

## Research Summary

Society remains tied to fossil fuels while increasing pressure on the climate suggests a transition to renewable energy resources. However, the efficiency of processes enabling such a transition has considerable room for improvement. Relevantly, natural systems have evolved enzymes that enable a very efficient conversion of small molecules such as H<sub>2</sub>, CO and CO<sub>2</sub>,<sup>1</sup> and perform these conversions more selectively and under milder conditions than current industrial processes. Many of these enzymes rely on multimetallic, and often heterometallic, active sites of abundant transition metals, for example in [NiFe] or [CuMo] carbon monoxide dehydrogenases.<sup>2</sup> In addition, close proximity between metal centers in multimetallic compounds is considered favorable to the occurrence of enhanced catalytic properties for a variety of reactions.<sup>3</sup> Thus, I studied the synthesis and properties of homogeneous bimetallic complexes of abundant, primarily first-row transition metals during my Link Foundation Energy Fellowship.<sup>4</sup>

A first component of the work supported by the Link Foundation Energy Fellowship involved the design and synthesis of a binucleating ligand that allows the selective synthesis of heterobimetallic complexes. Building on the Tilley group's previous work on dicopper complexes supported by a symmetrical naphthyridine-based ligand,<sup>5</sup> a related, unsymmetrical ligand platform that holds the metals in close proximity and features open or reactive coordination sites for both metals was designed and synthesized. This ligand features a dipyridyl binding pocket on one side (similar to that of previously reported symmetrical ligands) and a single coordinating phosphine on the other side. The presence of two very different binding sites (different coordination numbers and coordinating atoms) allowed the synthesis of a series of isostructural heterobimetallic complexes of abundant first-row transition metals, involving combinations of Cu<sup>I</sup> and M<sup>II</sup> (M = Mn, Fe, Co, Ni, Cu, Zn). Moreover, this synthesis is highly selective for the heterobimetallic complexes of interest compared to homometallic combinations, as evidenced through a variety of experimental characterization techniques such as NMR, cyclic voltammetry, ESI-MS and anomalous X-ray diffraction measurements. These results were presented at the 253<sup>rd</sup> ACS National Meeting (April 2017) and published in *Chemistry – A European Journal* (June 2018).<sup>6</sup>

A second component focused on how an unsymmetrical ligand environment would influence the reactivity at homobimetallic active sites, potentially allowing for differentiated electronic environments between the two metal centers which could in turn lead to increased catalytic activity. Again, building on previous Tilley group results on the use of symmetrical dicopper complexes in alkyne-azide cycloaddition catalysis (CuAAC, also called "click" reaction),<sup>7</sup> the potential of related unsymmetrical dicopper complexes was studied. Using the newly designed unsymmetrical ligand described earlier, a dicopper(I) complex was prepared. This complex performs an unusual activation of a tetraarylborate anion to yield a highly reactive phenyl-bridged dicopper complex.<sup>8</sup> The latter species was then used to activate a terminal alkyne, resulting in a dicopper alkynyl complex that proved to be an active CuAAC catalyst. Moreover, this unsymmetrical catalyst is more active than its symmetrical counterpart, performing the reaction an order of magnitude faster under identical conditions (concentration, temperature, catalyst loading). These results were presented at the 256<sup>th</sup> ACS National Meeting (August 2018) and are expected to be published in a peer-reviewed journal during the 2018 – 2019 academic year.

These two studies contribute to a better understanding of how symmetry (or the lack thereof) influences the reactivity and ultimately catalytic activity of multimetallic sites, providing tools to understand and rationally tune industrial catalysts in order to improve their efficiency. Notably, relatively few studies involve a platform that allows the systematic variation of metal precursors used to selectively provide a wide range of heterobimetallic combinations of coordinatively unsaturated

metal atoms, sterically allowing the coordination of small molecules and, ideally, their conversion into higher-value products (more complex chemicals or fuels).

Moreover, these two studies lay the foundation for additional investigations of these unsymmetrical systems. A few of them involve homobimetallic complexes, as they are relatively easier platforms to study. One goal is to study the underlying reasons behind the difference in catalytic rates observed for the click reaction catalysts (both through mechanistic and computational investigations). Moreover, preliminary results indicate differences in stability and reactivity of these dicopper complexes based on the ligand platform used; another future direction that will be actively investigated is the rational tuning of the ligand environment to maximize activity and minimize decomposition processes. This ligand optimization is also key to a better understanding of the reactivity of heterobimetallic complexes, which is another major future direction building on the results described above. Eventually, the study of more catalytically-relevant heterobimetallic combinations will also be investigated.

## References

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### Link Foundation Energy Fellowship Outcome

The Link Foundation Energy Fellowship granted to Amelie Nicolay helped support the following scholarly publications and presentations, and is/was acknowledged in the following:

#### Presentations:

- Synthesis, structure and reactivity of homo- and heterobimetallic complexes, *Graduate Research Seminar*, University of California, Berkeley, 9/29/2016
- Synthesis, structure and reactivity of homo- and heterobimetallic complexes, *253<sup>rd</sup> ACS National Meeting*, San Francisco, CA, 4/6/2017
- Unsymmetrical dicopper complexes: synthesis and enhanced reactivity, *256<sup>th</sup> ACS National Meeting*, Boston, MA, 8/22/2018
- Synthesis and Reactivity of Dicopper Catalysts, *Chemical Sciences Division Seminar*, University of California, Berkeley, 9/19/2018

#### Publications:

- Selective Synthesis of a Series of Isostructural  $M^I Cu^I$  Heterobimetallic Complexes Spontaneously Assembled by an Unsymmetrical Naphthyridine-Based Ligand, A. Nicolay, T. D. Tilley, *Chem. Eur. J.* **2018**, *24*, 10329.
- Unsymmetrical dicopper complexes: synthesis and enhanced reactivity, A. Nicolay, T. D. Tilley *et al.*, *in preparation*.

The Link Foundation Energy Fellowship helped me keep perspective in my research, actively focusing on studying models for small molecule transformations. It gave me the freedom to steer my research following my own interests, growing as an independent researcher, and to frame my fundamental organometallic work in the field of sustainable energy. In addition, the financial support provided by the Link Foundation was a major help to travel and attend conferences.