

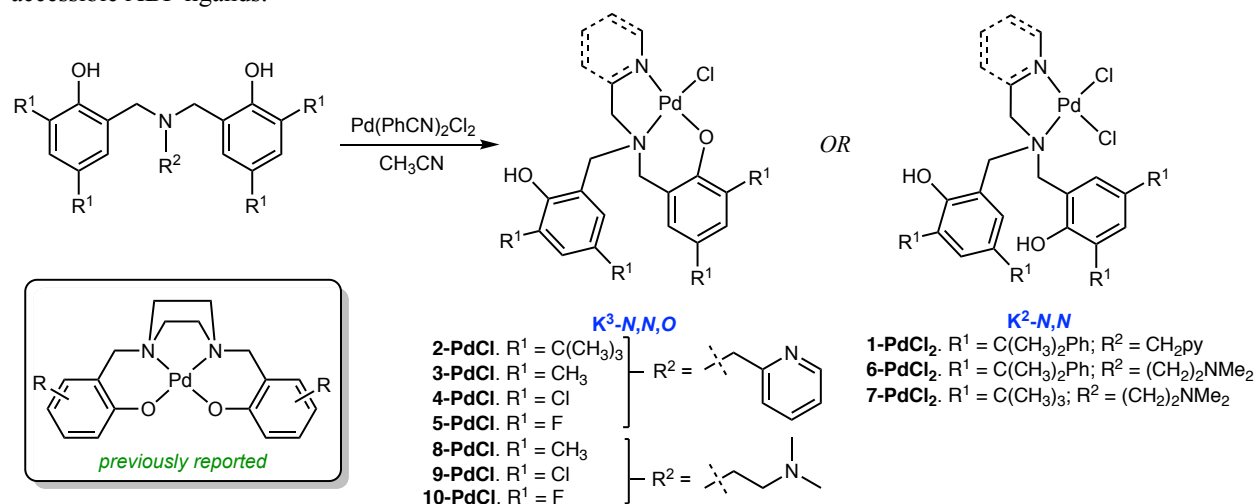
Progress Report – Year 2

Overview

In year two of this grant, our group completed characterization of a series of amine bis(phenolate) (ABP) palladium complexes featuring pendant amine donors. Through a combination of solution and single-crystal X-ray diffraction studies, the presence of both $\kappa^2\text{-N,N}$ and $\kappa^3\text{-N,N,O}$ binding modes was observed for these square planar complexes. For complexes with sterically less demanding phenolate donors, addition of external acidic or basic reagents allows for the selective masking of a coordination site at Pd. Complexes bearing bulky cumyl substituents on phenolate donors were found to exhibit unusual ^1H NMR spectroscopic features that are consistent with an anagostic interaction with the palladium center. These results have been reported in the literature and at national and local meetings.

Progress in Year 2

Palladium(II) complexes of these ligands may be readily prepared using equal molar quantities of $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ and the appropriate diprotic ligand in anhydrous acetonitrile (Scheme 1). Full characterization of these species using a combination of ^1H , ^{13}C , ^{19}F , and 2-dimensional NMR, IR, melting point, elemental analysis, and in some cases single crystal X-ray diffraction supported the assignments as shown in scheme 1. The $\kappa^2\text{-N,N}$ -PdCl₂ species bearing bulky cumyl or t-butyl substituents are somewhat atypical for this class of ligands, which may be attributed to the increased steric bulk proximal to the metal center, relative to ligands featuring methyl or halide-substituted phenol donors. These complexes all differ from the Pd ABP complexes reported prior to our work (four reports), in which bridging ABP ligands generate $\kappa^4\text{-N}_2\text{O}_2$ Pd species that are coordinatively saturated. We believe this represents an opportunity to extend the range of Pd catalysis to include these species derived from synthetically-accessible ABP ligands.



Scheme 1. Formation of $\kappa^2\text{-N,N}$ and $\kappa^3\text{-N,N,O}$ amine bis(phenolate) Pd(II) complexes, and previously reported $\kappa^4\text{-N}_2\text{O}_2$ Pd complexes (inset).

^1H NMR spectra for **1-PdCl₂** and **6-PdCl₂** reveal an unexpected downfield shift ($\Delta\delta > 1.73$ ppm relative to free ligand) for one aromatic C-H that is consistent with the presence of an anagostic interaction. While no close contacts were noted in the solid state structures for these species, the solution data suggest a more rigid ligand environment than has been observed for analogous iron and chromium complexes. Treating **1-PdCl₂**, **6-PdCl₂**, or **7-PdCl₂** with one molar equivalent of base generated a solution with spectral features consistent with the formation of a $\kappa^3\text{-N,N,O}$ chelate, as monitored by ^1H NMR. Additional reactivity studies were undertaken with **10-PdCl₂**, and monitored using a combination of ^1H and ^{19}F NMR. For **10-PdCl₂**, neither intentional addition of water or heating in anhydrous CDCl₃ led to a change in observed NMR features. The addition of anhydrous HCl resulted in rapid conversion to the formation of $\kappa^2\text{-N,N}$ complex, as evidenced by the disappearance of distinct ^1H NMR signals for diastereotopic methylene hydrogen atoms and a reduction in the number of ^{19}F NMR signals from four to two. Combined, these

observations suggest that interconversion of Pd(ABP) species between κ^2 -*N,N* and κ^3 -*N,N,O* coordination modes is relevant to complex speciation throughout a catalytic cycle.

In order to further clarify the influence of ligand substitution on complex speciation, computational studies were initiated in collaboration with Dr. Trilisa Perrine at Ohio Northern University. Computational analysis at the ω B97X-D/LAN2LDZ level of theory supported the assertion that such an anagostic interaction may play a role in stabilizing κ^2 complexes bearing a cumyl-substituted amine bis(phenolate) ligand. By comparing the energies of Pd complexes featuring either an O-H \cdots M or C-H \cdots M (anagostic) interaction (Figure 1), we were able to determine that the steric bulk of the *para*-substituent appears to play a significant role in the coordination mode of ABP ligands for these Pd(II) species.

Additional experiments have revealed that several novel base metal complexes of these ligands are isolable. Our group is currently undertaking full spectroscopic characterization of these species, and will conduct thorough studies of photophysical behavior as required based on preliminary data. Future work to characterize base metal complexes of this class of ligands is underway, and will be an area of focus for year three of this grant. We are currently exploring catalytic applications that might exploit this κ^2/κ^3 fluxionality. Additional computational efforts on this project will involve Ti(IV) (d^0) complexes, which are less computationally-intensive and relevant to the well-known group 4 polymerization catalysts featuring ABP ligands.

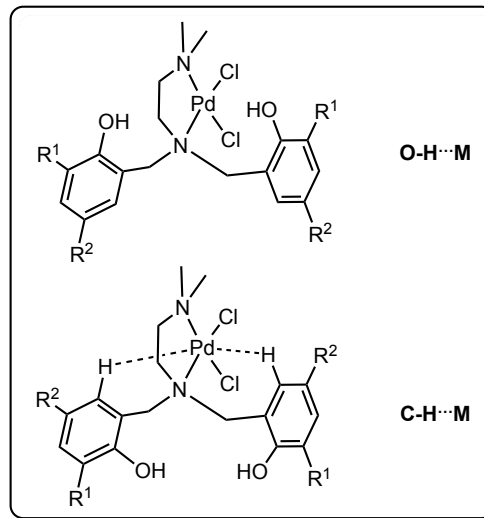


Figure 1. Approximate geometry of calculated species.

Impact on Students and Dissemination of Results

These findings have been reported at the 256th ACS national meeting in Boston, and in a research article published in *Inorganica Chimica Acta* (2019, 484, 185-196). This publication features five ONU undergraduate student co-authors, two of whom were supported by this grant during this grant year, and all of whom were supported in part by supplies purchased using this grant. Former students Brendan Graziano and Eric Collins are both entering their second year in chemistry graduate programs, and their inclusion as co-authors will add weight to their graduate fellowship applications, and assist them in demonstrating the quality of their undergraduate research experience. The other three student co-authors are current ONU students, and all are exploring or planning to attend graduate programs in the fall of 2019. Nathaniel McCutcheon has decided to pursue his interest in synthetic inorganic/organometallic chemistry based on his experience in my lab, and has demonstrated himself to be well suited to this work. Nicole Braunscheidel has chosen to pursue her interests in computational chemistry after her experiences working on this project and at a summer REU program. Claire Griffith is currently conducting polymer research, and exploring graduate programs as well as industrial research positions after graduation. Two additional students worked in my laboratory this summer.

Both Calum Bochenek and Victoria Ternes completed their freshman year prior to beginning summer research with me, and despite the steep learning curve, did thorough and diligent research. Victoria has continued to research with me this fall during her sophomore year. In all cases, this grant has permitted these students the opportunity to explore their own interests while addressing the main goals of the project, and encouraged them to continue as chemists. These substantial summer research experiences have been beneficial for my research students, and their continued involvement in my research program supports this claim. The collaboration with ONU faculty member Dr. Trilisa Perrine has been highly productive, and will result in future collaborative efforts. As a result of our work together on this project, Dr. Perrine and I are co-supervising Nicole Braunscheidel's senior research project, combining synthetic and computational chemistry.

The PRF grant has given my group the freedom to pursue this research project, despite the material costs associated with transition metal synthetic chemistry. I have submitted an application for sabbatical leave for the fall of 2019, and the results of this grant (specifically publications and conference presentations) will greatly assist in demonstrating to my institution the value of such a leave. If approved, I will plan to initiate new collaborations with faculty at the University of Toledo while considering how best to pursue future funding for this work. The PRF grant also allows me to demonstrate financial support for these research activities, and allows me to propose a more ambitious sabbatical plan. Overall, PRF funding has stimulated my research program, and led to specific experiences and opportunities for students in my group. We have all benefitted from the publications and presentations resulting from this work, and will continue to do so in the future.