

C₆F₅-Group Transfer from [MeB(C₆F₅)₃]⁻ to the Metal Center of L₂MMe⁺ (M = Ti, Zr) as a Deactivation Pathway in Olefin Polymerization Catalysis: A Combined Density Functional Theory and Molecular Mechanics Investigation

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We have carried out a combined density functional theory and molecular mechanics study of aryl group transfer reactions from [MeB(C₆F₅)₃]⁻ to the metal center of L₂MMe⁺ (M = Ti, Zr). This reaction which produces L₂MMe(C₆F₅) and MeB(C₆F₅)₂ is a possible deactivation pathway in metal-catalysed single-site olefin polymerization. The cationic catalyst systems L₂MMe⁺ include (NPR₃)₂MMe⁺, (Cp)(NPR₃)MMe⁺, (Cp)(NCR₂)MMe⁺, (Cp)(SiMe₂NR)MMe⁺ and (Cp)(OSiR₃)MMe⁺. With M = Ti, 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 reducing the aryl transfer reaction. The aryl group transfer is likely to take place for (Cp)(NCR₂)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*)(NCR₂)TiMe⁺ system.