

# Science and Technology Group Annual Report FY2020

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## 1 Introduction

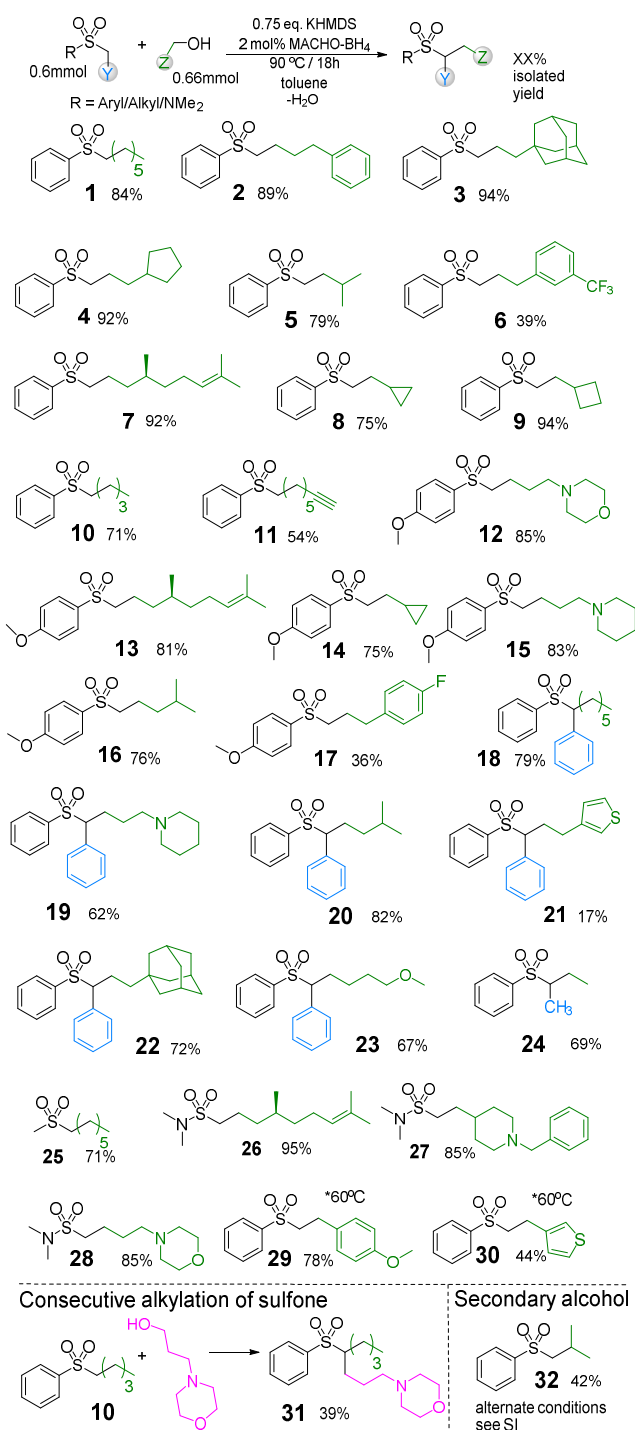
During FY2020 I published the linear sulfone catalytic chemistry that was earlier submitted to ChemArxiv. This publication appeared in the ACS journal ACS Catalysis.<sup>1</sup> A project that was started in FY2019 with my collaborator Dmitri Gusev in Canada, on unexpected reactivity of a catalyst routinely used for alcohol dehydrogenative coupling and ester hydrogenation, was also completed in the Fall of 2020 and was published in the Journal of the American Chemical Society.<sup>2</sup> I spent the rest of the year working on the second part of the collaboration, on other routinely used catalysts and their reactivity, which when examined in detail throws into doubt commonly accepted catalytic mechanisms. I published some papers with my collaborators at OIST as well. I did not go to any conferences this year due to the coronavirus and this situation may be continued in the next fiscal year as well.<sup>3-6</sup>

## 2 Activities and Findings

**Linear Sulfone summary:** We published the paper that was summarized in last year's review. Ultimately, we discovered and developed a novel, catalytic sulfone and alcohol coupling reaction that does not rely on utilizing halogen substrates which are usually more expensive and leave behind halogenated waste. By utilizing readily available alcohols, we can prepare a broad range of linear sulfone products with the only waste byproduct being water. Many of our products are liquids at ambient conditions, and they, along with the dimethyl sulfone derivatives might find use as solvents or electrolytes or as potential drug candidates in fragment screening assays. The obtained linear sulfones can also be further utilized in the Julia olefination, removing a major bottleneck in the utilization of this coupling reaction. The figure on the right is the library of substrates that was created by our catalytic method during this work.

### Modified Unexpected Catalyst behavior

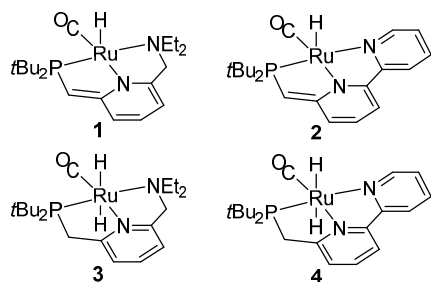
**summary:** The discovery of the ruthenium complexes **1** and **2** and the concurrent paradigm development of metal-ligand cooperation in substrate activation by ligand aromatization-dearomatization has attracted much attention and discussion in the recent literature. An important reaction of the 16-electron **1** is H<sub>2</sub> addition to give the well-characterized 18-electron dihydride **3**. Surprisingly, no experimental study of **2** has documented the analogous bipyridyl-based PNN dihydride **4**, although this complex



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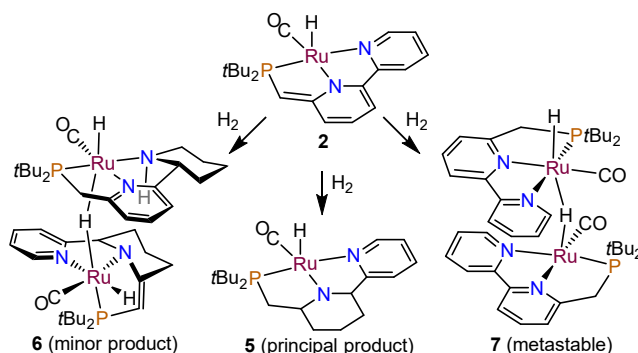
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featured prominently in the proposed mechanisms of the catalytic reactions of **2**. In our published study,<sup>2</sup> we demonstrated that **4** is an unstable species of which no direct evidence could be obtained because of facile H<sub>2</sub> loss resulting in formation of a metastable hydride-bridged dimer. Under reducing conditions, either under H<sub>2</sub> or upon heating in ethanol, the pyridine fragments of the PNN ligand are hydrogenated. The product compounds are highly active

Noyori-type catalyst for ester hydrogenation. A detailed mechanism of the catalytic ester reduction is proposed, and is supported by experiment and DFT calculations.

Our work and some previous examples, comprise substantive evidence indicating that the heteroaromatic fragments of the coordinated PN, PNN, and related polydentate ligands are susceptible to hydrogenation under reducing conditions. Theoretical studies of reactions of the metal complexes structurally related to Milstein catalyst **2**, and other similar complexes, should consider the previous studies detailing facile changes to the ligand architecture and should be supported by sufficient relevant experimental data.



### 3. Collaborations

I expect the collaboration with the Khusnutdinova group to continue as it has been very fruitful since 2019. I have recently helped synthesize a ligand that should block radical reactivity on the ligand backbone and thus stabilize low-valent Ni complexes.

The collaboration with Bernd Kuhn has led to a publication that appeared at the start of FY 2020 in April.<sup>6</sup> Me and Tomas Vojkovsky have made the first modified phosphate dye and have resolved an issue with the solubility of their workhorse ANNINE-6plus dye. I have a very interesting result with Ni for Prof Sydnes' ligand (Norway's Stavanger University), but do not have time to pursue this on my own. Hopefully the travel ban can finish soon and his student can come to help with the project.

### 4. Publications and other output

- (1) Vojkovsky, T.; Deolka, S.; Stepanova, S.; Roy, M. C.; Khaskin, E. Catalytic Sulfone Upgrading Reaction with Alcohols via Ru(II). *ACS Catal.* **2020**, *10*, 6810-6815.
- (2) Dawe, L. N.; Karimzadeh-Younjali, M.; Dai, Z.; Khaskin, E.; Gusev, D. G. The Milstein Bipyridyl PNN Pincer Complex of Ruthenium Becomes a Noyori-Type Catalyst under Reducing Conditions. *J. Am. Chem. Soc.* **2020**, *142*, 19510-19522.
- (3) Karimata, A.; Patil, P. H.; Khaskin, E.; Lapointe, S.; Fayzullin, R. R.; Stampoulis, P.; Khusnutdinova, J. R. Highly sensitive mechano-controlled luminescence in polymer films modified by dynamic CuI-based cross-linkers. *Chem. Commun. (Cambridge, U. K.)* **2020**, *56*, 50-53.
- (4) Karimata, A.; Patil, P. H.; Fayzullin, R. R.; Khaskin, E.; Lapointe, S.; Khusnutdinova, J. R. Triboluminescence of a new family of CuI-NHC complexes in crystalline solid and in amorphous polymer films. *Chem. Sci.* **2020**, *11*, 10814-10820.
- (5) Deolka, S.; Rivada-Wheelaghan, O.; Aristizabal, S. L.; Fayzullin, R. R.; Pal, S.; Nozaki, K.; Khaskin, E.; Khusnutdinova, J. R. Metal-metal cooperative bond activation by heterobimetallic alkyl, aryl, and acetylide PtII/CuI complexes. *Chem. Sci.* **2020**, *11*, 5494-5502.
- (6) Dalphin, N.; Dorgans, K.; Khaskin, E.; Kuhn, B. Voltage imaging of cortical oscillations in layer 1 with two-photon microscopy. *eneuro* **2020**, ENEURO.0274-0219.2020.