

Science and Technology Group Annual Report FY2021

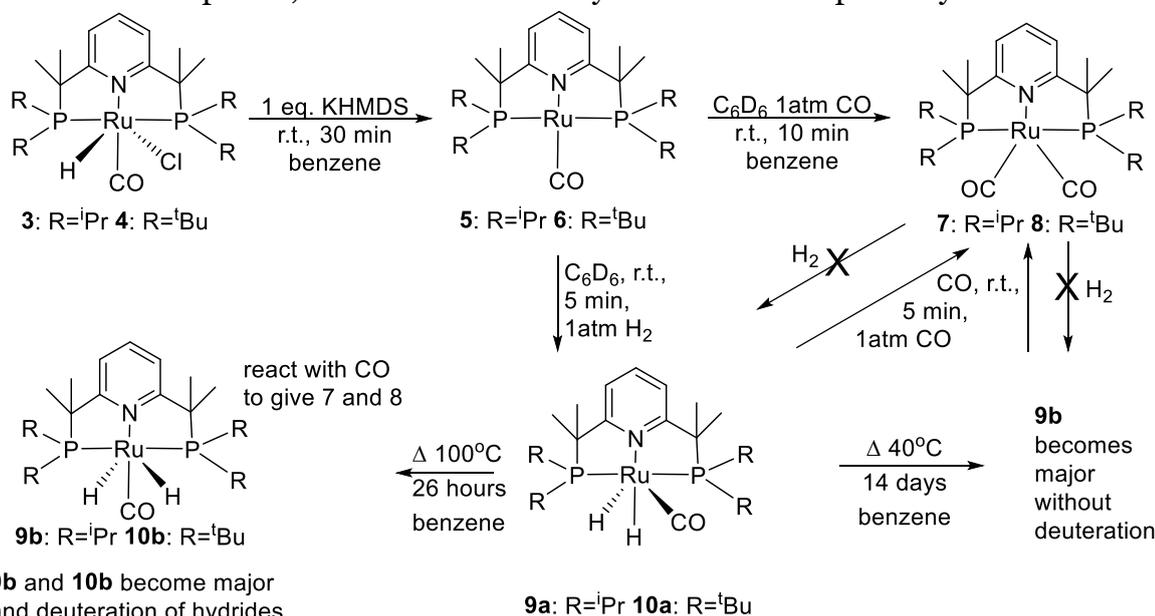
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1 Introduction

During FY2021 I published an article on the modification of pincer ligands to block metal ligand cooperation (MLC) on Ru catalysts. The article earlier appeared on ChemRxiv and was published online at the end of 2021 in Chemistry: A European Journal. ¹ MLC was assumed to be an important process for substrate activation that enabled dehydrogenative coupling of alcohols and amines to form esters and/or amides. Our findings showed that the catalytic reaction could take place even in the absence of MLC. However, this was an expansive work where we also studied the activation of small molecules with the new complexes that we made and found that the new ligands that blocked MLC allowed us to access the Ru(0) oxidation state, which is unusual in pincer Ru catalysts. This work was first started many years ago, and as it led to a complicated picture, it took going back to the project several times over the years to achieve a complete story. I also published other papers with my OIST collaborators. ²⁻⁵ My work with the collaborators varied from measuring and solving crystal structures, to more important contributions in the writing of parts of the papers and designing and carrying out some of the experiments.

2 Activities and Findings

We synthesized two 4Me-PNP ligands which block metal-ligand cooperation (MLC) with the Ru center and compared their Ru complex chemistry to their two traditional analogues used in acceptorless alcohol dehydrogenation catalysis. The corresponding 4Me-PNP complexes, which do not undergo dearomatization upon addition of base, allowed us to obtain rare, albeit unstable, 16 electron mono CO Ru(0) complexes. Reactivity with CO and H₂ allows for stabilization and extensive characterization of bis CO Ru(0) 18 electron and Ru(II) cis and trans dihydride species that were also shown to be capable of C(sp²)-H activation. Reactivity and catalysis are contrasted to non-methylated Ru(II) species, showing that an MLC pathway is not necessary, with dramatic differences in outcomes during catalysis between ⁱPr and ^tBu PNP complexes within each of the 4Me and non-methylated backbone PNP series being observed. Unusual intermediates were characterized in one of the new and one of the traditional complexes, and a common catalysis deactivation pathway was identified.



Scheme 1. Synthesis of Ru(0) complexes and their subsequent reactivity.

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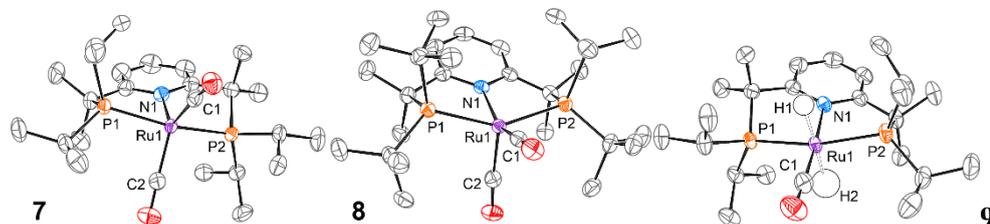
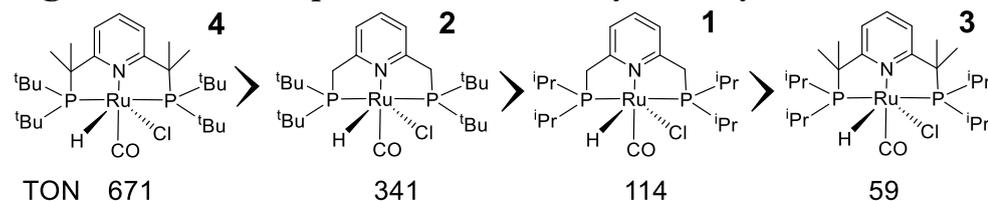


Figure 1. Ru(0) complexes and Ru(II) dihydride crystals structures



Scheme 2. Activity of synthesized complexes in catalysis.

In comparing ADC catalysis, we found that all four complexes performed differently, and no specific trend could be discerned (Scheme 2). In ethanol model reactions, complex **2** was, in contrast to the other three species, uniquely transformed to a hydrogenated backbone complex **18**, which is the first example of a 16 electron Ru(II) complex that is stable in ethanol solution. The other three complexes gave acetate species as the major products, hinting at a common deactivation pathway by alcohol disproportionation (Guerbet process). However, all reactions also gave a number of species that cannot be conclusively identified, highlighted by the isolation of the unusual Ru cluster **19** from solutions of **4**.

3 Collaborations

I'm continuing my collaboration with the Khusnutdinova and Kuhn units, and trying to keep up with my foreign collaborations: Sydnese Group in Norway, Dmitry Gusev in Canada, and Sebastian Kozuch in Israel, despite the travel ban due to the coronavirus. In FY2022, I may be able to get some of the collaborators to visit me and this should result in a collaborative work being published.

4 Publications and other output¹⁻⁵

Author list, *Title*, Journal or other reference, volume information (year)

- (1) Deolka, S.; Fayzullin, R. R.; Khaskin, E. Bulky PNP Ligands Blocking Metal-Ligand Cooperation Allow for Isolation of Ru(0), and Lead to Catalytically Active Ru Complexes in Acceptorless Alcohol Dehydrogenation. *Chem. - Eur. J.* **2022**, *28* (4), e202103778.
- (2) Deolka, S.; Govindarajan, R.; Khaskin, E.; Fayzullin, R. R.; Roy, M. C.; Khusnutdinova, J. R. Photoinduced Trifluoromethylation of Arenes and Heteroarenes Catalyzed by High-Valent Nickel Complexes. *Angew. Chem., Int. Ed.* **2021**, *60* (46), 24620.
- (3) He, Y.-T.; Karimata, A.; Gladkovskaya, O.; Khaskin, E.; Fayzullin, R. R.; Sarbajna, A.; Khusnutdinova, J. R. C-C Bond Elimination from High-Valent Mn Aryl Complexes. *Organometallics* **2021**, *40* (14), 2320.
- (4) Lapointe, S.; Pandey, D. K.; Gallagher, J. M.; Osborne, J.; Fayzullin, R. R.; Khaskin, E.; Khusnutdinova, J. R. Cobalt Complexes of Bulky PNP Ligand: H₂ Activation and Catalytic Two-Electron Reactivity in Hydrogenation of Alkenes and Alkynes. *Organometallics* **2021**, *40* (21), 3617.
- (5) Rivada-Wheelaghan, O.; Deolka, S.; Govindarajan, R.; Khaskin, E.; Fayzullin, R. R.; Pal, S.; Khusnutdinova, J. R. Construction of modular Pd/Cu multimetallic chains via ligand- and anion-controlled metal-metal interactions. *Chem. Commun. (Cambridge, U. K.)* **2021**, *57* (79), 10206.