

## Amine Catalyzed Solvent C–H Bond Activation as Deactivation Route for Cationic Decamethylzirconocene Olefin Polymerization Catalysts

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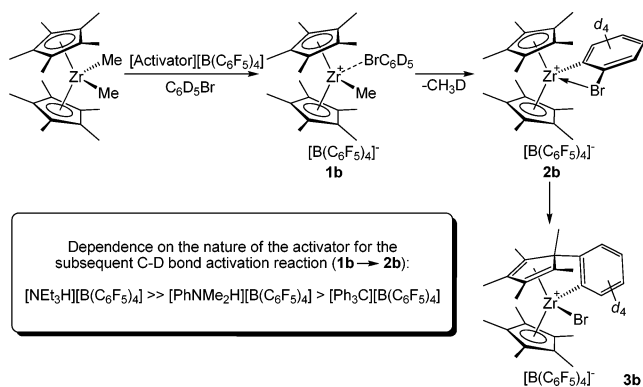
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The effectiveness of a catalyst is determined not only by its activity and selectivity but also by the lifetime of its active species.<sup>1</sup> It is therefore of key importance to get insight into catalyst deactivation processes for relevant catalytic transformations. For Lewis-acidic catalysts for olefin polymerization, C–H activation reactions are often involved in deactivation reactions.<sup>2,3</sup> Here we report that such deactivation reactions may be catalyzed by Brønsted basic coproducts of frequently used activators for olefin polymerization catalysts.

In 2004, Jordan and co-workers reported the C–D bond activation of *d*<sub>5</sub>-chlorobenzene by a cationic decamethylzirconocene compound as a new decomposition pathway for group 4 olefin polymerization catalysts.<sup>3</sup> In this particular solvent, ion-pair [Cp\*<sub>2</sub>ZrMe(ClC<sub>6</sub>D<sub>5</sub>-κCl)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**1a**) reacts via σ-bond metathesis, to give σ-aryl species [Cp\*<sub>2</sub>Zr(2-ClC<sub>6</sub>D<sub>4</sub>-κ<sup>2</sup>C,Cl)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**2a**), which subsequently degrades to [Cp\*(η<sup>4</sup>:η<sup>1</sup>-C<sub>5</sub>Me<sub>5</sub>C<sub>6</sub>D<sub>4</sub>)ZrCl][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**3a**). When we studied the same system in *d*<sub>5</sub>-bromobenzene solvent, we were not surprised to find a similar sequence, now involving the bromide analogues **1b–3b** (Scheme 1).<sup>4</sup> Nevertheless, we observed that the rate of formation of the σ-aryl compound (**2b**) depended strongly on the nature of the activator used to generate **1b** from Cp\*<sub>2</sub>ZrMe<sub>2</sub>.

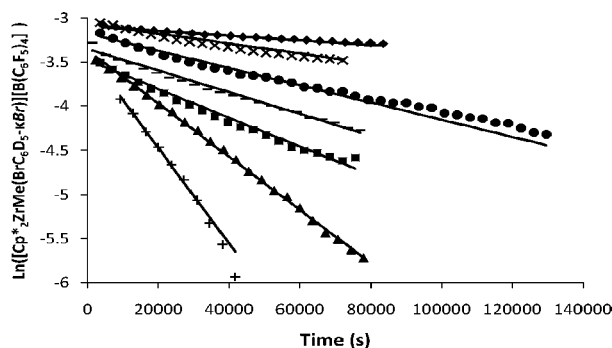
### Scheme 1



When the zirconocene methyl cation **1b** was generated in *d*<sub>5</sub>-bromobenzene solvent, by reaction of Cp\*<sub>2</sub>ZrMe<sub>2</sub> with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], slow conversion to complex **2b** was observed. When the Brønsted acid [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was used to generate **1b**, the formation of **2b** was faster than for trityl-generated **1b**, and in the case of [Et<sub>3</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as an activator, formation of **2b** was almost instantaneous. A Toepler pump experiment established that in this reaction 2 equiv of methane (identified by GC analysis) were formed per Zr.

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**Figure 1.** Ln(**1b**) versus time plot for the C–D bond activation reaction of *d*<sub>5</sub>-bromobenzene after activation of Cp\*<sub>2</sub>ZrMe<sub>2</sub> with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in the absence of *N,N*-dimethylaniline (♦) or in the presence of 1.1 (×), 2.6 (●), 3.6 (–), 5.1 (■), 10.6 (▲) and 21.1 (+) equivalents of *N,N*-dimethylaniline. Solid lines represent simulated data based on the kinetic model presented in eq 1.

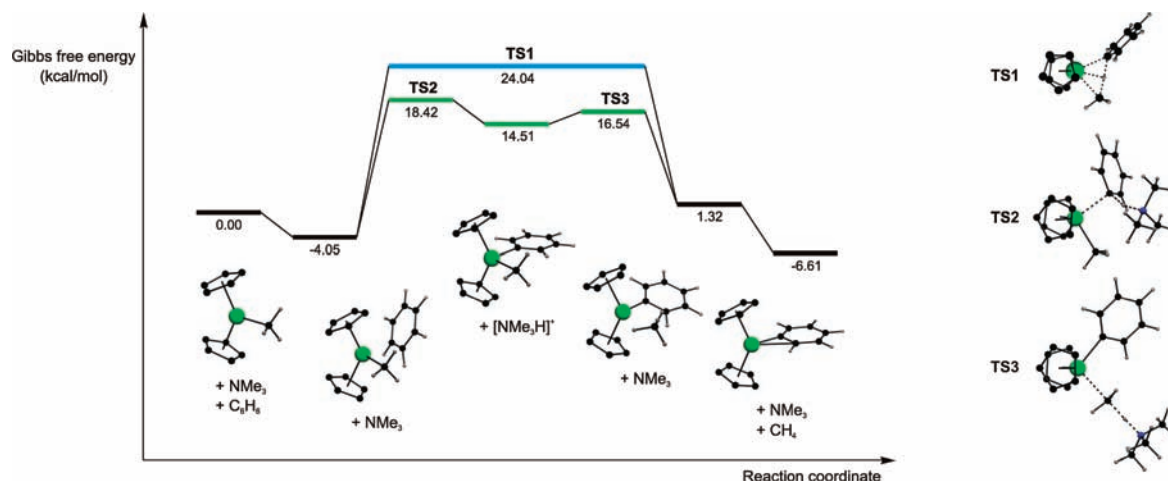
These results suggest that the solvent C–D bond activation reaction is catalyzed by the tertiary amine liberated in the generation of **1b** by ammonium salts. This was corroborated by the observation that formation of **2b** from **1b** generated by the trityl reagent can be accelerated by the presence of added PhNMe<sub>2</sub> or NEt<sub>3</sub>. Amine assisted C–H bond activation processes have precedent in late-transition metal chemistry,<sup>5</sup> though this is, to the best of our knowledge, the first time that an overall σ-bond metathesis reaction on an early transition-metal center is observed to be catalyzed by amines.

To further assess our hypothesis, we studied a) the effect of the basicity of the tertiary amine on the rate of the C–D bond activation reaction, and b) its dependence on the concentration of the amine. As expected, there is a qualitative correlation between the basicity of the amine and the rate of the C–D bond activation reaction (Et<sub>3</sub>N >> 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NMe<sub>2</sub> > *p*-*t*-BuC<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub> ≈ PhNMe<sub>2</sub> > *p*-BrC<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>).<sup>6</sup> Furthermore, the rate of the reaction increases with increasing *N,N*-dimethylaniline concentration (Figure 1). Kinetic data show that the rate of the amine-catalyzed C–D bond activation reaction is first order in both [**1b**] and [PhNMe<sub>2</sub>], whereas the uncatalyzed reaction is only dependent on the concentration of compound **1b**:

$$d[\mathbf{1b}]/dt = -(k_{\text{uncat}} + k_{\text{cat}}[\text{PhNMe}_2])[\mathbf{1b}] \quad (1)$$

Analysis of the data resulted in  $k_{\text{uncat}} = 2.69(8) \cdot 10^{-6} \text{ s}^{-1}$  and  $k_{\text{cat}} = 5.52(7) \cdot 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$ .

We decided to investigate the effect of the tertiary amine on the C–H bond activation reaction using DFT calculations (B3LYP).<sup>4</sup> As a model reaction, the C–H bond activation of benzene by [Cp<sub>2</sub>ZrMe]<sup>+</sup> was studied in the presence and absence of trimethyl-



**Figure 2.** Schematic representation of the reaction coordinate in the overall  $\sigma$ -bond metathesis reaction of  $[\text{Cp}_2\text{ZrMe}]^+$  with benzene in the absence (blue) and presence (green) of  $\text{NMe}_3$ . Energies at 298 K are listed in kcal/mol; hydrogen atoms on the cyclopentadienyl ring have been omitted for clarity.

amine. In this study, neither solvent nor counterion effects have been taken into account, but thermal corrections are included in the free energy discussions below (see also Figure 2).

In both cases, the initial step in the reaction involves coordination of benzene to the zirconocene methyl cation which, according to the calculations, is downhill by 4.05 kcal/mol. For the uncatalyzed reaction, a typical 4-membered transition state was found at 24.04 kcal/mol relative to the starting materials (**TS1**,  $\Delta G^\ddagger = 28.09$  kcal/mol).<sup>3,2e,7</sup> This barrier is higher than that found for the intramolecular C–H bond activation reaction in the linked Cp-arene titanium compound  $[\text{Cp}(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{-4-Me})\text{TiMe}]^+$  ( $\Delta G^\ddagger = 23.5$  kcal/mol).<sup>7c</sup> The initial product is the methane adduct of the phenyl cation,  $[\text{Cp}_2\text{ZrPh}(\text{CH}_4)]^+$ , which releases methane to generate  $[\text{Cp}_2\text{ZrPh}]^+$ . The geometry optimization of the phenyl cation shows a  $\beta$ -agostic interaction of the *o*-CH bond with the metal center resulting in a similar structure as that reported for other cationic  $\sigma$ -aryl species of zirconium.<sup>8</sup> The overall reaction is thermodynamically downhill by 6.61 kcal/mol.

For the amine catalyzed reaction, one could envision a stabilization of the aforementioned transition state (**TS1**) by hydrogen bonding interactions of the amine with the proton that is transferred from the coordinated benzene ligand to the methyl ligand. Instead, a two-step mechanism was found in which the benzene ligand is initially deprotonated in the coordination sphere of the metal center by the amine, generating  $\text{Cp}_2\text{ZrMePh}$  and  $[\text{Me}_3\text{NH}]^+$ . In a second step the methyl ligand is protonated by the ammonium salt to generate the observed products. The intermediate,  $\text{Cp}_2\text{ZrMePh}$  was found at 14.51 kcal/mol relative to the starting materials, and the transition state for the deprotonation (**TS2**) and protonation (**TS3**) reactions at 18.42 and 16.54 kcal/mol, respectively.<sup>9</sup> This results in a  $\Delta G^\ddagger = 22.47$  kcal/mol for the deprotonation reaction and  $\Delta G^\ddagger = 3.91$  kcal/mol for the protonolysis. The lowest energy transition state for the latter (**TS3**) resembles that of an  $\text{S}_{\text{E}}2$  reaction. The calculations suggest a small preference ( $\Delta\Delta G^\ddagger = 1.88$  kcal/mol) for phenyl cation over methyl cation formation upon treatment of  $\text{Cp}_2\text{ZrMePh}$  with ammonium borates. This is different to the observations made in THF and most likely a result of solvent effects.<sup>10</sup>

In conclusion, we have observed an increased rate of reaction for the C–H bond activation reaction of aromatic solvents by cationic decamethylzirconocene species. This is of major importance to the field of olefin polymerization catalysis, as trialkylammonium borate reagents are frequently applied as activators of transition metal dialkyl precursors. A computational study revealed a two-

step mechanism for the observed overall  $\sigma$ -bond metathesis reaction in the presence of tertiary amines, in which the amine effectively acts as a proton shuttle.

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**Supporting Information Available:** Text giving full experimental data and details on the kinetic model, as well as pdb files of stationary points of the reaction coordinate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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