The effectiveness of a catalyst is determined not only by its activity and selectivity but also by the lifetime of its active species. 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. 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 d5-chlorobenzene by a cationic decamethylzirconocene compound as a new decomposition pathway for group 4 olefin polymerization catalysts. In this particular solvent, ion-pair [Cp*2ZrMe(ClC6D5)- as a new decomposition pathway for group 4 olefin polymerization grades to [Cp*][ZrCl(C6D4-Cl)][B(C6F5)4](1a) reacts via σ-bond metathesis, to give σ-aryl species [Cp*2Zr(2-ClC6D5-κ2C)]([B(C6F5)4](2a), which subsequently degrades to [Cp*5(η5-η1)2CMe6Cl4ZrC])([B(C6F5)4](3a). When we studied the same system in d5-bromobenzene solvent, we were not surprised to find a similar sequence, now involving the bromide analogue 1b–3b (Scheme 1). 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*2ZrMe2.

When the zirconocene methyl cation 1b was generated in d5-bromobenzene solvent, by reaction of Cp*2ZrMe2 with [Ph3C][B(C6F5)4], slow conversion to complex 2b was observed. When the Brønsted acid [PhNMMe2][B(C6F5)4] was used to generate 1b, the formation of 2b was faster than for trityl-generated 1b, and in the case of [Et3NH][B(C6F5)4] 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.

Figure 1. Ln([1b]) versus time plot for the C–D bond activation reaction of d5-bromobenzene after activation of Cp*2ZrMe2 with [Ph3C][B(C6F5)4] in the absence of N,N-dimethylaniline (1b) or in the presence of 1.1 (•), 2.6 (○), 3.6 (●), 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 PhNMMe2 or NEt3. Amine assisted C–H bond activation processes have precedent in late-transition metal chemistry, 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 (Et3N >> 2.6-η-Pr2C6H3NMe2 > p-η-BuC6H4NMe2 ≈ PhNMMe2 ≈ p-BrC6H4NMe2). 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 [PhNMMe2], whereas the uncatalyzed reaction is only dependent on the concentration of compound 1b:

$$\frac{d[1b]}{dt} = -k_{uncat}[1b] + k_{cat}[PhNMMe2][1b]$$ (1)

Analysis of the data resulted in $k_{uncat} = 2.69(8) \times 10^{-6}$ s⁻¹ and $k_{cat} = 5.52(7) \times 10^{-3}$ L mol⁻¹ s⁻¹. We decided to investigate the effect of the tertiary amine on the C–H bond activation reaction using DFT calculations (B3LYP). As a model reaction, the C–H bond activation of benzene by [Cp2ZrMe]+ was studied in the presence and absence of trimethyl-
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). $^{3,2,7}$ This barrier is higher than that found for the intramolecular C–H bond activation reaction in the linked Cp-arene titanium compound [Cp(q$^-$)$^\sigma$-C$_6$H$_5$CMe$_2$C$_6$H$_4$-4- Me)TiMe]$^+$ ($\Delta G^\ddagger =$ 23.5 kcal/mol).$^{57}$ The initial product is the methane adduct of the phenyl cation, [Cp$_2$ZrPh(CH$_4$)]$^+$, which releases methane to generate [Cp$_2$ZrPh]$^+$. The geometry optimization of the phenyl cation shows a $\beta$-agostic interaction of the $\sigma$-CH bond with the metal center resulting in a similar structure as that reported for other cationic $\sigma$-aryl species of zirconium.$^8$ 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 Cp$_2$ZrMePh and [Me$_3$NH]$^+$. In a second step the methyl ligand is protonated by the ammonium salt to generate Cp$_2$ZrMePh and [NMMe$_3$]+. In a second step the methyl ligand is protonated by the ammonium salt to generate the observed overall C–H 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.

References


(4) See Experimental Section in the Supporting Information for details.


(9) Whereas different transition states have been considered for the different reaction steps, only those with the lowest energy have been included in the discussion. See Supporting Information for a complete overview.