Organometallics **2004,** *23,* 3847−3852 3847

C_6F_5-Group Transfer from $[MeB(C_6F_5)_3]^-$ to the Metal Center of L_2MMe^+ (M = Ti, Zr) as a Deactivation Pathway in Olefin Polymerization Catalysis: A Combined Density Functional Theory and Molecular Mechanics Investigation

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Received March 28, 2004

We have carried out a combined density functional theory and molecular mechanics study of aryl group transfer reactions from $[MeB(C_6F_5)_3]^-$ to the metal center of L_2MMe^+ (M = Ti, Zr). This reaction, which produces $L_2MMe(C_6F_5)$ and $MeB(C_6F_5)_2$, is a possible deactivation pathway in metal-catalyzed single-site olefin polymerization. The cationic catalyst systems L_2MMe^+ include $(NPR_3)_2MMe^+$, $(Cp)(NPR_3)MMe^+$, $(Cp)(NCR_2)MMe^+$, $(Cp)(SiMe_2NR)MMe^+$, and $(Cp)(OSiR_3)MMe^+$. With M = Ti and Zr, the results show that aryl group transfer is more facile for zirconium catalysts than for the corresponding titanium systems. Furthermore, electron-donating ligands and sterically demanding substituents play a crucial role in preventing the aryl transfer reaction. The aryl group transfer is likely to take place for $(Cp)(NCR_2)MMe^+$ with both titanium- and zirconium-ketimide complexes at about 100 °C. However, the decomposition temperature is raised to 250 °C for the corresponding $(Cp^*)(NCR_2)TiMe^+$ system.

Introduction

The development of new catalysts that do not exclusively contain the bis(cyclopentadienyl) (bis-Cp) ancillary ligands has recently been the subject of a great deal of interest.[1] A variety of strategies have been employed to explore the potential of other ligand systems. The most common way of developing such catalyst systems has been to replace one or both of the Cp ligands in the metallocenes by other donor groups. A notable example of this approach is the so-callled "constrained-geometry catalysts" first introduced by Bercaw[2] and later developed at Dow[3] and Exxon,[4] by combining Cp ligands with an amide functionality. More recently, a number of $Cp(L)TiX_2$ systems (L = OR,[5] NCR_2,[6] NR_2,[7] NPR_3,[8] SR,[9] and alkyl[10]) have been prepared and tested in olefin polymerization catalysis. Stephan et al. have also developed several families of highly active Ti-containing olefin polymerization catalysts with bis(phosphinimides) as ancillary ligands.[11] A wide range of Ti and Zr complexes containing amido,[12] diamido,[13] amidinates,[14] imidinophosphonamides,[15] pyridine-alkoxides,[16] aryloxides,[17] borolide,[18] boratabenzene,[19] pendant cyclopen-

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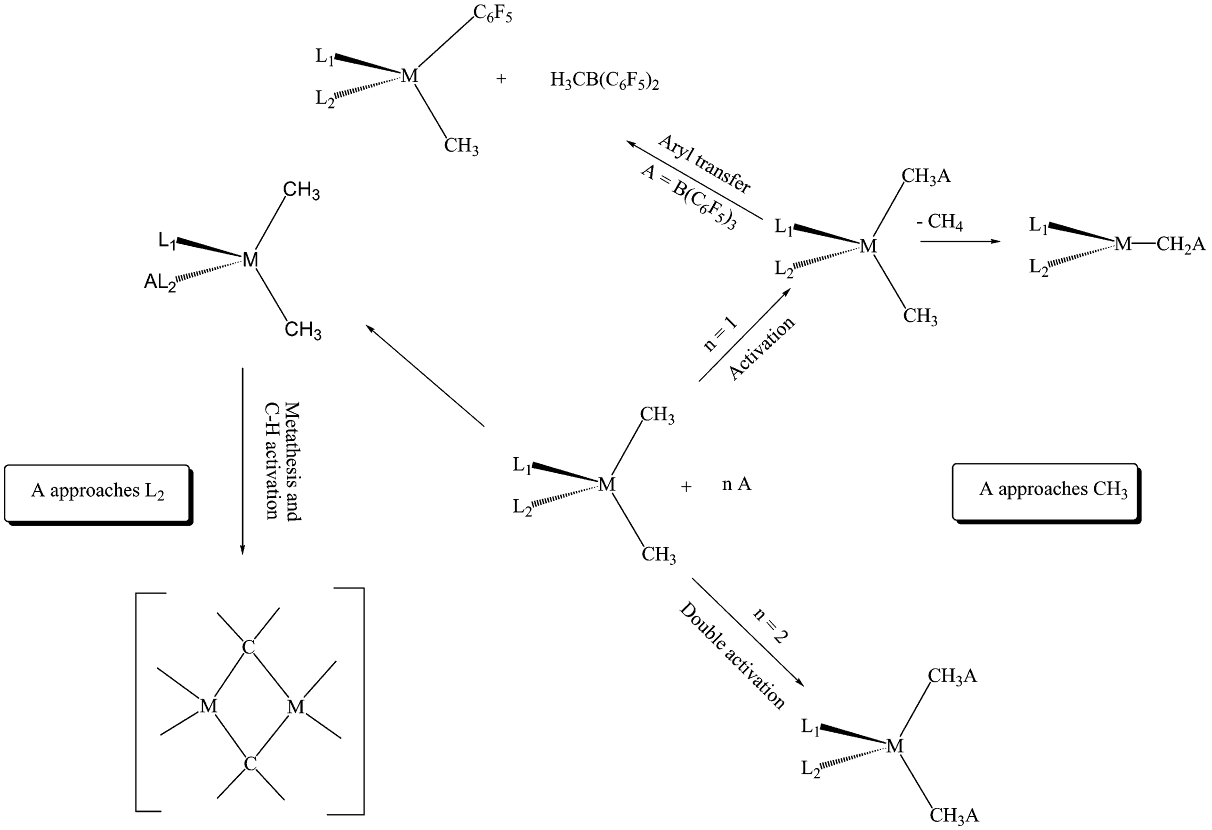
10.1021/om0497792 CCC: $27.50
Publication on Web 07/09/2004

Scheme 1. Possible Ion Pair Deactivation Pathways



tadienyl borane ligands,[20] trimethylene,[19] cyclopentadienylborate,[21] diketimine,[22] tropidinyl,[23] tridentate,[24] and macrocyclic ligands[25] have also been shown to exhibit appreciable catalytic activities. In general, in conjunction with activators such as methylaluminoxane (MAO), $B(C_6F_5)_3$, and $[A]^+[B(C_6F_5)_4]^-$ ($A = CPh_3$, HNR_3), the aforementioned complexes have been found to provide catalysts with moderate to high activity, making them viable alternatives to the metallocene systems.

However, these catalyst systems have also been found to undergo deactivating side reactions, leading to the eventual poisoning of the catalyst, thereby decreasing their productivity. An understanding of the deactivation mechanisms along with modifications that could prevent their occurrence would aid greatly in improving the design and development of nonmetallocene catalyst systems.

As shown in Scheme 1, a number of deactivation pathways have been observed for the catalyst systems involved in borane and trimethylaluminum activations. The most commonly observed deactivation pathway is C_6F_5 group transfer to the cationic metal center. We have recently reported another commonly observed deactivation pathway that involves hydrogen transfer from the bridging methyl group to the growing chain.[26] In this paper we report aryl group transfer from the counterion $[MeB(C_6F_5)_3]^-$ to the cationic metal, as shown in Scheme 1. To our knowledge, this is the first theoretical investigation of aryl group transfer from the counterion to the cationic metal for the catalyst systems depicted in Scheme 2. Similar C_6F_5 group transfer reactions have been previously observed experimentally.[27-29]

Computational Details and Methods

Density functional theory calculations were carried out using the Amsterdam Density Functional (ADF) program system, developed by Baerends et al.[30] and vectorized by Ravenek.[31] The numerical integration scheme applied was developed by te Velde et al.,[32] and the geometry optimization procedure was based on the method of Verslius and Ziegler.[33]

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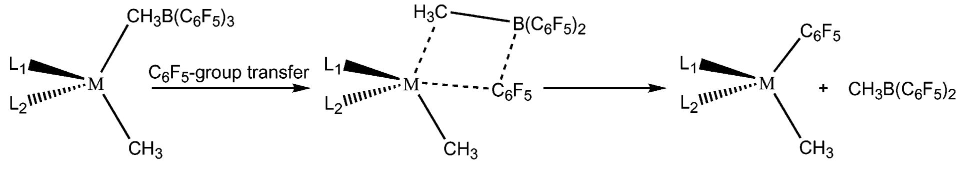
Scheme 2. Aryl Group Transfer Reaction



L_1, L_2 = Cp, Cp*, NCR_2, $CpSi(Me)_2NR$, NPR_3, $OSiR_3$

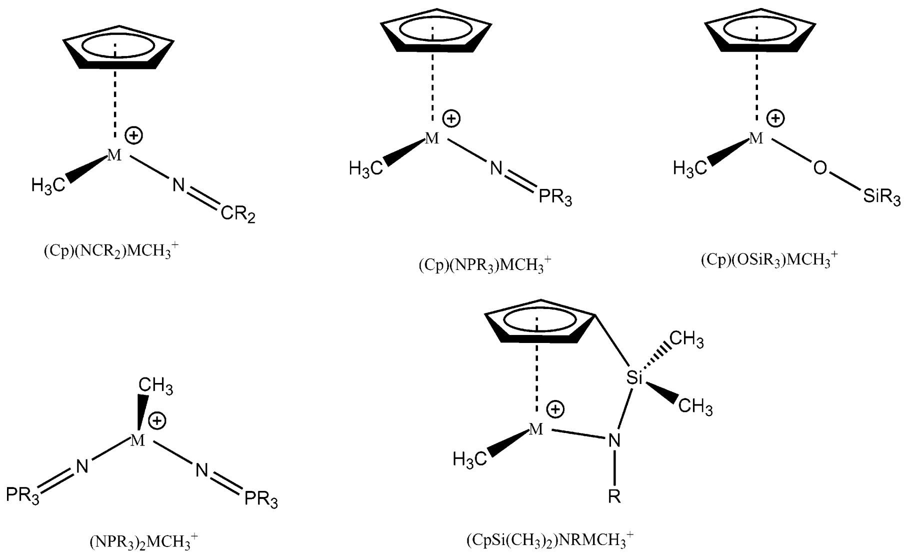


Figure 1. Structures of the catalyst systems under investigation.

Slater-type double-ς plus polarization basis sets were employed for H, B, C, N, O, F, Si, P, and Cl atoms, while triple-ς plus polarization basis sets were used for Ti and Zr atoms. All the calculations used the PW91 exchange−correlation functional.[34]

Combined quantum-mechanical (QM) and molecular-mechanical (MM) models (QM/MM) have been applied through out this study. In this model, the two perfluoro phenyl groups $(C_6F_5)_2$ in the counterion, $[MeB(C_6F_5)_3]^-$, were replaced by MM atoms and Cl atoms were used to cap the QM system, while the remaining C_6F_5 group was treated with full QM. QM/MM atoms were also used to model the tertiary butyl groups, with hydrogens used as capping atoms. The MM atoms were described using the SYBYL/TRIPOS 5.2 force field constants.[35] The code for QM/MM in ADF has been implemented by Woo et al.[36] The QM/MM model for $[MeB(C_6F_5)_3]^-$ has been validated in a previous study.[37]

Results and Discussion

In this paper, which is the first theoretical investigation of C_6F_5 group transfer from the counterion to the metal, we shall demonstrate how electronic and steric effects of the ancillary ligands can modulate the activation barrier. The role of the cationic metal in controlling the activation barrier will also be discussed.

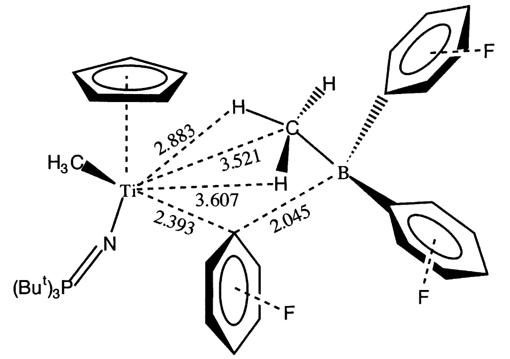


Figure 2. Optimized transition state geometries (Å) of the titanium-phosphinimide catalyst system.

The transition state structures were optimized for all of the complexes considered under this investigation. During the transition state search, as shown in Scheme 2, the B−C(C_6F_5) bond from the counterion $[MeB(C_6F_5)_3]^-$ was broken and an M−C(C_6F_5) bond was partially formed. Late transition states were predicted for most of the complexes. The optimized transition state structure of the Ti-phosphinimide system is presented in Figure 2 as a representative example.

The structures of the cationic catalyst systems considered in this study are given in Figure 1. Table 1 depicts C_6F_5 group activation barriers for the ketimide and phosphinimide generic systems in which all the tertiary butyl groups are replaced with hydrogens. As shown in Table 1, the activation barriers fall in the

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Table 1. Activation Energies (kcal/mol) for Aryl Group Transfer

catalyst	activation energy	
	M = Ti	M = Zr
(Cp)NPH_3MMe-μ-$MeB(C_6F_5)_3$	16.6	10.5
(Cp)(NCH_2)MMe-μ-$MeB(C_6F_5)_3$	12.4	2.5

Table 2. Activation Energies (kcal/mol) for Aryl Group Transfer (R = *tert*-butyl)

catalyst	activation energy	
	M = Ti	M = Zr
(Cp)NPR_3MMe-μ-$MeB(C_6F_5)_3$	21.0	10.8
(Cp)(NCR_2)MMe-μ-$MeB(C_6F_5)_3$	17.2 (13.3)[a]	7.7
(Cp*)(NCR_2)MMe-μ-$MeB(C_6F_5)_3$	29.2	17.1
($CpSiMe_2NR$)MMe-μ-$MeB(C_6F_5)_3$	17.7 (13.9)[a]	5.9
$(NPR_3)_2MMe$-μ-$MeB(C_6F_5)_3$	22.1 (10.3)[a]	10.6
(Cp)($OSiR_3$)MMe-μ-$MeB(C_6F_5)_3$	18.3	8.6

[a] First ethylene insertion barriers.

range 2.5−16.6 kcal/mol. The ketimide systems deactivate much faster than the phosphinimide catalysts. This is presumably due to the different electron donor abilities of the ketimide and the phosphinimide systems. It is also evident from the table that the Zr systems are more facile than the Ti analogues. The cause of this marked difference may be related to the significantly larger ionic radius of Zr, which facilitates C_6F_5 group transfer. It is therefore important to consider the nature of the ancillary ligands and the size of the cationic metal center in the development and design of single-site olefin polymerization catalysts. For example, the aryl transfer barrier can be increased from 2.5 to 16.6 kcal/mol by replacing the NCH_2 ligand framework with NPH_3 and the cationic metal Zr with Ti. Replacing the ancillary ligand NCH_2 with NPH_3 increases the transfer barrier by 8 and 4.2 kcal/mol for the Zr and Ti systems, respectively. However, replacing the metal Zr with Ti increases the barrier by 9.9 and 6.1 kcal/mol for ketimide and phosphinimide catalyts, respectively. Thus, the nature of the ancillary ligands and the size of the central metal play a crucial role in controlling the activation barrier.

Table 2 presents activation energies for all the catalyst systems considered in this study. In these systems, the hydrogen atoms are replaced with *tert*-butyl groups to investigate the influence of steric effects on the ancillary ligands. In general, these catalyst systems have higher activation barriers than the sterically open systems shown in Table 1. The Ti complexes are kinetically more stable than the corresponding Zr systems, again suggesting the role of Zr in promoting aryl group transfer. For M = Ti, steric factors play a significant role in determining the activation barrier for aryl transfer. The steric bulk of bis(phosphinimide) and phosphinimide complexes is considerably larger than the ketimide and constrained-geometry catalysts. This is reflected by the higher barriers reported for bis(phosphinimide) (22.1 kcal/mol) and phosphinimide (21.0 kcal/mol) catalysts. Therefore, aryl group transfer can be reduced if we employ sterically demanding substituents about the metal center. For systems occupying similar volumes about the metal center, electronic effects modulate the activation barrier for aryl group transfer. For example, the aryl group transfer barrier difference between Ti-based siloxy (18.3 kcal/mol) and phosphinimide (21.0 kcal/mol) complexes is believed to be due to the different electron-donating abilities of these ligands. Thus, for systems with similar steric properties, electron-donating substituents favor a higher activation barrier. We found the same trend for hydrogen transfer reactions.

For comparison, Table 2 also shows the first ethylene insertion barriers for the $(NPR_3)_2TiMe$-μ-$MeB(C_6F_5)_3$, (Cp)(NCR_2)TiMe-μ-$MeB(C_6F_5)_3$, and ($CpSiR_2NR'$)TiMe-μ-$MeB(C_6F_5)_3$ systems from our previous study. The C_6F_5 transfer barriers are about 4−12 kcal/mol higher than the first ethylene insertion barriers. Therefore, the above Ti-based catalysts are potential candidates for single-site olefin polymerization catalysis.

Stephan et al. have investigated deactivation pathways involving zirconium-phosphinimide complexes.[38] They synthesized and characterized zirconium-phosphinimide complexes of the form $Cp'Zr(NPR_3)X_2$ (Cp′ = Cp, Cp*; X = halide, alkyl, or aryl) and found poor catalytic activity for ethylene polymerization compared to the corresponding Ti complexes. The poor activity of Zr prompted the authors to further investigate the reaction of complexes of the form $Cp'Zr(NPR_3)Me_2$ (Cp′ = Cp, Cp*) with $B(C_6F_5)_3$. Under mild conditions, this reaction was shown to give the species $Cp'Zr(NPR_3)(C_6F_5)_2$, and this reactivity provides a highly efficient pathway for the destruction of the catalyst activity.

Piers et al. have recently reported a family of base-free dialkyl organoscandium complexes supported by bulky β-diketiminato ligands incorporating 2,6-diisopropylphenyl groups on nitrogen and either Me (L^1) or ^{t}Bu (L^2) substituents in the 2,4 positions of the ligand backbone.[39] The reaction of complexes of the form L^2ScMe_2 with $B(C_6F_5)_3$ gave the expected complex $[L^2ScMe]^+[MeB(C_6F_5)_3]^-$. Similarly, reaction of complexes of the form L^1ScMe_2 with 1 equiv of $B(C_6F_5)_3$ showed the formation of the expected zwitterion at 240 K. However, upon warming to 270 K, they observed rapid C_6F_5 transfer from the counterion to the metal center, along with the productions of $L^1Sc(Me)C_6F_5$ and $MeB(C_6F_5)_2$. Piers et al. did not observe C_6F_5 transfer for $[L^2ScMe]^+[MeB(C_6F_5)3]^-$. The authors underlined that the lower steric impact of L^1 versus L^2 reduces the barrier for aryl transfer, consistent with our observation.

Marks and co-workers investigated the thermal stability of $[L_2ZrMe]^+[MeB(C_6F_5)3]^-$ complexes.[40] For example, the moderately stable complex $[(TMS_2CP)_2ZrMe]^+[MeB(C_6F_5)3]^-$ slowly decomposes to $(TMS_2CP)_2Zr(Me)C_6F_5$ and $MeB(C_6F_5)_2$. According to their findings, the thermal stability is sensitive to the type of the ancillary ligands.

We have also examined the thermodynamic stability of ketimide and phosphinimide catalyst systems. The optimized geometries are given in Figure 3 for both titanium and zirconium systems. The enthalpies of aryl group transfer reactions are −4.3, −7.0, −9.0, and −10.4 kcal/mol for (Cp)(NCR_2)TiMe-μ-$MeB(C_6F_5)_3$, (Cp)(NCR_2)ZrMe-μ-$MeB(C_6F_5)_3$, (Cp)(NPR_3)TiMe-μ-$MeB(C_6F_5)_3$, and (Cp)(NPR_3)ZrMe-μ-$MeB(C_6F_5)_3$, respectively. Therefore,

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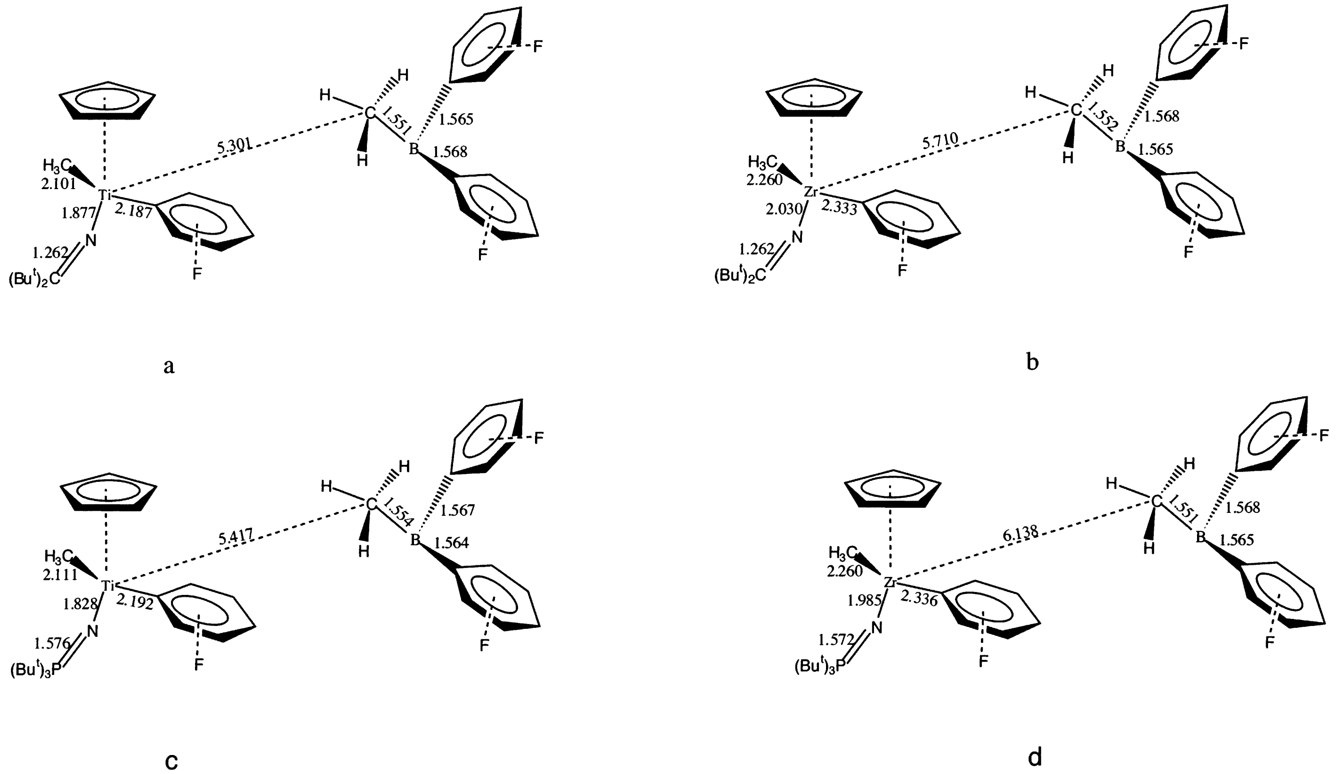

Figure 3. Optimized geometries (Å) of titanium-ketimide (a), zirconium-ketimide (b), titanium-phosphinimide (c), and zirconium-phophinimide (d) complexes formed from the decomposition of the corresponding ion pair.

the aryl group transfer reactions are exothermic, and the thermodynamic stability is dependent on the type of the ancillary ligand and the size of the central metal. The transfer reactions for the Zr-based systems are more exothermic than for the Ti analogues. As discussed above, the larger size of Zr atom facilitates the aryl group transfer reaction.

Furthermore, we investigated the kinetic stabilities of C_5Me_5- and C_5H_5-ligated ketimide systems. The Zr-based C_5Me_5-ligated catalyst systems have a lower barrier than the corresponding Ti complexes, consistent with our observation for C_5H_5-ligated systems. Again, this reflects the role of the larger ionic radius of the metal in facilitating the aryl group transfer. The introduction of methyl groups on the cyclopentadienyl ligand framework increases the activation barrier by 10 and 11 kcal/mol for Zr- and Ti-based ketimide catalyst systems, respectively. It is thus possible that this deactivation pathway can be eliminated entirely if we introduce bulky substituents such as *tert*-butyl groups on the Cp ring.

Industrial-scale olefin polymerization processes are usually performed at high temperatures with a minimum pressure of 5 bar. In gas-phase processes, the temperatures are kept in the range from 80 to 100 °C, whereas the solution processes require temperatures above 100 °C. The kinetics and deactivation of single-site olefin polymerization catalysts at higher temperatures and pressure are therefore of great interest for industrial-scale applications.

It is reasonable to assume that the catalyst systems considered in this study deactivate at a certain temperature T_x. We refer to T_x as the crossover temperature. At this temperature, the observed rate constant for the second ethylene insertion step is equal to the rate constant for the decomposition process. Details on the derivation of T_x from the transition state theory have been presented elsewhere and will not be discussed here.[26]

Table 3. Crossover Temperatures (K) for Aryl Group Transfer

catalyst	crossover temperatures M = Ti	 M = Zr[a]
(Cp)NPR$_3$MMe-μ-MeB(C_6F_5)$_3$	297	
(Cp)(NCR$_2$)MMe-μ-MeB(C_6F_5)$_3$	188	
(Cp*)(NCR$_2$)MMe-μ-MeB(C_6F_5)$_3$	561	165
(CpSiMe$_2$NR)MMe-μ-MeB(C_6F_5)$_3$	172	
(NPR$_3$)$_2$MMe-μ-MeB(C_6F_5)$_3$	333	
(Cp)(OSiR$_3$)MMe-μ-MeB(C_6F_5)$_3$	208	

[a] Most zirconium systems have lower barriers of decomposition. Thus, they will decompose at any temperature.

The crossover temperatures for the titanium-based catalyst systems are given in Table 3. The crossover temperatures range from 172 to 561 K. The highest crossover temperature was estimated for ketimide systems involving methyl substituents on the Cp ring. The crossover temperature can provide us qualitative pictures as to which of the catalyst systems considered in this study would survive at higher temperatures. As shown from Table 3, all the C_5H_5-ligated catalysts decompose at 100 °C. However, the ketimide catalyst systems involving methyl substituents on the Cp ligand do not decompose between 100 and 250 °C, reflecting the stability of these catalysts at higher temperatures. We are unable to estimate the crossover temperature for the C_5H_5-ligated zirconium systems, because the decomposition activation barriers (5.9−10.6 kcal/mol) are lower than the second ethylene insertion barrier (12.0 kcal/mol). That is, the propagation process in general must have a lower barrier than the decomposi-

Table 4. Total Bond Order around Ti and Aryl Transfer Activation Energies (kcal/mol) for Different Catalyst Systems

	total bond order around Ti			
catalyst	ion pair	transition state	thermodynamic product	activation energy
$(Cp)NPR_3MMe$-μ-$MeB(C_6F_5)_3$	4.23	4.26	4.33	21.0
$(Cp)(NCR_2)MMe$-μ-$MeB(C_6F_5)_3$	4.05	4.08	4.14	17.2
$(CpSiMe_2NR)MMe$-μ-$MeB(C_6F_5)_3$	4.15	4.20	*a*	17.7
$(NPR_3)_2MMe$-μ-$MeB(C_6F_5)_3$	4.46	4.51	*a*	22.1
$(Cp)(OSiR_3)MMe$-μ-$MeB(C_6F_5)_3$	4.19	4.24	*a*	18.3

[a] Not investigated.

tion process ($\Delta H^{\ddagger}_{p} < \Delta H^{\ddagger}_{d}$) for the catalyst to be active at any temperature range. However, this is not the case for aryl group transfer reactions. The C_5M_5-ligated zirconium-ketimide complex has a crossover temperature of 165 K; thus, it would not survive at 100 °C.

A bond order analysis[41] was done to evaluate the total bonding around the titanium metal center in the ion pair complexes as well as in the transition states. Table 4 summarizes the results obtained, along with the corresponding activation energies for the different systems.

From the results obtained, a clear correlation is observed between the activation barriers and the total bonding around the titanium metal center. The bis(phosphinimide) system has the highest activation barrier, as well as the highest bond order around the titanium metal center, in both the ion pair complexes and in the transition states. The phosphinimide system is second highest in terms of both the activation energies and the bonding around the titanium. A reasonable correlation exists for the three systems—the ketimide, the siloxy, and the constrained-geometry catalyst—between the bonding around the metal center and the corresponding activation barriers.

The explanation for this correlation lies in the ion pair separation energies of the catalyst systems. As shown in our previous work,[37] the ion pair separation energies decrease in the order CGC > ketimide > siloxy > phosphinimide > bis(phosphinimide).

Therefore, the two NPR_3 groups in bis(phosphinimide) provide the greatest electron density to the metal center, as evidenced by the lowest ion pair separation energy and the highest bond order around Ti. The constrained-geometry catalyst and ketimide provide the least electron density to the metal center. For the aryl group transfer reaction to take place, the counterion has to lose a phenyl group to the accepting metal center. The electron-rich titanium center in bis(phosphinimide) has the lowest tendency to accept the incoming phenyl group. This is reflected by the highest activation energy reported for bis(phosphinimide). Ketimide and the constrained-geometry catalyst have the lowest bond order around Ti. Thus, the electron-deficient metal center in ketimide and the constrained-geometry catalyst has the highest tendency to accept the aryl group, hence the corresponding lower activation barriers observed for these systems.

Conclusions

In summary, we have presented a combined density functional theory and molecular mechanics study of C_6F_5 group transfer form the counterion $[MeB(C_6F_5)_3]^-$ to the cationic metal center of L_2MMe^+ (M = Ti, Zr). The results give insights into the development and design of new temperature-resistant single-site olefin polymerization catalysts.

The aryl group transfer reactions are more facile for Zr complexes than the corresponding Ti systems. Thus, the size of the central metal plays a role in modulating the aryl group transfer reaction. Furthermore, the aryl group transfer reaction can be prevented if we employ bulky substituents on the ancillary ligands. For example, the sterically open systems deactivate much faster than systems that involve sterically demanding substituensts. Also, the aryl group transfer reaction can be eliminated if we employ methyl substituents on the Cp ring. This is reflected by the highest crossover temperature estimated for C_5M_5-ligated Ti-ketimide complexes.

Acknowledgment. This work was supported by the Natural Science and Engineering Research Council of Canada (NSERC) and by NOVA Research and Technology Corporation (NRTC).

Supporting Information Available: Cartesian coordinates (Å) for all optimized (QM/MM) ion pair and transition state (TS) geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0497792

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