

2018 Narrative Progress Report

PRF# 55989-DNI3

Project Title: A Structural Diphosphine Model to Predict Metal-Phosphorus Covalency Variations in Transition Metal Complexes

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The ACS Petroleum Research Fund supported ligand K-edge X-ray absorption spectroscopy (XAS) experiments aimed at determining how changes in diphosphorus ligand structure affect covalency in metal-phosphorus (M-P) bonds. We proposed that M-P covalency, which is known to govern certain aspects of chemical reactivity in transition metal complexes, could be used to develop predictive covalent bonding models using readily-available structural information obtained from single-crystal X-ray diffraction data. We have completed almost all the objectives put forth in our ACS-PRF proposal. In addition, we have developed new P K-edge energy standards for the XAS community (*J. Synchrotron Rad.* **2018**, 25, 529) and published a critical review of P K-edge XAS studies of M-P bonding (*Comments Inorg. Chem.* **2018**, 38, 54). Six PRF-supported manuscripts have been published, and several more are in preparation.

In our first study supported by the ACS-PRF, we collected P and Cl K-edge XAS data on solid $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]\text{PdCl}_2$ complexes (where $n = 1 - 4$) at the Stanford Synchrotron Radiation Lightsource (SSRL) in Menlo Park, CA. Our data showed that changes in diphosphine bite angle (P-M-P) do not track with anticipated changes in Pd-P covalency in these diphosphine complexes (Fig. 1). Notably, we discovered a unique and unexpected 10% increase in M-P covalency for $[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2]\text{PdCl}_2$. The experimental data was corroborated by DFT and TDDFT calculations, as well as similar XAS studies on isomorphous Ni(II) complexes. The results, which were published in the ACS journal *Inorganic Chemistry* (*Inorg. Chem.* **2015**, 54, 5646), suggested that the differences in M-P covalency could be modeled by taking into account the M-P-C angles in the complexes. However, more data was needed to test the validity of our model.

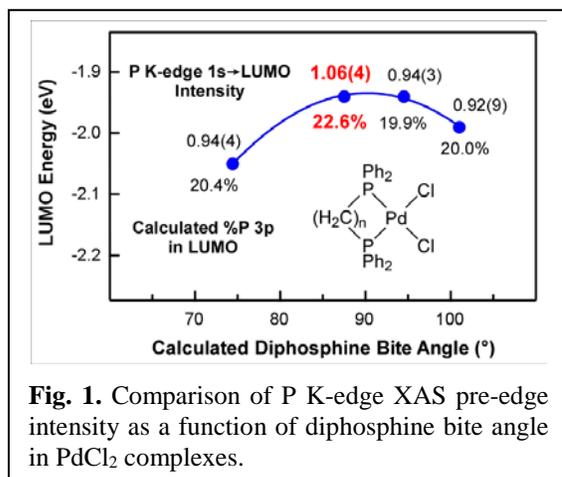


Fig. 1. Comparison of P K-edge XAS pre-edge intensity as a function of diphosphine bite angle in PdCl_2 complexes.

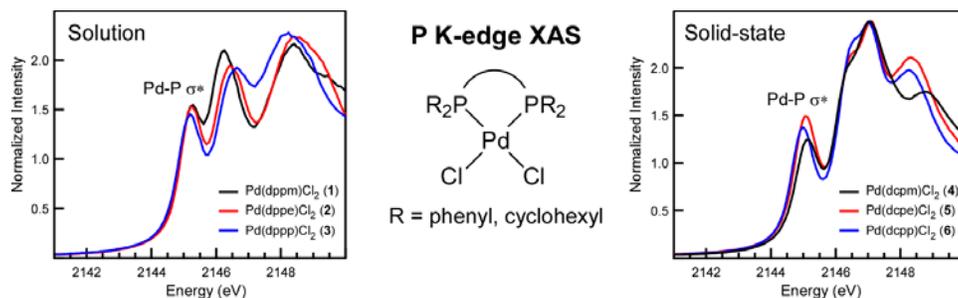


Fig. 2. Comparison of solution (left) and solid (right) P K-edge XAS data for $[\text{R}_2\text{P}(\text{CH}_2)_2\text{PR}_2]\text{PdCl}_2$ complexes.

We next set out to determine if the unique increase in solid-state Pd-P covalency observed for $[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2]\text{PdCl}_2$ was observed with (1) diphosphines containing different substituents attached to phosphorus, and (2) in solution (Fig. 2). P K-edge XAS data collected on the cyclohexyl-substituted complexes $[\text{C}_6\text{H}_{11}\text{P}(\text{CH}_2)_n\text{PC}_6\text{H}_{11}]\text{PdCl}_2$ (where $n = 1 - 3$) indeed revealed the same trend in Pd-P covalency observed for the phenyl-substituted complexes. To obtain the solution data, we designed a flow cell so we could collect solution P K-edge XAS data on the Pd complexes at ambient conditions. Most metal complexes rapidly decompose at room temperature during solution XAS data collection due to photodecomposition and the generation of solution radicals. We circumvented this problem by flowing a solution of the compounds through an XAS sample cell so that decomposition products were removed as they were generated. This allowed us to collect the first solution P K-edge data at room temperature on the $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]\text{PdCl}_2$ complexes. Remarkably, the solution data revealed that the unique 10% increase in Pd-P covalency observed for $[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2]\text{PdCl}_2$ in the solid-state disappeared in solution. All three $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]\text{PdCl}_2$ complexes, where $n = 1 - 3$, revealed statistically equivalent Pd-P σ covalency. These results

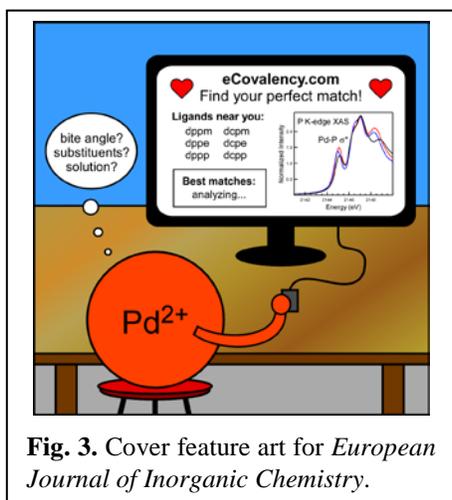


Fig. 3. Cover feature art for *European Journal of Inorganic Chemistry*.

With all of the XAS data now in hand, we have developed a structural model based on the observed experimental variations in metal phosphorus covalency. Our goal, as outlined in the PRF proposal, is to determine if our structural model can be used to predict relative differences in metal-phosphorus covalency in other diphosphine complexes using only structural data from single-crystal X-ray diffraction. We are currently testing our predictions based on the model, and our plan is to publish these results in the upcoming year.

Impact of research. Funding from the ACS PRF provided critical early career support needed to build a dedicated XAS program aimed at modeling M-P bonding and electronic structure in metal complexes. In addition to achieving the outlined objectives described here, PRF support has provided institutional knowledge, student training, and travel support needed to pursue separate, but parallel P, S, and Cl K-edge XAS studies in support of several other projects. Preliminary XAS results collected during our trips to SSRL were leveraged to successfully obtain a CAREER Award from the National Science Foundation (NSF), and supported a recent R01 proposal submitted to the National Institute of Health (NIH). Funding from the ACS PRF award has supported three PhD students as graduate research assistants. One student recently graduated with her PhD, and the other two students are scheduled to graduate with their PhD this upcoming academic year.

were recently published in the *European Journal of Inorganic Chemistry* (*Eur. J. Inorg. Chem.* **2018**, 2267) and the article was highlighted as a cover feature and was named a “Very Important Paper” (Fig. 3).

As described in our PRF proposal, we also began investigating Ti diphosphine complexes to determine how changes in metal identity and oxidation state affected M-P covalency as a function of bite angle (Fig. 4). $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]\text{TiCl}_4$ complexes have very different bite angles compared to PdCl_2 complexes containing the same diphosphine ligands. Despite the large structural differences, P K-edge XAS data and TDDFT calculations revealed identical relative trends in covalent M-P σ bonding as the number of methylene units were increased in the diphosphine backbone from one to three. Furthermore, because the Ti(IV) complexes have no d-electrons, we were able to experimentally quantify the σ -donor and π -acceptor properties of the diphosphines. These results were recently reported in the journal *Inorganic Chemistry* (*Inorg. Chem.* **2018**, 57, 10277).

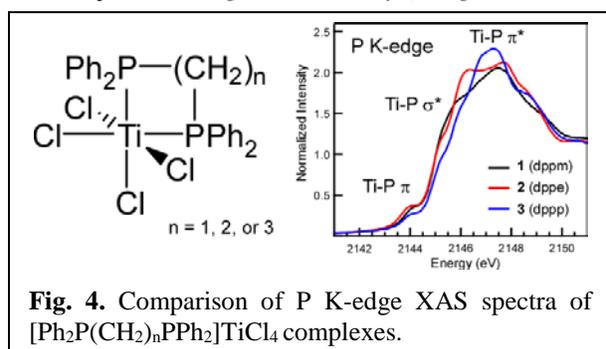


Fig. 4. Comparison of P K-edge XAS spectra of $[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]\text{TiCl}_4$ complexes.