Cationic Metallocene Olefin Polymerization Catalysts. Thermodynamic and Kinetic Parameters for Ion Pair Formation, Dissociation, and Reorganization

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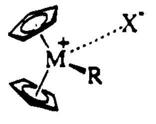
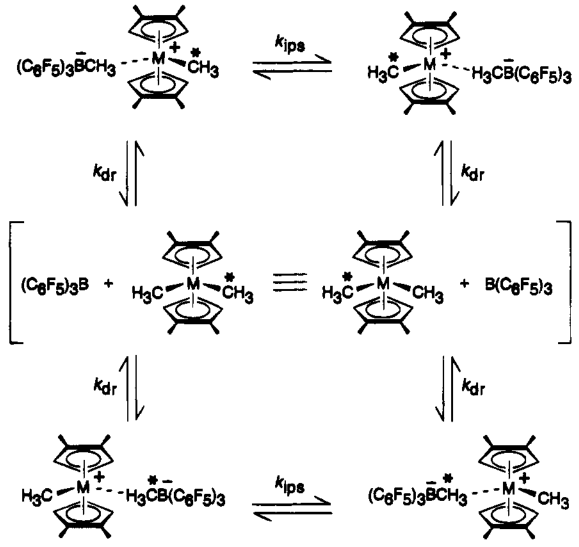
Cationic group 4 metallocene alkyl and hydride ion pairs (**A**) form the basis for broad classes of highly active, selective, and technologically important homogeneous olefin polymerization catalysts.[1,2] Although considerable empirical evidence now suggests that polymerization activity, stereoregulation, and chain transfer pathways are intimately connected with the nature of the ion pairing,[1-4] *quantitative* kinetic and thermodynamic data relating to the formation, dissociation, and stereomutation of such ion pairs as well as metal and solvent effects thereupon[3] are surprisingly sparse.[5] We report here the first detailed calorimetric thermodynamic and NMR spectroscopic kinetic study of a prototypical, structurally well-characterized[4a] metalloceniumcatalystsystem, $(1,2\text{-Me}_2\text{C}_5\text{H}_3)_2\text{MCH}_3{}^+\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3{}^-$ (M = Zr, Hf). From the acquired data, it is possible to map out the reaction coordinate(s) for the aforementioned ion pair formation/reorganization processes and to quantify several striking metal and solvent effects thereupon.[6]

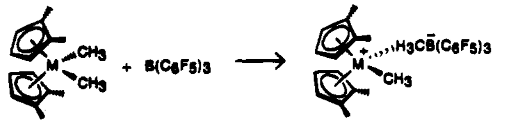


A

Scheme 1. Dynamic Ion Pair Reorganization Processes in $(\eta^5\text{-Me}_2\text{C}_5\text{H}_3)_2\text{M}^+\text{CH}_3\ \text{H}_3\text{CB}^-(\text{C}_6\text{F}_5)_3$ (M = Zr, Hf)



The thermodynamics of ion pair formation for eq 1 were measured by reaction titration calorimetry in toluene solution at 25 °C using instrumentation and techniques described elsewhere.[7] Noteworthy are the substantial methide abstraction exothermicities for M–CH$_3$ bonds having large homolytic bond disruption enthalpies[7c,8] and the inverse correlation of the magnitudes of ΔH_{abs} (Zr > Hf) with D(M–CH$_3$) trends (Hf > Zr).



(1)

1a M = Zr

1b M = Hf

2a M = Zr, ΔH_{abs} = -24.2 (5) kcal/mol

2b M = Hf, ΔH_{abs} = -21.4 (3) kcal/mol

The structure of **2** offers unique NMR probes[4a] of ion pairing reorganization dynamics and how they depend upon M and solvation environment. Thus, cation–anion separation processes which effect symmetrization of the disymmetric ion pair structure (Scheme 1) permute diastereotopic Cp methyl and C–H substituents (k_{ips}). Processes which involve B–CH$_3$ dissociation and subsequent recombination (k_{dr}) permute both B–CH$_3$/M–CH$_3$ sites and diastereotopic ring substituents. Variable-temperature NMR studies on **2** were carried out in toluene-d_8 using conventional 1-D (^{1}H, modified Bloch equation line shape analysis)[9] and 2-D (^{19}F, EXSY)[10] kinetic techniques. That the dynamic processes are unimolecular in metallocene is demonstrated by the invariance of methyl line shapes to a 20-fold variation in metallocene concentration. That the B–CH$_3$/

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[2] (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325–387 and reference therein. (b) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57–65 and references therein.

[3] For recent examples of metallocene ion pairing effects, see refs 1 and 2 and the following: (a) Chien, J. C. W.; Song, W.; Rausch, M. D. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2387–2393 (solvent effects on propylene polymerization rates and isospecificity). (b) Vizzini, J. C.; Chien, J. C. W.; Gaddam, N. B.; Newmark, R. A. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2049–2056 (anion effects on propylene polymerization rates and isospecificity). (c) Giardello, M. A.; Eisen, M. S.; Stern, S. L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3326–3327 (anion effects on propylene polymerization rates, chain transfer, and isospecificity). (d) Herfert, N.; Fink, G. *Makromol. Chem.* **1992**, *193*, 773–778 (solvent effects on propylene polymerization rates and syndiospecificity).

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[9] (a) The standard equation for initial line broadening was employed.[9b,c] Although ^{10}B/^{11}B quadrupolar effects vitiate use of the B–CH$_3$ signal, M–CH$_3$ signal broadening is adequate for k_{dr} determination. For intermolecular exchange processes[9d] involving nucleus i, $\tau_i^{-1} = k[\text{i}]^{n-1}f$([other species]), where τ is the mean preexchange lifetime and n is the order of the reaction. (b) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; pp 77–92. (c) Kaplan, J. I.; Fraenkel, G. *NMR of Chemically Exchanging Systems*; Academic Press: New York, 1980; pp 71–128. (d) Ham, N. S.; Mole, T. *Prog. Nucl. Magn. Reson. Spectrosc.* **1989**, *4*, 91–192.

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Table 1. Kinetic Data for Ion Pair Reorganization Processes in (1,2-$Me_2C_5H_3)_2M^+CH_3$ $CH_3B^-(C_6F_5)_3$ Complexes

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

[a] Rate constant at 25 °C derived from least-squares fitting of Eyring plot. [b] Eyring parameters derived from line shape analysis. Data taken over ≥40 °C range. Line widths are from the average of two or three independent determinations. [c] Rate too slow to determine: $k_{ips} \ll k_{dr}$.

M−CH_3 exchange involves rate-limiting $B(C_6F_5)_3$ *dissociation*, followed by rapid recombination (Scheme 1), is established by the following. First, this and the other dynamic processes are insensitive to the addition of a 10-fold molar excess of $B(C_6F_5)_3$ (ruling out S_E2-like associative M−CH_3 interchange). Second, EXSY experiments with 1 equiv of added $B(C_6F_5)_3$ reveal that B−CH_3/M−CH_3 and bound $B(C_6F_5)_3$/free $B(C_6F_5)_3$ exchange rates are indistinguishable.

Regarding kinetic specifics, the data (Table 1, entries 1 and 4) reveal that, in toluene-d_8 at 25 °C, ion pair symmetrization (k_{ips} in Scheme 1) is ~10× faster than $B(C_6F_5)_3$ dissociation/recombination (k_{dr}, Scheme 1) for M = Zr. However, there is a *complete reversal* of these trends for M = Hf, with both an enhanced k_{dr} (in accord with the smaller B−CH_3 bond enthalpy and a more product-like transition state[11]) and $k_{ips} \ll k_{dr}$. Eyring analysis of the variable-temperature kinetic data yields the activation parameters in Table 1, which are incorporated in comparative reaction coordinates (Figure 1). The degree to which k_{ips} describes ion pair separation processes was probed further via NMR kinetic studies in solvents of differing dielectric constant and coordinating tendencies. The data (Table 1, especially entries 2, 3, and 7−9) reveal *very large* enhancements in k_{ips} in polar solvents (up to ~2000×), consistent with solvent assistance of ion pair separation processes. A somewhat smaller and more variable solvent effect on k_{dr} is also observed, which may reflect solvation of/coordination to the 14-electron cation and/or to $B(C_6F_5)_3$. Efforts to detect discrete metallocenium halocarbon complexes[12] by a variety of NMR techniques have so far been unsuccessful.

The present results provide the first quantitative information on the thermodynamics and kinetics of metallocenium ion pair formation, dissociation, and stereomutation. The quantitative data indicate that the stability of the ion pairs with respect to the constituent neutrals is metal-dependent (Zr > Hf) and that processes which loosen the ion pairing and invert the local dissymmetry are also highly metal- and solvent-dependent. These results convey significant implications for catalyst stability, activity, and stereoregulation kinetics of the sterically-sensitive olefin insertion process.[1−3,13]

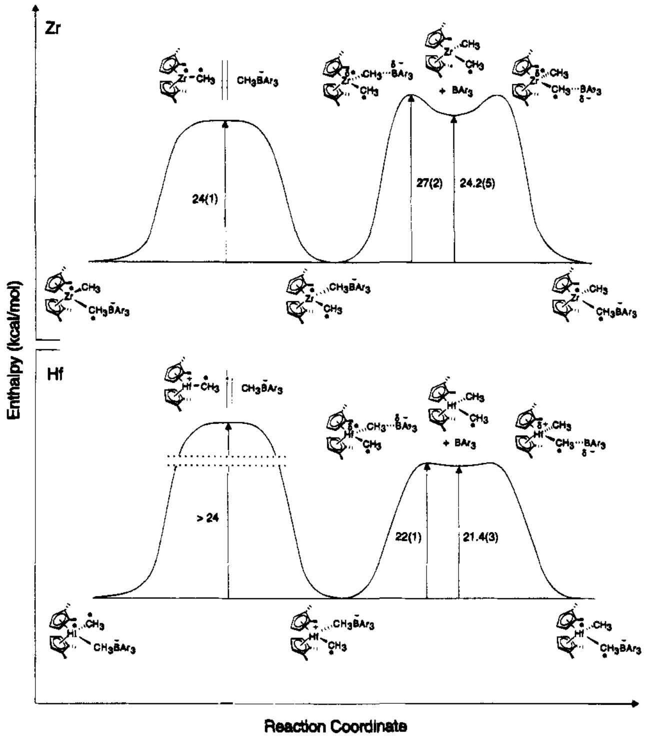

Figure 1. Enthalpic reaction coordinates for ion pair dissociation/recombination and symmetrization/separation processes in (η^5-1,2-$Me_2C_5H_3)_2MCH_3{}^+$ $CH_3B(C_6F_5)_3{}^-$ complexes (M = Zr, Hf) in toluene solution.

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