

Progress Report – Year 3

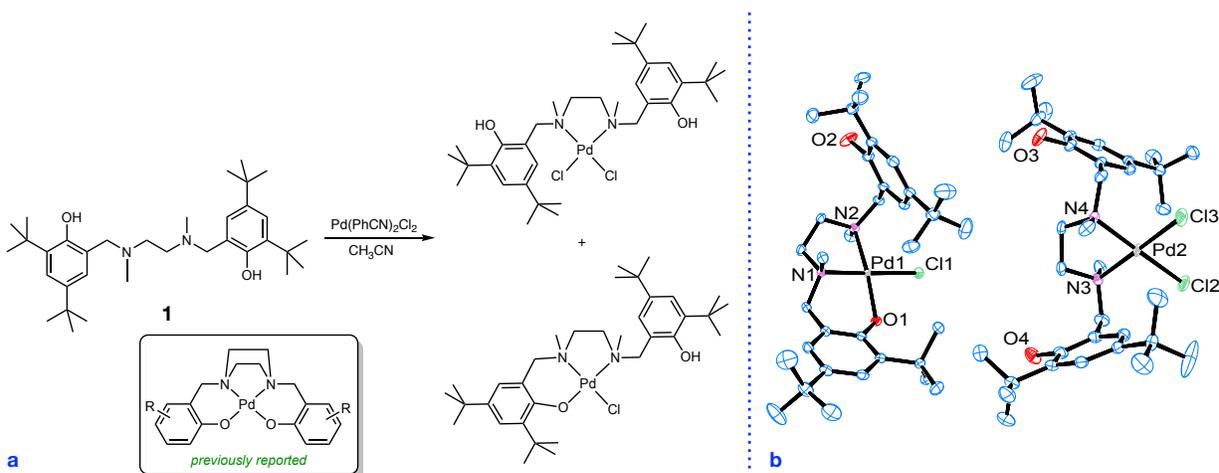
Overview

In year 3 of this grant, the Wile group continued to investigate the transition metal chemistry of the previously reported amine bis(phenolate) ligands. Our studies included a detailed investigation of the solid state structure of a mixed-coordination Pd(II) complex, and a synthesis and characterization of a series of novel Mn complexes. The results of the first study were communicated in a peer-reviewed publication, and the results of the second study are currently in the final stages of preparation for submission as a research article. Undergraduate student researchers supported by this PRF grant will serve as co-authors on all publications and posters related to this work.

Progress in Year 3

We have previously reported that palladium(II) complexes of pendant amine bis(phenolate) ligands adopt both κ^2 -N,N and κ^3 -N,N,O binding modes, based in part on the substitution pattern of the phenolate moieties. In contrast, related Pd(II) complexes (Scheme 1a) have been observed to adopt a κ^4 coordination mode. Seeking to determine which structural motif would dominate, our group investigated Pd complexes of the closely related bridging amine bis(phenolate) ligands (Scheme 1). Interestingly, single crystals of the compound isolated from the reaction of **1** with $(\text{PhCN})_2\text{PdCl}_2$ revealed both κ^2 -N,N and κ^3 -N,N,O coordination modes in the unit cell. We conducted a detailed structural analysis of this complex, and reported the results in a recent publication.

One implication of this observation is that in solution, ligand coordination modes can interconvert, suggesting that these amine bis(phenolate) ligands may operate as hemilabile donors. ^1H NMR spectra are a useful probe of complex speciation in solution. Upon coordination of a phenolate moiety, the methylene H's are rendered diastereotopic, and distinct from the methylene unit of the unbound arm. Thus, students can easily assess the extent of ligand binding in solution without the need for single crystals. Our group plans to continue working with our computational collaborator Dr. Trilisa Perrine (ONU) to better understand the energetic surface for these Pd(II) complexes. Initial calculations for this system include geometry optimization of free ligands, Ti(IV) complexes, and select Pd(II) complexes, and were conducted by former students in year 1 of this project. pH dependent binding has the potential to generate tunable complex behavior; our group is investigating applications of this phenomenon.



Scheme 1. a) Formation of Pd(II) complexes of a bridging amine bis(phenolate) ligand, and previously reported κ^4 Pd(II) amine bis(phenolate) complex (inset). b) ORTEP representation (displacement ellipsoids at 50% probability) of the two observed Pd(II) complexes of ligand **1**.

In addition, our group has investigated Mn complexes bearing a selection of the amine bis(phenolate) ligands featured in our palladium work. Overall, these species display coordination behavior similar to related Fe and Cr species. We are currently completing data collection for this set of novel compounds, including single crystal X-ray diffraction data, electronic spectra, and magnetic data for these paramagnetic species. These data offer insight to the electronic structure of these species. We are currently exploring applications of these complexes as magnetic

materials, and a manuscript describing these efforts is in the final stages of preparation. The Wile group will continue these studies beyond this grant period, with ligand elaboration to follow based on initial findings.

Impact on Students and Dissemination of Results

These findings have been reported at the 257th ACS national meeting in Orlando, FL, the 258th ACS national meeting in San Diego, CA, and the 50th ACS central regional meeting in Midland, MI, and in a research article published in *Acta Crystallographica* (2019, E75, 1265-1269). The first author of this publication is former student Brendan Graziano, whose work was supported by this grant. Notably, Brendan was also the first author on a previous publication from my group describing work supported by this grant in year 2. Brendan is currently a graduate student in an inorganic chemistry Ph.D. program, and this publication will demonstrate his continued impact on research in this field and at ONU. Former research students Nathaniel McCutcheon and Nicole Braunscheidel presented separate posters describing their senior research projects supported by this grant at the ACS meeting in Orlando. Nathan is currently a first year graduate student in inorganic chemistry, and Nicole is a first year graduate student in computational chemistry. Both students cited their ability to explore their research interests and their co-authorship on a previous publication (describing work supported by this grant in year 2) as key factors in their decision to pursue graduate degrees in the schools of their choice. Other former students supported by this grant are enrolled in a biochemistry graduate program, and pursuing chemistry BS and BA degrees at ONU, respectively.

This year, three students conducted summer research related to this project under my supervision. Hannah Morgan and Christina Bowen both completed their freshman year at ONU prior to starting their summer research projects. Although their learning curve has been steep, both students were extremely capable, and have generated significant results. Both students have expressed an interest in continuing to conduct research during their sophomore year. Victoria Ternes returned to my lab this summer, following her sophomore year at ONU. In addition to building on her previous lab experience, Vicki was able to take on a mentorship role for the more junior members of the lab. In all cases, these students had a chance to explore several research projects, asking questions, directing their short term efforts, and proposing new areas of interest based on their findings. No students are conducting research in the Wile lab during the fall semester while I am on sabbatical, but I continue to have requests to discuss research opportunities for the spring semester. I expect all of these students will serve as co-authors on manuscripts or posters describing their research efforts.

This PRF grant has allowed me the opportunity to pursue this research agenda, and facilitated conversations with a number of collaborators in the area. Characterization data for some complexes were obtained at Purdue University (X-ray), the Ohio State University (EPR), and Davidson College (HRMS data). During my sabbatical, I have begun investigating potential applications for these and related complexes at the University of Toledo. While early, I believe this interaction will allow me to expand my expertise in the applications of these and related metal complexes. I expect my future efforts to have a greater emphasis on catalytic and materials applications of the complexes we explored through this grant, and plan to pursue funding opportunities to support this. On a local level, my institution has continued to value the presence of funded undergraduate research opportunities such as those funded by this grant. PRF support has allowed me to leverage additional support for new laboratory initiatives (supplies) during the academic year in the form of a small Dean's research grant. Overall, PRF funding has been highly beneficial to my research agenda, and supported research activities for nine undergraduate students.