



# Graduate Students Seminar

Department of Chemistry

**Sunday, June 18<sup>th</sup>, 2023**

**Time 14:30**

**Bldg. 43 Room 015**

## Keren Iudanov

Under the supervision of Prof. Gabriel Lemcoff

### **Tuning Activity and Selectivity of Diiodo Latent Olefin Metathesis Catalysts**

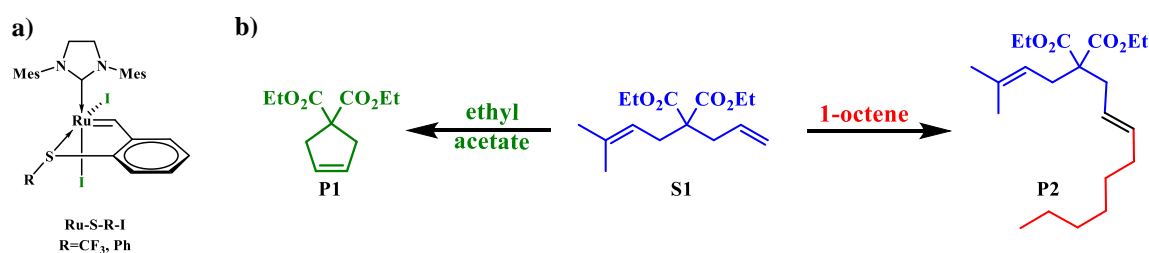
Olefin metathesis is a versatile reaction utilized in many processes in the chemical and pharmaceutical industry. This reaction is typically catalyzed by transition metal complexes, especially ruthenium, molybdenum, or tungsten. The metals are surrounded by a well-defined ligand shell; for example, Grubbs-type 16-electron ruthenium complexes contain two anionic ligands (usually chlorides), two neutral ligands (usually an N-heterocyclic carbene (NHC)) and a sulfur or chelating oxygen) and an active alkylidene ligand. The judicious tuning of the catalyst's ligand shell may result in novel reactivity. We have recently shown that replacing the typical chloride anionic ligands with iodides in sulfur-chelated ruthenium benzylidenes significantly affects their catalytic behavior. The iodide ligands inhibit coordination of non-terminal olefins to the metal center, which leads to an unprecedented change in chemical selectivity. For example, **Ru-SCF<sub>3</sub>-I** (Figure 1) only promoted ring closing metathesis (RCM) of **S1** (which contains a hindered terminus) at high concentrations of the substrate. By taking advantage of this behavior, selective cross-metathesis (CM) of **S1** with different substrates was studied. Surprisingly, coordinating additives enhanced RCM activity of the catalyst to form **P1**.



This finding highlights the influence of coordinating ligands on activity and the importance of matching catalysts to substrates in order to achieve specific olefin metathesis reactions.<sup>1</sup>

Ultimately, highly selective CM of **S1** and 1-octene (which is devoid of coordinating moieties) was achieved by utilizing **Ru-SCF<sub>3</sub>-I**. The 5-membered RCM reaction was only observed as a minor side reaction, and **P2** was obtained as the major product.

Indeed, with other metathesis catalysts, such as the non-latent Hoveyda Grubbs 2<sup>nd</sup> generation pre-catalyst and also with the chloride analogue **Ru-SCF<sub>3</sub>-Cl<sub>2</sub>**, the RCM product **P1** was formed exclusively. Given that many terpene natural products contain the ubiquitous prenyl moiety, by following the procedure described above, selective CM could also be achieved with myrcene, ocimene, and citronellene, known to readily afford RCM products with any other ruthenium catalyst. This unique selectivity is currently being further investigated and may provide an important new tool for the synthesis of derivatives of these significant natural products.



**Figure 1.** a) Sulfur-chelated ruthenium benzylidene with iodide anionic ligands.  
b) Reaction scheme for RCM and CM of **S1**.

(1) Nechmad, N.B., Iudanov, K., Tarannam, N., Kobernik, V., Kozuch, S., Lemcoff, N.G, *ChemCatChem*, **2023**, *15*, e202201690.