

Computational Approach to Understand the Active Site Opening Mechanism for Zirconium Bis(phenoxy-imine) Ion-pair

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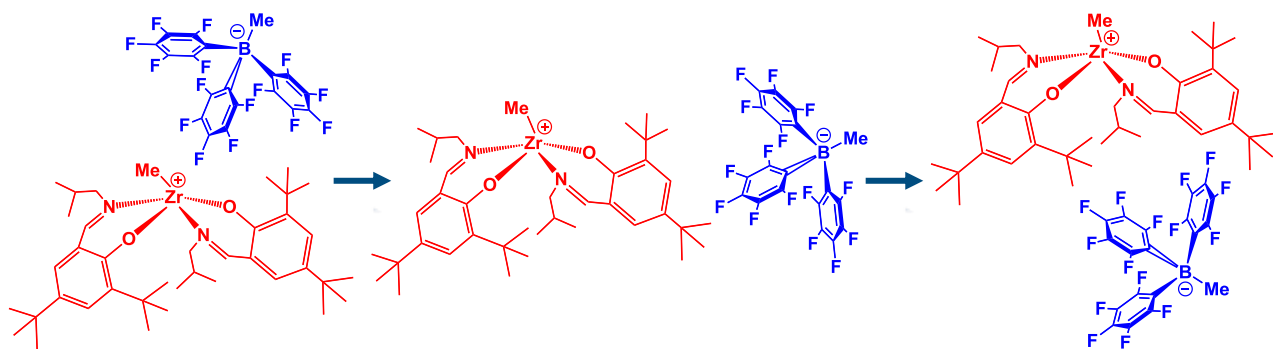
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One of the most influential breakthroughs was the discoveries of metal-phenoxy-imine (or FI: *Fenokishi-Imin*) catalysts that ignited the intense academic, and industrial research activities.^{1,2} To understand the geometrical features for the FI-catalyst, we have considered five important reactive species, viz, neutral, cation, cation & monomer (i.e., ethene), ion-pair and ion-pair & monomer, of zirconium bis(phenoxy-imine) catalyst.

The energetics among the five different isomers of neutral Zr-FI-catalyst have been assessed quantum mechanically. The Zr-cation can exist in three different isomers, viz, *cis*-N/*trans*-O (**A**), *cis*-N/*cis*-O (**B**), and *trans*-N/*cis*-O (**C**). The existing probability derived from the obtained free energy values suggests that isomer **C** is comparable with isomer **A**.³ The quantum mechanical (QM) calculations for ion-pair suggest that borate counteranion will be located on the opposite side of the methyl group, keeping the active site open (ASO⁴). Moreover, QM calculations of cation & monomer, and ion-pair & monomer also suggest that the active site will always completely open.

Since the ASO is a dynamic process, we have used molecular dynamics (MD) simulation technique to understand this dynamic process. During the MD simulation (Scheme 1), we have observed that the anion changed its coordination mode and finally keeping the active site always open. We have also confirmed the ASO process using the replica exchange molecular dynamics (REMD) method. The QM, MD and REMD results suggest that active site would always be opened for the Zr-FI catalyst. Keeping the active site always open could be one of the reasons for the higher reactivity¹ of FI catalyst.



Scheme 1: Schematic representation of observed ASO mechanism.

References:

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