometallics* **1982**, *1*, 1166−1174 and references therein. (g) Yoneda, G.; Lin, S.-M.; Wang, L.-P.; Blake, D. M. *J. Am. Chem. Soc.* **1981**, *103*, 5768−5771.

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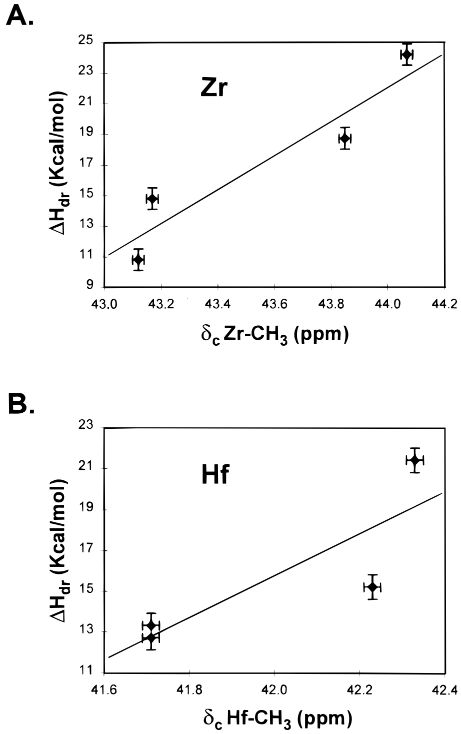


Figure 8. Relationship between the enthalpy of ion pair formation from the neutral precursors and the M$-{}^{13}CH_3$ chemical shift for a series of $(1,2\text{-}Me_2Cp)_2MCH_3{}^+CH_3B(C_6F_5)_3{}^-/CH_3B(C_6F_5)_2Ar^-$ complexes. The boranes are those of Table 4.

selection/olefin activation/facial selection processes.[1,3b,9,10,37] The present thermodynamic and kinetic data allow construction of quantitative experimental enthalpic reaction coordinates describing the energetics of the above processes. Figure 5 and Table 5 show that in toluene solution, $(1,2\text{-}Me_2Cp)_2ZrCH_3{}^+$ $CH_3B(C_6F_5)_3{}^-$ undergoes symmetrization more rapidly than borane dissociation/recombination while the opposite scenario holds for $(1,2\text{-}Me_2Cp)_2HfCH_3{}^+$ $CH_3B(C_6F_5)_3{}^-$. Both reaction coordinates indicate that the enthalpic barrier to ion-pair formation from the neutral reactants is very small; i.e., $\Delta H^\ddagger_{dr} - \Delta H_{dr}$ = a few kcal/mol at most. The same trend holds for the ion-pair complexes of the less Lewis acidic boranes in toluene solution (Table 4). In regard to dissociation of the ion pairs to neutrals, Figures 6 and 7 illustrate approximately linear, Brønsted/Hammett-like correlations[39] between the enthalpies and entropies of ion-pair dissociation into neutrals and the corresponding enthalpies and entropies of activation for the same processes. This demonstrates rather classical and well-behaved transmission of substituent effects in the methide abstraction process.

Figure 5 also depicts the effects of solvent polarity on the $(1,2\text{-}Me_2Cp)_2MCH_3{}^+$ $CH_3B(C_6F_5)_3{}^-$ ion-pair symmetrization, formation, and dissociation profiles. For both M = Zr and Hf, polar solvents substantially reduce the kinetic barrier to ion-pair separation, with rate enhancements reminiscent of more classical systems.[40] This is readily rationalized on the basis of solvation and/or complexation (**C**) effects. In the case of M = Zr, the barrier to dissociation to neutrals is also reduced. The reason is not immediately obvious since a more polar solvent might be expected to stabilize the charged ion pair versus the neutral constituents. One contributing explanation may be a Lewis acid–base interaction between the borane and chlorocarbon solvent (e.g., **E**). The Lewis acidity of $B(C_6F_5)_3$ is

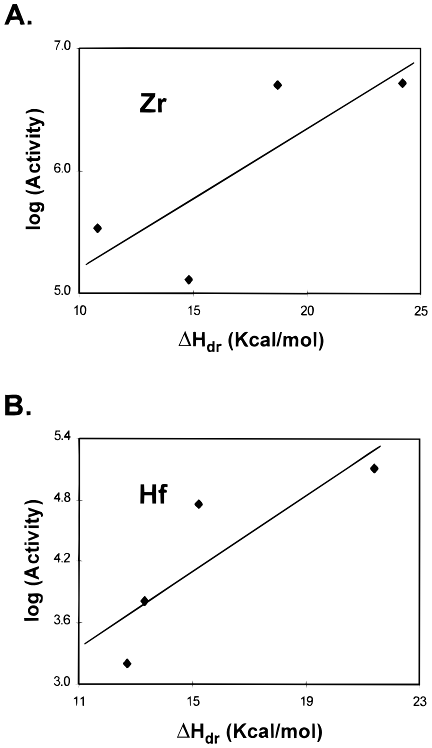
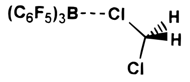


Figure 9. Relationship of $(1,2\text{-}Me_2Cp)_2MCH_3{}^+CH_3B(C_6F_5)_3{}^-/$ $CH_3B(C_6F_5)_2Ar^-$ ethylene polymerization activity to the enthalpy of ion pair dissociation to neutrals. The boranes are those of Table 4.

E



estimated to lie between that of BCl_3 and BBr_3.[13] However, in the M = Hf series where there is a larger database and where the magnitudes of both ΔH_{dr} and $\Delta H^\ddagger_{dr}$ are somewhat smaller, there is no evidence that polar solvents enhance the rate of dissociation to neutrals. Importantly, the data all indicate that the repositioning rate of the $CH_3B(C_6F_5)^-_3$ anion and $M-CH_3{}^+$ vector, from one side of the L–M–L plane to the other, increases dramatically in polar solvents.

Ion-Pair Thermodynamics, NMR Spectroscopic Parameters, and Polymerization Activity. To the extent that $\delta_c(M-CH_3)$ for a closely related, homologous series measures the electrophilicity/electron deficiency of the metallocenium metal center as modulated by the metallocenium ion-pair components, it can be seen in Figure 8 that there is a roughly linear relationship between the enthalpy of ion-pair formation and the ${}^{13}C$ NMR downfield shift of the $M-CH_3{}^+$ groups in the $(1,2\text{-}Me_2Cp)_2MCH_3{}^+$ $CH_3B(C_6F_5)_3{}^-/CH_3B(C_6F_5)_2{}^-Ar$ series. These results strongly argue that fluoroarylborane Lewis acidity modulates the electrophilicity/electron deficiency of the metallocenium cation.

Correlations of metallocenium physical observables with olefin polymerization activities are complicated by several factors. First, many of the $(1,2\text{-}Me_2Cp)_2MCH_3{}^+$ $CH_3B(C_6F_5)_2\text{-}Ar$ complexes are not completely in the cationic form for 0.140 mM solutions in toluene at 25 °C (Table 6). Second, the active forms of the catalysts in ethylene polymerization are either

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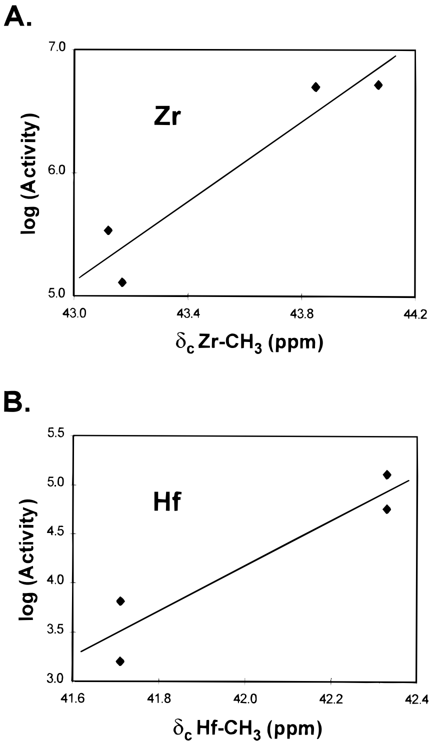

Figure 10. Relationship of $(1,2\text{-Me}_2\text{Cp})_2\text{MCH}_3{}^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3{}^-$/$\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_2\text{Ar}^-$ ethylene polymerization activity to the $\text{MCH}_3{}^+$ ^{13}C chemical shift. The boranes are those of Table 4.

polyalkyl ($L_2M(CH_2CH_2)_nH^+$ X^-) or hydrido (L_2MH^+ X^-) cations. The metallocenium steric and electronic environment is therefore not identical with that in the $L_2MCH_3{}^+$ X^- precursors, with differing alkyl steric encumberance and agostic interactions[1] expected in the former as well as differing cation−anion interactions likely in the latter.[3e] Nevertheless, plots of ethylene polymerization activity versus either ΔH_{dr} or $\delta(\text{M}-\text{CH}_3)$ for the $(1,2\text{-Me}_2\text{Cp})_2\text{MCH}_3{}^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3{}^-$/$\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_2\text{-Ar}^-$ series evidence a (surprising) positive correlation (Figures 9 and 10). Such phenomenological relationships should be useful in targeting future classes of highly active cationic olefin polymerization catalysts and certainly warrant additional scrutiny.

Conclusions

The thermodynamic propensity and kinetic facility of a series of triarylboranes and methylalumoxane to abstract the methide anion from group 4 metallocene and related complexes and to form highly electrophilic cations was quantified for the first time by titration calorimetry as well as by static and dynamic NMR spectroscopy. The energetics and kinetics of cation formation and structural reorganization are a sensitive function of borane acidity, metal ancillary ligation, and solvent polarity. Many of the trends can be interpreted in terms of the electron withdrawing power of the borane substituents, the ability of the metallocene ancillary ligands to stabilize the cationic charge, and the homolytic $\text{M}-\text{CH}_3$ bond dissociation enthalpies. Within the $(1,2\text{-Me}_2\text{Cp})_2\text{MCH}_3{}^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3{}^-$/$\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_2\text{Ar}^-$ series, qualitative correlations exist between the enthalpies of methide abstraction, the ^{13}C chemical shifts of the resulting $\text{M}-\text{CH}_3{}^+$ groups, and the ethylene polymerization activities.

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