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Significant Zirconium−Alkyl Group Effects on Ion Pair Formation Thermodynamics and Structural Reorganization Dynamics in Zirconocenium Alkyls

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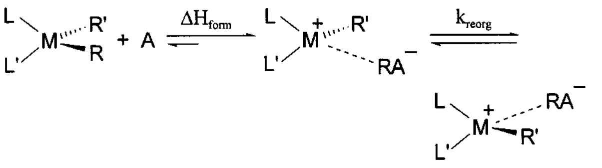
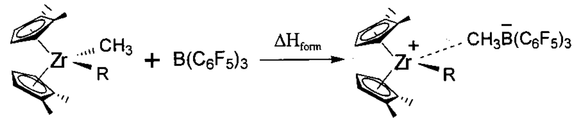
Summary: Substantial Zr−alkyl group (R) effects on ion pair thermodynamic stability as well as on ion pair solution structure and structural dynamics are reported in the $[(1,2\text{-}Me_2Cp)_2ZrR]^+[CH_3B(C_6F_5)_3]^-$ *series, where* $R = CH_3$, $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$, *and* $CH[Si(CH_3)_3]_2$. *These quantitative results underscore the effects such R moieties are likely to play in group 4 metallocene-mediated olefin polymerization catalysis.*

A growing database implicates metallocene ancillary ligation (L, L′), metal identity (M), and the nature of the abstractor/cocatalyst (A; eq 1) as key factors governing the thermodynamics and kinetics of single-site metallocenium catalyst activation as well as the stereochemical dynamics of the tight ion pairing.[1,2] The interplay of these variables influences catalyst activity, thermodynamic stability, chain transfer characteristics, and regio- and stereochemical aspects of monomer enchainment in ways that are not yet entirely understood. In actual polymerization catalytic systems, the identity of alkyls R and R′ can be quite variable, and little is known quantitatively about how alkyl group steric and electronic characteristics affect metallocenium ion pair thermodynamic stability with respect to the neutral precursors, solution phase structure, and stereochemical dynamics. We communicate here the first thermochemical and dynamic NMR study which indicates that R, R′ effects can be very large.[3]



(1)

Using the well-characterized and spectroscopically informative bis(1,2-dimethylcyclopentadienyl)zirconocene framework and $B(C_6F_5)_3$ as a prototypical abstractor/cocatalyst,[2,4,5] a series of metallocenium alkyl methylborate ion pairs (**2**) was synthesized from the corresponding methylalkyls (**1**)[6] (eq 2) and characterized by standard spectroscopic and analytical techniques.[7] The



(2)

		R
1a	**2a**	CH_3
1b	**2b**	$CH_2C(CH_3)_3$
1c	**2c**	$CH_2Si(CH_3)_3$
1d	**2d**	$CH[Si(CH_3)_3]_2$

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[1] For leading recent reviews of single-site olefin polymerization, see: (a) *J. Mol. Catal.* **1998**, *128*, 1−337 (special issue on metallocene and single site olefin catalysts; Jordan, R. F., Ed.). (b) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 144−187. (c) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255−270. (d) Brintzinger, H. H.; Fisher, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (e) Soga, K., Terano, M., Eds. *Catalyst Design for Tailor-Made Polyolefins*; Elsevier: Tokyo, 1994. (f) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1−29.

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[6] Methylalkylzirconocenes were prepared via the addition of 1 equiv of the corresponding lithium alkyl to the dichlorozirconocene followed by treatment with methyllithium or, alternatively, by addition of the lithium alkyl to a mixed chloromethylzirconocene. See the Supporting Information for details.

[7] For example, **2d** was synthesized when **1d** (0.21 g, 0.46 mmol) and $B(C_6F_5)_3$ (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 mixture 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 solution was filtered 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 (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$_3$). Anal. Calcd for $C_{40}H_{40}BF_{15}Si_2Zr$: C, 49.83; H, 4.19. Found: C, 49.39; H, 4.19. See the Supporting Information for other synthetic details.

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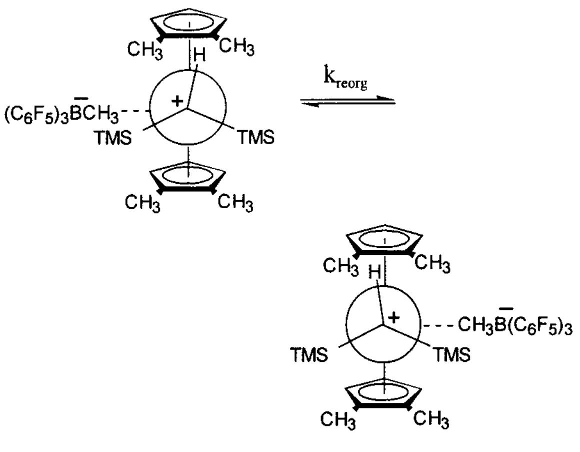
Table 1. Ion Pair Formation Thermodynamics and Ion Pair Reorganization Dynamics Data for Metallocene Alkyl Ion Pairs having the Formula $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrR}]^+[\text{CHB}(\text{C}_6\text{F}_5)_3]^-$ in Toluene Solution

entry no.	R	$\Delta H_{\text{formation}}$[a] (kcal/mol)	$\Delta G^{\ddagger}_{\text{reorganization}}$[b,c] (kcal/mol)	$\Delta H^{\ddagger}_{\text{reorganization}}$[b] (kcal/mol)	$\Delta S^{\ddagger}_{\text{reorganization}}$[b] (kcal/mol)	coalescence temp (°C in tol-d_8)
2a	CH_3	−24.6(8)[d]	17.6(2)[d]	22(1)[d]	13(2)[d]	110[d,f]
2b	$CH_2C(CH_3)_3$	β-Me elim	13.8(2)[e]	18(1)	15(2)	β-Me elim
2c	$CH_2Si(CH_3)_3$	−22.6(1.0)	13.8(2)	17(1)	10(3)	20[f]
2d	$CH[Si(CH_3)_3]_2$	−59.2(1.4)	8.0(4)[g]	9(2)[g]	7(4)[g]	−100[g,h]

[a] Determined calorimetrically. [b] Determined via VT NMR experiments. [c] At the indicated coalescence temperature. [d] See also ref 2c. [e] At 0 °C. [f] Coalescence of diastereotopic CpMe signals. [g] In $CDCl_2F$. [h] Coalescence of diastereotopic TMS groups.

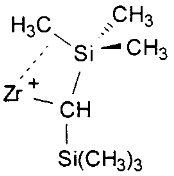
abstraction process is, within NMR detection limits, completely selective for the methyl anion.[8] The enthalpies of eq 2 (ΔH_{form}) were measured in toluene solution by reaction titration calorimetry using the rigorously anaerobic methodology and instrumentation described previously.[2c,9] ΔH_{form} for complex **2b** could not be measured because of facile β-CH_3 elimination above 0 °C.[10] The thermochemical results (Table 1) indicate that alkyl effects on ΔH_{form}, and hence stabilization of the cationic catalyst, can be rather large. Thus, while the exothermicity of eq 2 for R = $CH_2Si(CH_3)_3$ is comparable to or slightly less than that for R = CH_3, that for R = $CH[Si(CH_3)_3]_2$ is more than twice as large.

Some insight into the driving force(s) for eq 2 and the sensitivity of ion pair structural mobility on the R group is provided by variable-temperature NMR spectroscopy.[11] First, the *neutral precursor* complex **1d**[12] is found to be sterically congested, as indicated by restricted rotation of the $CH[Si(CH_3)_3]_2$ group ($\Delta G^{\ddagger} = 17.4$ kcal/mol at 85 °C).[13] The limited solubility of ion pair **2d** in toluene is suggestive of weak ion pairing,[2e,14] while the $CH_3B(C_6F_5)_3^-$ ^1H chemical shift (δ 0.40 in CD_2Cl_2, 1.24 in toluene-d_8) is similar to that of the free anion[10b,14] rather than to that in tightly ion paired complexes,[2c,4,5] i.e., those having strong $Zr^+ \cdots H_3CB(C_6F_5)_3^-$ interactions as assessed by X-ray diffraction. Variable-temperature NMR spectroscopy of **2d** in $CDCl_2F$ reveals an instantaneous structure at −126 °C in accord with eq 3, as indicated by four magnetically nonequivalent ring CH_3 groups, two magnetically distinct TMS (TMS = $-Si(CH_3)_3$) groups, and close C*H*TMS$_2$ methine proton proximity (as judged by NOE measurements) to *only one* 1,2-Me$_2$-Cp ring. Interestingly, at the lowest accessible temperatures, restricted rotation about one HC−TMS bond is observed, suggestive of cation−anion congestion and/or TMS group donor interactions toward the metal center (e.g., **I**), for which there is ample precedent in neutral lanthanocene anologues.[15] Steric destabilization of **1d**, together with interaction **I** and any β-cation stabilizing effects[16] of the $CHTMS_2$ group, likely account for the large negative ΔH_{form}. One consequence of the sterically encumbering/cation-stabilizing zirconocenium environment of **2d** is rather weak ion pairing, as evidenced by $\Delta G^{\ddagger}_{\text{reorg}} = 8.0(4)$ kcal/mol, $\Delta H^{\ddagger}_{\text{reorg}} = 9(2)$ kcal/mol, and $\Delta S^{\ddagger}_{\text{reorg}} = 7(4)$ cal/(K mol) for eq 3 in $CDCl_2F$. Although the slow exchange limit could not be reached in toluene-d_8, the similar line shape changes are consistent with similar activation parameters.



(3)

I



In contrast to the large R = $CHTMS_2$ effects on ΔH_{form} in **2d**, the thermochemical results (Table 1) for the R =

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(8) For examples of alkyl groups, other than and not in competition with methyl, abstracted by $B(C_6F_5)_3$ see ref 5c and: (a) Gielens, E. E. C. G.; Tiesnitsch, J. Y.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 1652−1654. (b) Horton, A. D.; de With, J. *Organometallics* **1997**, *16*, 5424−5436. (c) Pellecchia, C.; Immirzi, A.; Grassi, A.; Zambelli, A. *Organometallics* **1993**, *12*, 4473−4478.

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(10) ^1H NMR features of **1a** and isobutene are observed. For related examples of such processes, see: (a) Shaffer, T. D.; Canich, J. A. M.; Squire, K. R. *Macromolecules* **1998**, *31*, 5145−5147. (b) Horton, A. D. *Organometallics* **1996**, *15*, 2675−2677. (c) Guo, Z.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424−1432. (d) Kesti, M. R.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 3565−3567.

(11) Solution concentrations for variable-temperature NMR line shape measurements were precisely known and were typically within 5−10 mM.

(12) Spectroscopic and analytical details for **1d**: ^1H NMR (C_6D_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_6D_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 (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, 58.22; H, 8.83, 8.77.

(13) For related systems see: Jeffery, J.; Lappert, M. F.; Luong-Thi, N. T.; Webb, M.; Atwood, J. L.; Hunter, W. F. *J. Chem. Soc., Dalton Trans.* **1981**, 1593−1605.

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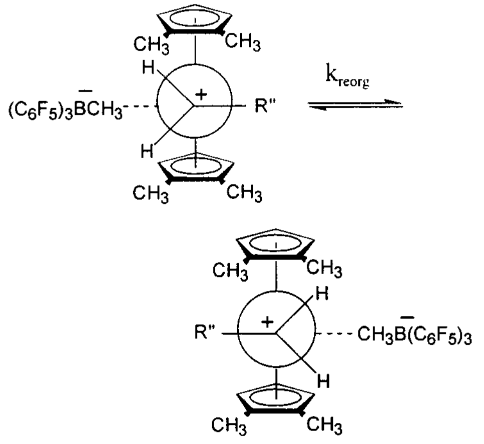
CH_2TMS ion pair (**2c**) evidence little overall silyl or alkyl stabilization of the cationic fragment, and ΔH_{form} is comparable to that in the R = CH_3 cation (**2a**) (−22.6(1.0) vs −24.6(8) kcal/mol, respectively). With regard to ion pair structure and structural dynamics, the R = CH_2TMS (**2c**) and $CH_2C(CH_3)_3$ (**2b**) cations differ markedly from both **2d** and **2a**. Unlike **2d**, the toluene solubility and $CH_3B(C_6F_5)_3^-$ ^1H chemical shifts in these complexes (δ = 0.06 in **2b** and −0.03 in **2c**) are consistent with tighter ion pairing (stronger $Zr^+\cdots H_3CB(C_6F_5)_3$ interactions).[2c,4,5] In accord with this observation, the enthalpic barriers to ion pair reorganization (eq 4) are now ~8−9 kcal/mol higher than in **2d** (~2 × 10^5 times slower reorganization rate at 25 °C), with limiting low-temperature spectra in accord with C_s-symmetric structures.[5,7] The small magnitude of $^1J_{C-H}$ in the **2c** $Zr-CH_2TMS$ group (107 Hz) may indicate a weak α-agostic interaction.[17] Magnetic equivalence of the TMS methyl groups down to the lowest accessible temperatures argues that interactions as in **I** must also be weak.[15] These results on ion pairing with bulky primary alkyls can be compared with those for the crystallographically characterized R = CH_3 ion pair (**2a**).[4] While the ΔH_{form} value is comparable to that in **2c** (Table 1) and δ $CH_3B(C_6F_5)_3^-$ differs marginally (δ 0.02), the barrier to ion pair reorganization (eq 4, R″ = H) is substantially larger (~4−5 kcal/mol; ~1 × 10^3 times slower reorganization rate at 25 °C), again illustrating significant alkyl group effects on the depth of the potential wells such structures occupy.



(4)

R"	
H	(**2a**)
$C(CH_3)_3$	(**2b**)
TMS	(**2c**)

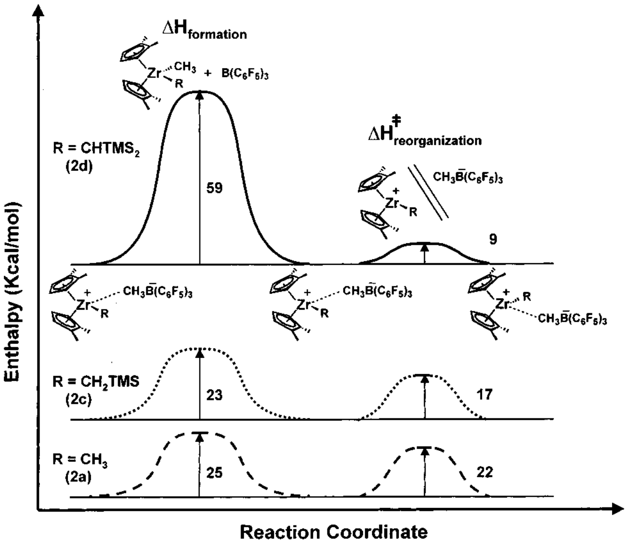


Figure 1. Enthalpic profiles for $[(1,2\text{-}Me_2Cp)_2ZrR]^+[CH_3B(C_6F_5)_3]^-$ ion pair formation from the neutral precursors and symmetrizing ion pair structural reorganization processes as a function of the R group in toluene solution: (---) R = CH_3; (···) R = CH_2TMS; (—) R = $CHTMS_2$.

The results of this study are summarized in the comparative energy surfaces of Figure 1. While the exact interplay of ancillary ligands, counteranion, metal, and alkyl substituent/growing polymer chain in the olefin activation and insertion process is not yet completely quantified, the present results indicate that variation in alkyl substituent can modulate the enthalpy of ion pair (catalyst) stabilization versus the neutral precursors (eq 1) by as much as ~37 kcal/mol (a factor of ~3 × 10^{25} times in equilibrium constant at 25 °C using ΔS_{form} from related systems[2c]). Furthermore, variation in the alkyl group can modulate the barrier to ion pair reorganization (eq 1) by as much as ~10−13 kcal/mol (a factor of ~2 × 10^8 times in reorganization rate).

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Supporting Information Available: Text giving experimental procedures and spectral and analytical data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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