Science and Technology Group
Annual Report FY2019

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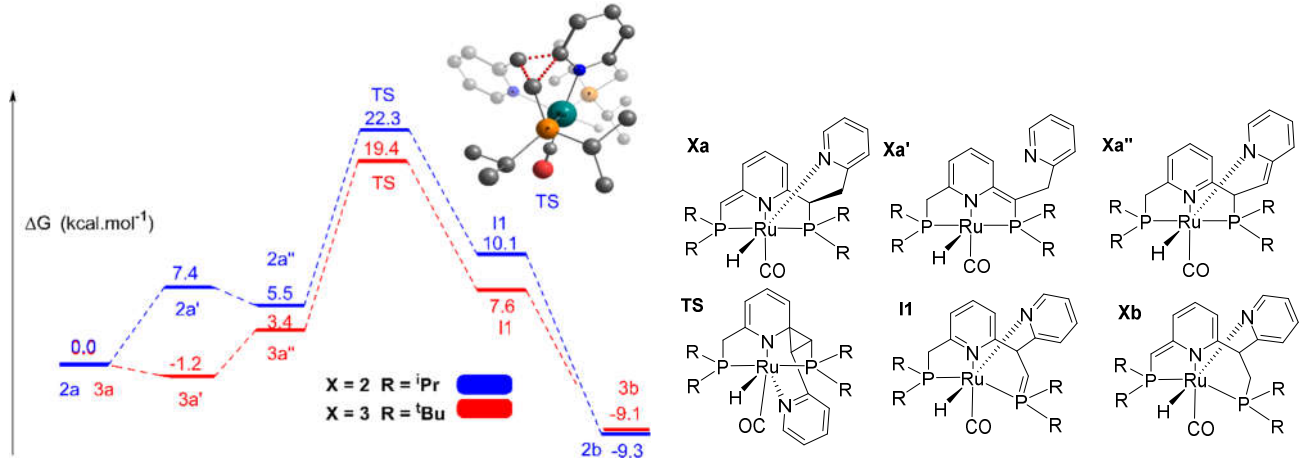
1 Introduction

During FY2019 I published the results of the C-C rearrangement study that was summarized in the FY 2018 report. [1] There was quite a bit of work done on the study by our DFT calculation collaborator from Israel which will be summarized below. This research was published in a Royal Society Journal (Chemical Communications) and the article was awarded a back cover, hopefully highlighting the research done by my lab. The linear sulfone chemistry was optimized and many new examples were synthesized. The linear sulfone work was written up for publication and submitted to the pre-print ChemArxiv server. I presented the results of the C-C rearrangement study and the general catalytic chemistry in my lab at a talk at the Markovnikov congress in Kazan, Russia (poster and talk) and a homogenous catalysis conference in Heidelberg Germany OMCOS 20 (poster). The presentations at the 100th Japanese Society of Chemistry meeting in March were cancelled due to the coronavirus. There were a number of other publications where I was not a corresponding author that came out during this time with my collaborators at OIST. [2,3]

2 Activities and Findings

C-C rearrangement summary:



As summarized last year, we explored 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 were completely inactive in alcohol dehydrogenation catalysis. This type of catalytic deactivation may be relevant to specialized alcohol substrates that contain heterocycles or heteroatoms, and shows that slight disruption of the coordination sphere can lead to dramatic effects in catalysis.
DFT and mechanistic studies suggest an intramolecular isomerization process via a spyrocycle cyclopropane intermediate, dependent upon arm pyridine coordination and ligand sterics. The figures below focus more on the DFT part, which was mostly finished in FY2019, and showed that complexes substituted with a ^{t}Bu on the phosphines could carry out this reaction at room temperature and that the most stable intermediate would be different than for the ^{i}Pr substituted complex. Accordingly, we managed to observe this intermediate by looking at the reaction in a different solvent which raised the activation barrier.

Linear Sulfone summary: Over the past year we performed optimization of the reaction that was summarized in last year's review. The extensive optimization allowed us to reach very high yields and good selectivity for the linear product that we wanted. We also were able to use sulfonamides in the reaction. Sulfones and sulfonamides are a class of valuable compounds

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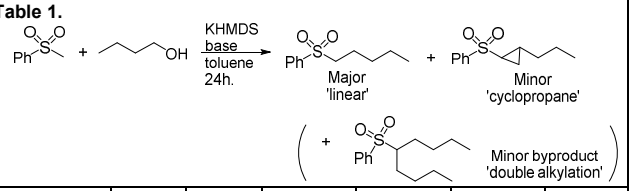
that are often used in the chemical industry, and they are a common functional group in many drugs and screening libraries. Our method enables for the synthesis of a diverse number of sulfones with bench stable and cheap reagents in one step, and creates less waste than other popular two or three step synthetic approaches. Alkyl sulfones have also recently found a use as possible electrolytic solvents in lithium ion batteries. To test scalability, we were able to show a TON of up to 3500 with 0.01 mol% catalyst loading after three days of reaction time with a 100 mol% loading of cheap base KO^{t}Bu, using our model phenyl methyl sulfone and butanol system. Shown to the left is a compiled, but not exhaustive table of our optimization results. The paper is likely to be peer reviewed and published in FY2020, at which time I will summarize the substrates that we were able to synthesize.

Table 1.



Entry/ Catalyst	mol%[a]	T °C	KHMDS (mol %)	Conc. [M] [b]	Ratio[c]	Yield %[d]
1.SNS-Ru	2	90	70	0.125	--	18
2.Ru PNN	2	90	70	0.125	--	12
3.MACHO	2	90	70	0.125	--	90
4.MACHO	1	90	120	0.125	17	73
5.MACHO	1	90	100	0.125	46	87
6.MACHO	1	90	70	0.125	60	91
7.MACHO	1	90	50	0.125	96	82
8.MACHO	1	80	75	0.125	60	91
9.MACHO	1	100	75	0.125	60	88
10.MACHO	3	90	75	0.125	103	88
11.MACHO	1	90	75	0.2	38	83
12.MACHO	1	90	75	0.1	85	73
13.MACHO	1	90	75	0.05	150	78
14.MACHO	2	90	75	0.05	202	85
15.MACHO	0.01	95[f]	100[e]	1.3	14	35
16.MACHO	0.05	90[g]	100[e]	1.2	147	76

For full optimization tables see SI. [a] mol percent catalyst based on starting sulfone; SNS-Ru-PPh3, Ru-aminePNN, and MACHO-BH4 used in entries [b] Initial concentration of phenyl methyl sulfone in toluene in M [c] ratio of linear over cyclopropane product (-- means undetermined); double alkylation minor product not included [d] Yield of linear sulfone product determined by GC/FID against internal standard mesitylene [e] KOtBu used instead of KHMDS [f] 72 h. reaction time; 3 eq. butanol [g] 48 h reaction time; 3 eq. butanol

3 Collaborations

The collaboration with the DFT group in Israel might continue on a new project on tetramethylated PNP pincer ligands and Ru(0) complexes, in 2020, depending on the experimental results.

The collaboration with Bernd Kuhn has led to a publication, likely at the very start of FY 2020 in April. I am making phosphate modified dies for his lab. As well, the previous collaboration with the Khusnutdinova unit will be continued. If Prof Sydnes' student can make it here from Norway's Stavanger University after the travel ban is eased, I expect lots publishable results there as well.

4 Publications and other output

(1) Deolka, S.; Tarannam, N.; Fayzullin, R. R.; Kozuch, S.; Khaskin, E. Unusual rearrangement of modified PNP ligand based Ru complexes relevant to alcohol dehydrogenation catalysis. *Chem. Commun. (Cambridge, U. K.)* **2019**, *55*, 11350-11353.

(2) Lapointe, S.; Khaskin, E.; Fayzullin, R. R.; Khusnutdinova, J. R. Nickel(II) Complexes with Electron-Rich, Sterically Hindered PNP Pincer Ligands Enable Uncommon Modes of Ligand Dearomatization. *Organometallics* **2019**, *38*, 4433-4447.

(3) Sarbajna, A.; He, Y.-T.; Dinh, M. H.; Gladkovskaya, O.; Rahaman, S. M. W.; Karimata, A.; Khaskin, E.; Lapointe, S.; Fayzullin, R. R.; Khusnutdinova, J. R. Aryl-X Bond-Forming Reductive Elimination from High-Valent Mn-Aryl Complexes. *Organometallics* **2019**, *38*, 4409-4419.

For presentations see 'Introduction' section