Young Career Focus: Professor Johanna Blacquiere (Western University, Canada)

Background and Purpose. SYNFORM regularly meets young up-and-coming researchers who are performing exceptionally well in the arena of organic chemistry and related fields of research, in order to introduce them to the readership. This Young Career Focus presents Professor Johanna Blacquiere (Western University, Canada).

Biographical Sketch

Prof. J. Blacquiere

Johanna Blacquiere was born and raised on Prince Edward Island, Canada. She obtained a B.Sc. with an Honours in Chemistry from Mount Allison University (Canada) in 2005, during which she completed research with Steve Westcott. She then completed a summer research position at Los Alamos National Laboratory (USA) under the supervision of Tom Baker. She obtained her Ph.D. at the University of Ottawa (Canada) with Deryn Fogg on the design of ruthenium complexes for olefin metathesis and N_2 activation. She was an NSERC postdoctoral fellow in the laboratory of Jim Mayer at the University of Washington (USA). In 2013, she began her independent career at Western University (Canada) and in 2019 she was promoted to Associate Professor.

INTERVIEW

SYNFORM *What is the focus of your current research activity?*

Prof. J. Blacquiere Our goal is to design, understand, and deploy transition-metal catalysts toward the synthesis of valuable organic targets. We prioritize reactions that do not require additives and that generate minimal waste. In this vein, we have designed catalysts for selective alkyne hydrofunctionalization, and acceptorless dehydrogenation of amines.

SYNFORM *When did you get interested in synthesis?*

Prof. J. Blacquiere In the first year of my undergraduate degree at Mount Allison University, I got the opportunity to volunteer in Steve Westcott's research lab. The research group was called the Wild Toads and it was a fun and inspiring training ground for undergrad researchers. I was intending to do a biology degree, but by the end of second year I'd switched to chemistry and I spent the next two summers doing research with the Wild Toads! I loved that we were exploring new chemical space, that understanding experimental outcomes was like solving mysteries, and that there's a lot of creativity in synthesis.

SYNFORM *What do you think about the modern role and prospects of organic synthesis?*

Prof. J. Blacquiere I think that it's imperative that chemists are central players in reducing anthropogenic environmental impacts. This should certainly include new synthetic methodologies that allow for more abbreviated and less wasteful routes to high-value molecules, like pharmaceuticals. It should also include many other areas, like the synthesis of new classes of monomers for degradable polymers, or catalysts that can harness abundant small molecules, such as O_2, as chemical feedstocks. It's exciting that central to many of these grand practical challenges are basic questions about cleavage/formation of bonds, and strategies that may shift the paradigm of conventional chemical reactivity.

SYNFORM *Could you tell us more about your group's areas of research and your aims?*

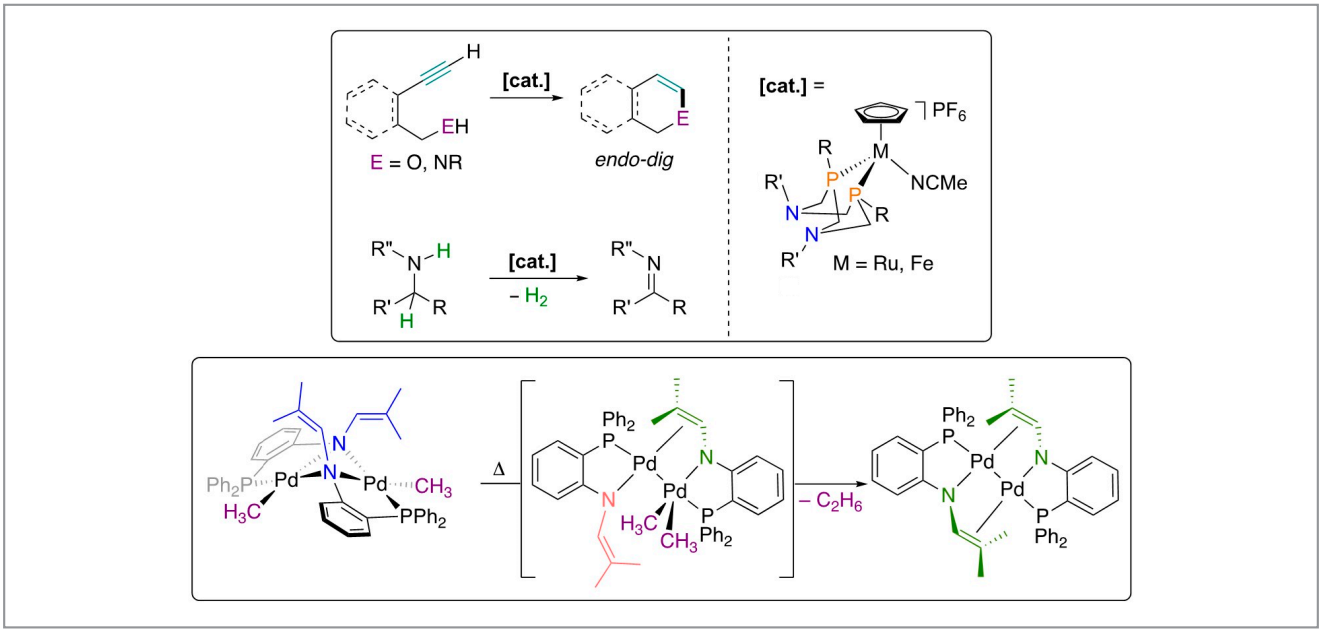
Prof. J. Blacquiere We study cooperative metal ligand reactivity, behaviour which we exploit in catalysis for the construction of synthetically valuable functionalities. We have predominantly focused on two types of cooperative ligands.

 Synform **2023/03**, A49–A50 • Published online: February 13, 2023 • DOI: 10.1055/s-0040-1720588

First, we have extensively explored catalysts with $P^{R}_{2}N^{R'}_{2}$ ligands, bisphosphines with pendent tertiary amine groups, that can shuttle protons to/from the metal and/or the organic substrate (Scheme 1, top). Since the ligand can mediate proton transfer steps, exogenous Brønsted base additives are eliminated as a reaction component. We've exploited this type of catalyst structure toward hydrofunctionalization of alkynes and acceptorless dehydrogenation of amines. Second, we have designed a phosphine 1-azaallyl ligand that can readily and reversibly change coordination mode, which induces metal-based reactivity (Scheme 1, bottom). We have shown that the ligand induces metal–metal synergy through a dinuclear reductive elimination pathway, and it can readily stabilize operationally unsaturated complexes. We are excited to exploit both of these features in catalysis.

SYNFORM *What is your most important scientific achievement to date and why?*

Prof. J. Blacquiere Our mechanistic study of C–C reductive elimination from a dinuclear palladium complex (Scheme 1, bottom). This was the outcome of a valuable collaboration between Kyle Jackman, who recently completed his PhD and who did all the experimental work, and Guangchao Liang, a postdoc with Paul Zimmerman (UMichigan, USA), who studied the reaction computationally. The mechanism involved alkyl transfer from one palladium centre to the other followed by reductive elimination from one palladium atom, all within a dinuclear framework. This mechanism is distinct from the vast majority of bond-forming steps mediated by palladium, which occur from mononuclear compounds. Integral to the dinuclear pathway was our phosphine 1-azaallyl ligand that can bridge metals through several different coordination modes. More critically, the capacity of the ligand to readily and reversibly switch between coordination modes facilitated C–C reductive elimination over a competing C–H activation pathway. There are many other examples in the literature of reactions promoted by ligands with dynamic coordination chemistry. Yet, as synthetic chemists, we most often design and exploit ligands that are rigid and that have a static coordination mode. Such ligands have led to enormous success in many areas of catalysis, but a complementary approach with dynamic ligands could open new and unusual catalytic methodologies.



Scheme 1 Catalytic intramolecular hydrofunctionalization of alkynes and acceptorless dehydrogenation of amines, promoted by ruthenium or iron cooperative catalysts (top). C–C reductive elimination from a dinuclear palladium complex, induced by changes in the coordination mode of the phosphine 1-azaallyl supporting ligand (bottom).

