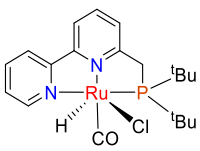
Science and Technology Group Annual Report FY2025

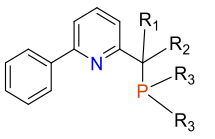
Eugene Khaskin

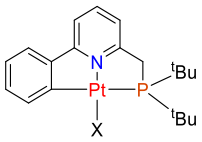
1 Introduction

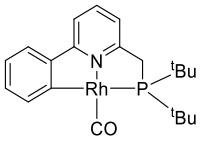
During FY2025, as my main research output I published two articles as a corresponding author. One is a long-standing collaboration with Dmitri Gusev, where we detailed how substituting the bipyridine core for a phenanthroline on the ligand backbone gives an interesting hydrogenation pattern of the complex under ester hydrogenation catalytic conditions, but catalysis is shut down. We also argued that it's hydrogenation of the outer ring of the bipyridine catalyst that causes the highest activity and we plan to prepare this complex in the future. [1] The second article started from a mistake in the identity of metal precursors when making a new complex. I discovered that Pt, unexpectedly, made an air-stable complex with a PNC pincer ligand, and the published paper was the culmination of the work of two interns who worked with me three months each. They are co first-authors on the resulting paper. It is this work that will be discussed (mostly pictorially) in more detail below. [2] There were also three more publications where I was a co-author. [3-5]

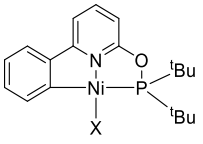
2 Activities and Findings

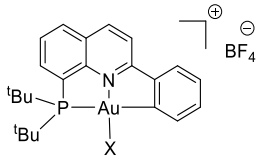






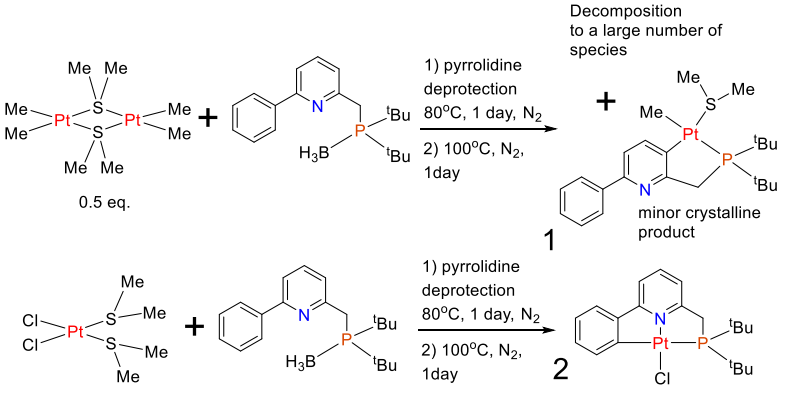


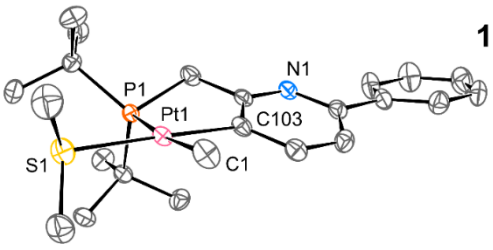


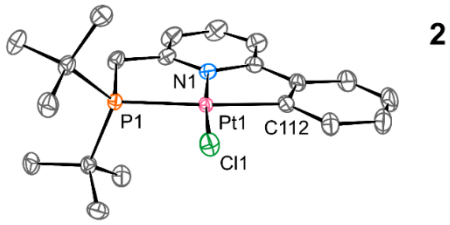


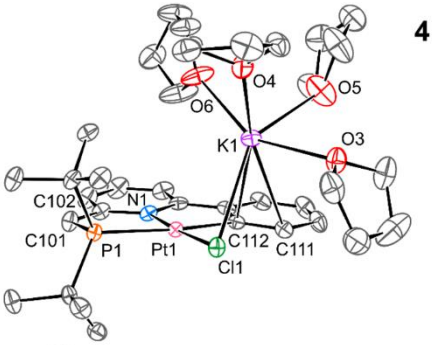
The PNC ligand motif, like other de-aromatizable ligands explored by us, can be easily modified via out protecting group synthetic strategy. It has been reported by van der Vlugt and Klein. While the initial plan was to use it for Ru ester hydrogenation, a side project on Pt, and possible CH activation chemistry, developed (after using the wrong metal precursor) to explore coordination chemistry.

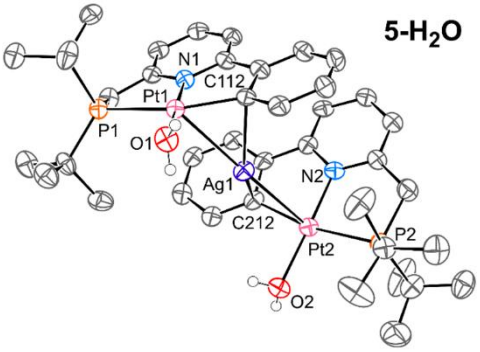
Pt-Me precursor fails; Pt-Cl succeeds











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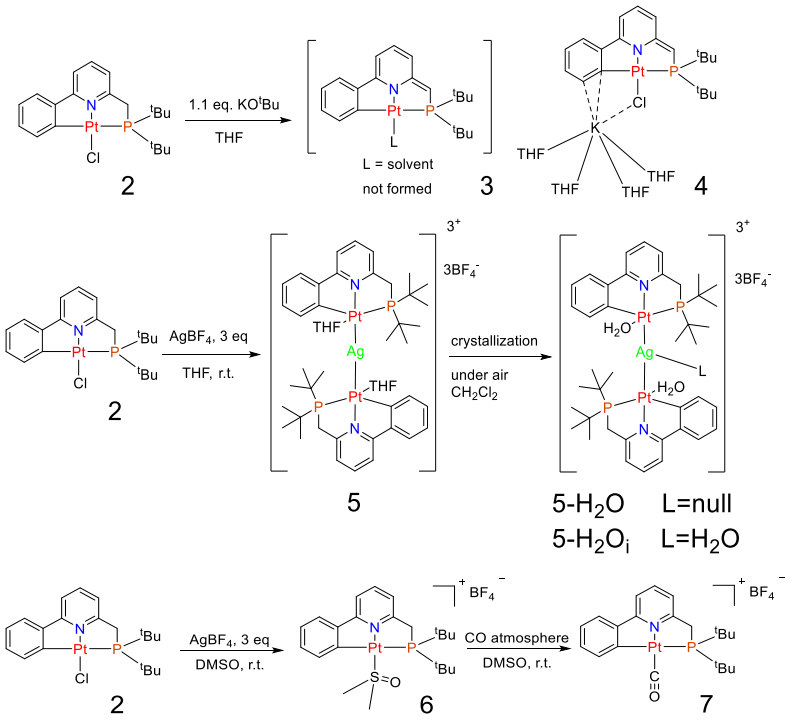
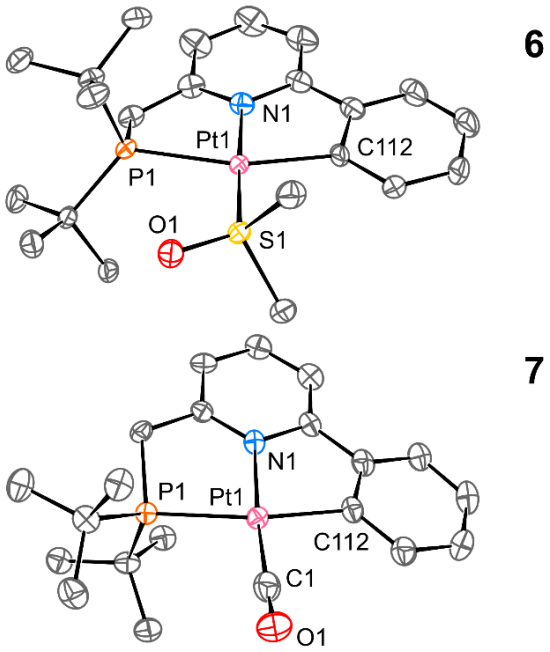
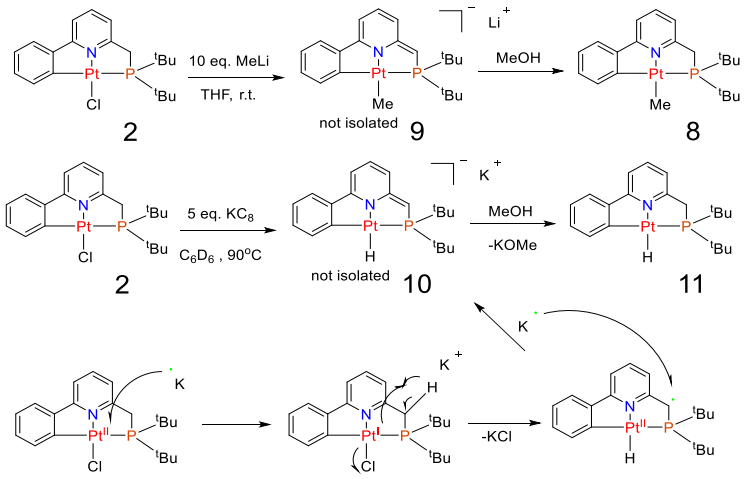
'Weakly bound' L ligand doesn't leave…

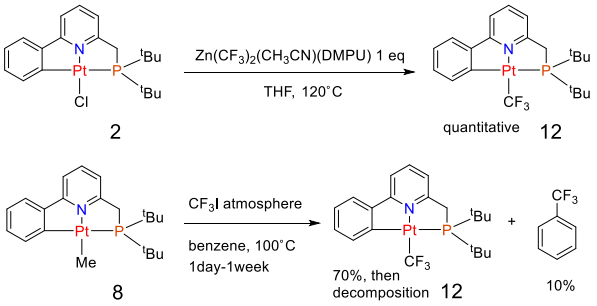




CH$_3$ and H complexes synthesized (no CH activation…)



(sub)-Stoichiometric CH activation



3 Collaborations

My work with OIST collaborators this year (besides the Gusev Paper), included publications 3-5 in the list below, where in the first one my contribution including the measuring of X-ray crystal structures, while in the second I designed the ligand and contributed heavily to the editing of the paper and certain concepts. In the final paper I measured X-ray structures and contributed to the editing of the paper.

I am continuing my collaboration with Dmitri Gusev, which should culminate in the publication of one of the best (highest TON; lowest temperature) ester hydrogenation catalyst reported in the literature sometime in the near future according to preliminary results. In FY2026, I will also likely work with interns on the PNC-Pt project, and this may lead to a new collaboration with the Magne Sydnes group in Norway.

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4 Publications and other output

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

(1) Sherstiukova, D. B.; Dawe, L. N.; Khaskin, E.; Gusev, D. G. Complex Speciation of bipy- and phen-NNP Pincer Complexes of Ruthenium under Catalytic Ester Reduction Conditions. *ACS Catal.* **2025**, *15* (18), 16094-16105.
(2) Losev, M. A.; Yessengazin, A.; Fayzullin, R. R.; Khaskin, E. Synthesis of a series of PNC pincer ligand-supported Pt complexes, and an initial exploration of their reactivity. *Dalton Trans.* **2025**, *54* (36), 13712-13721.
(3) Karimata, A.; Ilatovskii, D.; Fayzullin, R. R.; Komoto, S.; Bruhacs, A.; Khaskin, E.; Khusnutdinova, J. R. Mechanoluminescence from amorphous solids of heteroleptic copper complexes and common luminophores induced by non-destructive mechanical stimuli and fabrication of flexible mechanoluminescent films. *Chem. Sci.* **2025**, *16* (47), 22376-22386.
(4) Pandey, D. K.; Gridneva, T.; Khaskin, E.; Fayzullin, R. R.; Vasylevskyi, S.; Khusnutdinova, J. R. Distinct reactivity of iron dihydride vs. iron(hydride)(borohydride) bearing the same bulky PNP ligand in hydrogenation of alkenes and alkynes. *Dalton Trans.* **2025**, *54* (39), 14809-14820.
(5) Sorvanov, A.; Deolka, S.; Khaskin, E.; Fayzullin, R. R.; Vasylevskyi, S.; Khusnutdinova, J. R. Self-Assembly of a Customizable Library of Nickel Trifluoromethylation Catalysts via Selective CF and CO Bond Cleavage. *Angew. Chem., Int. Ed.* **2025**, *64* (32), e202509042.