A Density Functional Study of Ion-Pair Formation and Dissociation in the Reaction between Boron- and Aluminum-Based Lewis Acids with $(1,2\text{-}Me_2Cp)_2ZrMe_2$

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Calculations have been carried out on the reaction between the olefin polymerization precatalyst $(1,2\text{-}Me_2Cp)_2ZrMe_2$ (P) and a number of Lewis acids (A) to form the methide-bridged (contact) ion pair $(1,2\text{-}Me_2Cp)_2ZrMe(\mu\text{-}Me)A$ (**I**; $P + A \rightarrow \mathbf{I} + \Delta H_{ipf}$). This is the first step in the activation of P to becoming an olefin polymerization catalyst. The calculated enthalpies of formation (ΔH_{ipf}) for **I** were as follows (A, ΔH_{ipf} in kcal/mol): $B(C_6F_5)_3$ (**1a**), −23.8; $B(C_6F_5)_2(C_6H_3F_2)$ (**1b**), −21.5; $B(C_6F_5)_2(C_6H_5)$ (**1c**), −18.3; $B(C_6F_5)_2(C_6H_3(CH_3)_2$ (**1d**), −18.0; $B(C_6H_5)_3$ (**1e**), −6.7; $B(C_{10}F_7)_3$ (**1f**), −25.8; $(MeAlO)_6$ (**2a**), −15.9; $(MeBO)_6$ (**2b**), −22.3; $AlMe_3$ (**2c**), −8.1; $Al(C_6F_5)_3$ (**2d**), −30.8. The charge separation between the $(1,2\text{-}Me_2Cp)_2ZrMe^+$ and AMe^- fragments in **I** was calculated for all A, and it was found that the charge separation as well as $-\Delta H_{ipf}$ increases through the series **1e**, **1c**, **1b**, and **1a** with the number of fluorine atoms. A good activating Lewis acid (A) has the equilibrium shifted strongly from P and A toward **I**, and this is the case for all A except **1e** and **2c.** Also considered was the complete dissociation in solution (toluene) of **I** into the counterions $[(1,2\text{-}Me_2Cp)_2ZrMe]^+$ and AMe^- with the dissociating enthalpy ΔH_{ips} as well as the formation from I of the solvent-separated ion pair (S = toluene) $[(1,2\text{-}Me_2Cp)_2ZrMe]^+{-}S{-}[AMe]^-$ with the reaction enthalpy ΔH_{ss}. The two types of separation processes have both been postulated as the second and final steps in the activation of P. The calculated values are as follows (A, ΔH_{ips} and ΔH_{ss} in kcal/mol): **1a**, 38.0, 18.7; **1f**, 43.6, 18.9; **2a**, 57.0, 32.4; **2b**, 46.9, 35.3; **2c,** 69.2, 35.3; **2d,** 48.3, 20.6. It is concluded that the formation of $[(1,2\text{-}Me_2Cp)_2ZrMe]^+{-}S{-}[AMe]^-$ is the more likely separation process. Consideration has also been given to the influence of solvent polarity on the separation process, with S = toluene, chlorobenzene, and 1,2-dichlorobenzene. Finally discussed are ΔH_{ips} and ΔH_{ss} for the ion pair $[(1,2\text{-}Me_2Cp)_2ZrMe]^+[A]^-$ (**III′**); $A^- = B(C_6F_5)_4^-$ (**3a**), $Al(C_6F_5)_4^-$ (**3b**), $[(C_2B_9H_{11})_2Co]^-$ (**3c**), and $\{^tBuCH_2CH[B(C_6F_5)_2]H\}^-$ (**3d**)), where **III′** is formed from the reaction of P with the activator $[CPh_3^+][A^-]$. Here the calculated values are as follows (A^-, ΔH_{ips} and ΔH_{ss} in kcal/mol): **3a**, 22.1, −4.2; **3b**, 26.2, 0.7; **3c**, 34.9, 7.5; **3d**, 26.7, −0.5. It is found that **III** type ion pairs are easier to dissociate than **I** held together by a methide bridge.

I. Introduction

Group 4 metallocenes $Cp_2M(Me)_2$ (Cp = C_5H_5; M = Zr, Hf, Ti) and their derivatives have been the subject of intense scrutiny over the past decade because of their ability to act as olefin polymerization precatalysts. The metallocenes $Cp_2M(Me)_2$ are only active after treatment with a Lewis acidic cocatalyst, A, and the catalytic activity has been attributed[1−4] to the cationic, coordinatively unsaturated complex Cp_2MMe^+ and its derivatives. This species is assumed to be formed by methide abstraction from $Cp_2M(Me)_2$ by A.

Careful studies[1,4] have shown that the first step in the activation of Cp_2MMe_2 by A involves the formation of the methide-bridged species $Cp_2M(Me)\text{-}(\mu\text{-}Me){-}A$ according to

$$Cp_2M(Me)_2 + A \rightarrow Cp_2M(Me)\text{-}(\mu\text{-}Me){-}A + \Delta H_{ipf} \quad (1)$$

The methide-bridged species is often described as the contact ion pair $[Cp_2M(Me)]^+[MeA]^-$ with full charge separation. The contact ion pair **Ia**, formed from the reaction between the precatalyst $(1,2\text{-}Me_2Cp)_2ZrMe_2$ (P) and the cocatalyst $B(C_6F_5)_3$ (**1a**), is shown in Scheme 1. The enthalpy ΔH_{ipf} for the (contact) ion pair formation reaction of eq 1 has been measured for a few Lewis acids by Marks et al.[2]

NMR experiments[2] in solution clearly indicate that $Cp_2M(Me){-}(\mu\text{-}Me){-}A$ is in equilibrium with species where the contact between the metal and the methide

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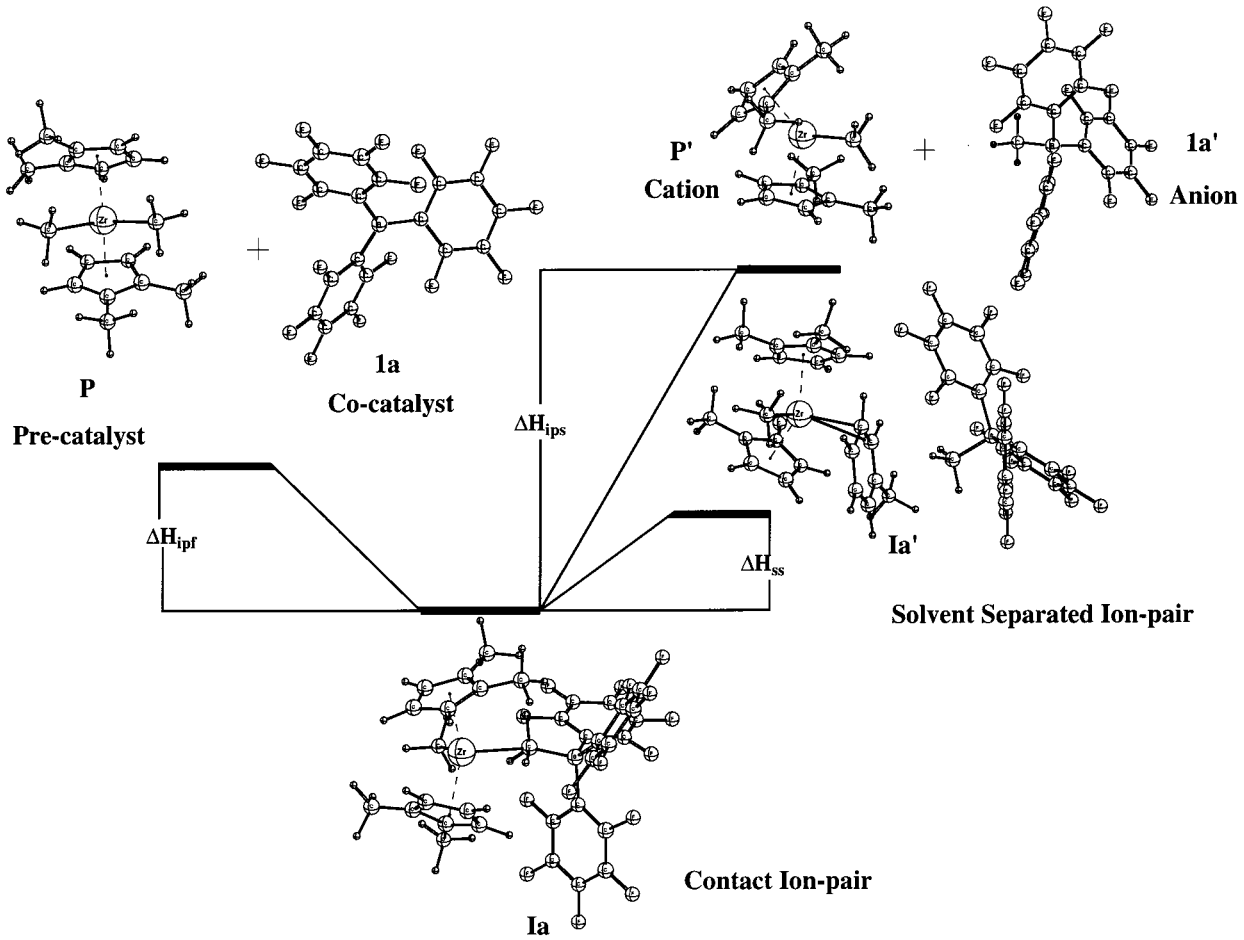
Scheme 1. Possible Reactions of the Contact Ion Pair $[(1,2Me_2Cp)_2ZrMe]^+[B(C_6F_5)_3Me]^-$ in Toluene



group is broken. The disruption of the metal−methide contact is often presented as a simple ion pair separation process

$$(Cp_2M(Me)-(\mu\text{-}Me)-A)_{solv} \rightarrow (Cp_2MMe^+)_{solv} + (MeA^-)_{solv} + \Delta H_{ips} \quad (2)$$

in which the two ions dissociate completely in solution, as illustrated in Scheme 1 for the dissociation of $(1,2\text{-}Me_2Cp)_2ZrMe-(\mu\text{-}Me)-B(C_6F_5)_3$ (**Ia**) into $(1,2\text{-}Me_2Cp)_2ZrMe^+$ (P′) and $B(C_6F_5)_3(Me)^-$ (**1a′**). However, experimental evidence does not rule out the formation of a solvent-separated ion pair

$$(Cp_2M(Me)-(\mu\text{-}Me)-A)_{solv} \rightarrow ([Cp_2MMe]^+-S-[MeA]^-)_{solv} + \Delta H_{ss} \quad (3)$$

in which a solvent molecule is sandwiched by the two counterions. Scheme 1 illustrates the different species involved in the activation of $(1,2\text{-}Me_2Cp)_2ZrMe_2$ by $B(C_6F_5)_3$. A good activator should have a sufficiently large $-\Delta H_{ipf}$ value to convert the precatalyst completely to the contact ion pair in eq 1. At the same time olefin should have easy access to the cationic metal center in $[Cp_2M(Me)]^+[MeA]^-$, which means that the ion pair dissociation energies of eqs 2 and 3 should be low.

Methylalumoxane (MAO) has typically been the most commonly used cocatalyst in industry. There have been experimental investigations conducted to determine the structure of MAO[2] and to test the polymerization activity of model compounds for MAO.[3] Other activators that have been studied experimentally include boron[4] and aluminum[5] compounds. More recently[6] salts of carbenium ions have been used successfully as activators

$$Cp_2M(Me)_2 + [CPh_3]^+A^- + S \rightarrow [Cp_2MR]^+-S-[A]^- + MeCPh_3 \quad (4)$$

with the anion A^- represented by carboranes and boranes.

Theoretical studies of the activation processes in eqs 1−4 have just started to emerge. In their pioneering work, Lanza et al.[7] studied the activation of $Me_2Si(Me_4\text{-}Cp)(t\text{-}BuN)TiMe_2$ by $B(C_6F_5)_3$ using ab initio methods. Their work clearly underlined that the anions MeA^- as

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well as the solvent strongly influence the initial steps of the olefin polymerization process. Klesing et al.[8a] used density functional theory (DFT) to study dimerization and ion pair formation enthalpies for silicon-bridged bis-(indenyl) zirconocenes with a hexameric 3-D model for MAO used as cocatalyst. Their results demonstrated that the degree of steric bulk on the precatalyst can influence the way in which MAO acts as an activator. Models of MAO have also been considered by Fusco et al.[8b−c]

We have previously conducted DFT studies[8d] on the activation of different metallocene precatalysts by the same Lewis acid, B(C_6F_5)$_3$. The present investigation considers on the other hand various activators applied to the same precatalyst, (1,2-Me$_2$Cp)$_2$ZrMe$_2$. We shall first investigate the borane-based activators B(C_6F_5)$_3$ (**1a**), B(C_6F_5)$_2$($C_6H_3F_2$) (**1b**), B(C_6F_5)$_2$(C_6H_5) (**1c**), B(C_6F_5)$_2$(C_6H_3(Me)$_2$) (**1d**), B(C_6H_5)$_3$ (**1e**), and B($C_{10}F_7$)$_3$ (**1f**), already considered experimentally by Marks et al.[4e] The emphasis is here on understanding how different flourinated substituents attached to boron will influence the thermochemistry of reactions 1−3. Considerations will also be given to MAO (**2a**), its boron analogue MBO (**2b**), AlMe$_3$ (**2c**), and Al(C_6F_5)$_3$ (**2d**), as well as the influence of different solvents on the processes in eqs 2 and 3. We shall finally discuss the merits of the new types of activators [CPh_3^+][A^-] for different anions A^- = B(C_6F_5)$_4^-$ (**3a**), Al(C_6F_5)$_4^-$ (**3b**), [($C_2B_9H_{11}$)$_2$Co]$^-$ (**3c**), and {^{t}BuCH$_2$CH[B(C_6F_5)$_2$]H}$^-$ (**3d**).

II. Computational Details

The density functional theory calculations were carried out using the Amsterdam Density Functional (ADF) program, version 2.3.3, developed by Baerends et al.[10] and vectorized by Ravenek.[11] The numerical integration scheme applied was developed by te Velde et al.,[12] and the geometry optimization procedure was based on the method of Verslius and Ziegler.[13] Geometry optimizations were carried out using the local exchange-correlation potential of Vosko et al.[14] without any symmetry constraints. The electronic configurations of the molecular systems were described by a triple-ζ basis set on zirconium for 4s, 4p, 4d, and 5s, augmented with a single 5p polarization function. Double-ζ STO basis sets were used for carbon (2s, 2p), hydrogen (1s), and nitrogen (2s, 2p), augmented with a single 3d polarization function, except for hydrogen, where a 2p polarization function was used. A set of auxiliary s, p, d, f, and g STO functions centered on all nuclei was used to fit the molecular density and represent Coulomb and exchange potentials accurately in each SCF cycle.[15] The gas-phase energy difference was calculated by augmenting the local density approximation energy with Perdew and Wang's nonlocal correlation and exchange corrections (PWB91).[16] The energy differences in solution were corrected from the gas-phase energy by accounting for the solvation energy calculated by the Conductor-like Screening Model (COSMO) that has recently been implemented into the ADF program.[17] The solvation calculations were performed with the dielectric constants 2.38 for toluene, 5.71 for chlorobenzene, and 9.93 for dichlorobenzene. The radii used for the atoms (in Å) were as follows: hydrogen, 1.16; boron, 1.15; carbon, 2.0; oxygen, 1.5; fluorine, 1.2; zirconium, 2.4. These values were obtained by optimization using least-squares fitting to experimental solvation energies. The charge distribution study was carried out by Mulliken analysis.[18]

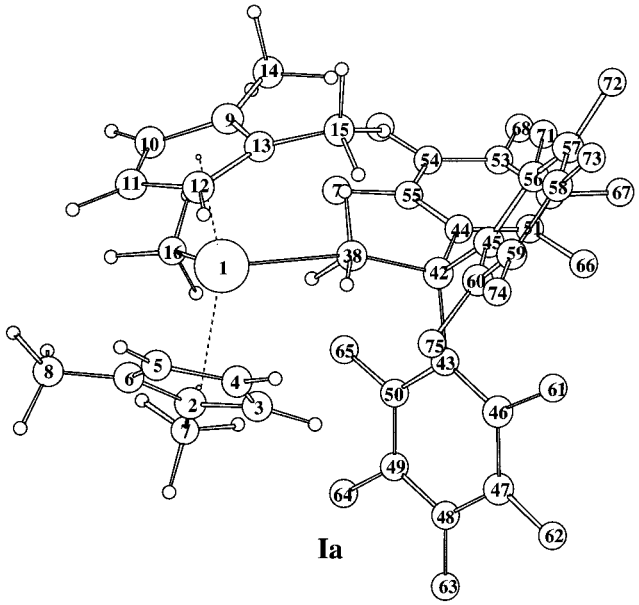

Figure 1. LDA optimized structure of the [(1,2-Me$_2$Cp)$_2$ZrMe]$^+$[B(C_6F_5)$_3$Me]$^-$ contact ion pair.

III. Results and Discussion

a. Ion-Pair Formation. (i) Activation Using Boranes. The activation of (1,2-Me$_2$Cp)$_2$ZrMe$_2$ (P) by B(C_6F_5)$_3$ (**1a**) to give the ion pair [(1,2-Me$_2$Cp)$_2$ZrMe]$^+$-[MeB(C_6F_5)$_3$]$^-$ (**Ia**) has been studied experimentally.[4a,b] The crystal structure of the ion pair that was obtained from these studies revealed that the cation was attached to the anion by a (μ) Zr−Me−B bridge. The Zr−Me-(bridging) bond was found to be 0.15 Å longer than the terminal Zr−Me distance. Further, the terminal B−C distances in B(C_6F_5)$_3$ were found to be only slightly longer (0.03 Å) than the bonds in the anionic B(C_6F_5)$_3$Me$^-$ species.

The obtained calculated structures are similiar to those obtained experimentally. The optimized ion pair is shown in Figure 1. A comparison of selected bond angles and bond lengths with the corresponding values in the crystal structure are given in Table 1. The comparison of the optimized B(C_6F_5)$_3$Me$^-$ anion (**1a′**) and the neutral cocatalyst **1a** reveals that the three C−B−C angles in the neutral cocatalyst are all roughly equal to 120° while the corresponding angles in the

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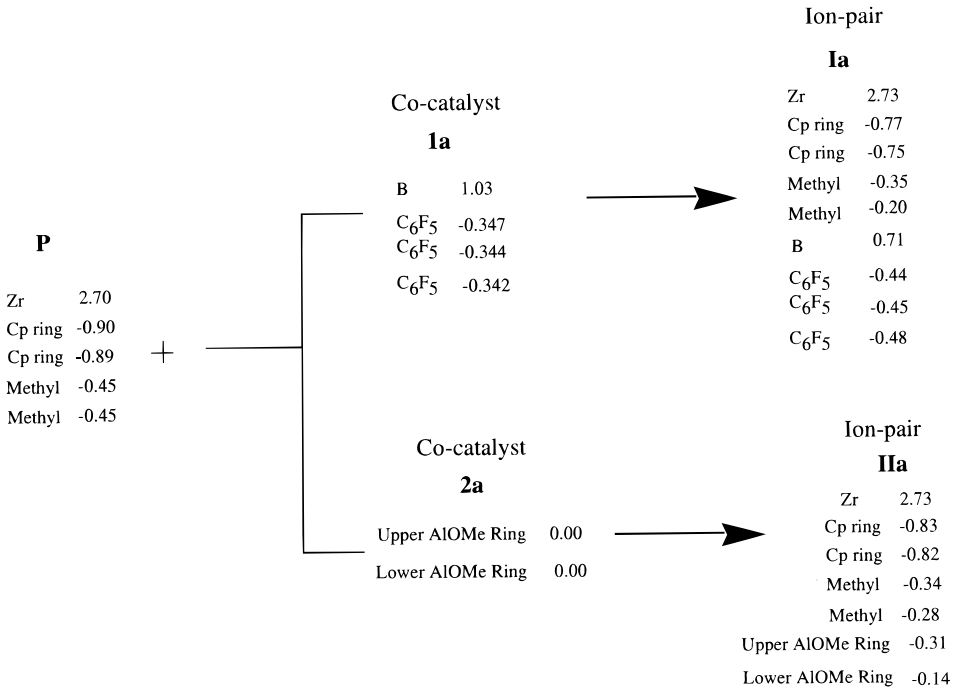


Figure 2. Charge analysis of ligands and functional groups in the neutral precursors and ion pair for the $[(1,2\text{-}Me_2\text{-}Cp)_2ZrMe]^+[B(C_6F_5)_3Me]^-$ system and the $[(1,2\text{-}Me_2Cp)_2ZrMe]^+[MAOMe]^-$ system.

Table 1. Selected Experimental and Calculated Bond Distances (Å) and Bond Angles (deg) for Contact Ion Pair Ia

distance[a]	exptl[b]	calcd	angle[a]	exptl[b]	calcd
Zr−C_2	2.543	2.557	C_{43}−B−C_{45}	106.5	106.8
Zr−C_3	2.487	2.493	C_{43}−B−C_{44}	112.0	114.7
Zr−C_4	2.483	2.431	C_{44}−B−C_{45}	114.3	114.1
Zr−C_5	2.469	2.447	C_{38}−B−C_{43}	112.7	108.1
Zr−C_9	2.524	2.535	C_{38}−B−C_{44}	114.3	111.1
Zr−C_{10}	2.475	2.475	C_{38}−B−C_{45}	108.7	101.8
Zr−C_{11}	2.455	2.431	Zr−C_{38}−B	161.8	163.7
Zr−C_{12}	2.498	2.431	C_{16}−Zr−C_{38}	92.0	93.0
Zr−C_{16}	2.252	2.263			
Zr−C_{38}	2.549	2.411			
B−C_{38}	1.663	1.635			
B−C_{43}	1.643	1.613			
B−C_{45}	1.665	1.615			

[a] For the numbering scheme, see Figure 1. [b] Reference 4a.

Table 2. Formation Energies (ΔH_{ipf}) for Methide Bridge Ion Pairs Containing Borates

cocatalyst	ion pair	ΔH_{ipf} calcd[b,c]	ΔH_{ipf} exptl[a,c]	activity[a,d,e]
$B(C_6F_5)_3$ (**1a**)	**Ia**	−23.8	−24.2	5.2×10^6
$B(C_6F_5)_2(C_6H_3F_2)$ (**1b**)	**Ib**	−21.5	−18.7	5.0×10^6
$B(C_6F_5)_2(C_6H_5)$ (**1c**)	**Ic**	−18.3	−14.8	1.3×10^5
$B(C_6F_5)_2\{C_6H_3(CH_3)_2\}$ (**1d**)	**Id**	−18.0	−10.8	3.4×10^5
$B(C_6H_5)_3$ (**1e**)	**Ie**	−6.7		
$B(C_{10}F_7)_3$ (**1f**)	**If**	−25.8		

[a] Reference 4e. [b] Corresponding to the process $Cp_2M(Me)_2 + A \rightarrow Cp_2M(Me)\text{−}(\mu\text{-}Me)\text{−}A + \Delta H_{ipf}$. [c] In units of kcal/mol. [d] Ethylene polymerization activities. [e] In units of $(\text{mol catalyst})^{-1}$ $(\text{atm } C_2H_4)^{-1}$ h^{-1}.

bound anion are decreased to 113° in order to accommodate the methide group. The B−C distances in the anion are also found to increase to 1.62 Å in the anion from 1.54 Å in the neutral for the same reason. The enthalpy of ion pair formation ΔH_{ipf} for **Ia** was calculated to be −23.8 kcal/mol, which compares very favorably with the experimentally[4a,b] determined value of −24.0 kcal/mol.

Changes in the electronic density due to the formation of the ion pair from the precursors was analyzed by conducting a charge analysis on the precursors P and **1a** and the ion pair **Ia**. The scheme for the charge analysis is shown in Figure 2. The total charge on each of the functional groups was calculated by adding the charge present on each atom of the functional group. The total charge on the functional groups was calculated for the precursors as well as for the ion pair formed. The charge analysis underlines a distinct flow of electron density from the neutral catalyst precursor to the borane anion in the ion pair. The total charge on the cyclopentadienyl rings increased from around −0.90 to about −0.75 in the ion pair. The charge on the boron atom decreased from 1.03 in the neutral precursor to 0.71 in the ion pair. The charge on the C_6F_5 rings decreased from −0.34 in the neutral precursor to about −0.45 in the ion pair. It is clear that the cocatalyst activator $B(C_6F_5)_3$ is quite effective in withdrawing electron density from the precatalyst and this explains why the stability of the subsequent ion pair formed is quite high. Our charge analysis is consistent with a formulation of the contact ion pair **Ia** as $[(1,2\text{-}Me_2\text{-}Cp)_2ZrMe]^{q+}[MeB(C_6F_5)_3]^{q-}$ with $q = 0.85$.

Varying the number of fluorine atoms in the cocatalyst was found to have a significant effect on the value of ΔH_{ipf}. Deck et al.[4e] had experimentally determined that the polymerization activity decreased with the decrease in the number of fluorine atoms in the cocatalyst. We optimized the structures **Ia**−**f** and calculated the value for ΔH_{ipf} for each case. The results are summarized in Table 2. The value of ΔH_{ipf} was found to increase almost linearly with the number of fluorine atoms contained in the cocatalyst. The polymerization activities determined by Deck et al.[4e] are also shown in the table. A graph of ΔH_{ipf} against the number of fluorine atoms is shown in Figure 3.

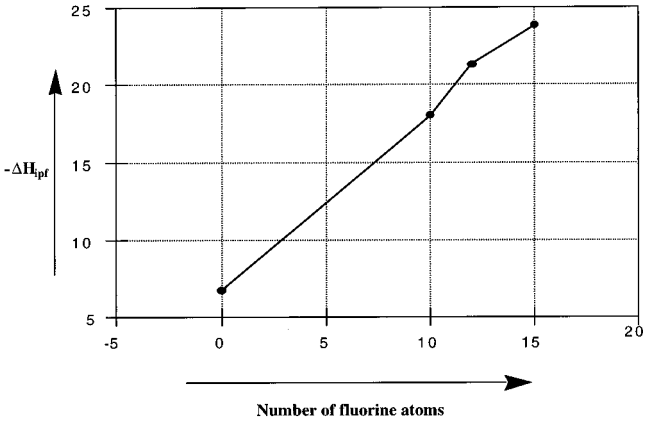


Figure 3. Plot of the negative enthalpy of ion pair formation against the number of fluorine atoms for a series of ion pairs with borates as the cocatalyst.

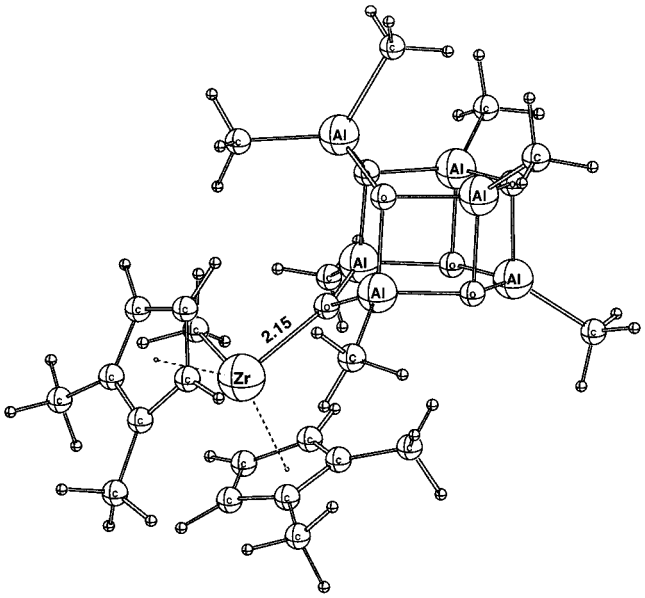
Table 3. Total Charge on the C_6F_5 Group in the Neutral Cocatalyst A and Corresponding Ion Pair (1,2-Me$_2$Cp)$_2$ZrMe−(μ-Me)−A

cocatalyst A	charge (cocatalyst A)[a]	charge (ion pair **I**)[b]	charge flow[c]
$B(C_6F_5)_3$	−0.34	−0.48	−0.14
$B(C_6F_5)_2C_6H_3F_2$	−0.36	−0.47	−0.11
$B(C_6F_5)_2C_6H_5$	−0.38	−0.46	−0.08

[a] Total average charge on each C_6F_5 group in neutral cocatalyst A. [b] Total average charge on each C_6F_5 group in (1,2-Me$_2$Cp)$_2$ZrMe−(μ-Me)−A. [c] Total average flow of charge to each C_6F_5 group on ion pair formation.

The electron-withdrawing effect of the fluorine atoms is quite clear from the graph—an increase in acidity of the boron center with the addition of more fluorines was found to lead to greater stability of the ion pair formed. The resultant increased charge separation between the ions in the ion pair would also facilitate the separation of the ions in solution. This would explain the higher polymerization activity of ion pair systems with more fluorine atoms in the cocatalyst, as experimentally observed by Deck et al.[4e] and shown in Table 2. A charge analysis was conducted along the same lines as in the case of **Ia** for each cocatalyst. It was found that the flow of charge decreased with increasing replacement of the fluorine atoms by hydrogens. A "relative" charge flow index is displayed in Table 3—here we see the difference in charge of a C_6F_5 group in the neutral precursor $B(C_6F_5)_2A$ (where "A" would be C_6F_5, $C_6H_3F_2$, etc.) compared to the charge of the same C_6F_5 group in the corresponding anion. It is quite clear from the table that increasing the number of fluorine atoms has a decisive effect on increasing the charge flow.

One way of improving the activity (and $-\Delta H_{ipf}$) of the cocatalyst would be to try and increase the number of fluorine atoms in the cocatalyst. This strategy has already been used by Li et al.[4d] in substituting perfluorophenyl groups by perfluoronaphthyl groups. Despite the steric problems associated with increasing the size of the cocatalyst, thereby making it more difficult to approach the precatalyst, this tris(β-perfluoronaphthyl)-borane cocatalyst (**1f**) was found to improve catalyst performance. Calculations were done on the **1f**−P system. The ΔH_{ipf} value was determined to be −25.8 kcal/mol (Table 2), which shows that this cocatalyst would indeed be more effective in extracting the methide group from the precatalyst.



2a

Figure 4. LDA optimized structure of the contact ion pair formed with MAO as the cocatalyst.

(ii) Aluminum-Based Cocatalysts. To date, the structure of MAO remains unknown. Harlan et al.[3] tested experimentally a hexameric (^{t}BuAlO)$_6$ unit as a three-dimensional model for MAO and found that it reacted exothermically at room temperature with Cp$_2$-ZrMe$_2$ to give an activated ion pair complex. In line with the experimental work of Harlan et al.,[3] we have employed the hexameric species (MeAlO)$_6$ (**2a**) as a model for MAO in the reaction with (1,2-Me$_2$Cp)$_2$ZrMe$_2$ to produce the ion pair **IIa** of Figure 4. The activation occurred with the cleavage of one Al−O bond in the model cocatalyst **2a**, followed by coordination of the cationic zirconium center to oxygen and migration of one methyl group from zirconium to aluminum. In the optimized ion pair structure (Figure 4), the Zr−C bond distance has increased to 4.6 Å and the Al−C distance adopts the normal bond distance for a Al−C bond of 1.9 Å. The Al−O distance has increased from the normal bond length of 1.8 Å in **2a** to 3.34 Å in **IIa** so as to facilitate the activation. The key geometrical features of the optimized ion pair **IIa** compares well with the corresponding parameters in the experimentally determined[3] ion pair structure resulting from the reaction between (^{t}BuAlO)$_6$ and Cp$_2$ZrMe$_2$.

The charge analysis of the ion pair and the precursors is interesting—it shows that there is a flow of charge to the upper ring of two Al−O hexagons. From a 0.0 charge in the neutral species, the upper ring acquires a charge of −0.31, while the lower ring acquires a charge of −0.14. This charge flow in the upper ring is 3 times the charge flow in the corresponding $B(C_6F_5)_3$ case, indicating that the charge transfer for the activation using MAO is much more effective than for the boron cocatalysts studied. The scheme for the charge analysis involving the MAO system with precatalyst P, cocatalyst **2a**, and ion pair **IIa** is shown in Figure 2.

The value for ΔH_{ipf} was calculated to be −15.9 kcal/mol, which compares reasonably well with the experimentally obtained estimate of −10.9 kcal/mol[4e] (Table 4). The relatively low value for $-\Delta H_{ipf}$ can be attributed

Table 4. Formation Energies (ΔH_{ipf}) for Methide Bridge Ion Pairs without Borates

cocatalyst	ion pair formed	ΔH_{ipf},[a] kcal/mol calcd	exptl[b]
MAO (**2a**)	**IIa**	−15.9	−10.9
MBO (**2b**)	**IIb**	−22.3	
$AlMe_3$ (**2c**)	**IIc**	−8.05	
$Al(C_6F_5)_3$ (**2d**)	**IId**	−30.8	

[a] Corresponding to the process $Cp_2M(Me)_2 + A \rightarrow Cp_2M(Me)-(\mu\text{-}Me)-A + \Delta H_{ipf}$. [b] Reference 4e.

Table 5. Enthalpy of Ion Pair Dissociation (ΔH_{ips})[a] for Contact Ion Pairs with a Methide Bridge

cocatalyst	ion pair	calcd ΔH_{ips}[b,c]
$B(C_6F_5)_3$ (**1a**)	**Ia**	38.0
$B(C_{10}F_7)_3$ (**1f**)	**If**	43.6
MAO (**2a**)	**IIa**	57.0
MBO (**2b**)	**IIb**	46.9
$AlMe_3$ (**2c**)	**IIc**	69.2
$Al(C_6F_5)_3$ (**2d**)	**IId**	48.3

[a] Corresponding to the process $(Cp_2M(Me)-(\mu\text{-}Me)-A)_{solv} \rightarrow ([Cp_2MMe]^+)_{solv} + ([MeA]^-)_{solv} + \Delta H_{ips}$. [b] In units of kcal/mol. [c] The solvent is toluene.

to the cost of cleaving completely one Zr−O bond. The boron equivalent of MAO—"MBO" (**2b**)—was constructed by replacing the aluminum atoms with borons in the 3-D model used for MAO. Ion pair formation with MBO was also done to test the ability of **2b** to act as a cocatalyst. The value of $-\Delta H_{ipf}$ was calculated to be 22.3 kcal/mol, which is higher than for the corresponding MAO model **2a**, indicating that it might be a better cocatalyst than MAO, if it can be synthesized.

The aluminum analogue of $B(C_6F_5)_3$, $Al(C_6F_5)_3$ (**2d**), was also examined as a cocatalyst. The value of ΔH_{ipf} was calculated to be −30.3 kcal/mol, which means that the ion pair formed is about 6 kcal/mol more stable than with $B(C_6F_5)_3$. The reason for this increased stability is the stronger Zr−C(bridging) bonding in the $Al(C_6F_5)_3$ case. The Zr−C(bridging) bond was found to be shorter (2.373 Å) in comparison to the Zr−C (bridging) bond (2.411 Å) in the ion pair formed with $B(C_6F_5)_3$.

We have finally looked at the possibility of $AlMe_3$ acting as a cocatalyst, since the reaction between $AlMe_3$ and Cp_2ZrMe_2 as well as Cp_2ZrCl_2 has been studied by Siedle et al.[5a] The reaction between $(1,2\text{-}Me_2Cp)_2ZrMe_2$ and $AlMe_3$ to produce the ion pair **IIc** is only slightly exothermic, with $\Delta H_{ipf} = -8.05$ kcal/mol. Thus, entropy would easily overcome the small favorable ion pair formation energy and drive the equilibrium toward the two neutral constituents $(1,2\text{-}Me_2Cp)_2ZrMe_2$ and $AlMe_3$. It is quite clear that $AlMe_3$ would do a poor job as a catalyst activator. The small charge flow to the "anion" formed in **IIc** also bears out this view. Thus, according to our charge analysis **IIc** should be formulated as $[(1,2\text{-}Me_2Cp)_2ZrMe]^{q+}[AlMe_4]^{q-}$ with $q = 0.48$. Structural data for all the contact ion pairs with a methide bridge are given as Supporting Information.

b. Ion Pair Dissociation. (i) Contact Ion Pairs with a Methide Bridge. We have calculated the energy (ΔH_{ips}) required in toluene to separate completely a number of methide-bridged contact ion pairs (**Ia**,**f**, **IIa**−**d**) into $[(1,2\text{-}Me_2Cp)_2ZrMe]^+$ and $[AMe]^-$ according to eq 2 (Table 5). The required energy is substantial in all cases with $\Delta H_{ips} = 38.0$ kcal/mol (A = $B(C_6F_5)_3$) and $\Delta H_{ips} = 43.6$ kcal/mol (A = $B(C_{10}F_7)_3$) for the borane systems at the lower end and $\Delta H_{ips} = 69.2$ kcal/mol for A = $AlMe_3$ at the upper limit. In the intermediate range are $\Delta H_{ips} = 46.9$ kcal/mol (*A* = MBO), $\Delta H_{ips} = 48.3$ kcal/mol (A = $Al(C_6F_5)_3$), and $\Delta H_{ips} = 57.0$ kcal/mol (*A* = MAO). The trend correlates to some degree with the size of AMe^- and its ability to approach the cation without too much steric congestion. Thus, ΔH_{ips} is largest for A = $AlMe_3$, where steric repulsion might be at a minimum in the contact ion pair, and smallest for A = $B(C_6F_5)_3$, $B(C_{10}F_7)_3$, where steric congestion is highest. The generally large values calculated for ΔH_{ips} in the case of the contact ion pairs (**Ia**,**f**, **IIa**−**d**) can in part be attributed to the strength of the zirconium−methide bond. Chan et al.[8d] have shown that isomers to **Ia** in which the borate is bound to zirconium through fluorines rather than the methide group are higher in energy.

The calculations would indicate that a complete separation of the methide bridge contact ion pair into $(1,2\text{-}Me_2Cp)_2ZrMe^+$ and the AMe^- anion is unlikely. Deck et al.[4b] have measured an enthalpy of activation of 24.2 kcal/mol for a process in which the methide group in the contact ion pair **Ia** is completely transferred from zirconium to boron. Our calculations would indicate that this process is unlikely to be the complete ion separation of eq 2, for which we calculate a value of $\Delta H_{ips} = 38.0$ kcal/mol. We shall later show that the process observed by Deck et al.[4b] might be consistent with the formation of a solvent-separated ion pair according to eq 3.

(ii) Contact Ion Pairs without a Methide Bridge. We have also considered the complete separation of the contact ion pair $[(1,2\text{-}Me_2Cp)_2ZrMe]^+[A]^-$ according to the process

$$([(1,2\text{-}Me_2Cp)_2ZrMe]^+[A]^-)_{solv} \rightarrow ([(1,2\text{-}Me_2Cp)_2ZrMe]^+)_{solv} + (A^-)_{solv} + \Delta H_{ips} \quad (5)$$

where [(1,2-Me2Cp)2ZrMe]$^+$[A]$^-$ is formed in the reaction between $(1,2\text{-}Me_2Cp)_2ZrMe_2$ and the activator $[CPh_3]^+A^-$. The calculated values for ΔH_{ips} of eq 5 are shown in Table 6 in the case of $A^- = B(C_6F_5)_4^-$, $Al(C_6F_5)_4^-$, $(C_2B_9H_{11})_2Co^-$, and $[^tBuCH_2CH(B(C_6F_5)_2)_2H]^-$. This choice reflects key prototypes currently used in experimental studies of $[CPh_3]^+A^-$ activators.

The $[(1,2\text{-}Me_2Cp)_2ZrMe]^+[A]^-$ systems are in general found to have a lower dissociation energy (ΔH_{ips}) than the methide-bridged contact ion pairs due to the larger steric bulk of A^- in comparison to AMe^- as well as the lack of a zirconium−methide interaction in $[(1,2\text{-}Me_2Cp)_2ZrMe]^+[A]^-$.

The ion pairs formed from the borates $B(C_6F_5)_4^-$ (**3a**) and $[^tBuCH_2CH(B(C_6F_5)_2)_2H]^-$ (**3d**) have the lowest ion pair dissociation energies of $\Delta H_{ips} = 22.06$ kcal/mol (**3a**)

Table 6. Enthalpy of Ion Pair Dissociation (ΔH_{ips})[a−c] for Contact Ion Pairs without a Methide Bridge

counterion	ion pair	calcd ΔH_{ips}
$B(C_6F_5)_4^-$ (**3a**)	**IIIa**	22.06
$Al(C_6F_5)_4^-$ (**3b**)	**IIIb**	26.20
$[(C_2B_9H_{11})_2Co]^-$ (**3c**)	**IIIc**	34.86
$\{^tBuCH_2CH[B(C_6F_5)_2]_2H\}^-$ (**3d**)	**IIId**	26.70

[a] Corresponding to the process $([Cp_2M(Me)]^+[AMe]^-)_{solv} \rightarrow ([Cp_2MMe]^+)_{solv} + ([MeA]^-)_{solv} + \Delta H_{ips}$. [b] In units of kcal/mol. [c] The solvent is toluene.

Table 7. Influence of Solvent on the Calculated Ion Pair Dissociation Energy (ΔH_{ips})[a,b]

		ΔH_{ips}			
cocatalyst	ion pair	gas phase	toluene	chloro-benzene	1,2-dichloro-benzene
$B(C_6F_5)_3$ (**1a**)	**Ia**	81.6	38.0	23.4	22.5
$B(C_{10}F_7)_3$ (**1f**)	**If**	77.9	43.6	27.7	22.8
MAO (**2a**)	**IIa**	101.8	57.0	34.5	30.2
MBO (**2b**)	**IIb**	91.4	46.9	26.6	20.4
$AlMe_3$ (**2c**)	**IIc**	110.8	69.2	41.6	35.1
$Al(C_6F_5)_3$ (**2d**)	**IId**	85.7	48.3	31.2	25.9

[a] Corresponding to the process $(Cp_2M(Me)-(\mu\text{-}Me)-A)_{solv} \rightarrow ([Cp_2MMe]^+)_{solv} + ([MeA]^-)_{solv} + \Delta H_{ips}$. [b] In units of kcal/mol.

Table 8. Enthalpy of Formation of Solvent-Separated Ion Pairs (ΔH_{ss})[a,b] Formed from Contact Ion Pairs with a Methide Bridge

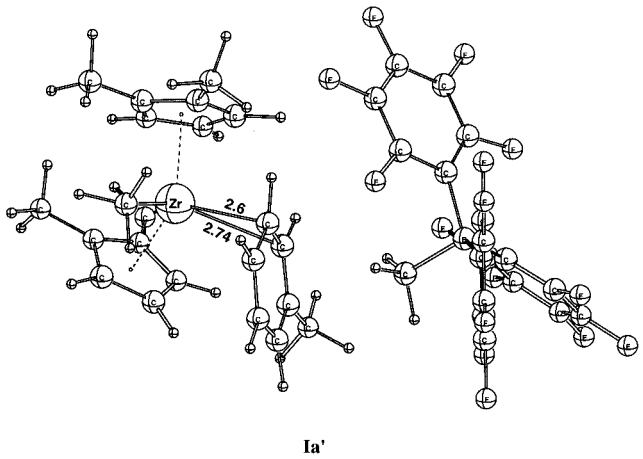
		ΔH_{ss}	
cocatalyst	solvent-sep ion pair	calcd	exptl[c]
$B(C_6F_5)_3$ (**1a**)	**Ia′**	18.7	24.2
$B(C_{10}F_7)_3$ (**1f**)	**If′**	18.9	
MAO (**2a**)	**IIa′**	32.4	
MBO (**2b**)	**IIb′**	25.3	
$AlMe_3$ (**2c**)	**IIc′**	35.3	
$Al(C_6F_5)_3$ (**2d**)	**IId′**	20.58	

[a] Corresponding to the process $(Cp_2M(Me)-(\mu\text{-}Me)-A)_{solv} + S \rightarrow ([Cp_2MMe]^+-S-[CH_3A]^-)_{solv} + \Delta H_{ips}$. [b] In units of kcal/mol. [c] Reference 4e.

and ΔH_{ips} = 26.7 kcal/mol (**3d**). They are, aside from Coulombic forces, held together by two weak Zr−F interactions. The Zr−F contact distances were found to be 2.56 Å, which is much longer than the regular Zr−F bond length of 2.14 Å. The low value for the ΔH_{ips} calculated would account for the high polymerization activity[6c] observed for ion pair systems with $B(C_6F_5)_4^-$ as counterion. The low ΔH_{ips} value of the anion **3d** suggested by Li et al.[6c] is presumably because of its large size. Williams et al.[6d] have recently developed similar borate anions. Substituting boron in **3a** with aluminum in **3b** increased the value of ΔH_{ips} by around 4 kcal/mol, primarily because the fluorines on **3b** are more negative and thus better able to coordinate to the electrophilic zirconium center. The anion $Al(C_6F_5)_4^-$ has not been synthesized. However, $Al(C_{12}F_9)_3F^-$ has been examined by Chen et al.[6g]

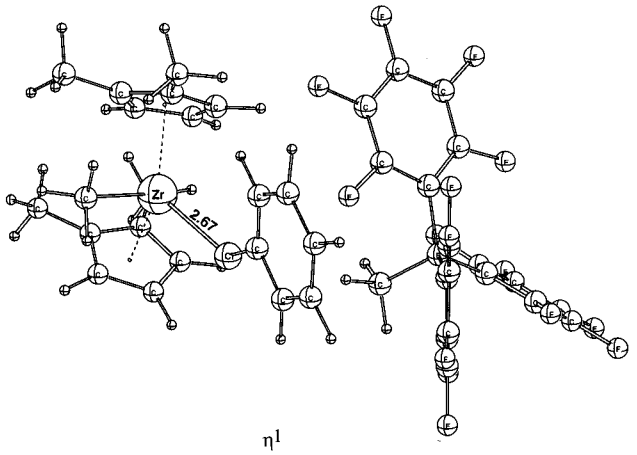
Carborane anions have been used successfully as A^- in $[CPh_3]^+[A^-]$ and $[PhNMe_2H]^+[A]^-$ type activators by Hlatky et al.[6a] We have carried out calculations on the contact ion pair[6a] (**IIIc**) formed between $[(C_2B_9H_{11})_2Co]^-$ (**3c**) and $(1,2\text{-}Me_2Cp)_2ZrMe^+$. It follows from Table 6 that the ion pair dissociation energy (ΔH_{ips} of eq 5) for **IIIc** is the highest among the contact ion pairs without a methide bridge. We attribute this to a strong Zr−H interaction with a contact distance of 2.0 Å. It is possible that the introduction of perhalogenated carboranes[6e,f] would reduce ΔH_{ips}. Structural data for all the contact ion pairs without a methyl bridge are given as Supporting Information.

c. Influence of Solvent on Ion Pair Separation. (i) Implicit Effect. The bulk influence of the solvent on the energy of complete dissociation (ΔH_{ips}) has been studied for a number of contact ion pairs, as shown in Table 7. The dissociation energies (ΔH_{ips}) were evaluated for three different solvents of increasing polarity—toluene (ϵ = 2.379), chlorobenzene (ϵ = 5.71), and 1,2-dichlorobenzene (ϵ = 9.93)—and compared to the ΔH_{ips} values determined for the gas phase. Solvent effects were included within the continuum approximation by employing the conductor-like screening model (COSMO) due to Klamt,[17a] as implemented in the ADF program.[17b] It follows from Table 7 that ΔH_{ips} is reduced by 50% in going from the gas phase to the nonpolar toluene solvent and another 50% in going from toluene to the polar 1,2-dichlorobenzene solvent. The dependence of solvation energies[17a,b] on the dielectric constant ϵ suggests that adding solvents more polar than 1,2-dichlorobenzene will reduce ΔH_{ips} only marginally. Siedle et al.[5a] found that using dichloromethane (ϵ = 9.08) allowed them to activate Cp_2ZrMe_2 by MAO, whereas MAO had failed as a cocatalyst (activator) in toluene (ϵ = 2.379).



Ia'

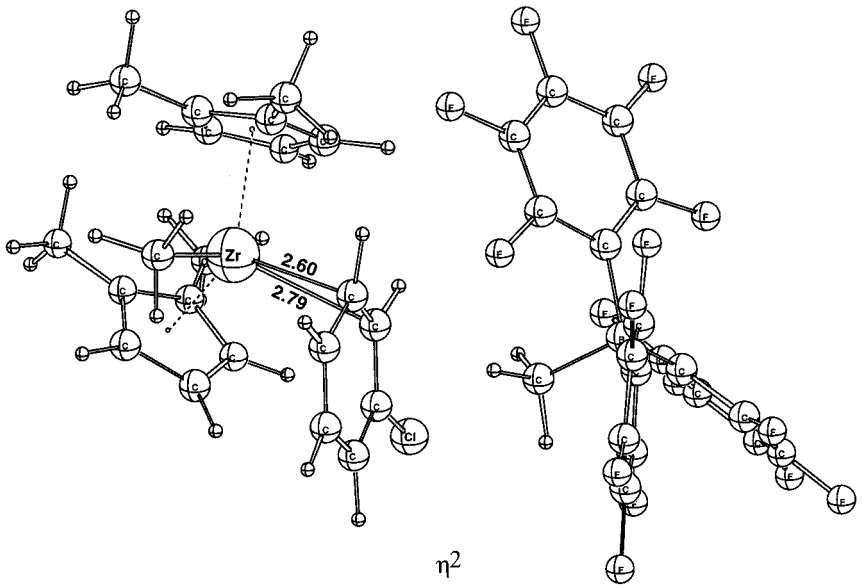
Figure 5. LDA optimized structure of the solvent-separated ion pair formed by the $[(1,2\text{-}Me_2Cp)_2ZrMe]^+$-$[B(C_6F_5)_3Me]^-$ system in toluene.



1a''(i)

Figure 6. LDA optimized structure of the solvent-separated ion pair formed by the $[(1,2\text{-}Me_2Cp)_2ZrMe]^+$-$[B(C_6F_5)_3Me]^-$ system in chlorobenzene, with the solvent coordinating through the chlorine.

(ii) Explicit Solvent Effect. Deck et al.[4b] employed NMR to detect a process in which the methide group in **Ia** is completely dissociated from the zirconium metal center. The process was determined to have a dissociation energy of 24.2 kcal/mol in toluene. Our much higher calculated ΔH_{ips} value of 38.0 kcal/mol (in toluene) would indicate that the process observed by Deck et al.[4b] is different from a complete ion pair dissociation (eq 2).



Ia'' (ii)

Figure 7. LDA optimized structure of the solvent-separated ion pair formed by the $[(1,2\text{-}Me_2Cp)_2ZrMe]^+[B(C_6F_5)_3Me]^-$ system in chlorobenzene, with the solvent coordinating through two carbons of the benzene ring.

An alternative process accounting for the dissociation of the zirconium−methide bond involves the formation of the solvent-separated ion pair (eq 3), in which a solvent molecule (S) is sandwiched between two counterions. There is experimental[9] and theoretical[7a] evidence to support such an explicit role of a single solvent molecule. Thus, Eisch et al.[9] were able to use NMR to demonstrate the formation of $[Cp_2TiMe]^+-S-[AlCl_4]^-$ when $Cp_2TiMeCl-AlCl_3$ was added to arene solvents. In this section we shall study the possible explicit role of a single solvent molecule in the dissociation of (contact) ion pairs. Our investigation will include ion pairs with (**Ia**,**f** and **IIa**−**d**) and without (**IIIa**−**d**) a methide bridge.

The energies (ΔH_{ss}) required to convert the methide bridge species **Ia**−**f** and **IIa**−**d** into solvent-separated ion pairs are given in Table 8. The optimized structure for the species **Ia′** related to **Ia** is displayed in Figure 5. We find in general that the formation of a solvent-separated ion pair (ΔH_{ss}) for this class of species is more facile than the full ion pair separation process (ΔH_{ips}) by 15−20 kcal/mol. For the dissociation of the zirconium−methide bridge in **Ia** to form **Ia′,** we find a value (Table 8) of $\Delta H_{ss} = 18.7$ kcal/mol, which compares reasonably well with the zirconium−methide dissociation energy of 24.2 kcal/mol observed by Deck et al.[4b]

The contact ion pairs without a methide bridge (**IIIa**−**d**) are also seen to prefer separation by a single solvent molecule (ΔH_{ss}) to complete dissociation of the counterions (ΔH_{ips}; Table 9). Interestingly, for the borates $[B(C_6F_5)_4]^-$ and $[^tBuCH_2CH(BC_6F_5)_2H]^-$ the formation of **IIIa′** and **IIId′**, respectively, is exothermic. Thus, the borate-based species **IIIa**−**d** can be expected to exhibit the highest degree of separation among all the investigated contact ion pairs. The value of ΔH_{ss} is close to zero (0.8 kcal/mol) for $[P'-Al(C_6F_5)_4^-]$ and 7.5 kcal/mol for the carborane $[(C_2B_9H_{11})_2Co]^-$. Thus, **IIIb** and **IIIc** can be expected to exhibit a high degree of separation as well.

Table 9. Enthalpy of Formation of Solvent-Separated Ion Pairs (ΔH_{ss})[a,b] Formed from Contact Ion Pairs without a Methide Bridge

counterion	solvent-sep ion pair	calcd ΔH_{ss}
$B(C_6F_5)_4^-$ (**3a**)	**IIIa′**	−4.2
$Al(C_6F_5)_4^-$ (**3b**)	**IIIb′**	0.76
$[(C_2B_9H_{11})_2Co]^-$ (**3c**)	**IIIc′**	7.5
$\{^tBuCH_2CH[B(C_6F_5)_2]_2H\}^-$ (**3d**)	**IIId′**	−0.58

[a] Corresponding to the process $([Cp_2M(Me)]^+[AMe]^-)_{solv} + S \rightarrow ([Cp_2MMe]^+-S-[MeA]^-)_{solv} + \Delta H_{ips}$. [b] In units of kcal/mol.

Table 10. Enthalpy of Formation of Solvent-Separated Ion Pairs (ΔH_{ss})[a] for Ion-Pair Ia in Three Different Solvents

solvent	solvent-sep ion pair	ΔH_{ss} calcd	ΔH_{ss} exptl[b]
$C_6H_5CH_3$	**Ia′**	18.7	24.2
η^1-C_6D_5Cl[c]	**Ia″(i)**	15.1	11.0
η^2-C_6D_5Cl[d]	**Ia″(ii)**	15.4	11.0
η^1-1,2-$C_6D_4Cl_2$[c]	**Ia‴(i)**	15.9	12.0
η^2-1,2-$C_6D_4Cl_2$[d]	**Ia‴(ii)**	13.8	12.0

[a] In kcal/mol. [b] Reference 4e. [c] Coordination through one chlorine. [d] Coordination through two carbons.

(iii) Coordination of Solvent in Arene-Separated Ion Pairs. Deck et al.[4b] have measured the enthalpy of activation for the dissociation of the zirconium−methide bond in **Ia** for three different solvents—toluene, chlorobenzene, and 1,2-dichlorobenzene. We have optimized the corresponding solvent-separated ion pair geometries for **Ia** and calculated the related separation enthalpies ΔH_{ss}. In the case of toluene the solvent binds to the zirconium through η^2 coordination of two carbons in the arene ring. For chlorobenzene and 1,2-dichlorobenzene there are two possibilities—the solvent can coordinate to zirconium in an η^2 fashion as in toluene or it can coordinate through the chlorine(s). Both of these possibilities were investigated for these two solvents. The results are summarized in Table 10. The optimized η^1 and η^2 structures for the solvent-separated

ion pairs with chlorobenzene (**IIIa″(i)** and **IIIa″(ii)**) are shown in Figure 6 and Figure 7, respectively. For chlorobenzene it was found that the solvent preferred to coordinate through the chlorine (η^1 coordination). However, the η^2-coordinated conformer was only slightly less stable. The energy required to form the solvent-separated ion pair for the η^1 case was 15.1 kcal/mol, while the corresponding energy required to form the η^2 conformation was 15.4 kcal/mol. Thus, it is to be expected that the two conformers could exist in equilibrium with each other. For 1,2-dichlorobenzene, however, the η^2-coordinated ion pair structure was found to be more stable than the η^1 conformation by 2.1 kcal/mol. The η^1 coordination is less favorable for 1,2 -dichlorobenzene (−0.20). The Zr−Cl bond distance is also greater (2.69 Å) for 1,2-dichlorobenzene than for chlorobenzene (2.67 Å).

IV. Conclusions

A DFT-based study has been carried out on the reaction between the olefin polymerization precatalyst (1,2-Me$_2$Cp)$_2$ZrMe$_2$ (P) and a number of Lewis acids (A) to form the methide-bridged (contact) ion pair (1,2-Me$_2$Cp)$_2$ZrMe−(μ-Me)−A (**I**; eq 1). The acids include the boranes B(C$_6$F$_5$)$_3$ (**1a**), B(C$_6$F$_5$)$_2$(C$_6$H$_3$F$_2$) (**1b**), B(C$_6$F$_5$)$_2$(C$_6$H$_5$) (**1c**), B(C$_6$F$_5$)$_2$(C$_6$H$_3$(CH$_3$)$_2$ (**1d**), B(C$_6$H$_5$)$_3$ (**1e**), and B(C$_{10}$F$_7$)$_3$ (**1f**), as well as (MeAlO)$_6$ (**2a**), (MeBO)$_6$ (**2b**), AlMe$_3$ (**2c**), and Al(C$_6$F$_5$)$_3$ (**2d**). The charge separation between the (1,2-Me$_2$Cp)$_2$ZrMe$^+$ and MeA$^-$ fragments in **I** was calculated for all A, and it was found that the charge separation as well as $-\Delta H_{ipf}$ (negative of the formation enthalpy) increases through the series **1e, 1c, 1b**, and **1a** with the number of fluorine atoms. A good activating Lewis acid (A) has the equilibrium shifted strongly from P and A toward **I**, and this is the case for all A except **1e** and **2c**.

Also considered was the complete dissociation in solution (toluene) of **I** into the counterions [(1,2-Me$_2$Cp)$_2$ZrMe]$^+$ and [AMe]$^-$ with the dissociation enthalpy ΔH_{ips} as well as the formation from **I** of the solvent-separated ion pair (S = toluene) [(1,2-Me$_2$Cp)$_2$ZrMe]$^+$−S−[AMe]$^-$ with the reaction enthalpy ΔH_{ss}. The two types of separation processes have both been postulated as the second and final step in the activation of P. It is concluded that the formation of [(1,2-Me$_2$Cp)$_2$ZrMe]$^+$−S−[AMe]$^-$ is the more likely separation process. Consideration has also been given to the influence of solvent polarity on the separation processes with S = toluene, chlorobenzene, and 1,2-dichlorobenzene.

Finally discussed are ΔH_{ips} and ΔH_{ss} for the ion pair (1,2-Me$_2$Cp)$_2$ZrMe$^+$[A]$^-$ (**III**) with A$^-$ = B(C$_6$F$_5$)$_4^-$ (**3a**), Al(C$_6$F$_5$)$_4^-$ (**3b**), [C$_2$B$_9$H$_{11}$)$_2$Co]$^-$(**3c**), and {^{t}BuCH$_2$CH-[B(C$_6$F$_5$)$_2$H}$^-$ (**3d**), where **III** is formed from the reaction of P with the activator [C(C$_6$H$_5$)$_3^+$][A$^-$]. It is found that **III** type ion pairs are easier to dissociate than **I** held together by a methide bridge.

Under catalytic polymerization conditions, olefin might take the place of S in the solvent-separated ion pairs as the first step in the polymerization process.[7a] Initial studies by Chan et al.[8d] indicate that the substitution of S by olefin is exothermic by 10−13 kcal/mol in group 4 metallocenes, where the steric bulk of the Cp rings only allows for a weak η^2 coordination of the arene solvent to the metal center. We shall in a subsequent study[19] discuss how the contact ion pairs with and without a methide bridge are converted into an active polymerization catalyst in the presence of olefin.

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Supporting Information Available: The optimized geometries of the structures reported (Cartesian coordinates, in Å). This material is available free of charge via the Internet at http://pubs.acs.org.

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