

Group : Laboratory of Organic Chemistry
Project : **Heterobimetallic Ruthenium catalysts for C-C bond formation**
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Keywords. Ruthenium catalysis, heterobimetallic complexes, C-H bond functionalization.

Introduction. C-C bond formations are considered high-efficiency reactions in organic synthesis.^[1] Developing new methods to accomplish these reactions on a wider scale is desired to improve synthesis paths for various chemicals in academia and industry. Ruthenium is the least expensive platinum group transition metal and has therefore been the target of extensive study, leading to various Ru-based catalysts being developed.^[2-5] However, there is still a room for development of efficient Ru-based catalytic systems. Heterobimetallic complexes are complexes containing two different metals, usually one transition metal and one main group metal. These complexes have been found to have enhanced catalytic activity compared to complexes only containing one a transition metal, with the Lewis acidic main group metals acting as σ -acceptors, stabilizing the transition metal complex, accelerating reductive elimination, and improving the coordination strength between transition metals and otherwise unreactive substrates such as CO₂.^[9-10] When correctly selected, the main group metal is able to improve the stability and activity of an organometallic complex for various catalytic reactions.

Goal. Recently, our group made a Ruthenium(0) complex containing a BINAP ligand,^[11] which was found capable of shifting between binding modes, stabilizing the otherwise unstable Ru(0) and preventing intramolecular C-H bond activations from occurring, whilst also still being reactive enough to perform intermolecular C-H bond activations. Despite its promising properties, the complex has not been tested yet for C-C bond formations. We desire to improve the activity of this catalyst for C-H activation and C-C bond formation by turning this Ruthenium complex into a heterobimetallic Ru-M complex (M = Li, Mg, Zn, Al, Sn) and optimize it for enantioselective C-C bond formation so this catalyst can be used elsewhere in organic synthesis.

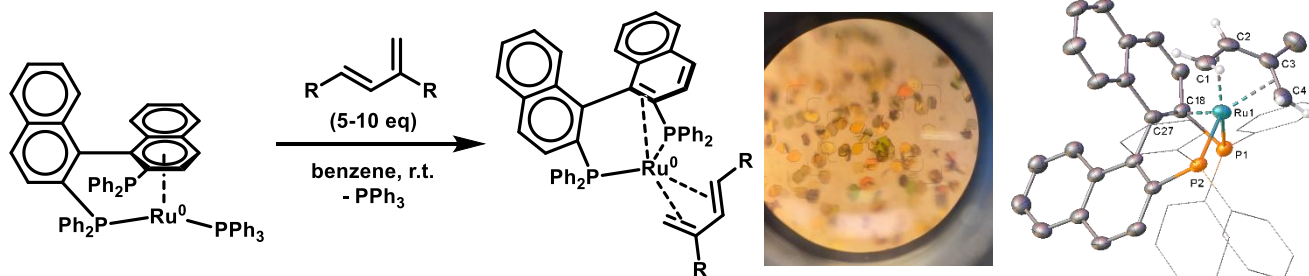


Figure 1. Ru(BINAP)(PPh₃) and example of its activity in diene coordination.

Topics to be studied. This project will involve the synthesis of a variety of heterobimetallic Ruthenium complexes based on the Ru(BINAP)(PPh₃)HCl precursor and their analysis by NMR and single crystal XRD. Furthermore, the project will include an analysis of the effects of including main group metals into a Ru(BINAP)(L)MR complex on its ability to perform C-H bond functionalization reactions. Beyond this, the synthesized complexes can be modified further to introduce stereochemical control in order to achieve enantioselective C-C bond formations.

Techniques to be used. Inorganic synthesis, Schlenk techniques, Glove box, Crystallization, NMR, IR, single crystal XRD.

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