Research project objectives/Hypothesis

The main goal of this research project is a systematic study of selected, non-standard carbenes and their potential use in homogenous chemical catalysts directed toward better understanding of the fundamental aspects of their action. The main part of this project consists of the design and modelling of new anionic, cationic and mesoionic N-heterocyclic carbene derivatives, which can be used as transition metal complexing agents to produce new catalysts. We will focus on ruthenium-based complexes as candidates for efficient metathesis, hydrogenation, transfer hydrogenation and hydrosilylation catalytic reactions. For these complexes we will computationally explore all possible catalytic reactions paths and degradation paths and select the best candidates for efficient catalysts for the synthesis. The second theme of this proposal is the development of new computational methods to accurately describe newly designed complexes not only at the atomic level but also at the nano/mesoscale level. This task will be carried out in an interdisciplinary team consisting of scientists, experts in rational design and modeling of transition metal complexes, organometallic chemistry and physics. The results of this project will allow for an accurate characterization of a series of new carbenes and complexes and allow to develop a general methodology, which will be used in the future to design new, better catalysts.

Research methodology

In the "catalyst design" part of this project we will first describe the electronic properties of new anionic, cationic and mesoionic carbenes. We will then *in silico* modify the known ruthenium-based metathesis, hydrogenation, transfer hydrogenation and hydrosilylation catalysts and computationally study their stabilities and catalytic activities. The *in-silico* designed catalysts will be modeled and tested for their optimum geometry, stability and electron-donor properties using some the latest density functional methods, including the M06 functional with dispersion correction, in medium-sized and large basis sets (lacv3p**++, 6-311++G**) using the Jaguar 7.x-8.x and Orca 3.x software. Such approach was shown by us to give results which are in perfect agreement with experimental data for many ruthenium complexes. Selected compounds with optimal stabilities and properties from DFT calculations will be subject to more complex simulations to find their full mechanisms and estimate the energy barriers of the most favorable reaction pathways. The best candidates for catalysts with desired properties will be synthesized and tested for their catalytic activity.

In the "methods development" part of this project we will use results from the accurate calculations and experimental studies of new carbenes and their Ru complexes to parametrize the Ru-based catalyst for the reactive force field ReaxFF method, Density Functional based Tight Binding approach and PM6/PM7 semiempirical methods. These three powerful methods allow to computationally study chemical reactions in systems consisting of thousands to tens of thousands atoms. Such an approach will grant us insight not only into the atomic-scale mechanisms governing these catalytic reactions, but also into the nano/mesoscale level. It also allows to incorporate additional physical phenomena, such as diffusion, into the theoretical description of the reaction mechanisms, resulting in a more detailed view of the entire catalytic process.

Research project impact

The proposed project will contribute to a better understanding of how structural changes in complexes affect their catalytic activities and incorporate a new class of chemical compounds into the large family of ruthenium-based catalytic systems. The mechanistic studies of degradation paths of selected complexes will offer new insight into the rational design of new catalysts, while the novel carbene complexes will offer new challenges for synthetic chemists, increase our knowledge about them and, in the future, promise to create faster and more efficient catalysts. The proposed, comprehensive, theoretical approach to this problem will provide us with an accurate characterization of new systems and will lead to the development of a new methodology for the rational design of new catalysts. The nano/mesoscale approach, proposed for the first time for Ru-based catalysts, will deepen our knowledge about various chemical and physical phenomena occurring during catalytic cycles. New Ru-catalysts parametrizations for ReaxFF, DFTB and PM6/PM7 methods will be also released and available freely to the scientific community. This project will also strengthen research in Poland. We believe that a project lead by an expert in theoretical description of catalytic systems is timely and relevant for the Polish catalysis landscape. We believe that it will also increase the competitiveness of Poland in the field of chemical synthesis and catalysis, and its results will be useful to the Polish and international chemical community in better understanding the relationships between structure and reactivity of various catalysts.