(De)Activation of olefin metathesis catalysts

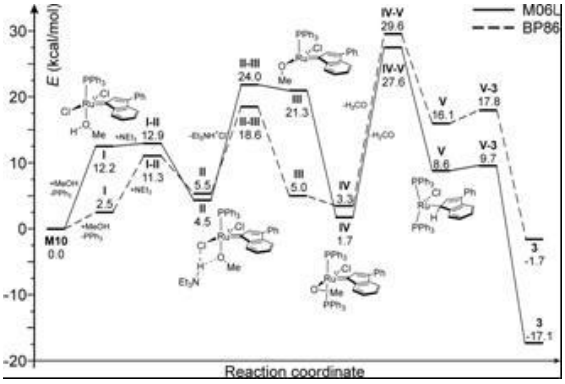
Albert Poater[1,2] and Luigi Cavallo[2]

1 Catalan Institute for Water Research (ICRA), H2O Building, Scientific and Technological Park of the University of Girona, Emili Grahit 101, E-17003 Girona, Spain; apoater@icra.cat (A.P.); mpoch@icra.cat (M.P.)

2 Dipartimento di Chimica e Biologia, Università di Salerno, Via ponte don Melillo, I-84084 Fisciano (SA), Italy

In recent years olefin metathesis catalyzed by N-heterocyclic carbene ruthenium complexes has attracted remarkable attention as a versatile tool to form new C=C bonds. [1] The last developed (pre)catalysts show excellent performances, and this achievement has been possible because of continuous experimental and computational efforts to understand the laws controlling the behavior of these systems. This perspective talk rapidly traces the ideas and discoveries that computational chemistry contributed to the development of these catalysts, with particular emphasis on catalysts presenting a N-heterocyclic carbene ligand. Specifically, one of the most important challenges in ruthenium-catalyzed olefin metathesis is to increase the stability of the catalysts under reaction conditions and this hopefully without loss of activity. Although, in the solid state, most ruthenium-based olefin metathesis catalysts are stable to oxygen and moisture, in solution decomposition usually occurs readily. Understanding the decomposition routes of catalysts is extremely important as any insight gained in this area can guide catalyst design efforts.

The well-defined and easily accessed [$RuCl_2(PPh_3)_2$(3-phenylindenylidene)], although not efficient in olefin metathesis itself, is an important synthon used in the preparation of a number of classes of ruthenium-based olefin metathesis catalysts. Although slightly stable in solution under anaerobic and anhydrous conditions, it exhibits rapid decomposition in the presence of alcohols. The instability of ruthenium olefin metathesis complexes to alcohols is often encountered. Indeed, in methanol, these complexes are prone to methanolysis and lead to the formation of hydrido-carbonyl complexes.



An unusual indenylidene to indenyl rearrangement has been uncovered,[2] leading to the rather facile formation of a new ruthenium indenyl complex. This complex, formally a decomposition product from an olefin metathesis catalyst, displays exceptional activity in the racemisation of chiral alcohols. DFT calculations permitted assembling all the experimental information into an energy profile. To facilitate the computational effort, MeOH was used as the model alcohol.[2] The discussed energies have been calculated with the M06L and BP86 functionals.

[1] G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2009**, *110*, 1746-1787B.
[2] S. Manzini, C. A. Urbina-Blanco, A. Poater, A. M. Z. Slawin, L. Cavallo, S. P. Nolan, *Angew. Chem. Int. Ed.* **2012**, *51*, 1042-1045.

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