

Theoretical characterization of first and second generation Grubbs catalysts in styrene cross-metathesis reactions: insights from conceptual DFT

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Resumen

The differences between the first and second generation Grubbs catalysts have been the subject of much interest in olefin metathesis. In this direction, we revised in detail the dissociation reaction of 16e Grubbs precatalysts and the rotameric change between 14e inactive to active catalysts using a distortion/ interaction model (called here the reorganization energy ΔE_{reorg} and interaction energy ΔE_{int}) combined with DFT-based reactivity descriptors. We have found that there are no great changes between both generations in terms of the interaction energies and electronic descriptors; however, a lower reorganization energy for the conformational change in the second generation was shown to be significant, in agreement with the reverse trans effect proposed recently, confirming that structural effects play a key role in the reactivity of these Ru-based complexes. Furthermore, the difference of the Grubbs catalysts in the formation of the ruthenacyclobutane intermediate, RCB, shows that the biradical species needed to generate this type of compound is more easily formed by the second generation than by the first, with $\Delta E_{\text{reorg}}^{\text{T-T}}(14) = -3.6 \text{ kcal mol}^{-1}$ vs. $11.8 \text{ kcal mol}^{-1}$, respectively. As a consequence, the different electronic features of the first and second generation Grubbs catalysts are manifested in the formation of ruthenacyclobutane intermediates, which allow us to propose that the higher catalytic activity of the second generation of Ru-based complexes also has its origin in these effects and not only in structural changes. Finally, we have also found that the dielectric polarizability change was shown to be a suitable property to describe the intensity of polarization effects in the formation of ruthenacyclobutane as well as in the identification of productive and non-productive processes.

Palabras clave

KeyWords Plus: DENSITY-FUNCTIONAL THEORY; HETEROCYCLIC CARBENE LIGANDS; AB-INITIO PSEUDOPOTENTIALS; IMIDO ALKYLIDENE COMPLEXES; OLEFIN-METATHESIS; NONCOVALENT INTERACTIONS; NOBEL LECTURE; MECHANISM; POLYMERIZATION; APPROXIMATION

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