Ab Initio Studies on Ruthenium-Based Olefin Metathesis Catalysts Mechanism

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Abstract:

We examine the mechanism of the Grubbs catalyst using density functional theory (DFT). This work in progress is validating DFT as an accurate method to examine this mechanism by correctly predicting structures and energetics of known Grubbs catalyst species. Several popular mechanisms for Grubbs olefin metathesis are examined. Support for a mechanism with phosphine disassociation followed by trans carbene/phosphine association of the olefin is presented.
Grubbs catalyst mechanism important species:

A (Starting Catalyst)  B (Activated Species--lost phosphine)

C (Olefin bound to Ru)  D (Form metallacycle)
Phosphine Dissociation (a closer look)

Phosphine-Ru Distance

$\text{exp} \sim 25\text{kcal/mol}$

(exchange rate of labeled PR3)