

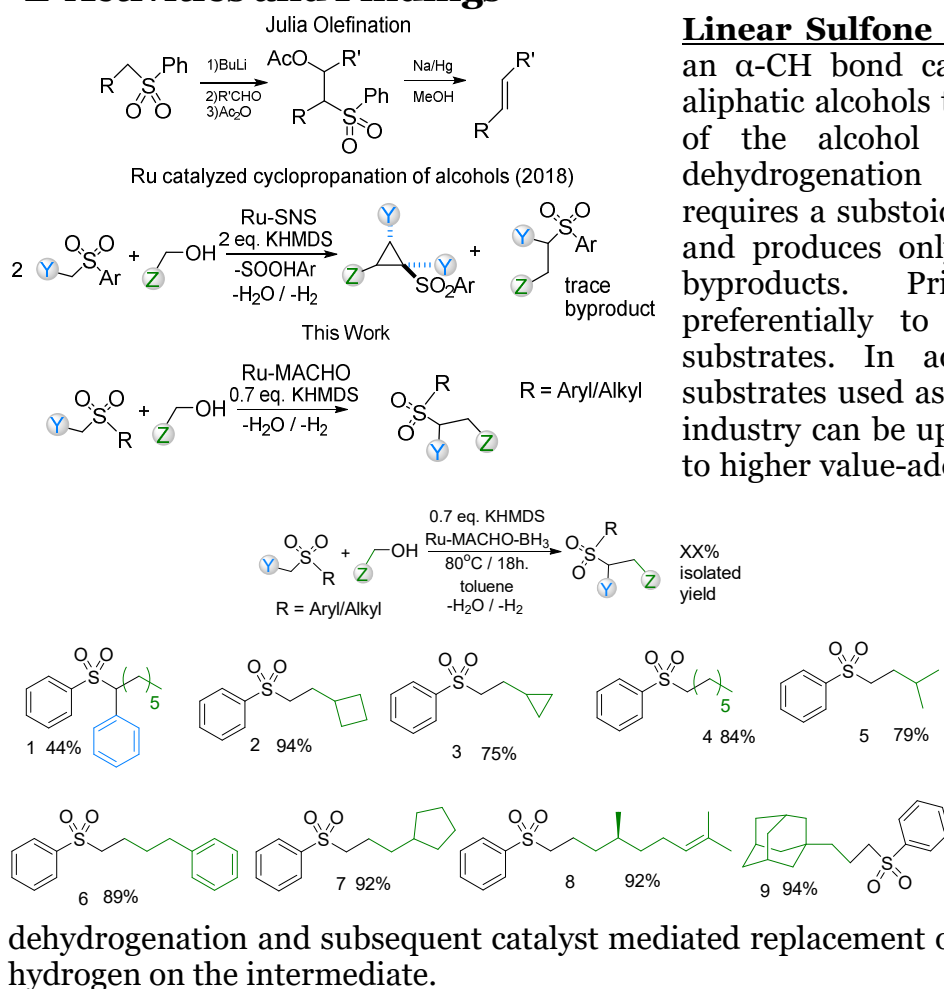
Science and Technology Group Annual Report FY2018

Eugene Khaskin
Science and Technology Associate

1 Introduction

During FY2018, I published the results of the highly diastereoselective sulfone cyclopropane synthesis (summarized in FY2017 report) first in an open access ChemArXiv and afterwards a final version in an organometallics journal.¹ This research was highlighted in SynFacts, a journal which summarizes most promising organic reactions each year. The first author of the paper is a former OIST intern. Based on this work a patent was granted and funding was secured for a POC grant from OIST to explore the possibility of commercializing the findings. The grant led to the hiring of an experienced synthetic chemist who optimized the synthesis of linear sulfones, research that will be prepared for publication in FY2019. This work was presented at the Japanese Society of Chemistry 99th annual March meeting (lecture). In addition, an earlier collaboration with the Kuhn unit led to the preparation of an earlier published Annine-6plus and a novel dimethyl-Annine-6plus neuron dye, with the work being submitted for publication in 2019. A collaboration with Magne Sydnes from Stavanger University in Norway led to the preparation of a number of complexes with a novel ligand architecture that will be tested for catalysis in the next fiscal year. Collaboration with the Khusnutdinova unit led to the publication of two papers in FY2018: one where I designed the ligand and project² and one where I carried out XRD work.³ Recently a paper was submitted for publication that took up a significant amount of research time in FY2018 where we synthesized a new ligand and observed an unusual and highly rare C-C cleavage and formation reaction. As this final work is will not be reported on by other units, it will be summarized below. This work was done in collaboration with researchers in Ben Gurion University in Israel and Kazan University in Russia.

2 Activities and Findings

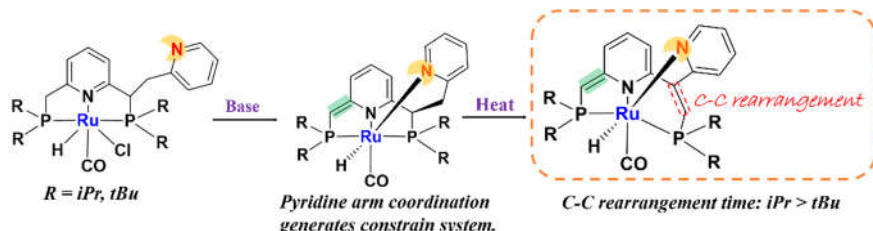


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C-C rearrangement summary. We report the synthesis of 'hangman-type' PNP pincer ligands and their associated Ru complexes. Upon deprotonation, the complexes undergo sp^2 - sp^3 C-C bond cleavage and subsequent C-C formation processes to form a new, one carbon unit longer backbone motif. Unlike the starting geometry, the products are completely inactive in alcohol dehydrogenation catalysis. DFT and mechanistic studies suggest an intramolecular isomerization process via a spirocycle cyclopropane intermediate, dependent upon arm pyridine coordination and ligand sterics.



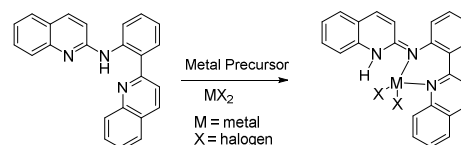
isomerization process via a spirocycle cyclopropane intermediate, dependent upon arm pyridine coordination and ligand sterics.

C-C cleavage and formation

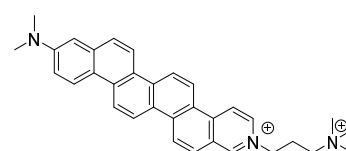
reactions mediated by metal complexes are rare, yet it occurs readily at room temperature in one of the complexes. We tested the new rearranged complexes in catalysis and found out that they are inactive. However, the original unmodified complex was tested by us under strictly controlled conditions and we found that it can act as a living catalyst for alcohol dehydrogenation as long as the atmosphere is well controlled. Thus, this type of rearrangement process is likely not involved in the catalyst decomposition pathways for ordinary alcohol and amine coupling catalytic systems, however it suggests that strained sp^3 - sp^2 carbon systems can be utilized in Ru catalyzed processes in the future.

3 Collaborations

With Magne Olav Sydnes from Stavanger University on the synthesis of new complexes with a potentially electron shuttling ligand that was developed by the Norwegian group.



With Bernd Kuhn unit on the synthesis of neuronal dyes. The dimethyl dye structure that was synthesized and successfully tested this year is presented to the right. We are exploring the possibility of further modifying the dyes to make them selective for particular cells.



Collaboration with Israel (DFT calculations) and Russia (crystallography) labs are summarized above under 'C-C rearrangement' and collaboration with the Khusnutdinova until will be summarized by that unit's annual report, with the two published papers presented below.

4 Publications and other output

- (1) Jankins, T. C.; Fayzullin, R. R.; Khaskin, E. Three-Component [1 + 1 + 1] Cyclopropanation with Ruthenium(II). *Organometallics* **2018**, *37*, 2609-2617.
- (2) Lapointe, S.; Khaskin, E.; Fayzullin, R. R.; Khusnutdinova, J. R. Stable Nickel(I) Complexes with Electron-Rich, Sterically-Hindered, Innocent PNP Pincer Ligands. *Organometallics* **2019**, *38*, 1581-1594.
- (3) Sarbajna, A.; Patil, P. H.; Dinh, M. H.; Gladkovskaya, O.; Fayzullin, R. R.; Lapointe, S.; Khaskin, E.; Khusnutdinova, J. R. Facile and reversible double dearomatization of pyridines in non-phosphine Mn(I) complexes with N,S-donor pyridinophane ligand. *Chem. Commun. (Cambridge, U. K.)* **2019**, *55*, 3282-3285.

Presentation: Khaskin E. (presenting author); Deolka, S.; Stepanova, S.; Vojkovsky, T., *Cyclopropanation of aliphatic esters and alcohols extended to one-step catalytic linear sulfone synthesis*, Japanese Society of Chemistry 99th annual meeting at Konan University, March 16-19, 2019.