

Among the many types of transition-metal reactions of carbon-carbon double bond formation, metathesis is the one that draws increasing attention of organic chemists. It has been adopted in many fields ranging from pharmaceutical and material science to petrochemical industry and its importance is constantly growing. The widespread use of metathesis was associated with the development of ruthenium catalysts, which were not compromised by most of the chemical groups found in organic molecules. Moreover, several types of products can be obtained with the same catalyst, depending on the reaction conditions and substrates used. Since cross metathesis allows for a direct bond creation, and as an equilibrium controlled reaction favours formation of stronger, polar bond, it is not surprising that the question arose about the possibility of conducting it between two functionally different unsaturated partners. In 80's and 90's scientists conducted first experiments on reaction between diazo compounds, containing N=N bond and Fischer carbenes - an early catalysts for this reaction. To the best of our knowledge, a catalytic cross metathesis with Ru-based catalyst and diazenes to imines has not yet been reported, either computationally or synthetically.

The main goal of the proposed research project is a systematic study of novel ruthenium-based catalysts able to catalyze hetero-functional cross metathesis reaction between diazo compounds and alkene to introduce a relevant new tool into imine synthesis. Molecules of this type, containing carbon-nitrogen double bond, belong to important class of chemical compounds. The imine motif can be often found in pharmacologically relevant compounds, for e.g. drugs for Alzheimer's disease, drugs against osteoporosis. The reversible nature of the imine bond makes it an excellent reactant for construction of imine-based molecular motors, which have been awarded the Nobel Prize. The use of readily available diazenes as substrates for such transformation seems an obvious choice to further expand the scope of cross metathesis, because - as commonly used dyes - they are available in functionalized form and in large quantities. The working hypothesis of the current proposal is based on the assumption that cross metathesis between functionally different unsaturated compounds can be realized, and a properly designed metathesis catalyst will allow to carry out this process catalytically. Our mechanistic study will expand the understanding of structure-activity relationships for the non-stoichiometric azo cross-metathesis transformations. We will focus on the impact of both the substrate and the catalyst structural framework, such as the presence of specific ligands/substituents, on the reactivity of the catalysts. Density functional theory methods will be applied in this project to thoroughly study the entire catalytic cycle of azo metathesis, as well as all possible competitive reactions causing degradation of metal catalyst.

In light of the importance of the imines in various chemistry fields, a theoretical approach to new reactions that introduce nitrogen functionality is undoubtedly attractive and extends available methods. This project offers the possibility to further study the still unclear reaction mechanisms of azo metathesis and will provide a rational design of novel ruthenium cross metathesis protocols, with the possibility of future use in catalytic access to imines. The proposed project contributes also to a better understanding the mechanisms and crucial intermediates / transition states in the hetero-functional cross metathesis reaction, the mechanisms of decomposition of ruthenium-based catalysts under the conditions of these reactions, as well as about the relationship between the structure and electronic properties of selected ruthenium catalysts in these new reactions.