

Is the Polymerization of linear α -olefins by Transition Metal Carbene Complexes a Viable Process? A Theoretical Study Based on Density Functional Theory.

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Gradient-corrected density functional theory has been used to study the mechanism of α -olefin polymerization catalyzed by transition metal carbene complexes. Taking the $[\text{CH}_2=\text{Re}(\text{NO})_2(\text{PMe}_3)]^+$ complex as an example we investigate the possible elementary steps of the polyethylene formation. This "carbene-to-metallacycle" style mechanism based on a pure carbene intermediate starts with the coordination of the ethylene. Then ethylene react with the carbene complex by a [2+2] addition. Metallacyclobutane decomposition to a new carbene complex takes place by an α -hydrogen transfer reaction. We have also investigated the possible side reactions for the metallacyclobutane decomposition by metathesis reaction, cyclization and β -hydride transfer reactions. Calculations have been performed on the monomer and carbene complexes, on the possible intermediates, ethylene π -complexes, metallacyclobutanes, cyclopropyl complexes, cyclopropyl hydride complexes, propylidene complexes, propene π -complexes, allyl-hydride intermediates, and transition states. The results show that when the $[\text{CH}_2=\text{Re}(\text{NO})_2(\text{PMe}_3)]^+$ complex is used as a catalyst, the β -hydride transfer is both kinetically and thermodynamically favored over the α -hydride transfer reaction, therefore ethylene polymerization is not viable. Modifying the catalyst by changing ligands and metals we have increased the preference for β -elimination over α -elimination. The application of very strong electron donor ligands can make the metal center enough electron rich and stabilize the new propylidene ligand over the formation of an olefin π -complex.