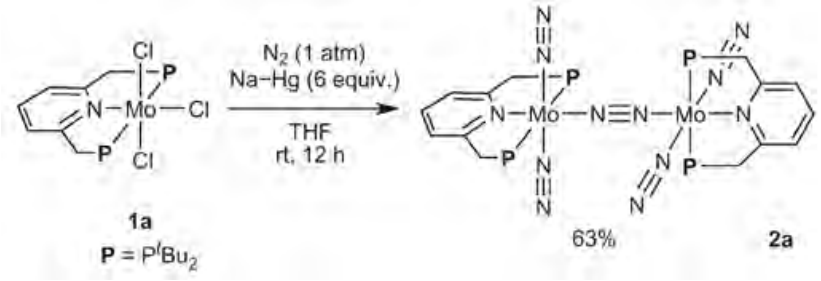
Emma Farley/Yoshiaki Nishibayashi

Research: the synthesis of transition metal complexes for catalysis.

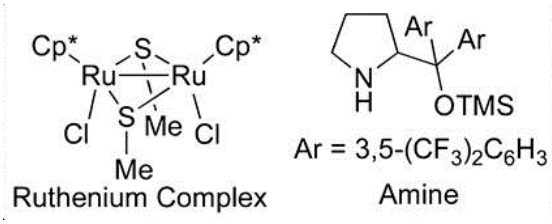
Professor Nishibayshi's research group focuses on the design of transition metal complexes for use as catalysts. His two main areas of synthetic interest are nitrogen fixation and development of catalytic systems for the synthesis of complex organic molecules.

The search for a method for transition-metal-catalyzed nitrogen fixation stems from a desire to replace the costly Haber-Bosch process, which requires high temperatures and pressures, with a catalytic reaction that could be performed at ambient conditions. Inspiration for this comes from nature: nitrogen-fixing bacteria do so at ambient temperature and pressure in the soil with the aid of a metallic FeMo-cofactor. The mechanism of biological nitrogen fixation is unknown, but the Nishibayashi group has successfully designed several molybdenum- and iron- based catalysts for the conversion of dinitrogen into both ammonia and silylamines: the catalyst used for the former process is shown below.



Synthesis of catalyst **2a** for catalytic nitrogen fixation (figure 1 from *Nature Chemistry* **2011**, *3*, 120-125.)

The Nishibayashi group has also constructed catalytic systems for the synthesis of complex organic compounds, including propargylic allylation of propargylic alcohols. In this case they linked two catalytic cycles, one transition metal catalyzed, one organocatalyzed, to synthesize allylated products selectively and in high yields. A ruthenium complex (below) was used to activate the propargylic alcohol towards allylation by an a,b-unsaturated aldehyde, which in turn activated by its conversion into an enamine by reaction with the aminocatalyst below.



Catalysts used by the Nishibayashi group (abstract in *Organometallics,* **2012**, *31*, 3810-3813.)

1. Cooperative catalysis: http://pubs.acs.org/doi/abs/10.1021/om300286b
2. Catalytic nitrogen fixation I: http://www.nature.com/nchem/journal/v3/n2/full/nchem.906.html
3. Catalytic nitrogen fixation II: http://pubs.acs.org/doi/abs/10.1021/ja109181n