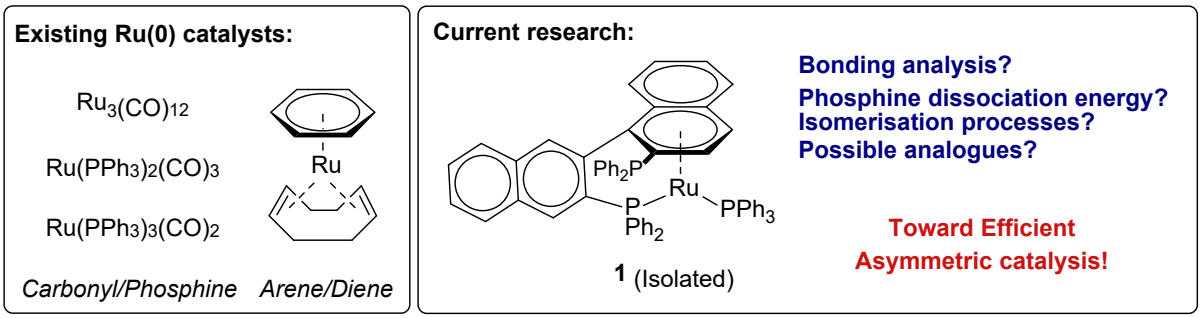
Groups	**:**	Theoretical Surface Chemistry / Homogeneous Catalysis & Biomimetic Synthesis
Project	**:**	**Computational Study of Ru(0) complexes Towards Asymmetric Catalysis**
Supervisors	**:**	Guanna Li and Fedor Miloserdov

Keywords: DFT Calculations, Mechanistic Studies, Transition Metal Catalysis

Introduction. In this project you will perform ***in silico*** study of properties and reactivity of novel asymmetric catalysts based on Ru(0) metal center.

While catalytic systems based on Ru(II) are well-known and widely used in both academia and industry, the application of Ru(0) complexes in homogeneous catalysis is much less common. In the same time it is known that Ru(0) complexes can mediate a number of unique transformations.[1-3] The development of efficient ***asymmetric*** catalytic systems around Ru center in oxidation state zero will open novel synthetic possibilities toward highly valuable chiral bio-organic molecules.

For many years the field of Ru(0) catalysis was dominated by non-chiral Ru(0) carbonyl and arene complexes, which are typically quite inert because of the strong backdonation of electron density from Ru center to ligands.[1] Mixed phosphine/arene complexes of Ru(0) would be a valuable alternative to existing coordination systems, as they offer the high variability of the ligand environment, and the possibility to induce chirality by using ready available tethered arene/phosphine ligands. Very recently we developed a synthetic access to the first complex of this type, [Ru(BINAP)(PPh_3)] (**1**), which contains BINAP in a highly unusual π-arene/σ-P coordination mode.



Topics to be studied. With the most advanced computational techniques, the bonding and reactivity of complex **1** will be elucidated and it's potential to deliver asymmetric catalysis will by studied. A particular attention will be given to isomerization processes connecting different coordination modes at Ru-center, estimation of energies of phosphine dissociations and the stability of possible analogues of complex **1**. This work will be done in parallel with the experimental studies on the properties and catalytic activities of **1**, and will contribute to the overall mechanistic picture and understanding of the reactivity patterns of Ru(0) complexes in π-arene/σ-P coordination mode.

Approach. The project is focused on the computational studies. The work will involve quantum modeling work on supercomputer. Gaussian and GaussView packages will be used to build the molecular models of Ru(0) complexes, estimate the isomerization and dissociation processes and screen potential analogues.

Techniques to be used. By this project, you will learn the operation on Unix system and supercomputer cluster, prevalent quantum modeling package of Gaussian, and general DFT (density functional theory) computational methods including geometry optimization, spectroscopic simulation and transition state search.

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