

MULTI-EDGE X-RAY ABSORPTION NEAR-EDGE SPECTROSCOPIC ANALYSIS
OF PALLADIUM COMPLEXES IN II, III AND IV OXIDATION STATES

By

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A thesis submitted in partial fulfillment
of the requirements for the degree

of

Masters of Science

in

Chemistry

MONTANA STATE UNIVERSITY
Bozeman, MT

November 2013

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DEDICATION

I dedicate this thesis to my family. Throughout the highs, lows and mediocre times, they were always willing to listen critically and lovingly. I want to individually thank my brother, Wes, for his advice in making decisions throughout my graduate career. Extra special thanks go to my husband, Ross, for he has endured a “not-so-ideal” work environment to support me in this endeavor. I am forever grateful for his love and belief in me, and for those days when all I needed was a smile to brighten my day.

ACKNOWLEDGEMENTS

First, I want thank the Chemistry and Biochemistry program at Montana State University for allowing me to pursue this degree with full financial support.

I owe gratitude especially to my advisor, Robert Szilagyi, for always being an advocate for my success. I will always recall my first meeting with him in his office as being the most exciting moment after becoming a graduate student. It was during this meeting that he introduced a project based on simple palladium complexes. That simple idea grew beyond either of our expectations to that which is presented in this work. I also thank Allan van Asselt for showing me the beauty of inorganic chemistry as a junior in undergraduate school and for Jan Bryson, my high school chemistry teacher, for showing me how cool this science can be.

I also want to thank my group members for their guidance in helping me understand synchrotron science and computational chemistry. Individually, I want to thank Matt Queen for the many discussions and reflections had over science. Whether they were in the office or on the scary roads to Saskatoon, I appreciate your view on the world and the zeal you have in share your curiosities.

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ABSTRACT

Palladium-based complexes have profoundly impact on the synthetic tools of organic chemists due to their importance as catalysts in a myriad of chemical transformations. Palladium in the 0, II, III and IV oxidation states have all been experimentally observed to have catalytic activity in carbon-carbon bond coupling reactions. A common organometallic research aim is to improve catalytic activity of these complexes by designing and optimizing new ligand systems to access more difficult transformations. In order to understand the electronic effects that ligand systems have on reactivity, X-ray absorption spectroscopy is used to characterize the electronic structure of the ligand and metal components of pre-catalysts and palladium model complexes. The multi-edge X-ray absorption near-edge absorption spectroscopic technique (XANES) is an element specific technique that excites core electrons of the 1s (K-edge) and 2p (L-edge) orbitals to frontier unoccupied molecular orbitals, providing a ground state picture of a complex's ligand and metal electronic structure. This thesis will describe a comparative analysis between homoleptic chloropalladium complexes and interesting heteroleptic palladium based complexes of II, III and IV oxidation states to understand the stabilizing effects of a unique ligand environment. Furthermore, it will emphasize the benefits of using multi-edge XANES technique in rationalized catalyst design.

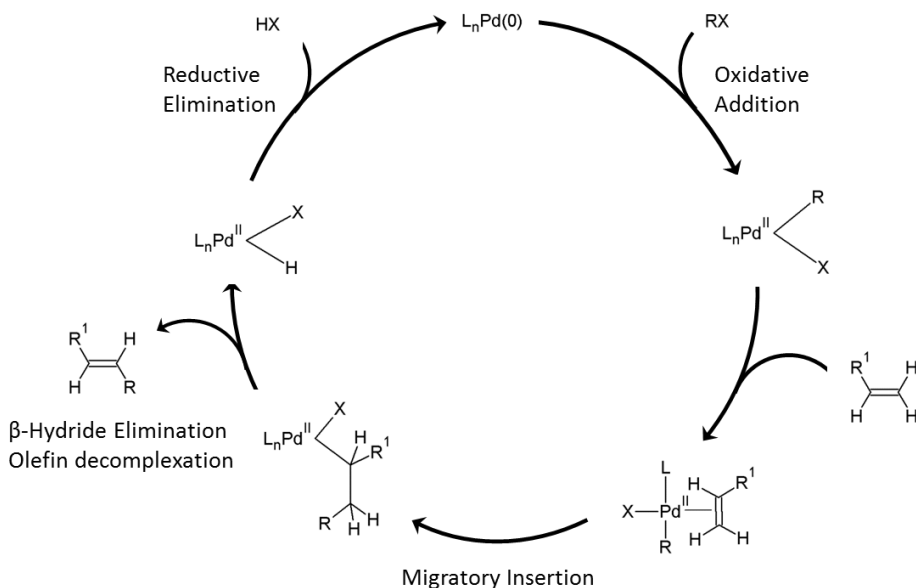
CHAPTER 1

PALLADIUM AS CATALYSTS IN Pd⁰, Pd^{II}, Pd^{III} and Pd^{IV} OXIDATION STATESIntroduction

Palladium-based complexes have profoundly impacted the synthetic tools of organic chemists due to their importance as catalysts in a myriad of chemical transformations. The Nobel Prize in Chemistry was awarded to Heck, Negishi and Suzuki in 2010 for their initial developments of palladium-based catalysts in the Pd⁰ and Pd^{II} oxidation states.⁵ This family of catalysts are particularly known for their remarkable stability with oxygen and moisture and their tolerance to a wide variety of reagents and functional groups.¹ These desirable qualities have led current research towards ligand tuning and optimization to access specific organic transformations. Even so, non-optimized traditional phosphane ligands such as triphenyl or tricyclohexyl phosphane, paired with Pd⁰ and Pd^{II} metal centers, dominate the organic literature due to their catalytic activity.^{1,4} Due to the synthetic usefulness palladium, a wide range of reactions have been developed for Pd⁰, Pd^{II}, and recently for Pd^{IV} and Pd^{III} oxidation states with their most notable activity in carbon-carbon bond coupling,^{1,3,4} carbon-heteroatom coupling,^{2,4} and C-H bond functionalization reactions.¹⁸ The thesis work presented herein revolves around the novelty of palladium catalysts and utilizes combined experimental spectroscopic and theoretical approaches to improve our understanding of their electronic structure.

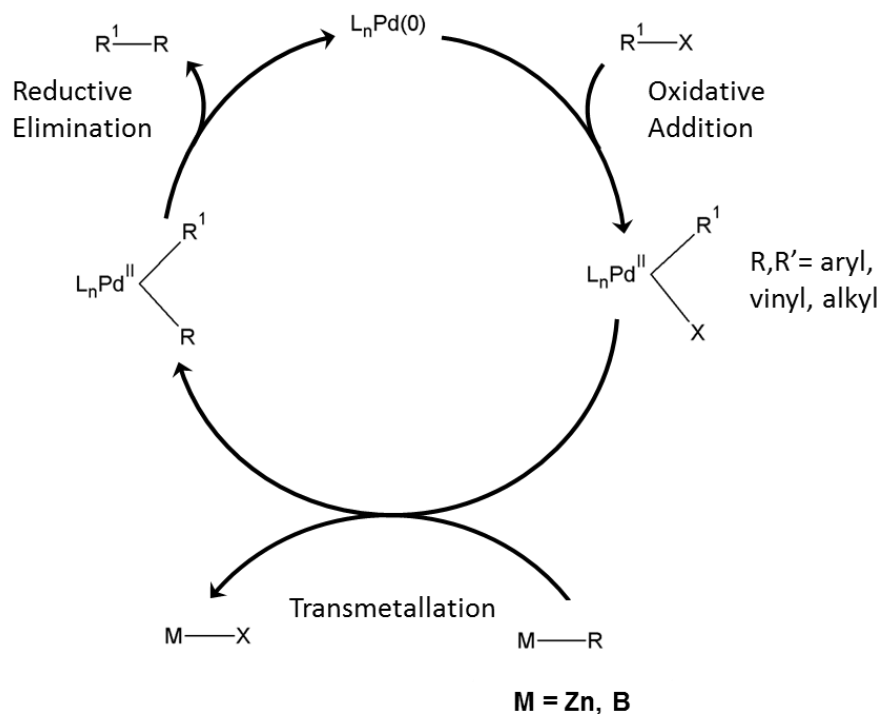
Pd⁰- and Pd^{II}-based Catalysis

Heck pioneered the advancement of palladium as a catalyst in the late 1960s. His name reaction, Scheme 1, is the formation of a carbon-carbon bond between an aryl halide and an olefin using a Pd⁰ catalyst.^{7,35} The proposed mechanism for the Heck Reaction begins with an oxidative addition of an aryl halide to a Pd⁰ metal center, causing a formal two-electron oxidation to Pd^{II}. Olefin coordination to the Pd^{II} center is followed. Migratory insertion forms a palladium-carbon bond and inserts the R group to the adjacent carbon. β -hydrogen elimination encourages the olefin to reform and non-coordinate from the Pd^{II}, whereby reductive elimination of a hydrogen halide regenerates the catalytically active Pd⁰ metal center. The Heck reaction remains a powerful process to date for synthetic chemists as they consider this reaction a basic tool in organic chemistry.³⁵



Scheme 1: Mechanism of the Heck Reaction. Adapted from Ref. [35]

In the early 1970s, Negishi was also active in investigating palladium as a catalyst, recognizing that the transition metal had the ability to afford remarkable yields in carbon-carbon bond formation reactions. The addition of an alkylzinc reagent, which behaves as a nucleophilic partner with palladium, exchanges a halide from the palladium for a functionalized alkyl group.^{8,9} This step, termed transmetallation, replaces the migratory insertion step used in the Heck Reaction. The alkylzinc reagent can be generated by direct insertion of zinc metal into an arylbromide bond with I_2 catalyst.⁶³ These mild reagents superseded the yields observed with popular reactions Grignard reagents, copper- catalyzed coupling and organolithium reagents.¹⁰ Similar to Negishi's



Scheme 2: Mechanism of Negishi and Suzuki coupling reactions. Adapted from Ref. [10]

progress, Suzuki saw the capability of organoboron reagents to perform as a nucleophilic partner with palladium via transmetallation. Like the zinc counterparts, boron reagents are very tolerant of functional groups and can operate under mild reaction conditions. The only difference between these reagents are that organoboron reagents must be activated with a base.^{11,12} Scheme 2 shows the Negishi and Suzuki coupling mechanisms.

Carbon-heteroatom bond forming reactions are significant due to their abundance throughout all of chemistry but have particular importance for the pharmaceutical industry for synthesizing biologically active molecules with these bonding schemes.^{13,93} Coupling of alkyl groups and amines became prominent in literature with the design of new ligand systems with Pd^{II} metal centers.⁶⁴⁻⁶⁶ Ligand systems specifically designed for Pd-catalyzed amination reactions include BINAP¹⁴ and N-heterocyclic carbenes.¹⁵ However, amines often have crowded environments, which make coordination to palladium difficult and side reactions prevalent.⁶⁶ One of the leaders in developing new classes of ligands for Pd-catalyzed amination reactions is Buchwald. Examples of his group's work are the dialkylbiaryl phosphane ligands, which offer high yields, mild reaction conditions and minimized sensitivity to air and moisture.¹³ Figure 1.1 shows the

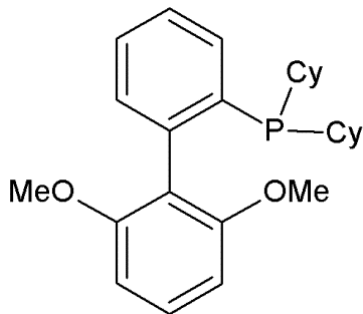


Figure 1.1: Buchwald's SPhos ligand used in amination reactions

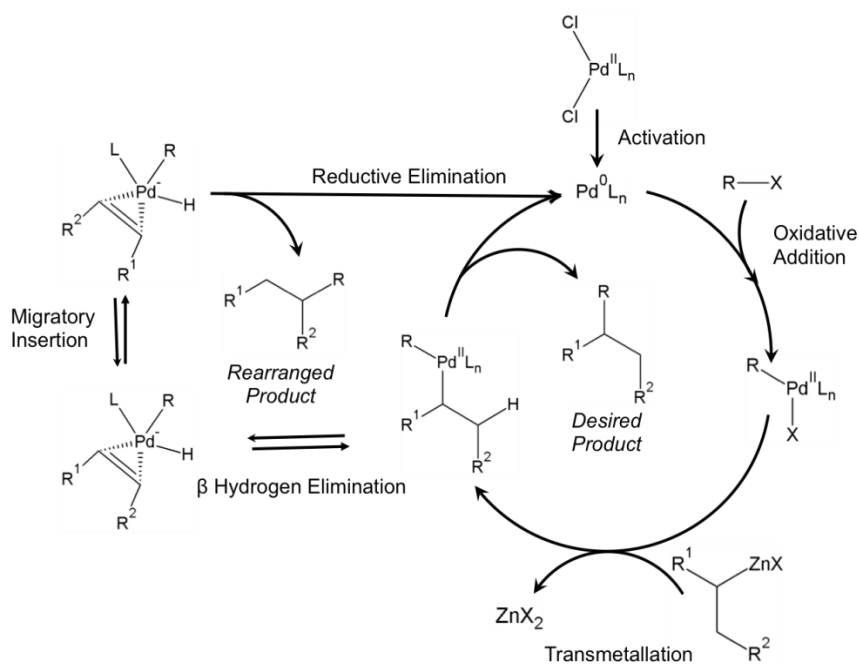
the mechanism of Pd-catalyzed amination reactions is similar to that of the Heck reaction. However, the olefin coordination step is replaced by amine binding. The addition of a base deprotonates the amine and drives the reaction towards reductive elimination and product formation.¹³

The modest set of representative examples presented above already well illustrates how palladium-based catalysts are being evolved to accomplish difficult transformations. Using the foundations established earlier by Heck, Negishi and Suzuki and their coworkers and collaborators, ligand modifications have become a focus in organometallic research for improving reaction rates and yields but also access to coupling reactions between bulky reagents. A limitation of simple Pd-based catalysts in the Negishi and Suzuki mechanisms is the coupling of secondary or tertiary alkanes. Once bulky reagents are added to the metal center through transmetallation, β -hydride elimination competes with reductive elimination. If β -hydride elimination advances through the catalytic cycle, rearrangement of branched substrates occurs and reductive elimination results in coupling of primary carbons. A depiction of this is shown in Scheme 3.

An exceptional example, in terms of the ease to modify the ligand for minimizing β -hydride elimination is seen in the PEPPSI (pyridine-enhanced pre-catalyst preparation, stabilization and initiation) catalysts developed by Organ and co-workers.¹⁶ Pd^{II}-based pre-catalysts have been designed with modified N-heterocyclic carbenes and pyridine to

favor reductive elimination. These pre-catalysts show broad functional group tolerance, high catalytic activity and versatility in being tuned by electronic and steric means.⁶⁷

Figure 1.2 shows the Pd^{II} -PEPPSI-i-Pr complex.¹⁷



Scheme 3: Proposed Negishi cross-coupling mechanism. Adapted from Ref. [18]

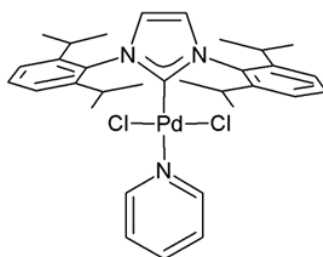


Figure 1.2: PEPPSI-iso-propyl complex.

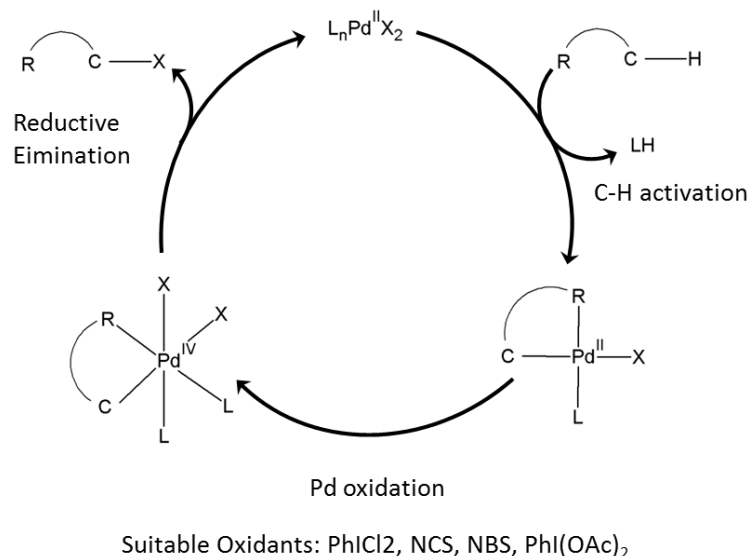
PEPPSI complexes are characterized by the N-heterocyclic carbene (NHC) backbone that occupies one of four coordination sites on the Pd^{II} metal center. Adding

substituents at ortho and para positions of the aryl groups creates an envelope like structure around the metal center. The rationale of this design is that increased crowding around the metal center protects it from oxidation, but also facilitates reductive elimination. Once a bulky alkyl group is added via transmetallation from the alkylzinc reagent, those steric interactions will lower the energy needed for reductive elimination to occur and favor coupling at the secondary carbon.^{3,17} Electronic modifications can also be made to the N-heterocyclic carbene, by adding substituents to the backbone. Increased selectivity towards branched products is favored regardless of whether electron withdrawing chlorides or electron donating methyl groups are added to the NHC.¹⁷ The combination of these modifications shows almost exclusive branched product formation.¹⁷

Pd^{IV}-Based Catalysis

Palladium-based catalysts of the Pd^{IV} oxidation state, while not as prevalent as Pd^{II} catalysts, offer complementary and sometimes, improved reactivity for carbon bond coupling reactions.⁴⁷ Developments in Pd^{IV} catalysis are more recent than those of Pd^{II} due to the instability of Pd^{IV} species, which poses experimental difficulties in their studies. Investigations of Pd^{II}/Pd^{IV} catalytic cycles however, show improvements over Pd⁰/Pd^{II} cycles with the ability to avoid β -hydride elimination and undergo facile reductive elimination.^{18,20,22} Because of this thermodynamically favored step, Pd^{IV} catalysts are also active in C-X bond functionalization, where X=halide in addition to C-C and C-N bond coupling reactions. Their ability to make CF₃-carbon linkages, as demonstrated by Stanford and coworkers, has been important for the pharmaceutical

industry.^{22,24} Overall, Pd^{IV} catalysts are primarily used for ligand directed C-H functionalization reactions,¹⁸⁻²¹ for creating new carbon-heteroatom linkages.²² The only caveat in Pd^{IV} catalysis is that strong oxidants are crucial toward the formation of high-valent species from the intrinsically more stable Pd^{II} complexes (bottom part of Scheme 4). The remarkable activity toward directed C-H functionalization has motivated current research to make Pd^{IV} catalysts more chemo-, regio- and stereoselective. Thus, optimizing the ligand environment is a continuing endeavor for improved functionality.



Scheme 4: Mechanism of C-H bond functionalization via low-to-high valent Pd^{II}/Pd^{IV} reaction cycle. Adapted from [47].

Pd^{III} Complexes as Catalysts

Mechanistic investigations of Pd^{II}/Pd^{IV} catalytic cycles have proposed mononuclear Pd^{III} intermediates in C-H functionalization reactions, however they are typically short lived and yet to be observed in operando.^{48,49} Pd^{III} complexes are rare in comparison to the abundant Pd⁰, Pd^{II} and Pd^{IV} complexes. The first Pd^{III} complex,

NaPdF₄, was synthesized in 1982²⁵ and the first organometallic and catalytically active Pd^{III} complex was not synthesized until 2010 by the Mirica group;²⁶ Figure 1.3. The stability of the complex shown has allowed for detailed mechanistic analysis of one-electron oxidations and has contributed to the understanding of the role of catalyst with odd-electron Pd^{III} metal centers.

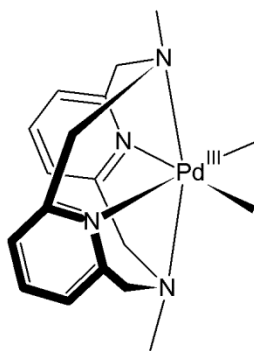
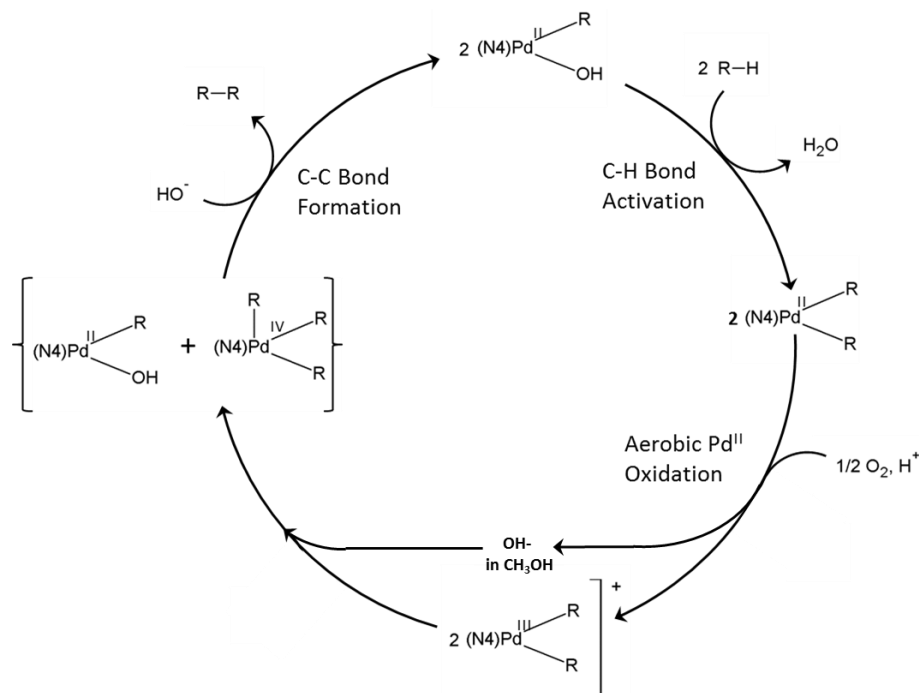


Figure 1.3: Schematic structure of ^{Me}N₄Pd^{III}Me₂

The organometallic complex in Figure 1.3 has been identified as an intermediate in C-H bond activation and C-C bond formation reactions.^{26,27,28} As previously mentioned, Pd^{IV} catalysts are used for C-H bond activations, yet strong oxidants are needed. The novel use of the “N₄” ligand has allowed for oxidation to occur using a mild and green oxidant, O₂.²⁷ A mechanism was proposed for the catalytic cycle of C-H activation and C-C bond formation via an aerobic oxidation step by the Mirica group, Scheme 5.

A brief history of Pd⁰, Pd^{II}, Pd^{III} and Pd^{IV} complexes as catalysts demonstrates the importance of their role in C-C and C-heteroatom coupling reactions and C-H functionalization reactions. Some of the first palladium catalysts still in-use shows up frequently in current literature, as they remain powerful reagents for organic chemists.

The design and optimization of new ligand systems for Pd-based catalysts continue to diversify these reagents for allowing access into more difficult transformations.



Scheme 5: Proposed mechanism for aerobic oxidative coupling of C-H bonds. Adapted from Ref. [27]

Experimental spectroscopic and combined theoretical approaches will improve the understanding of the electronic structures of palladium pre-catalysts and palladium complexes. To obtain ground state pictures of bonding in Pd^{II} , Pd^{III} and Pd^{IV} complexes, multi-edge X-ray absorption spectroscopy (XAS) will be utilized.

X-ray Absorption Spectroscopy

X-ray absorption spectroscopy is an element-specific technique that uses a synchrotron radiation source to generate continuous or pulsed on ps time-scale, high flux light, which is tunable in the range of core ionization energies. It can be used with solid,

liquid or frozen samples that are either paramagnetic or diamagnetic. An XAS spectrum consists of two main regions, as illustrated by Figure 1.4. X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) provide high-resolution information about the electronic and geometric structures of the absorbing atom, respectively. In the XANES pre-edge region, as core electrons reach their ionization potential, they populate unoccupied molecular orbitals, providing a

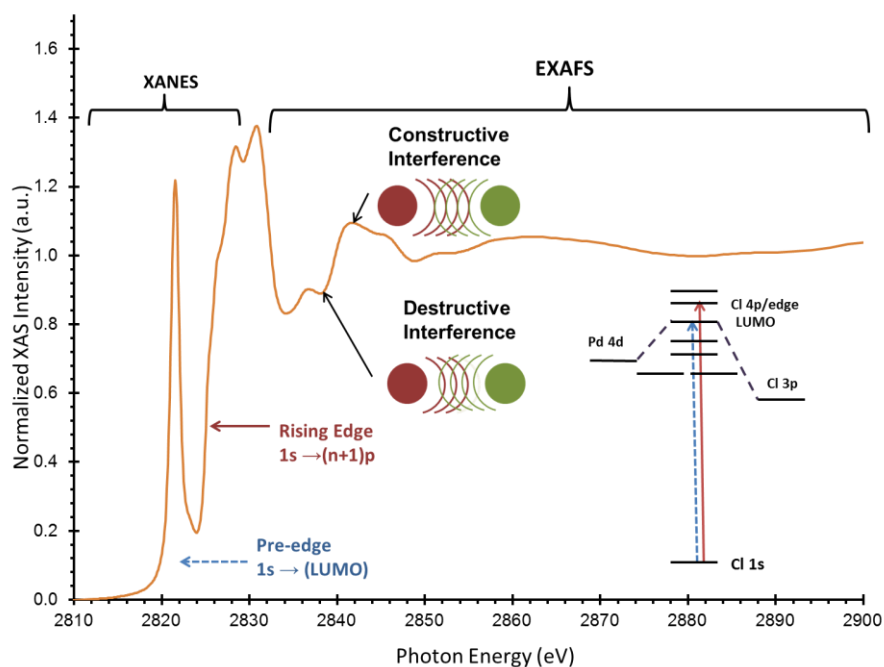


Figure 1.4: Representative spectrum of the Cl K-edge used to illustrate the XAS regions and their origin

quantitative probe of bond covalency in that LUMO. The rising-edge region in the XANES spectrum directly reflects the ionization threshold and the effective nuclear charge of the absorbing atom. After an electron is ionized, its electron wave function can constructively and/or destructively interfere with its back-scattered wave off of

neighboring atoms. Peak and troughs in the XANES region are a result of these interactions. Through Fourier transform of the data, geometric information about the neighboring atoms can be obtained.

The XAS technique is particularly useful for palladium catalysts with chloride ligands. The core Cl 1s and Pd 2p ionization energies are within 350 eV of one another in the “tender” X-ray region of 2-4 keV. Due to their proximity, single scans can capture the ionization of core Cl 1s (Cl K-edge, $n=1$) and Pd 2p (Pd L-edge, $n=2$) electrons without different beamline set-up procedures or need for preparation of new samples. Hard X-rays (above 4 keV) are used to probe Pd 1s electrons at the Pd K-edge ($n=1$).

Multi-edge analysis of a complex provides complementary ground state descriptions of bonding between the metal and ligand. Pre-edge features at the Cl K-edge are a result of the dipole allowed transition from Cl 1s $\rightarrow$ Cl 3p. If Cl 3p character is present in the unoccupied frontier molecular orbitals, pre-edge features will arise in the XANES region. Similarly, Pd L-edge pre-edge features represent the dipole allowed transitions from Pd 2p $\rightarrow$ Pd 4d orbitals. Complementary bonding information is obtained if the same unoccupied frontier orbital is probed at the Cl K-edge and then at the Pd L-edges with Cl 3p and Pd 4d characters.

The Pd L-edge is split into two distinct regions as a result of core hole spin-orbit coupling. The L_{III} -edge represents excitations from the 2p orbital with $J=3/2$ state and the L_{II} -edge from the $J=1/2$ state. Both L-edges are used in quantitative analysis because they stem from the same ground state electronic structure. Because covalent bonding descriptions in inorganic, coordination and organometallic complexes is often between

metal d orbitals and ligand p orbitals, pre-edges features at the ligand and metal edges provide complementary information about bond character and bond covalency from the same LUMO. The edge positions are indicative of effective charges of the absorbers and thus provide information about the ionic bonding among the metal and ligand centers.

Theoretical considerations have proven that integrated pre-edge feature intensities in the XANES region are directly proportional to the ligand atomic character in a covalent bond formed with an open-shell metal.⁶⁹ A proportionality constant, also called in the literature the transition dipole integral, is used to convert analytical areas of pre-edge features into chemically relevant covalency values through the dipole expression for the ligand K-edge pre-edge features:

$$D_0 = \frac{1}{3} \frac{h}{A} \alpha^2 I_{1s \rightarrow 3p} \quad \text{Equation (1)}$$

where D_0 is the normalized analytical area in eV, h is the number of electron holes in the complex, N is the number of absorbing atoms, α^2 is the total covalency per hole and I is the transition dipole integral, reported in eV.

A firm foundation of the ground state, quantitative analysis has been laid for the Cl K-edge using the complex Cs_2CuCl_4 .²³ EPR data provided the Cu 3d orbital character in the d^9 copper complex. From complementarity for homoleptic complexes, the remaining electron density from 100% less the metal character can be attributed to Cl 3p character. This Cl 3p character, α^2 , is used to define a transition dipole integral for Cl 1s $\rightarrow$ 3p transitions and can be applied to analyze complexes beyond chloride ligands in copper complexes, but to any metal complex with terminal chloride ligands. The method

for defining transition dipole integrals is what makes correlating pre-edge intensities with orbital compositions at edges beyond the Cl K-edge possible.

The XAS technique will be used to characterize the electronic structure of homoleptic and heteroleptic palladium-based complexes and pre-catalysts. Pre-edge and rising-edge energy position analysis will illustrate the relative orbital energies of metal and ligand environments between palladium complexes. Transition dipole integrals will be defined for both the ligand K and the metal L-edge pre-edge features and applied to quantitatively analyze the orbital character of Pd-Cl bonds in catalytically interesting heteroleptic complexes. The combination of the two edges provides rich information content from which reactivity information can be deduced and further optimization of catalysts can be carried out.

Scientific Motivations

The introduction has outlined the importance of palladium catalysis and the use of XAS as a spectroscopic probe for analyzing electronic structure. XAS is well established in the bioinorganic community for correlating electronic structure of active sites to reactivity.²⁹⁻³² This thesis extends the XAS approach to Pd-containing inorganic and organometallic complexes to evaluate quantitative structure and activity relationships of structurally and compositionally well-defined pre-catalysts. The multi-edge approach, as defined in the literature,²⁹ will be applied to Pd-Cl bonding throughout this thesis.

Initial progress has already been described in the literature toward establishing Pd L-edge X-ray absorption spectroscopy for homoleptic chloropalladium complexes.³³ Using the quantitative orbital composition from the Cl K-edge,²³ complimentary analysis

of Pd L-edge was carried out for complexes of Pd^{II} and Pd^{IV} oxidation states. Quantitative analysis of spectral features defined orbital contributions of each participating atom and defined Pd-Cl bonds in complexes with terminal chlorides and bridging chlorides.

Chapter 2 will provide an independent confirmation of the Pd L-edge method development. Furthermore, it will apply the methodology to describe the complete electronic structure of a homoleptic chloropalladium dimer.

Chapter 2 will demonstrate that the multi-edge XAS technique for Cl K-edge and Pd L-edges give intense pre-edge features with great sensitivity to electronic structural changes. Naturally, the next step is to extend developments made to more interesting heteroleptic palladium catalysts and pre-catalysts. Chapter 3 will highlight a remarkable set of palladium-based complexes in the oxidation states of II, III, IV from the Mirica Laboratory in Washington University, St. Louis, MO. Since the complete electronic structure of homoleptic chloropalladium complexes is known, they will be used to compare and contrast differences seen in the spectra of heteroleptic complexes. Moreover, the Cl K-edge and Pd L-edge analysis will be used to make inferences about a unique nitrogen-based ligand system and its influences on three different oxidation states of palladium.

Chapter 4 will describe the theoretical ground state and excited state methods used to further understand the three complexes analyzed by XAS in Chapter 3. In the current presentation, Density Functional Theory will be used to describe orbital compositions using ground and excited state methods. These calculations are used to

support the interpretation of pre-edge energy positions and their spectral assignments through a variety of approaches.

Chapter 5 will expand the XAS method to a large series of palladium catalysts from the Organ Laboratory, York University, Canada, which highlight ligand modifications that impact reactivity. These catalysts are commercially available for performing difficult carbon-carbon bond coupling reactions, but further optimization of the catalyst is desired to achieve improved selectivity. This chapter will highlight the future direction of the multi-edge approach toward characterizing catalytically active species in situ. The potential to expand the multi-edge XAS technique is transformative in organometallic catalysis, whereby this thesis lays the foundation of exploration into this field of XAS analysis.

CHAPTER 2

MULTI-EDGE X-RAY ABSORPTION NEAR-EDGE SPECTROSCOPIC ANALYSIS
OF BRIDGING AND TERMINAL CHLORIDES IN THE HOMOLEPTIC DIMER
COMPLEX HEXACHLORODIPALLADATE(II)

Introduction

X-ray absorption spectroscopy has now become a well-established core ionization technique that is used to examine the electronic and geometric structure of metal-based complexes.³⁶ Quantitative analysis of peak intensities in the XANES region of ligand K-edges and metal L-edges provides information about bond covalency, orbital character and effective nuclear charge of the absorbing atom at each edge. Previous work has determined the entire electronic structure of homoleptic chloropalladium complexes by using multi-edge XAS technique at the Cl K-edge and Pd L-edge.³³ This work was carried out by Ryan Boysen, M.Sc., a former graduate student in the Szilagyi Lab at MSU.

The initial methods developed by Boysen for XANES feature analysis of Pd L-edges shows that the quantitative treatment used at the ligand K-edge is a viable technique for L-edges.³³ The scope of this chapter will confirm Boysen's previous work, using parallel methods for independent measurements to determine transition dipole integrals for Pd^{II} and bridging chloride environments. Application of these transition dipole integrals will be used to define the complete electronic structure of $[\text{Pd}_2\text{Cl}_6]^{2-}$, which contains two Pd^{II} metal centers, and bridging and terminal chloride ligands.

Boysen's work led to the complete electronic structural characterization of centrosymmetric and homoleptic complexes, K_2PdCl_4 , K_2PdCl_6 and $PdCl_2$.³³ It was concluded that Pd-Cl bonds are very covalent with nearly 50%/50% sharing of electron density among Pd and Cl in all of the mentioned complexes with experimental chlorine 3p character per chlorine for K_2PdCl_4 , K_2PdCl_6 and $PdCl_2$ as $12\pm2\%$, $17\pm2\%$ and $25\pm4\%$, respectively and Pd 4d character as $51\pm1\%$, $48\pm1\%$ and $45\pm3\%$, respectively.³³ Three methods were developed in his research for determining palladium transition dipole integrals. Due to the splitting of Pd L-edges, Pd 4d orbital character can be quantified from the pre-edge features at the L_{III} -edge, L_{II} -edge, or the sum of pre-edges at both edges.

A brief description of the methods Boysen used in his 2008 publication is outlined here, as the same methods are used for data analysis in this chapter. By starting with a well-defined Cs_2CuCl_4 complex^{33,37,38} with a known covalency value of 7.3% per Cl bond,³⁹ a transition dipole integral for the terminal chlorides can be defined. The area under the pre-edges in a Cl K-edge spectrum reflects the chlorine character in a metal-chlorine bond, thus integrated area of the pre-edge (D_0 , eV) is proportional to the Cl 3p character. Using the dipole expression:

$$D_0 = \frac{1}{3} \frac{h}{A} \alpha^2 I_{1s \rightarrow 3p} \quad \text{Equation (1)}$$

where D_0 is the integrated pre-edge area, h is the number of d-orbital holes, α^2 is the covalency and $I_{Cl\ 1s \rightarrow 3p}$ is the electronic dipole integral for Cl 1s-to-3p excitations. A transition dipole integral for terminal chlorides (I_{Cl_t} , eV) is determined and used to correlate D_0 and α^2 for other complexes with metal-terminal Cl bonds. By applying the

reverse procedure, taking the known Cl character in Pd-Cl bonds, the Pd character can be calculated from complementarity in homoleptic complexes. Thus, a transition dipole integral of Pd^{II} and Pd^{IV} oxidation states can be determined. Pd^{II} covalency in PdCl₂ was used to determine, from complementarity, the character and transition dipole integral for bridging chlorides.

The dimer complex, [Pd₂Cl₆]²⁻, was highlighted at the end of Boysen's publication,³³ hinting that the since bridging chloride and terminal chloride dipole integrals were different, they could be applied along with the transition dipole integral for Pd^{II} to determine the complete electronic structure of a complex with both terminal and chloride ligand environments present. Since Boysen's initial work, the dimer complex has been synthesized allowing for the extension and validation of his method development at the Pd L-edge. This chapter will confirm Boysen's method developments and apply the experimentally determined dipole integrals to the dimer complex, tetraethylammonium hexachlorodipalladate(II).

Materials and Methods

Samples

All samples were obtained from commercial sources and used without further purification as in Boysen's work³³ with the exception of the dimer complex, tetraethylammonium hexachlorodipalladate(II) (TEA₂Pd₂Cl₆), whose synthesis is described in the following section. Samples were ground, undiluted with BN, thinly pasted onto Kapton dots, mounted onto a copper sample rod and placed into the sample

chamber for measurement. The sample chamber was evacuated to 10^{-6} to 10^{-7} torr pressures.

Synthesis of Dimer Complex

The $\text{TEA}_2\text{Pd}_2\text{Cl}_6$ complex was synthesized using modified techniques from literature.⁴⁰ The amount of 0.08 mol PdCl_2 was dissolved in warm methanol over 24 hours. Once dissolved, one equivalent of tetraethylammonium chloride was dissolved in a small amount of methanol and added to the PdCl_2 solution. A color change from yellow to orange was observed. The solvent was evaporated off with vacuum, leaving a red powder. The powder was recrystallized in methanol and washed three times with ice-cold deionized water and dried over vacuum.

The dimer complex was characterized via solid-state UV/vis. Previous literature reports d $\rightarrow$ d and LMCT peak positions for $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{Pd}_2\text{Cl}_6]$ with using CH_3CN .⁹⁴ However, duplicate acetonitrile UV/vis measurements with the $(\text{TBA})_2[\text{Pd}_2\text{Cl}_6]$ complex did not correlate with published values but solid state measurements did. Solid state UV/vis pellets were made with mM concentrations of the complex in KBr. Samples were ground via mortar and pestle and hydraulically pressed into pellets with 1500lbs/in². Pellets were mounted into an Agilent Cary 60 UV/vis Spectrophotometer for measurement.

Resolvable peak positions for $[\text{Pd}_2\text{Cl}_6]^{2-}$ solid state measurements are as follows: 20300cm⁻¹, 23200cm⁻¹, 29000cm⁻¹, 35500cm⁻¹, and 42500cm⁻¹. Higher lying features cannot be resolved above 47000cm⁻¹ due to the KBr cutoff point. These energy positions, while shifted lower by about 2000cm⁻¹ from reported values⁹⁴ due replicate the spectral

trends for d→d transitions and LMCT bands resultant from bridging and terminal chlorides. There are also significant differences in spectral features between the dimer and PdCl₂ and [PdCl₄]²⁻ solid state measurements. More features are present in the dimer spectrum due to the combination of terminal and bridging chloride environments.

Data Collection

All data was measured at the Advanced Light Source (ALS) on beamline 9.3.1 and collected in October of 2011. The same sample chamber and detection methods were used during this data collection as those used by Boysen.³³ The energy was scanned in 0.1 eV step sizes 15 eV prior to the rising-edge and 25 eV after the rising-edge. Before and after this region the energy was scanned in 2.0 eV and 0.5 eV step sizes. To minimize noise, data for each of the complexes is an average of three scans.

Data Analysis

Spectra at the Cl K-edge and Pd L-edge were calibrated using the pre-edge peak of Cs₂CuCl₄ at 2820.2 eV.³⁷ Data reduction was performed using MatLab.⁴¹ A second or third order polynomial, fit to the pre-edge region, was used to subtract the background from the raw data. Data were normalized by fitting second order spline to the post-edge region then normalizing to the spline at 2840 eV. Pd L-edges were analyzed using three different methods. Using Method I, where only the Pd L_{III}-edge is considered, a background was fit to the pre-edge of the L_{III}-edge and normalized to 1 at 3195 eV, after the L_{III}- rising-edge. Method II is parallel to Method I, however a background was fit at the pre-edge of the L_{II}-edge and normalized with a spline to 1 at 3345 eV, after the L_{II}-

rising-edge. In Method III, the L_{III} - and L_{II} -edges are treated as inseparable edges. A second order background was fit to the pre-edge of the Pd L_{III} -edge and a spline was fit to the post-edge of the Pd L_{II} -edge. The entire spectrum was normalized to 1 at the L_{II} -edge jump at 3345 eV.

Fitting Spectral Features

Peak positions of pre-edges were obtained from the inflection point in the first derivative plots. Inflection points that define the rising-edge position in the raw data were obtained from the first maximum after the pre-edge inflection point in the first-derivative spectrum. Normalized spectra were fit using the program Peak Fit v4.12 (SeaSolve) in a 13 eV energy range from 2815-2828 eV in the Cl K-edge spectra. Rising-edges were fit with Lorentzian Cumulative Ascending function, which model the edge-jump with excited state lifetime broadening. Pre-edge features at the Cl K-edge were fit using a 1:1 mixture of Lorentzian and Gaussian line shapes as a consideration of broadening due to excited state lifetime and beamline optics.⁴²⁻⁴⁵ The number of peaks that were used to fit the pre-edges was defined by the second-derivative spectrum. One peak was used to fit the single feature in PdCl_2 and two peaks for the two features in $[\text{Pd}_2\text{Cl}_6]^{2-}$.

Pd^0 has no pre-edge feature at the Pd L-edge due to the closed shell $4d^{10}$ electron configuration. This enables the use this spectrum as a model the Pd edge jump from the allowed $2p \rightarrow 5s$ transition, and the broad rising-edge in each of the Pd^{II} complexes. Pre-edges at the Pd L-edge are broader, when compared to the Cl K-edge, due to different excited-to-ground state relaxation channels between the metal L-edge and ligand K-edge, thus peak shapes were allowed to vary by changing the Gaussian-Lorentzian mixing

ratios. Fits were done over an energy range of 3165-3180 eV and 3325-3345 eV for the Pd L_{III}-edge and L_{II}-edge, respectively.

Results and Analysis

Cl K-edge XANES

Peak Position Analysis. The XANES features of the core ionization of Cl 1s electrons to the LUMO of the complex can provide direct experimental information about bond covalency, orbital composition, effective nuclear charge and electro- or nucleophilicity of the absorbing chlorine atom. Figure 2.1a shows the Cl K-edge spectra for three homoleptic complexes, [PdCl₄]²⁻, PdCl₂ and [Pd₂Cl₆]²⁻ compared to Cs₂CuCl₄.

Rising-edge energy positions reflect the effective nuclear charge (Z_{eff}) of the chlorine atoms. Higher lying rising-edge energy positions correlate with more oxidized chlorine absorbers. Rising-edge positions were determined by taking the first maximum after the rising edge in the first derivative plots (Figure 2.1b). The rising-edges of these complexes increase in energy in the order Cs₂CuCl₄, [PdCl₄]²⁻ = [Pd₂Cl₆]²⁻ and PdCl₂, indicating that the chloride ligands in the copper complex are the most negative and the bridging chlorides in PdCl₂ are the least negative. Similar to previous trends,³³ terminal chloride ligands in [PdCl₄]²⁻ are more negative than bridging chlorides in PdCl₂. This trend indicates that bridging chlorides are donating more electron density to the metal center and are therefore form more covalent Pd-Cl bonds than terminal chlorides. Thus, the rising-edge of [Pd₂Cl₆]²⁻ reflects only the ionization potential of the terminal chloride ligands. Since data supports that bridging chlorides in PdCl₂ have a greater Z_{eff} , the

rising-edge for bridging chloride ligands should be shifted up by 1.4 eV, as indicated by the two pre-edges in the dimer complex. Lack of experimental resolution around the rising-edge prevents the actual quantitative deconvolution of the terminal vs. bridging rising-edge analysis.

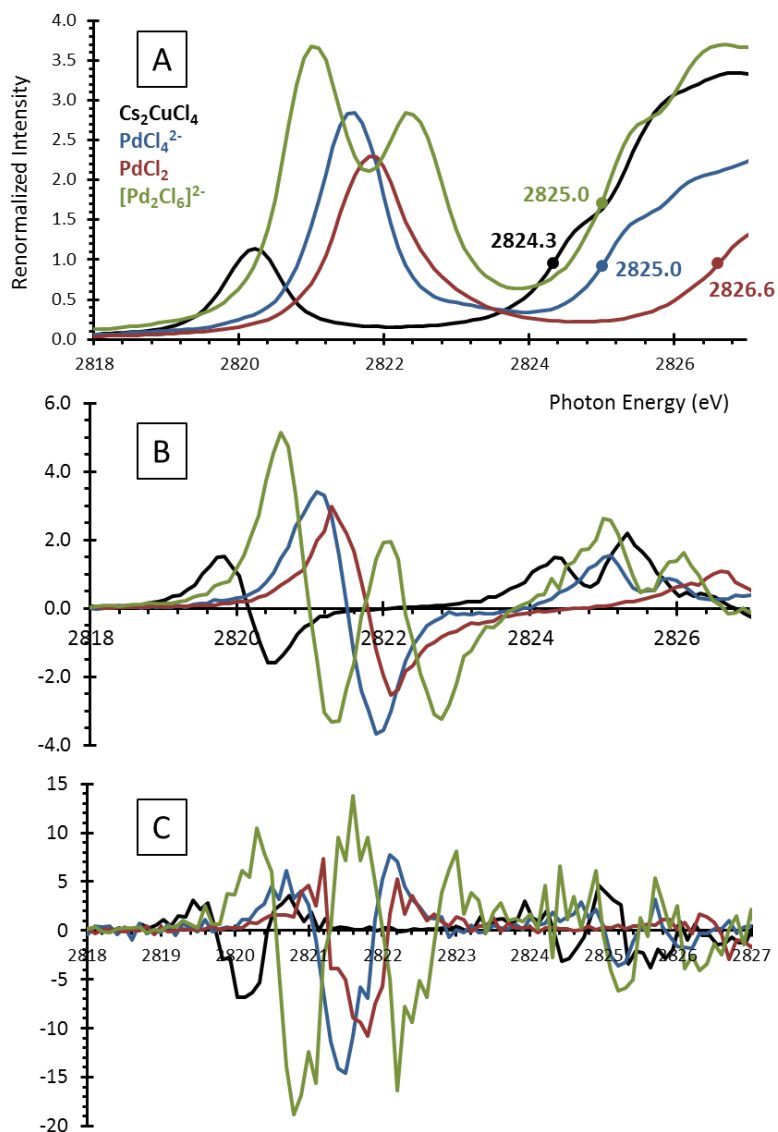


Figure 2.1: (a) Spectra of homoleptic complexes Cs_2CuCl_4 (black), $[\text{PdCl}_4]^{2-}$ (blue), PdCl_2 (red) and $[\text{Pd}_2\text{Cl}_6]^{2-}$ (green) at the Cl K-edge used for energy position analysis. (b) and (c) are the First-and second-derivatives of the respective data.

Pre-edge energy positions are a result of the metal oxidation state, d-manifold energy, d-orbital splitting, and the charge on the chlorine atom. Pre-edge energies were assigned by finding the first position that the first-derivative crosses zero (Figure 2.1b) as data quality was not good enough to use the second-derivative. All three palladium complexes have a square planar geometry around the palladium metal center. Thus, the pre-edge peaks are a result of a Cl $1s \rightarrow 3p$ excitation into the LUMO of the complex, which has Cl 3p and Pd $4d_{x^2-y^2}$ character. The single pre-edge feature in the $[\text{PdCl}_4]^{2-}$ spectrum is representative of the doubly unoccupied b_{1g}^* LUMO and is located at 2821.5 eV. The main pre-edge in PdCl_2 is located at 2821.7 eV and represents two doubly unoccupied LUMOs of b_{2u}^* and b_{3g}^* symmetry. The spectrum of $[\text{Pd}_2\text{Cl}_6]^{2-}$ shows two well resolved pre-edge features; the first, at 2821.0 eV and the second at 2822.4 eV are representative of terminal chloride and bridging chloride $1s \rightarrow 3p$ excitations into two doubly unoccupied LUMOs with the same symmetry as PdCl_2 . Assignment of the peaks was made using the relative energy shifts of the separate terminal chloride and bridging chloride pre-edge energies in $[\text{PdCl}_4]^{2-}$ and PdCl_2 . Since in the dimer $[\text{Cl}^t_2\text{PdCl}^b_2\text{PdCl}^t_2]^{2-}$ complex, the same LUMOs are being probed in both pre-edge features but from different chlorine absorbers, the first peak can be assigned to terminal chlorides and the second to bridging chlorides with lower and higher Z_{eff} , respectively. Data for all energy positions, line widths, intensities, analytical areas and covalency values are given in Table 2.1.

Peak Intensity Analysis. Pre-edge area fits show that the normalized area for $[\text{PdCl}_4]^{2-}$ and PdCl_2 are 2.0 eV and 3.5 eV respectively. The total Cl 3p covalency per d orbital is 45% for $[\text{PdCl}_4]^{2-}$ which is in agreement with previous results³³. Depending on

the method used to determine Pd covalency in the L-edge analysis, three covalency values are possible for PdCl_2 : $44\pm 2\%$, $41\pm 2\%$ or $42\pm 2\%$ from Methods I, II, or III, respectively. These values are slightly lower than previous results as reported in the introduction of this chapter. Self-absorption could explain an increase in pre-edge areas as it causes less intense and broadened features. Regardless of these differences, Pd-Cl bonds are still experimentally shown to be very covalent.

Given the overlapping edges from two different chloride ligands, the intensity of the two pre-edge features in the $[\text{Pd}_2\text{Cl}_6]^{2-}$ spectrum had to be separately renormalized to account for the 4 terminal chlorides and 2 bridging chloride absorbers.⁴⁶ Renormalized intensities are 2.3 eV and 3.3 eV for terminal and bridging chlorides, respectively. The terminal environment has $26\pm 1\%$ Cl 3p character per d orbital hole and bridging chlorides have an average of $19\pm 3\%$ Cl 3p character per d orbital hole.

Pd L-edge XANES

Peak Position Analysis. The spectra of the homoleptic complexes $[\text{PdCl}_4]^{2-}$, PdCl_2 and $[\text{Pd}_2\text{Cl}_6]^{2-}$ are shown in Figure 2.2a with the reference Pd^0 . The rising-edge positions increase in energy from Pd^0 , $[\text{PdCl}_4]^{2-}$, PdCl_2 and $[\text{Pd}_2\text{Cl}_6]^{2-}$, located at 3173.4 eV, 3180.1 eV, 3180.6 eV, and 3180.8 eV, respectively. All three palladium complexes have formally Pd^{II} metal centers, which is reflected by the ~ 7 eV shift up in energy from the rising-edge position of Pd^0 . The rising-edge energy positions among the chloropalladium complexes however, vary only slightly by 0.7 eV. This is expected since all of the

complexes have similar ligand environments in square planar geometries around the metal center.

Pre-edge features all show one intense peak, which is the same LUMO or LUMO-s being probed at the Cl K-edge. Pre-edge energy positions for $[\text{PdCl}_4]^{2-}$ and $[\text{Pd}_2\text{Cl}_6]^{2-}$ are both located at 3175.7 eV and 3332.6 eV at the L_{III} - and L_{II} -edges, respectively. The pre-edge for PdCl_2 is located 0.1 eV lower in energy at 3175.6 eV and 3332.5 eV for the Pd L_{III} - and L_{II} -edges. The gap between the rising-edge of $[\text{PdCl}_4]^{2-}$ and PdCl_2 (0.7 eV) and rising-edges (0.1 eV) indicates that the ligand field splitting is smaller for the PdCl_2 complex.

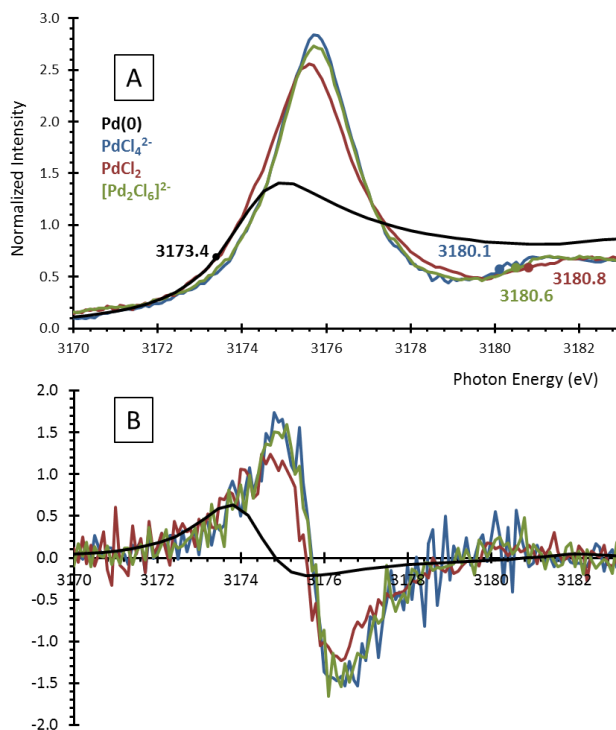


Figure 2.2: (a) Pd L_{III} -edge spectra of Pd^0 (black), $[\text{PdCl}_4]^{2-}$ (blue), PdCl_2 (red) and $[\text{Pd}_2\text{Cl}_6]^{2-}$ (green) used for energy position analysis. (b) First-derivative spectra of the respective complexes.

Table 2.1

Chlorine K-edge data measured at ALS 9.3.1. Bridging chlorides analyzed using Methods I, II, and III. (see text)

Compound	Edge	Method	Rising- edge (eV)	Pre-edge (eV)	Amplitude	Line width (HHLW , eV)	Intensity (D ⁰ , eV)	Total Intensity (D ⁰ , eV)	Renormalized Intensity (D ⁰ , eV)	Number of Absorbers	Number of Holes	Total Cl 3p Covalency	Transition Dipole Integral
Cs ₂ CuCl ₄	Cl K	--	2825.4	2820.2	0.5	0.98	0.6			4	1	29 ± 2%	26.4 I _{Cl_t}
K ₂ PdCl ₄	Cl K	--	2825.0	2821.6	1.4	1.09	2.0			4	2	47 ± 3%	26.4 I _{Cl_t}
				2823.2	0.1	1.10	0.1	2.1					
PdCl ₂	Cl K	<i>Method III</i>	2826.6	2821.8	2.3	1.21	3.5			2	2	42 ± 2% ^a	29.6 I _{Cl_b}
				2823.2	0.3	1.39	0.6	4.1					
Tea ₂ Pd ₂ Cl ₆	Cl K	--		2821.0	1.2	1.04	1.6		2.3 ^b	4	4	26 ± 1%	26.4 I _{Cl_t}
Tea ₂ Pd ₂ Cl ₆	Cl K	<i>Method III</i>	2825.0	2822.4	0.8	1.04	1.1		3.3 ^b	2	4	17 ± 1%	29.6 I _{Cl_b}

(a): Chlorine 3p character calculated from 1-PdCl₂ 4d character -0.02³³ from Method III (b): Renormalized to that type of Cl in the complex⁴⁶.

Table 2.2

Palladium LIII-edge data measured at ALS 9.3.1 analyzed by Methods I, II, and III (description in text)

Compound	Rising-edge (eV)	Pre-edge (eV)	Amplitude	Line width (HHLW,eV)	Intensity, Renormalized (D ⁰ , eV)	Intensity (D ⁰ , eV)	Number of Absorbers	Number of Holes	Total Pd 4d Covalency	Transition dipole integral (I, eV)
<i>Method I</i>										
Pd	3173.4									
K ₂ PdCl ₄	3180.1	3175.7	2.87	2.30	10.2		1	2	51 ± 1% ^a	30 ^b
PdCl ₂	3180.8	3175.6	2.50	2.73	10.7		1	2	54 ± 2%	30
[Pd ₂ Cl ₆] ²⁻	3180.6	3175.7	2.71	2.32	9.8		2	4	49 ± 1%	30
<i>Method II</i>										
K ₂ PdCl ₄	3336.6	3332.6	2.27	2.31	8.2		1	2	51 ± 2% ^a	24 ^b
PdCl ₂	3337.6	3332.5	2.19	2.70	9.3		1	2	57 ± 2%	24
[Pd ₂ Cl ₆] ²⁻	3337.3	3332.6	2.44	2.42	9.3		2	4	57 ± 1%	24
Compound	Edge	Pre-edge (eV)	Amplitude	Line width (HHLW,eV)	Intensity, Renormalized (D ⁰ , eV)	Intensity (D ⁰ , eV)	Number of Absorbers	Number of Holes	Total Cl 3p Covalency	TDI
<i>Method III</i>										
K ₂ PdCl ₄	Pd L _{III}	3175.7	1.71	2.30	6.1					
	Pd L _{II}	3332.6	0.91	2.33	3.3	9.4	1	2	51 ± 1% ^a	28 ^b
PdCl ₂	Pd L _{III}	3175.6	1.64	2.72	6.9					
	Pd L _{II}	3332.5	0.79	2.72	3.4	10.3	1	2	56 ± 1%	28
[Pd ₂ Cl ₆] ²⁻	Pd L _{III}	3175.7	1.80	2.32	6.5					
	Pd L _{II}	3332.6	0.89	2.36	3.2	9.7	2	4	53 ± 1%	28

a: Pd 4d character is 1-Cl 3p character - 0.02³³, b: transition dipole integral calculated using the dipole expression and Total Pd 4d Covalency

Peak Intensity Analysis. As outlined in Boysen's publication and described in the Materials and Methods section, three methods can be used to analyze Pd L-edge spectra. These methods result in different Pd 2p→4d transition dipole integrals and thus a range of Pd 4d character in LUMO-s of PdCl₂ and [Pd₂Cl₆]²⁻. This range of values gives larger uncertainty for Pd character. Pre-edge intensities for all complexes and all methods of fitting can be seen in Table 2.2. Palladium 4d orbital character is 51 ± 1% for [PdCl₄]²⁻. PdCl₂ and [Pd₂Cl₆]²⁻ have an average of 56 ± 2% and 53 ± 1% over the three methods.

Using the Pd 4d character in [PdCl₄]²⁻, a transition dipole integral for Pd^{II} complexes is derived using the dipole expression (Equation (1) above). The dipole integrals are 30 eV, 24 eV and 28 eV for Methods I, II, and III, respectively. As seen in the Cl K-edge, the Pd 4d covalency values are complementary to the Cl K-edge, showing that Pd-Cl bonds are very covalent, with nearly 50% of the electron density being palladium based.

Discussion

Cl K-edge

The Pd-Cl bonding for terminal and bridging chlorides were examined through the analysis of the Cl K-edge features of [PdCl₄]²⁻ and PdCl₂. Derived dipole integrals were used to determine the ground state electronic structure of [Pd₂Cl₆]²⁻. Terminal chlorides in [PdCl₄]²⁻ were found to have a total of 47 ± 3% Cl 3p character or, 12% electron donation per Cl. Bridging chlorides in PdCl₂ were calculated to have 42 ± 2% Cl 3p character or 21% electron donation per Cl ligand. The near 50% Cl 3p character

confirms previously reported³³ data and supports that Pd-Cl bonds are very covalent. It also verifies that bridging chlorides are more covalent than terminal chlorides, donating electron density to two metal centers via two different Cl 3p orbitals.

The dipole integral for terminal chlorides (I_{Clt}) was determined from the reference Cs_2CuCl_4 , with a value of 26.4 eV. The dipole integral for bridging chlorides (I_{Clb}), was determined through PdCl_2 analysis and was defined for this study as 29.6 eV. It was shown by Boysen, that a new dipole integral was needed due to the difference in chemical bonding between bridging and terminal chlorides.³³ Using the terminal chloride description for a bridging chloride, the sum of the chlorine and palladium characters become more than 100%, which is physically impossible. The data presented here for the PdCl_2 confirms previous results.

Furthermore, the use of the terminal and bridging dipole integrals in the dimer complex $[\text{Pd}_2\text{Cl}_6]^{2-}$ confirms that the methods developed by Boysen can be used to define the electronic structure of terminal and bridging environments as well as palladium metal centers. Terminal and bridging Cl 3p character are calculated to be $26 \pm 1\%$ and $17 \pm 1\%$ per chlorine atom. These values correlate to 13% per Pd-Cl bond terminal chloride donation to two palladium metal centers and 17% per Pd-Cl bond bridging chloride donation to the same metal centers. The dimer complex, with the two different chlorine ligand environments, supports that bridging chlorides are more covalent with 8% more character in Pd-Cl bonding than terminal chlorides.

Pd L-edge

The Pd L_{III}- and L_{II}-edges were analyzed at the XANES region to quantify Pd 4d character in homoleptic chloropalladium complexes. While three methods are presented, Method III is preferred for XANES analysis of L-edge data because the J=3/2 and J=1/2 core excited states stem from the same ground state. The ratio of the metal L_{III} to L_{II} edge-jump should theoretically be 2. The ratio between the Pd L-edges is close to this value with 1.8 intensity ratio between the two, and explains why all three methods give reasonable Pd 4d character values. However, not all metal L-edges follow this theoretical ratio. Therefore, Method III is the most desirable method to quantify any transition metal L-edge data. Separate normalization of L_{III} and L_{II}-edges may results in distortion in the pre-edge areas due to the loss of the electronic structural information stored in branching ratio.

Method III data analysis shows that Pd 4d character is $49 \pm 1\%$, $57 \pm 2\%$, and $53 \pm 1\%$ for $[\text{PdCl}_4]^{2-}$, PdCl_2 and $[\text{Pd}_2\text{Cl}_6]^{2-}$, respectively. Comparison of PdCl_2 Pd L-edge data between Boysen and those reported herein indicates that features are broader for the more recent data collection. This broadening is not observed in the other two chloropalladium complexes. Due to this broadening, an 8% larger Pd 4d covalency value is reported in this study. Broadening could be a result of self-absorption, which would artificially increase the intensity of the feature. However, we do not have enough data at this moment to ensure that this is the case. Further data measurement with multiple detection methods are planned at the Photon Factory in November 2013 accompanied by careful sample preparation toward obtaining a reproducible and reliable data analysis.

Conclusion

The data presented here confirms that the methods developed by Boysen in his 2008 paper are reliable for Pd L-edge analysis. Dipole integrals were determined for Pd^{II} metal centers with bridging chlorides for multi-edge XANES analysis at the Pd L-edge and Cl K-edge. The dimer complex [Pd₂Cl₆]²⁻ was used to evaluate the transferability of transition dipole integral for bridging chlorides. It was confirmed that the method used to find a new transition dipole integral using complementarity of metal and ligand character in homoleptic complexes is transferrable to other palladium complexes with both terminal and bridging ligand environments. Finally, this work also confirms that bridging chlorides need a different transition dipole integral in order to account for their differences in bonding from terminal chlorides.

CHAPTER 3

MULTI-EDGE X-RAY ABSORPTION NEAR-EDGE SPECTROSCOPIC ANALYSIS
OF THE Pd^{II}, Pd^{III} and Pd^{IV} REDOX SERIESIntroduction

Palladium-based homogeneous catalysts have rapidly emerged as versatile coordination compounds in organometallic chemistry. Catalysts in the Pd^{II} and Pd^{IV} oxidation states are used to perform C-H activations, C-C bond coupling and C-heteroatom bond coupling.^{1,47} It is commonly accepted that mechanisms of palladium-based transformations occur through two electron oxidations and reductions. However, it has been proposed that Pd^{II}/Pd^{IV} catalytic cycles may include one electron oxidations to Pd^{III} intermediates in C-H activations as depicted in Scheme 5 (page 10).^{48,49} While these species have been only postulated, experimental evidence of their presence is limited. Naturally, understanding the role of Pd^{III} species in catalytic cycles is needed in order to further the optimization of Pd^{IV} catalytic species.

The electron configuration of Pd^{II}, Pd^{III} and Pd^{IV} oxidation states are 4d⁸, 4d⁷ and 4d⁶, respectively as seen in Figure 3.1. Pd^{II} complexes are typically square planar complexes with the primary bonding interaction arising from the metal 4d_{x²-y²} orbital with ligand 2p/3p-orbitals. Pd^{IV} complexes are singlet octahedral complexes with quadruply unoccupied e_g* orbitals. Pd^{III} complexes are paramagnetic species with a single electron in a singly occupied molecular orbital (SOMO). The addition of an

unpaired electron in the d-manifold, from d^6 to d^7 , causes Jahn-Teller distortion which destroys the degeneracy of the e_g^* symmetry and lowers the symmetry to C_2 .

Figure 3.1 shows the approximate electron configurations in the bottom diagrams for complexes to be considered in this chapter.

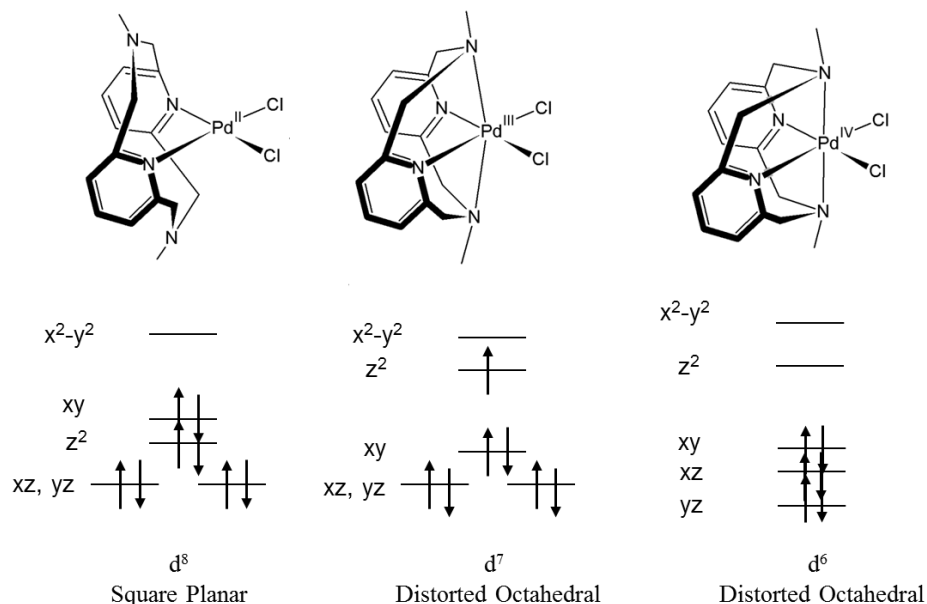


Figure 3.1: $MeN_4Pd^xCl_2$ complexes in the Pd^{II}, Pd^{III}, Pd^{IV} oxidation states. The d-manifold electron configuration and orbital energy ordering for each complex is below. Adapted from [51].

Pd^{III} coordination complexes have been synthesized and studied since the 1980s,²⁵ but until 2010 no one had isolated organometallic Pd^{III} complex.²⁶ The stability of these complexes has led to novel studies of Pd^{III} reactivity in carbon-carbon bond formation and C-H bond activation reactions. The Mirica group uses the macrocyclic ligand, N,N'-di-tert-butyl-2,11-diaza[3,3](2,6)pyridinophane ("N4"), to stabilize the Pd^{III} metal center. Two pyridine N-atoms coordinate in the equatorial plane, adjacent to two methyl groups

(chlorides in Figure 3.1), while the amine N-atoms weakly coordinate at the axial positions. The strain induced from all N-atoms coordinated to the metal forces a distorted angle of 153.5° between the axial amines and palladium center.⁵⁰ The ligand strain stabilizes the electronic configuration in such a favorable way, that the Pd^{III} oxidation state is preferred among the analogous Pd^{II} and Pd^{IV} complexes. Figure 3.2 shows this distorted octahedral environment with representative bond lengths and angles.

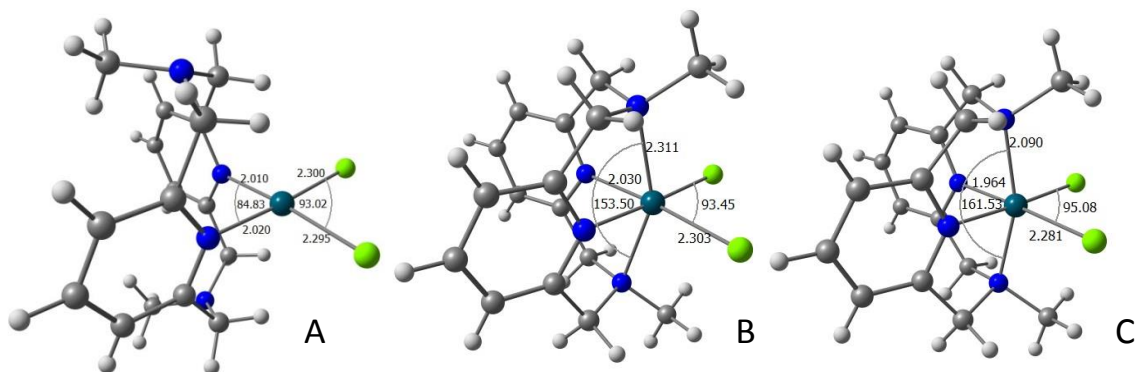


Figure 3.2: Bond lengths and bond angles as reported from crystal structures for $\text{Me}^{\text{N4}}\text{Pd}^{\text{II}}\text{Cl}_2$ (A), $\text{Me}^{\text{N4}}\text{Pd}^{\text{III}}\text{Cl}_2$ (B) and $\text{Me}^{\text{N4}}\text{Pd}^{\text{IV}}\text{Cl}_2$ (C).

The series of palladium complexes with the "N4" ligand coordination are differentiated by their geometric characteristics. The Pd^{II} species is four coordinate, as expected, with the pyridine N-atoms coordinated in the equatorial plane. The bond distance between Pd-Cl bonds and Pd-N_p bonds is 2.3 Å and 2.0 Å, respectively. The amine N-atoms are pointed away from the metal center, thus no coordination is possible. The Pd^{III} complex has the same equatorial pyridine coordination, but with a more electrophilic palladium center, the amine N-atoms approach the metal center. As a result, they are weakly coordinated with a long bond length of 2.3 Å. The Pd^{IV} species is structurally similar to the Pd^{III} complex with tetradentate "N4" ligand coordination.

However, all of the nitrogen based ligands are bound more tightly to the metal center with shorter Pd-N bond lengths and a more obtuse angle of 161.53° is adopted as the complex approaches an octahedral coordination geometry. The remarkable qualities of this series show that the Pd^{III} complex is preferentially stable over the Pd^{II} and Pd^{IV} complexes. The engineering of the ligand system and the strain that it imparts on the structure stabilizes the $4d^7$ electron configuration. In fact, mixing of equimolar amounts of Pd^{II} and Pd^{IV} complexes, comproportionate to the Pd^{III} species.

The ligand design presented above has opened up a path for studying the role of Pd^{III} intermediates in C-C bond formation, C-H bond activations and O_2 oxidation of Pd^{II} catalysts. By understanding the steric interactions and electronic structure of these ligand systems, further optimization of ligand environments can be made to study targeted reactions. Electronic structural characterization can be carried out with multi-edge XAS, a profound technique for obtaining electronic structural details about the ligand and metal components within a complex. XAS is an element specific technique and is capable of measuring diamagnetic and paramagnetic species, making it ideal for examining differences in electronic structures among the three analogous complexes shown in Figure 3.1.

The Cl K-edge results from the Cl $1s \rightarrow 3p$ excitation and provides information about the bond covalency, Cl 3p orbital character and effective nuclear charge of the Cl^- ligands. The Pd L-edge is a result of Pd $2p \rightarrow 4d$ excitations and provides complementary information to the Cl K-edge, only focused on the palladium absorber. Since pre-edge features at the Cl K-edge and Pd L-edges are a result of the same unoccupied frontier

molecular orbitals, together, they can provide a complete picture of the bonding between palladium and chlorine atoms.

As shown in Chapter 2, the chlorine K-edge and palladium L-edges have intense features that are sensitive to changes in the electronic structure of a complex. The approach to the analysis of Cl K-edge and Pd L-edge of chloropalladium complexes will be extended in this chapter to examine the electronic structures of more exciting heteroleptic complexes. In order to analyze pre-edge and rising-edge features of these complexes, another well-studied complex must be used for comparison to interpret the energy and intensity shifts reliably. The electronic structure of the homoleptic complexes of K_2PdCl_4 and K_2PdCl_6 are well understood,³³ and will serve as the reference spectra for heteroleptic complex XAS analysis. The homoleptic complexes have similar coordination environments to their heteroleptic counterparts, so they will be important for understanding how bond character in Pd-Cl bonds changes and allowing for better understanding about the electronics of the “N4” ligand system.

Methods

Sample Sources

The complexes $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$, $[^{\text{Me}}\text{N4Pd}^{\text{III}}\text{Cl}_2]^+ \text{ClO}_4^-$, and $[^{\text{Me}}\text{N4Pd}^{\text{IV}}\text{Cl}_2]^{2+} (\text{BF}_4^-)_2$ were synthesized and characterized by the Mirica group and provided as solid powders.²⁸ Other samples used in this study were K_2PdCl_4 and K_2PdCl_6 , which were purchased as pure compounds from Strem Chemicals and used without further purification.

X-ray Absorption Measurements

All measurements of the homoleptic chloropalladium species and the $^{Me}N_4PdCl_2$ oxidation state series were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) under storage ring (SPEAR 3) conditions of 96-81 mA current and 3 GeV energy. The Cl K-edge and Pd L-edge XANES regions were collected on beamlines 6-2 and 4-3 for the homoleptic and heteroleptic complexes, respectively. Pd K-edge data was collected at beamline 7-3.

Beamline 6-2 is a 56-pole, 0.9T and beamline 4-3 is a 20-pole, 2.0 T Wiggler beamline equipped with a liquid N₂ cooled Si(111) double-crystal monochromator. Beamline 6-2 and 4-3 were optimized at 2750 eV and 2575 eV, respectively. Cs₂CuCl₄ was used as the calibrant. The maximum of the pre-edge feature was set at 2820.2 eV. Chlorine K-edge spectra were collected in the energy range of 2770-3150 eV using an unfocused beam in a He-purged beam path at room temperature using a Lytle fluorescence detector. All of the samples were prepared in an anaerobic N₂ purged glovebox, diluted with boron nitride and mounted onto contaminant-free Kapton tape. The samples, while not particularly air sensitive, were protected from oxidation and moisture contact by mounting a thin polypropylene window in front of the Kapton tape. At least three scans were collected and averaged to obtain improved signal-to-noise ratios. Radiation damage was not observed during any of the data collection as the second scan looked practically identical to the first.

Data Work-up and Normalization

Before fitting and analyzing XAS data, baseline subtraction, background correction and normalization procedures were followed using the Automated Data Reduction Protocol developed by Gardenghi.⁵² The baseline subtraction and background correction are often done in a single step. The background correction of the raw data is then fit with a second order polynomial to the pre-edge region, which is subtracted from the original data to produce the background corrected data (Figure 3.3a). A linear line is then fit to the post-edge region, which is used to generate a constraint for the first derivative of a spline function. The spline is used to normalize the spectrum by scaling the Cl K-edge to 1 at 2840 eV, Figure 3.3b.

Similar procedures were followed for the Pd L-edge. A second order polynomial was fit to the pre-edge of the L_{III} -edge and subtracted from both the L_{III} - and L_{II} -edges to generate background corrected data. Following Method III in Chapter 2, a second order spline was fit to the post-edge of the Pd L_{II} -edge region and normalized to 1 at 3345 eV.

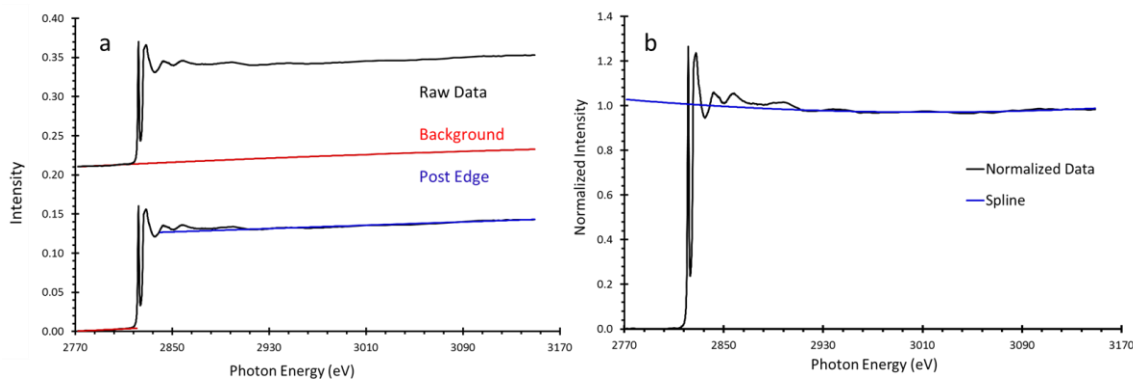


Figure 3.3: (a) Representative Cl K-edge data illustrating background subtraction, and polynomials fit to the pre-edge and post-edge. (b) Post-edge second order polynomial used as a spline to normalize background corrected data.

Spectral Correction due to Presence of Counter-ions

The ClO_4^- counterion for the $[\text{Me}_4\text{N}^+\text{Pd}^{\text{III}}\text{Cl}_2]^-$ complex caused interference with normalization procedures. Because measurements were taken at the Cl K-edge, the chlorine absorber of the perchlorate counterion is also measured, and the spectrum is a result of two chlorine ligands and the perchlorate ion. The normalized spectra of the Pd^{III} complex and NaClO_4 are shown in Figure 3.4a. The intense feature in both spectra at 2835.5 eV is a result of the Cl-O bonds in the ClO_4^- ion. Fortunately, the formal oxidation of Cl in ClO_4^- is +7 and the rising-edge energy position is high enough in energy that it does not overlay with the chlorine ligand XANES feature. Furthermore, given this large energy separation the spectral contributions can be readily corrected due to the presence of perchlorate anion. In order to correct for the perchlorate features, simple subtraction of the counter-ion spectrum was used, followed by renormalization of the edge.

Three subtraction methods were employed to correct for the perchlorate feature interfering with intensity of the edge jump. A simple stoichiometric subtraction was used based on chemical reasoning, for every two chloride ligands, one perchlorate is present. Assuming that there are three different chlorine absorbers present in equimolar amounts, the $[\text{Me}_4\text{N}^+\text{Pd}^{\text{III}}\text{Cl}_2]^-$ complex spectrum was renormalized to 3. The normalized NaClO_4 spectrum was subtracted, accounting for one third of the rising-edge intensity. The subtracted spectrum was then renormalized to two for the two chlorine ligands within the complex. The second and third subtraction methods were based on fitting a second and third order polynomial to the ratio of complex to counter-ion intensities at four points

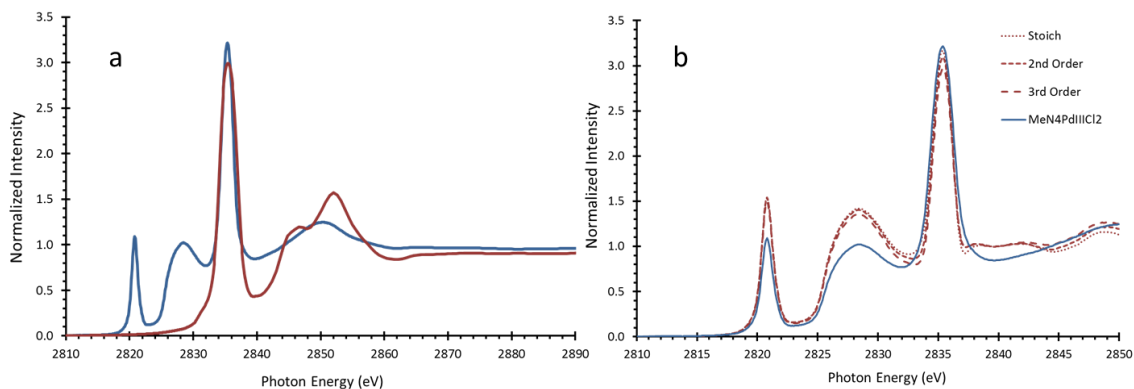


Figure 3.4: (a) Spectra of $[\text{MeN}_4\text{Pd}^{\text{III}}\text{Cl}_2]^+ \text{ClO}_4^-$ (blue) and NaClO_4 (red) overlaid to show the overlap of the Cl K-edge edge-jump. (b) Spectra of normalized $[\text{MeN}_4\text{Pd}^{\text{III}}\text{Cl}_2]^+ \text{ClO}_4^-$ (blue) alongside renormalized data after subtraction methods were performed: stoichiometric subtraction (---), second-order subtraction (- - -) and 3rd order subtraction (-- --).

(2835.5 eV, 2852 eV, 2870 eV, and 2880 eV). These four points represent the energy positions of the three features in the perchlorate spectrum and an arbitrary energy after the edge-jump. The ratio between the values between the two spectra at each point was used to scale the perchlorate spectrum, followed by the stoichiometric subtraction method. The three subtraction methods and the change in pre-edge intensity are shown in Figure 3.4b; importantly, there is negligible variation among them.

XANES Data Fitting

Fitting of the Cl K-edge and Pd L-edge XANES region was achieved by using PeakFit v4.12 (Seasolve Software, Inc.). The fits were based on a molecular orbital-based picture, where the pre-edge is defined to represent the LUMO from symmetry adapted linear combinations of Cl 3p and Pd 4d orbitals. Respective fits of each spectrum at each edge is shown in Figure 3.5. The single feature in each heteroleptic spectrum was fit with a 1:1 sharing of Gaussian/Lorentzian line shapes at the Cl K-edge. This mixing is based

on broadening due to excited state lifetimes and beamline optics. The rising-edge was fit using the spectrum of NaCl, which represents the “free” chloride ligand edge-jump. There are no existing pre-edge features in the XANES region of NaCl, thus it is used to model the rising-edge of any complex with chlorine absorbers at the Cl K-edge by shifting and scaling the data.

Similarly, the Pd L-edge rising-edge was modeled with the spectrum from metallic Pd⁰ powder. Pd powder has a closed shell 4d¹⁰ electron configuration and no pre-edge features. The shape of the rising-edge is used to model the rising-edge for Pd^{II}, Pd^{III} and Pd^{IV} spectra by shifting and scaling. Pre-edge features at the Pd L-edge are fit with peaks that are allowed to vary in the amount of Gaussian/Lorentzian mixing. Line shapes at metal L-edges are broader than at the Cl K-edge, thus the 1:1 lineshape does not fit well. This variation in the lineshape is a result of the different fluorescence relaxation channels at the metal L- vs. ligand K-edge.⁹¹ The spectrum of [^{Me}N4Pd^{IV}Cl₂]²⁺ has two pre-edge features. These features were fit using shared linewidths as the transitions result from the same Cl 1s orbital.

Renormalization

In order to appropriately show the intensity related to the number of chlorine absorbers in each complex, spectra were renormalized by the number of chloride ligands in each complex. Since [PdCl₄]²⁻ has twice as many chloride ligands as ^{Me}N4Pd^{II}Cl₂, it was renormalized to two while the heteroleptic complex is normalized to one. The renormalized spectra correct for the intensity for the total number of chlorides in each system. Similarly, the Cl K-edge spectrum of [PdCl₆]²⁻ needs to be renormalized to

three when compared to the heteroleptic complex $[\text{MeN4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$.

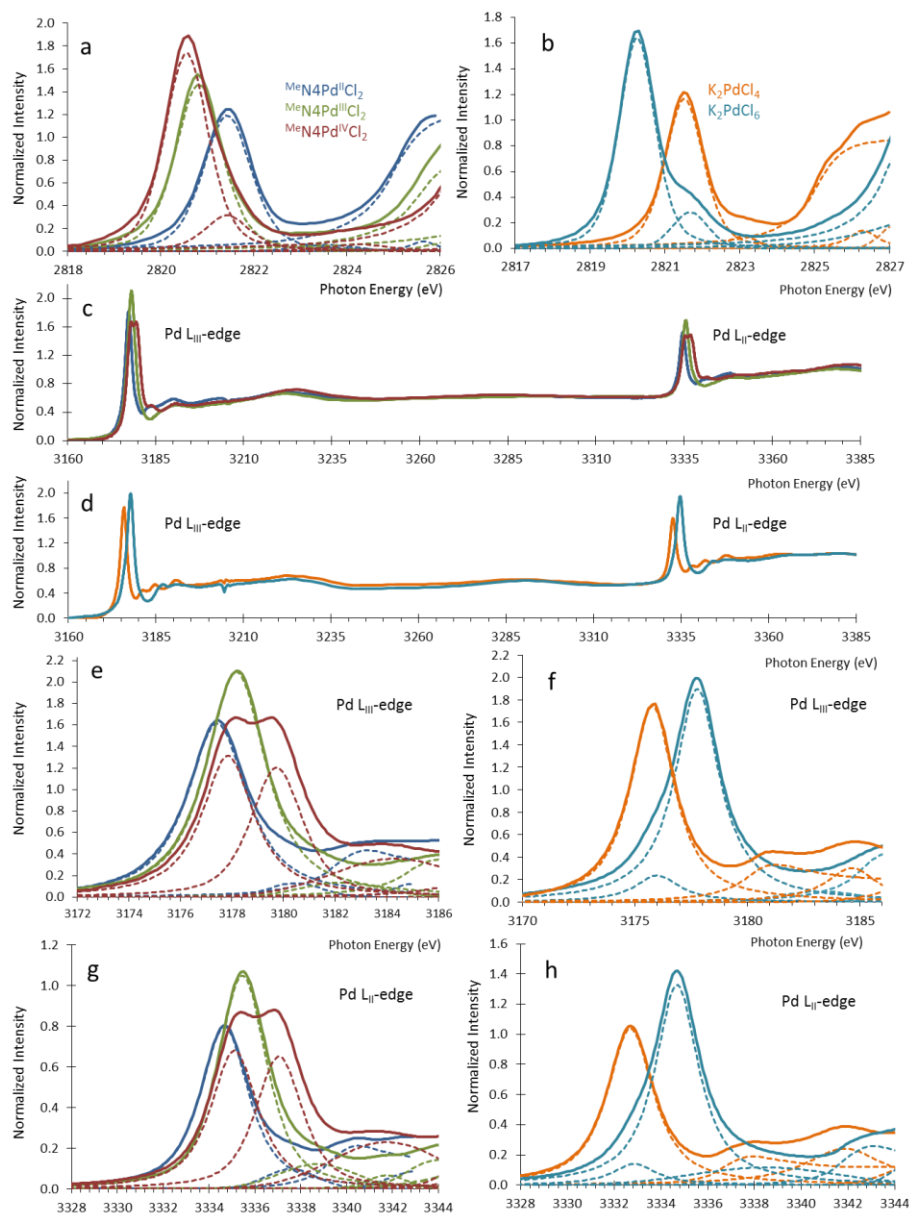


Figure 3.5: Representative fits for all heteroleptic and homoleptic complexes with normalized data (solid lines) and fitted features (dotted lines). Plots (a), (e) and (g) show the Cl K-edge, Pd L_{III}-edge and Pd L_{II}-edge fits for $[\text{MeN4Pd}^{\text{II}}\text{Cl}_2]$ (blue), $[\text{MeN4Pd}^{\text{III}}\text{Cl}_2]^+$ (green) and $[\text{MeN4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$ (red), respectively. Plots (b), (f) and (h) show Cl K-edge, Pd L_{III}-edge and Pd L_{II}-edge fits of $[\text{PdCl}_4]^{2-}$ (orange) and $[\text{PdCl}_6]^{2-}$ (turquoise), respectively. Plots (c) and (d) show the normalized Pd L-edge data, using Method III.

Results and Analysis

The XANES region of the Cl K-edge provides direct experimental information about bond covalency, orbital composition, Z_{eff} and nucleo- or electrophilicity of an absorber. This region can be used to understand electronic structural differences between complexes and allows for understanding of chemical reactivity. The information content from the XANES spectrum is better understood and more reliably analyzed when compared to similar or comparable complexes. To make inferences about the electronic structure of the analogous $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$, $[^{\text{Me}}\text{N4Pd}^{\text{III}}\text{Cl}_2]^+$ and $[^{\text{Me}}\text{N4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$ complexes, homoleptic chloropalladium complexes $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$ are used as model complexes for comparisons. Differences between spectral features at the Cl K-edge between the homoleptic and heteroleptic complex of the same formal oxidation state will indicate differences in Pd-Cl bonding. Shifts in pre-edge intensity and rising-edge energy positions will indicate how the N-donor ligand in the heteroleptic complex influences the electronic structure of the complex by replacing chloride donor ligands. These comparisons allow for indirect observations to be made about the unique macrocyclic “N4” ligand system present in the three palladium complexes.

Palladium^{II} Complex Analysis

Cl K-edge

Energy Position Analysis of XANES Features. Figure 3.6a shows the renormalized data for Cs_2CuCl_4 , K_2PdCl_4 , and $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$. Rising-edge inflection points were

determined through the First-derivative spectrum (Figure 3.6b) as the first inflection point after the last resolved feature in the XANES region. Rising-edges are often correlated with the effective nuclear charge of the Cl 1s core orbital and are assigned to the dipole allowed Cl 1s→4p transition. Rising-edge energy positions for Cs₂CuCl₄, [PdCl₄]²⁻ and ^{Me}N₄Pd^{II}Cl₂ are 2824.3 eV, 2824.9 eV and 2825.1 eV, respectively. Pre-edge energy positions were obtained from the first minima in the second derivative spectrum (Figure 3.6c) and correspond to the dipole allowed Cl 1s → 3p transition. ^{Me}N₄Pd^{II}Cl₂ has a single pre-edge at 2821.4 eV. K₂PdCl₄ has two pre-edge features: the first, and most intense, at 2821.5 eV and the second at 2823.1 eV (Figure 3.6). The reference Cs₂CuCl₄ complex has a single pre-edge feature at 2820.2 eV.

Both Pd^{II} complexes have square planar geometry with a doubly unoccupied LUMO. The LUMO in each complex is a Pd 4d_{x²-y²} based orbital with Cl 3p character. The first feature in the [PdCl₄]²⁻ spectrum is assigned to the LUMO of b_{1g}* while the weaker second feature is attributed to the ¹A_{1g} excited state due to double occupation of b_{1g}* (4d_{x²-y²} orbital) and de-occupation of b_{2g} (4d_{xy} orbital) into the ground state.³³ The generally large separation between b_{1g} and b_{2g} for tetragonal complexes can be reduced by the presence of counterions from the crystal packing environment above and below the plane of the molecule by lowering orbitals with ‘z’ components, which in turn results in raising the energy of orbitals with dominantly ‘x’ and ‘y’ components. The reduced energy separation induces degeneracy and allows for electronic state mixing. Both features were used in quantitative analysis since they originate from the same ground

state. All data regarding edge positions and intensities at the Cl K-edge can be found in Table 3.1.

Cs_2CuCl_4 is a well-defined homoleptic complex in which the electronic structure has been determined quantitatively.³⁶ Hereby, the spectrum of Cs_2CuCl_4 is shown as a comparison to aid the assessment of relative intensities and energy shifts. Cs_2CuCl_4 has one hole in its 3d manifold that is able to accept electron density from terminal chlorides, while Pd^{II} complexes have two holes in the 4d manifold. The rising-edge position for Cs_2CuCl_4 is located at 2824.3 eV; 0.6 eV lower in energy than the palladium complexes. This decrease in rising-edge position indicates that the chlorine Z_{eff} is smaller due to less electron donation to the Cu d-manifold. The additional hole in the Pd^{II} d-manifold allows the chloride ligands to increase their donation, thus becoming effectively less negative.

By comparing the two Pd^{II} complexes, several similarities can be found in their electronic structures. The rising-edge energy positions of the two complexes are 0.2 eV apart from one another. These energy positions are assigned to the Cl 1s $\rightarrow$ 4p transition. Cl 4p Rydberg orbitals do not significantly contribute to the Pd-Cl bond, thus the rising energy position estimates the difference in the Cl Z_{eff} between the homoleptic and heteroleptic complexes. The 0.2 eV increase in rising-edge experimentally shows that the Cl 1s orbital from the heteroleptic complex is 0.2 eV lower in energy than the $[\text{PdCl}_4]^{2-}$ counterpart. The gap between the rising-edge features (0.2 eV) is also larger than the gap in the pre-edge energy position (0.1 eV), indicating that there is 0.1 eV increase in d-manifold splitting in the heteroleptic complex. These differences are measurable, but small, indicating that the electronic structures of the two Pd^{II} complexes are similar.

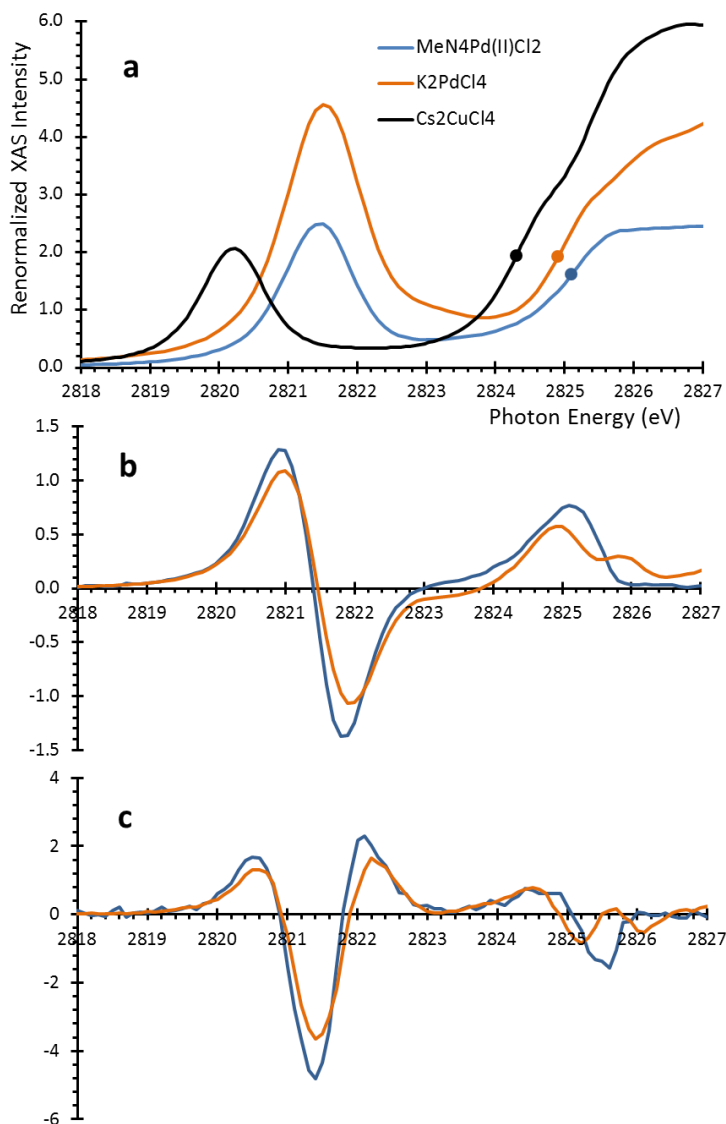


Figure 3.6: (a) Renormalized spectra of Cs_2CuCl_4 (black), K_2PdCl_4 (orange) and $\text{Me}_4\text{N}_4\text{Pd}^{\text{II}}\text{Cl}_2$ (blue) used for energy position analysis. (b) and (c) First- and second-derivative plots of respective complexes

Intensity Analysis of Pre-edge Features. Analytical areas of the renormalized pre-edge features are 3.68 ± 0.09 eV for $\text{Me}_4\text{N}_4\text{Pd}^{\text{II}}\text{Cl}_2$ and 7.71 ± 0.32 eV for $[\text{PdCl}_4]^{2-}$. Both pre-edge areas correspond to the Cl $1s \rightarrow 3p$ transition, where the Pd $4d_{x^2-y^2}$ based LUMO contains some Cl $3p$ character. Integrated area of pre-edge is directly proportional to the Cl $3p$ character in the LUMO. Using the established Cl $3p$ character (7.3% per absorber)

in Cs_2CuCl_4 and the corresponding analytical area from the data presented a conversion constant was obtained to relate analytical areas to bond covalency. The pre-edge areas correspond to $12.0 \pm 0.3\%$ and $9.6 \pm 0.2\%$ Cl 3p character per hole and per absorber for $[\text{PdCl}_4]^{2-}$ and $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$, respectively. Since the metal oxidation states are both formally Pd^{II} the decrease in Cl 3p covalency in the heteroleptic complex is attributed to better σ -donation from the pyridine N-atoms of the “N4” ligand.

Pd L-edge

Energy Position Analysis of XANES Feature. In Figure 3.7a, the two Pd^{II} heteroleptic and homoleptic complexes are shown at the Pd L_{III} -edge. Pd^0 serves as the reference spectrum for the Pd L-edge since it has a filled d-manifold with no ligand environment and thus it does not show a pre-edge feature in the XANES region. Two edges are present at the L-edge as a result of 2p core hole spin-orbit coupling. The Pd L_{II} -edge is about 150 eV higher in energy. It is a result of the excitation from 2p orbitals to the $J=1/2$ excited state with a core hole left behind in the 2p manifold that has an antiparallel coupled spin and orbital angular momentum. Its features are similar to the L_{III} -edge, which is a result of excitations to the $J=3/2$ state with parallel spin and orbit angular momentum. Energy position analysis can be performed using either edge; however, the Pd L_{III} -edge features are more intense, it is presented in all the figures for analysis.

Table 3.1

Chlorine K-edge data measured at SSRL, Beamlines 4-3 and 6-2.

Compound	Beamline	Rising-edge (eV)	Pre-edge (eV)	Amplitude	Intensity, D ₀ (eV)	Sum (eV)	Renormalized Intensity	Line width (HHLW, eV)	Number of Absorbers	Number of Holes	Total Cl 3p Bond Covalency per hole	Covalency per chloride
NaCl	4-3	2825.5	--	--	--	--		--	1	--	--	
Cs ₂ CuCl ₄	6-2	2825.4	2820.2	0.47	0.58		2.34	0.95	4	1	29 ± 1% ^a	7%
	4-3	2825.4	2820.2	0.48	0.70		2.80	1.15	4	1	29 ± 1% ^a	7%
K ₂ PdCl ₄	6-2	2824.9	2821.5	1.16	1.78	1.93	7.71	1.20	4	2	48 ± 1%	12%
			2823.1	0.10	0.14							
^{Me} N ₄ Pd ^{II} Cl ₂	4-3	2825.1	2821.4	1.21	1.84		3.68	1.25	2	2	19 ± 1%	10%
K ₂ PdCl ₆	6-2	2827.0	2820.3	1.65	2.37	2.79	16.76	1.14	6	4	52 ± 1%	9%
			2821.7	0.28	0.42			1.14				
^{Me} N ₄ Pd ^{IV} Cl ₂	4-3	2826.3	2820.6	1.73	2.51	2.97	5.94	1.09	2	4	16 ± 1%	8%
			2821.4	0.32	0.45			1.09				
^{Me} N ₄ Pd ^{III} Cl ₂	4-3	2825.4	2820.8	1.02	2.28		4.56	1.20	2	3	16 ± 1%	8%

a: Ref. from [29]

The first derivative of each spectrum is shown in Figure 3.7b, where the first maximum after the pre-edge feature determines the rising-edge energy position. The rising-edges inflection points are a result of Pd 2p $\rightarrow$ 5s transitions and increase in the order of Pd⁰, [PdCl₄]²⁻ and ^{Me}N₄Pd^{II}Cl₂. The corresponding energy positions are 3173.8 eV for palladium powder, 3180.2 eV for [PdCl₄]²⁻ and 3181.9 eV for ^{Me}N₄Pd^{II}Cl₂.

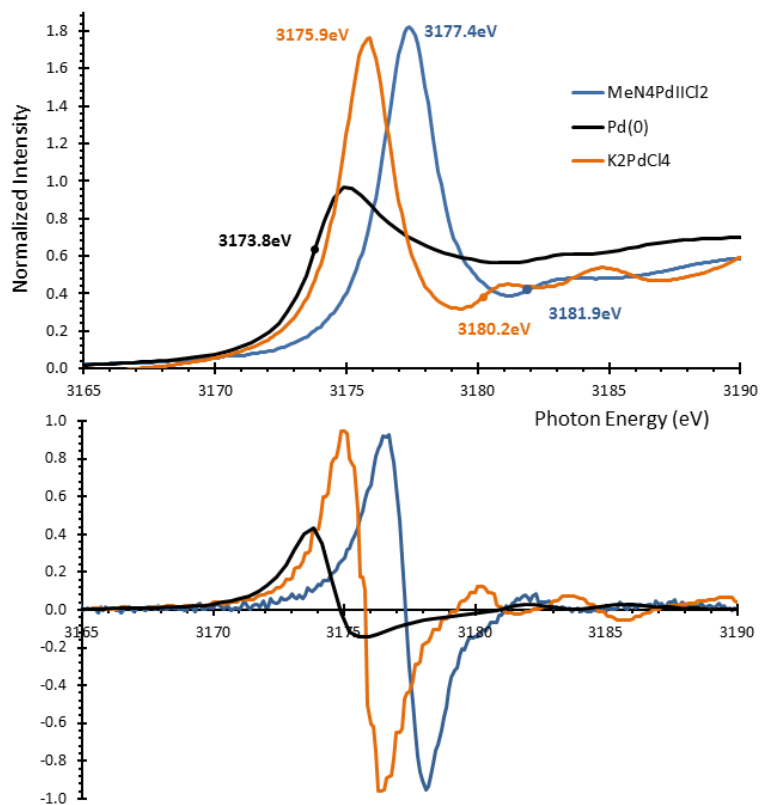


Figure 3.7: (a) Normalized data of Pd⁰ (black), K₂PdCl₄ (orange) and ^{Me}N₄Pd^{II}Cl₂ (blue).
(b) First-derivative spectra

Pre-edge energy positions were determined using the energy axis intercept of the pre-edge in the first-derivative spectrum. Intense pre-edge features are located at 3175.8 eV and 3177.4 eV for [PdCl₄]²⁻ and ^{Me}N₄Pd^{II}Cl₂, respectively and correlate to the Pd

2p→4d dipole allowed transition. Table 3.2 lists the energies in eV, intensities (unit less due to normalization), half-height full line widths in eV and analysis of the pre-edge features. The same LUMO is being probed at the Pd L-edge as the Cl K-edge, so it is expected to have one intense pre-edge feature, as seen in the Cl K-edge. These pre-edge features provide complementary information about the bonding between metals and ligands, from the perspective of the metal component.

The rising-edge position of $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$ is 1.7 eV is higher in energy than K_2PdCl_4 , which corresponds to a 1.7 eV lower Pd 2p core orbital energy for the heteroleptic complex. This is a modest difference considering that a formal 2 electron oxidation from Pd^0 is about a 7 eV shift. It is predicted that the pyridine ligand, while participating as a good σ -donor in this complex, is also withdrawing electron density from the palladium into its π^* frontier orbitals. The LUMO contour plot in Figure 3.8 illustrates the symmetry adapted linear combination of two pyridine σ^* orbitals forming back-bonding interactions with the occupied Pd $4d_{xy}$ orbital. However, this interaction is too small to justify the 2 eV energy difference between rising-edge features of the complexes. The rising-edge represents the total Z_{eff} and not just the electron donation associated with the covalent interaction of the Pd 4d and N 2p/Cl 3p orbitals. Higher lying Pd 5s and 5p orbitals may participate in bonding, but to a smaller extent than the Pd 4d. Overlap between Cl 3p and Pd 5s/5p orbitals is greater than the combination of the N 2p and 5s/5p overlap due to the differences between the radial part of the orbital's wave function. The 5s/5p and 3p overlap allows for more covalent interaction than the 5s/5p and 2p overlap. Considering that Cl 3p orbitals can donate to more Pd-based orbitals

Table 3.2

Pd L-edge data measured at SSRL, Beamline 4-3 and 6-2.

Compound	Beamline		Rising-edge (eV)	Pre-edge (eV)	Amplitude	Intensity, D ₀ (eV)	Sum (eV)	Line width (HHLW, eV)	Number of Absorbers	Number of Holes	TDI	Total Pd 4d Covalency per hole
Pd(0)	4-3		3173.8	--	--	--	--	--	1	--	--	--
K ₂ PdCl ₄	6-2	L3	3180.2	3175.8	1.75	6.31	10.02	2.36	1	2	29.8	50.5 ± 1%
		L2	3337.2	3332.7	1.05	3.71		2.36				
^{Me} N4Pd ^{II} Cl ₂	4-3	L3	3181.9	3177.4	1.63	6.89		2.81	1	2	29.8	49.2 ± 1%
		L2	3338.2	3334.7	0.79	2.88	9.76	2.48				
K ₂ PdCl ₆	6-2	L3	3184.6	3175.9	0.26	0.97		2.36	1	4	20.3	47.5 ± 1%
				3177.8	1.87	6.85						
		L2	3342.2	3332.7	0.12	0.44		2.27				
				3334.7	1.33	4.62	12.89					
^{Me} N4Pd ^{IV} Cl ₂	4-3	L3	3188.3	3177.9	1.31	4.88		2.44	1	4	20.3	50.5 ± 1%
				3179.8	1.22	4.15						
		L2	3347.1	3335.1	0.68	2.47		2.46				
				3337.1	0.65	2.20	13.71					
^{Me} N4Pd ^{III} Cl ₂	4-3	L3	3184.9	3178.17	2.09	8.60	12.31	2.76	1	3	25.4	48.5 ± 1%
		L2	3342.7	3335.47	1.05	3.71		2.55				

(a_{1g}^* and e_u^* in D_{4h}), than N 2p orbitals, the palladium would become effectively more reduced in the homoleptic complex. Although not well resolved, shoulders along the Cl K-edge rising-edge of $[\text{PdCl}_4]^{2-}$ can be correlated with these covalent interactions involving the Pd 5s/5p Rydberg-type orbitals.

The gap between the rising-edge (1.7 eV) and rising-edge positions (1.5 eV) between shows that the ligand field splitting is 0.2 eV higher for the $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$ complex, which supports findings from the Cl K-edge with respect of the s-donor pyridine ligands generate intermediate strength ligand field in addition to the π -acid character as well.

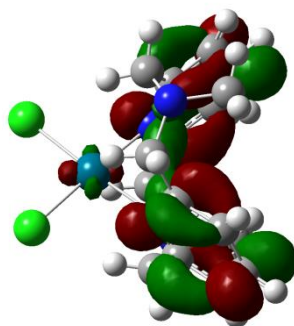


Figure 3.8: LUMO of $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$ indicating π -bond back donation from the Pd $4d_{xy}$ orbital. The orbital contour plot was calculated at BHandHLYP/def2-TZVP level

Intensity Analysis of Pre-edge Features. Core electron excitations from the Pd 2p orbitals involve the same LUMO probed at the Cl K-edge. Both complexes have square planar geometries, thus the LUMO is Pd $4d_{x^2-y^2}$ based. However, in addition to Pd-Cl bonds, the Pd L-edge feature also reflects electron density shared between the Pd- N_{py} bonds in the $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$ complex. Analytical areas of the pre-edges are 10.0 eV and 9.76 eV for $[\text{PdCl}_4]^{2-}$ and $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$, respectively. Using the chemically more reasonable

Method III, detailed in Chapter 2, the Pd 4d character is calculated to be $51 \pm 1\%$ and $49 \pm 1\%$ for the homoleptic and heteroleptic complex, respectively. These values indicate that, regardless of the ligand environment, Pd^{II} metal centers saturates at about 50% of the electron density, which is consistent with previous conclusions.³³

Palladium^{IV} Complex Analysis

Cl K-edge. Parallel to the Pd^{II} complex analysis, the homoleptic [PdCl₆]²⁻ complex will serve as a reference complex for the analysis of Pd^{IV} complexes. By comparing the energy positions and analytical areas between the homoleptic and heteroleptic complexes, comparisons and inferences about the electronic structure of [Me₄NPd^{IV}Cl₂]²⁺ and the [PdCl₆]²⁻ will be made.

[PdCl₆]²⁻ and [Me₄NPd^{IV}Cl₂]²⁺ complexes both have a six-coordinate ligand environment; however, the molecular symmetry greatly differs. The homoleptic complex has O_h symmetry and the heteroleptic complex is closer to C₂ symmetry. The heteroleptic complex can be approximated with a distorted octahedral structure with the axial ligands moved away from the z-axis. The “N4 ligand” system, when coordinated to the Pd^{IV} metal center, is coordinated by the equatorial pyridine N atoms and by amine N atoms at the axial positions. Because the amines and pyridine arms of the “N4 ligand” are tethered together via methyl bridge at the ortho positions of the aromatic system, the strain of the tetradentate ligand system reduces the N-Cu-N bite angle that causes distortion from the ideal octahedral to 161.5°. ⁵⁰

Energy Position Analysis of XANES Features. Figure 3.9a shows the XANES regions of Cs_2CuCl_4 , $[\text{PdCl}_6]^{2-}$ and $[\text{MeN4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$. Rising-edge inflection points were assigned by the first maximum after the pre-edge in the first-derivative spectra. Rising-edge energy positions are located at 2827.0 eV and 2826.3 eV for $[\text{PdCl}_6]^{2-}$ and $[\text{MeN4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$, respectively. Two pre-edge energy features are present in both Pd^{IV} complexes. $[\text{PdCl}_6]^{2-}$ have an intense feature at 2820.3 eV and less intense shoulder at 2821.7 eV. The spectrum of $[\text{MeN4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$ has one intense feature at 2860.6 eV with an unresolved peak on the higher energy side of the peak. The transitions for $[\text{PdCl}_6]^{2-}$ are a result of the excitation from the Cl 1s orbital to a quadruply unoccupied e_g^* LUMO. It is expected that the spectrum would only have only one intense feature due to the degeneracy in the ground state orbitals. However, a higher energy shoulder is seen after the intense feature. This feature can be attributed to excited state Jahn-Teller distortion effect, where the single occupied e_g^* excited state split into two levels, similar to the high spin d^4 and d^9 ground state electron configurations.⁷⁰ Since both of these features arise from the same ground state, both peaks are used in the quantitative pre-edge analysis. Unlike the excited state effects observed in the homoleptic complex, the two features present in the heteroleptic complex are described by the splitting of the e_g^* set in the ground state due to the low symmetry ligand environment. The strain on the axial component of this complex results in poor overlap of the N 3p orbital with the Pd $4d_{z^2}$ orbital, therefore the $4d_{z^2}$ orbital energy drops below that of the $4d_{x^2-y^2}$. An unfavorable overlap between Cl 3p and Pd $4d_{z^2}$ orbitals results in the observed in the shoulder of the pre-edge.

Ground state orbital energy levels however, do not correctly describe the ordering of the XANES features. Δ SCF calculations performed using the ADF package and TDDFT calculations performed using the ORCA program indicate that the $4d_{x^2-y^2}$ orbital, upon occupation by the excited Cl 1s electron, relaxes to a lower energy due to better overlap between the Cl 3p and Pd 4d orbitals and thus the more covalent. The details of the theoretical calculations are described in Chapter 4. The intense feature in $[\text{Me}_4\text{N}4\text{Pd}^{\text{IV}}\text{Cl}_2]^{2+}$ is assigned to Cl $1s \rightarrow \text{Pd } 4d_{x^2-y^2}$ based LUMO and the higher energy feature to a Cl $1s \rightarrow \text{Pd } 4d_{z^2}$ based LUMO transition. Both features are used to evaluate chlorine bond character.

The rising-edge positions of the palladium complexes are about 2 eV higher in energy than the rising-edge of Cs_2CuCl_4 . In contrast, the 0.6 eV gap observed between the Pd^{II} complexes and this copper complex. A 2.0 eV gap is attributed to three more holes in the Pd^{IV} d-manifold. Chloride donation overwhelmingly increases due to this electronic structural difference and becomes effectively more oxidized. The gap between the rising-edge positions of $[\text{PdCl}_6]^{2-}$ and $[\text{Me}_4\text{N}4\text{Pd}^{\text{IV}}\text{Cl}_2]^{2+}$ is 0.7 eV higher. Since the formal oxidation states of the metal centers are the same between these complexes, the increase in rising-edge energy position indicates that chloride ligands are more negative in the heteroleptic complex. This must be a result of the coordinated nitrogen ligands donating more electron density to the palladium center than the chloride components similarly to the Pd^{II} heteroleptic complex.

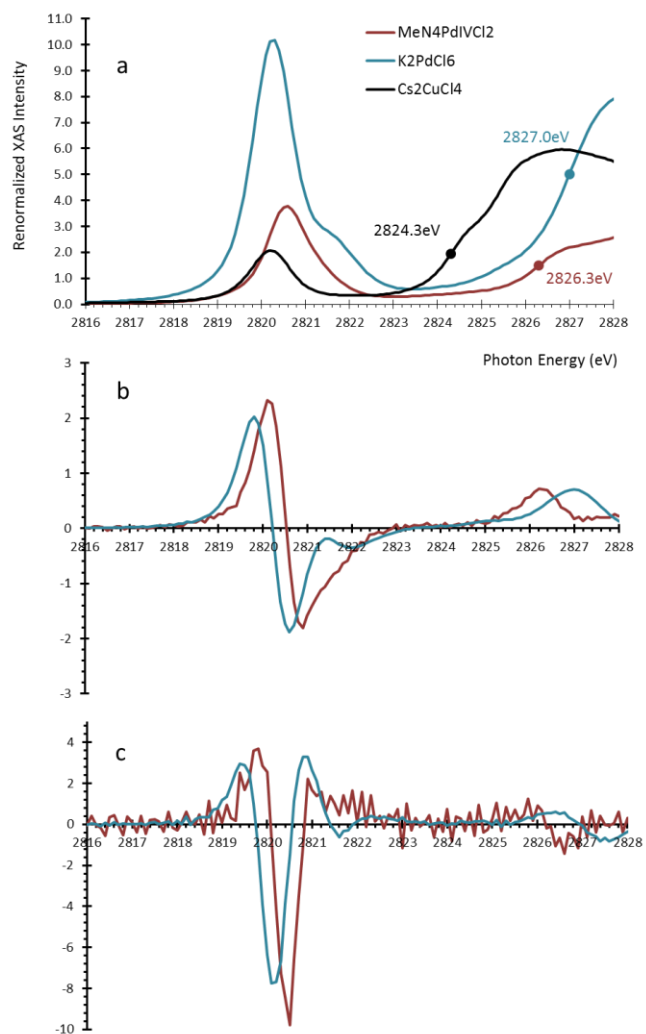


Figure 3.9: (a) Renormalized spectra of Cs_2CuCl_4 (black), K_2PdCl_6 (turquoise) and $[\text{MeN4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$ (Red). (b) and (c) First- and second-derivative plots of respective complexes.

Pre-edge peak positions are indicators of Pd effective nuclear charge, d manifold energy and ligand field splitting. The most intense features of the palladium complexes are located at 2820.3 eV and 2820.6 eV for $[\text{PdCl}_6]^{2-}$ and $[\text{MeN4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$, respectively. The gap between the rising-edges (0.7 eV) and the gap between the pre-edges (0.3 eV)

indicate that the ligand field splitting of $[\text{PdCl}_6]^{2-}$ is greater than $[\text{Me}_4\text{N}[\text{Pd}^{\text{IV}}\text{Cl}_2]^{2+}]$. This is as expected, since the ligand field splitting ($10Dq$) is greatest in octahedral environments.

Intensity Analysis of Cl K-edge Pre-edge Features. The total normalized analytical area under the pre-edges are 2.69 ± 0.05 eV and 2.97 ± 0.05 eV for $[\text{PdCl}_6]^{2-}$ and $[\text{Me}_4\text{N}[\text{Pd}^{\text{IV}}\text{Cl}_2]^{2+}]$, respectively. The ratio between known Cu-Cl bond covalency in Cs_2CuCl_4 and its pre-edge intensity was used to convert analytical areas into experimental Cl 3p Pd-Cl bond covalency in the LUMOs of the complexes. The total chlorine 3p Cl character is $52 \pm 1\%$ and $19 \pm 1\%$ for $[\text{PdCl}_6]^{2-}$ and $[\text{Me}_4\text{N}[\text{Pd}^{\text{IV}}\text{Cl}_2]^{2+}]$, respectively. These values reflect the covalency of all chlorines in each complex. With three times as many chlorides in the homoleptic complex, it is useful to normalize these covalency values to a per chloride basis to understand how covalent bonding changes. Adjusted, the Cl 3p covalency per hole is 9% and 8% for the homoleptic and heteroleptic complexes, respectively. Pd^{II} complex analysis showed that pyridine N-atoms are better donors than chloride ligands. As holes open up in the d-manifold from the Pd^{II} complex, donation from the amine and pyridine N-atoms are greater than for the chloride ligands, despite a modest overlap of amine N-atoms in the distorted structure.

Theoretical Analysis of the Cl K-edge spectrum of K_2PdCl_6 . The XANES structure of $[\text{PdCl}_6]^{2-}$ at the Cl K-edge has two features, and counters the ground state electronic structure description that there should only be one feature due to the quadruply unoccupied, degenerate e_g^* LUMO in the octahedral structure. The origin of the second feature has been proposed as a satellite shake-up transition,³³ photodegradation of the

complex and contamination.⁵³ The latter two can be disregarded due to the fact that pure compounds, purchased from Strem, were used for this study, with more than 99% purity. Lack of any isosbestic point between the two features upon multiple scans is indicative of lack of radiation damage. Thus, an excited state effect must be used to describe the second feature. Traditional and modified Kohn-Sham TDDFT calculations using the ADF package were not able to replicate the second feature seen in experiment (see Chapter 4). Therefore, the second feature is not a result of any excited state relaxation effects, but configuration interaction of excited states in the ground state picture or Jahn-Teller excited state distortion.

The Tanabe-Sugano (TS) diagram of a d^7 electron configuration as a result of core electron excitation of the parent d^6 electron configuration in Figure 3.10 can be used to justify the presence of the second feature. Excitation of the core Cl 1s electron populates the e_g^* molecular orbital, adding an extra electron to the d-manifold, hence using the d^7 TS diagram. The excited state electron configuration, $t_{2g}^6 e_g^1$, is represented by the ^2G term at the weak field limit. With increasing ligand field strength, this term splits into ^2E_g , degenerate $^2T_{2g}$ and $^2T_{1g}$ and $^2A_{1g}$ representations.⁵⁴ The second feature observed in the XAS spectrum is proposed to be the population of the degenerate $^2T_{2g}$ and $^2T_{1g}$ excited states.

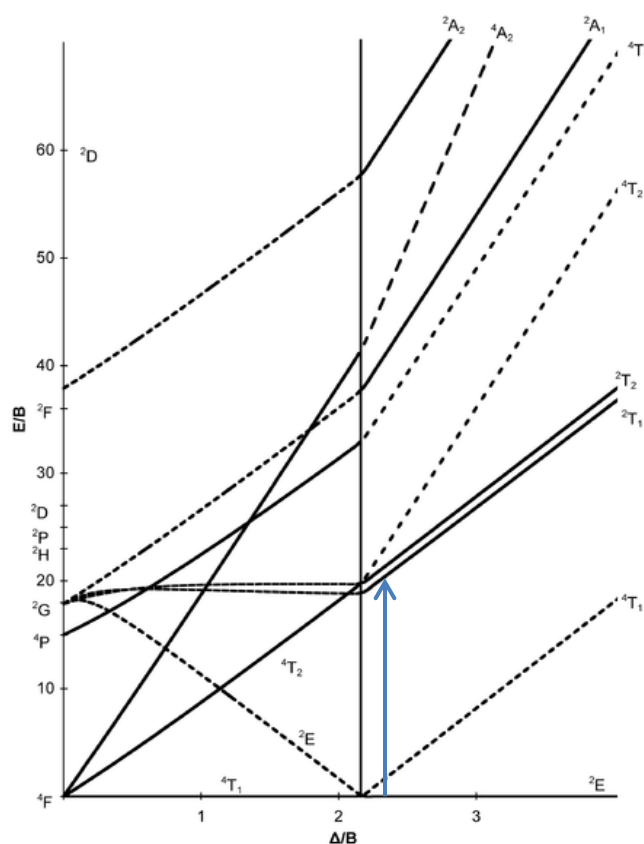


Figure 3.10: Tanabe-Sugano diagram for d^7 electron configuration for core-level excited state configuration of Pd^{IV} with $4d^6$

From the experimental data, we know the energy spacing between the first and second features is about 1.4 eV, or $11,292\text{cm}^{-1}$, for the octahedral complex. The Pd^{IV} complex is low spin due to the radial function of the 4d orbitals and thus the Δ/B value should be greater, but not too much than the discontinuity line at around 2.2. Assuming that the 1.4 eV energy separation corresponds to the ${}^2\text{T}_1/{}^2\text{T}_2$ and ground state ${}^2\text{E}_g$ gap of about 20, the electron-electron repulsion term B can be calculated as 565 cm^{-1} . The free ion value for Pd^{4+} is about 1000 cm^{-1} , which gives a nephelauxetic reduction factor of about 56%. This is a somewhat large percentage for the known electron cloud expansion effect and thus it questions the adequacy of this assignment. From the about 2.5 Δ/B

value, the ligand field splitting of $10Dq$ or Δ_0 can be calculated to be $14,125\text{ cm}^{-1}$, which is quite significantly less than the theoretical ground state Δ_0 value from density functional theory calculations (see Chapter 4) of $18,961\text{ cm}^{-1}$. Thus, it is more likely that the second pre-edge feature is due to the Jahn-Teller effect, which has been observed for Ti^{3+} , low spin Fe^{2+} , low spin Co^{3+} complexes.^{71-73,92}

Pd L-edge

Energy Position Analysis of XANES Feature. Figure 3.11a shows the spectrum of Pd^0 , $[\text{PdCl}_6]^{2-}$ and $[\text{Me}_4\text{N}(\text{Pd}^{\text{IV}}\text{Cl}_2)]^{2+}$ at the Pd L_{III} -edges. Both L_{III} - and L_{II} - edges are used in the intensity analysis (Method III from Chapter 2). Since the energy shifts of pre-edges are equivalent at both L-edges, only the Pd L_{III} -edge is used for energy position analysis. Rising-edge features increase in the order of Pd^0 , $[\text{PdCl}_6]^{2-}$ and $[\text{Me}_4\text{N}(\text{Pd}^{\text{IV}}\text{Cl}_2)]^{2+}$ with values of 3173.8 eV, 3184.6 eV and 3188.3 eV respectively. The pre-edge for the homoleptic complex is expected to have one intense feature corresponding to the excitation of the Pd $2p_{3/2}$ to the quadruply unoccupied e_g^* set of the octahedral complex, however similarly to the Cl K-edge, there are two features. The main peak position of $[\text{PdCl}_6]^{2-}$ is at 3177.8 eV with a non-resolved shoulder on the lower energy side. This shoulder is due to the Jahn-Teller distortion of the excited state as described above. Two defined pre-edge features exist for the heteroleptic complex at 3177.9 eV and 3179.8 eV. These features are assigned to the same orbitals described at the Cl K-edge.

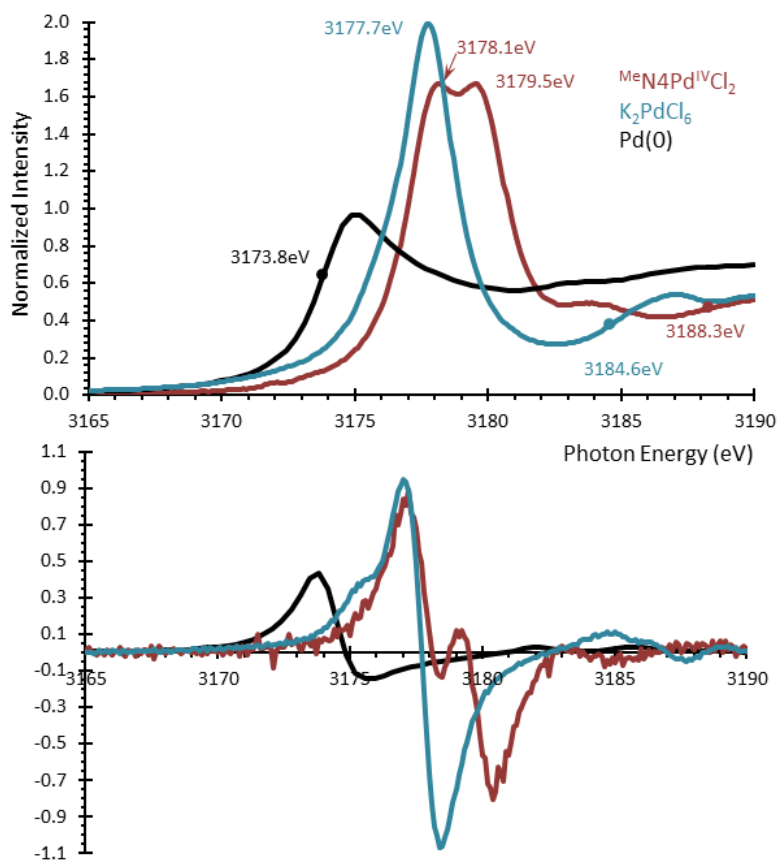


Figure 3.11: (a) Normalized data of the Pd L_{III}-edge used for energy position analysis. Pd⁰ (black), [PdCl₆]²⁻ (turquoise) and [Me₄N][PdCl₄]²⁺ (red). (b) First-derivative of respective data

The first peak is assigned to the Pd 2p_{3/2} → Pd 4d_{z²} transition and the second to the Pd 2p_{3/2} → Pd 4d_{x²-y²} transition.

The rising-edge feature in the spectrum of [Me₄N][PdCl₄]²⁺ is shifted up by 3.7 eV from the rising-edge of [PdCl₆]²⁻. As observed with the Pd^{II} complexes, this positive energy shift can be attributed to the lack of orbital overlap between N 2p and Pd 5s/ 5p orbitals; while the overlap is present for the Cl 3p orbitals. Furthermore, while a reduction from four chlorides in [PdCl₄]²⁻ to two chlorides in Me₄N[PdCl₂]²⁺ resulted in a

1.7 eV difference between the Pd L-edge rising-edges, a reduction from six to two chloride ligands in $[\text{PdCl}_6]^{2-}$ and $[\text{Me}_4\text{N}4\text{Pd}^{\text{IV}}\text{Cl}_2]^{2+}$ results in an even larger, 3.7 eV difference. The gap between the rising-edge (3.7 eV) and between the pre-edges (~ 1.1 eV) experimentally also shows that the ligand field splitting for the $[\text{PdCl}_6]^{2-}$ complex is larger.

Intensity Analysis of Pre-edge Features. The intense pre-edge feature and lower lying shoulder in the $[\text{PdCl}_6]^{2-}$ spectrum have a total normalized analytical area of 12.9 ± 0.3 eV. The two intense features of $[\text{Me}_4\text{N}4\text{Pd}^{\text{IV}}\text{Cl}_2]^{2+}$ have a total analytical area of 13.7 ± 0.3 eV. Using the transition dipole integral (Table 3.2) for Pd^{IV} oxidation states, the analytical areas can be converted into Pd 4d character. Total Pd 4d character is $48 \pm 2\%$ and $51 \pm 1\%$ for $[\text{PdCl}_6]^{2-}$ and $[\text{Me}_4\text{N}4\text{Pd}^{\text{IV}}\text{Cl}_2]^{2+}$, respectively. Similar to the Pd^{II} complex, palladium character for Pd^{IV} complexes remains about 50%, regardless of the ligand environment.

Extending the Scope of XAS to Pd^{III} Complexes

Cl K-edge XANES. The electronic structure descriptions of the Pd^{II} and Pd^{IV} heteroleptic complexes have been straightforward with the use of their homoleptic counterparts. Due to the lack of data for homoleptic Pd^{III} complex, the heteroleptic complexes will be used to analyze the paramagnetic $[\text{Me}_4\text{N}4\text{Pd}^{\text{III}}\text{Cl}_2]^+$ complex spectrum and extend the XAS technique to the analysis of Pd^{III} complexes. For the sake of simplicity, the heteroleptic Pd compounds will be referred to as Pd^{II} , Pd^{III} , and Pd^{IV} for $\text{Me}_4\text{N}4\text{Pd}^{\text{II}}\text{Cl}_2$, $[\text{Me}_4\text{N}4\text{Pd}^{\text{III}}\text{Cl}_2]^+$ and $[\text{Me}_4\text{N}4\text{Pd}^{\text{IV}}\text{Cl}_2]^{2+}$, respectively.

Energy Position Analysis of XANES Features. Figure 3.12a shows the comparison of the spectra of the heteroleptic complexes. From a quick glance at the spectra, it is evident that total Cl 3p bond character and Cl 1s effective nuclear charge both increases as the palladium complexes go through one electron oxidations. The first and second derivatives (Figures 3.12b and 3.12c, respectively) of the spectra were used to define rising-edge energy and pre-edge peak positions. Rising-edge energy positions increase in the order of Pd^{II} , Pd^{III} and Pd^{IV} with energies of 2825.1 eV, 2825.4 eV and 2526.3 eV, respectively and pre-edge peak positions are 2821.5 eV, 2820.6 eV and 2820.5 eV, respectively.

It is expected that with each one-electron oxidation, chloride donation increases thus effectively making the chlorine absorber less negative. Rising-edge energy positions Z_{eff} . The oxidation from complex Pd^{II} to Pd^{III} results in a 0.3 eV shift, while another one electron oxidation to Pd^{IV} results in a 0.9 eV shift. The small and then large energy differences among the three rising-edge positions indicate unique electronic structure features vs. a monotonic change in going from Pd^{II} to Pd^{IV} through Pd^{III} formal oxidation states. It should be noted that the shape of the first-derivative spectrum of the paramagnetic complex Pd^{III} is different from the other two complexes, characterized by a broader rising-edge. This change in slope could indicate that spin polarization in the paramagnetic complex, which leads to different orbital energies for the α - and β -spin electron excitations. Thus, the rising-edge could be a mixture of different spin polarized Cl 1s $\rightarrow$ 4p dipole allowed transitions.

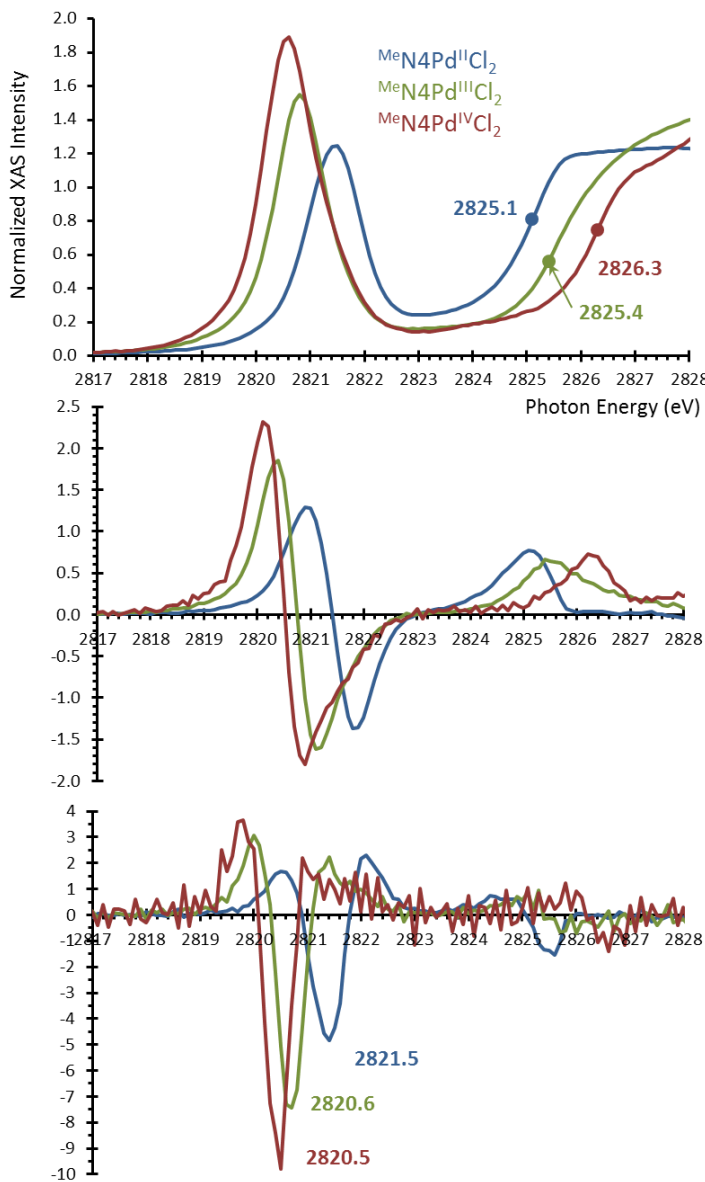


Figure 3.12: (a) Normalized spectra of Pd^{II} (blue), Pd^{III} (green) and Pd^{IV} (red) analogous complexes. (b) and (c) First- and second-derivative plots of respective complexes. increase in energy as the Cl 1s electron move to lower energies as a result of increased

Pre-edge energy positions decrease in energy in the order of Pd^{II} , Pd^{III} and Pd^{IV} , with energies of 2821.5 eV, 2820.6 eV and 2820.5 eV, respectively. A decrease in energy position correlated with each, one electron oxidation indicates that the d-manifold is lowering in energy. The $\text{Pd } Z_{\text{eff}}$ increases with each oxidation, causing a lowering of all

Pd orbital energies. The decrease in Pd orbital energies correlates with smaller transition energy between the Cl 1s orbital and LUMO. Assignment of Cl 1s transitions has been described in previous sections for the Pd^{II} and Pd^{IV} complexes. The intense pre-edge for complex Pd^{III} is assigned to the transition of Cl 1s electron into two frontier molecular orbitals. One transition occurs to singly occupied LUMO with Pd based 4d_{z²} character. The second transition occurs to a doubly unoccupied Pd 4d_{x²-y²} based molecular orbital. Experimental resolution limits the detection of two separate transitions; therefore, one transition envelope feature was used to represent both frontier orbitals.

The gap between the pre-edges of Pd^{II} and Pd^{III} is 0.9 eV while the pre-edge difference between complexes Pd^{III} and Pd^{IV} is 0.1 eV. The 0.9 eV decrease in energy from complex Pd^{II} to Pd^{III}, likely represents a true one electron oxidation of the metal center. It is nearly half of the energy shift (1.6 eV) seen between the [PdCl₄]²⁻ and [PdCl₆]²⁻ complexes. The smaller energy gap between complexes Pd^{III} and Pd^{IV} indicates that while there is a one electron oxidation, but increased electron donation from the “N4” ligand effectively reduces the palladium center. Since bond angles and bond distances change to favor better overlap in Pd^{IV} (Figure 3.2), more donation from the nitrogen ligands can take place.

Since pre-edge energy positions are affected by the d-manifold energy, d orbital splitting and the Pd Z_{eff} , the difference in the rising-edge (0.3 eV) and the pre-edge (1.6 eV) energy positions between complexes Pd^{II} and Pd^{III} show that the d-manifold of complex Pd^{III} is 1.9 eV lower in energy from Pd^{II}. The difference in the pre-edge energy (0.1 eV) and the rising-edge (0.9 eV) energy positions for the oxidation from Pd^{III} to

Pd^{IV} , indicates that the Pd^{III} d-manifold is 1.0 eV lower in energy from Pd^{IV} . The smaller drop in d-manifold energy from the first oxidation to the second oxidation is a combination of increased “N4” electron donation and greater d-manifold splitting of the Pd^{IV} complex.

Intensity Analysis of Pre-edge Features. The pre-edge analytical area of the Pd^{III} is 2.28 ± 0.1 eV and corresponds to total Cl 3p character per d-manifold hole of $16 \pm 1\%$. The total Cl 3p character per hole for complex Pd^{II} and Pd^{IV} are $19 \pm 1\%$ and $16 \pm 1\%$, respectively. Chlorine 3p character per hole goes down from Pd^{II} to Pd^{III} , but stays the same between the Pd^{III} and Pd^{IV} complexes. The trend in Cl 3p donation among Pd^{II} , Pd^{III} and Pd^{IV} complexes can be correlated with the change in the coordination environment. Pd^{II} is only four coordinate with a $[\text{N}_2\text{Cl}_2]$ inner sphere, facilitating better Cl 3p donation to Pd 4d compared to the high valent complexes. The similarities in Pd-Cl bond covalencies for the Pd^{III} and Pd^{IV} complexes is due to the similar, hexa-coordinate environment with a $[\text{N}_4\text{Cl}_2]$ inner sphere. When an electron hole opens up in the out-of-plane $4d_{z^2}$ orbital, it is partially filled with N 2p donation. The Pd center becomes more electron rich and reduces the Pd-Cl bond covalancy in the equatorial plane. Since the chlorine covalency per hole remains the same, it suggests that the pyridine and amine N-atoms dominate electron donation to the metal center.

Pd L-edge

Energy Position Analysis of XANES Features. Figure 3.13a shows the Pd L_{III} -edge spectra of complexes Pd^{II} , Pd^{III} and Pd^{IV} . Rising-edge inflection points increase in

energy in the order of Pd^{II} , Pd^{III} and Pd^{IV} with energy positions of 3181.9 eV, 3184.9 eV and 3188.3 eV. The pre-edge energy position of complex Pd^{III} is located at 3178.1 eV.

Rising-edge energy positions increase in energy with each formal one-electron oxidation. The gap between the rising-edges is 3.0 eV and 3.4 eV and corresponds to one electron oxidation each. It is expected that the rising-edge energy shift be nearly the same, as each oxidation reflects an increase in Z_{eff} seen by the Pd 2p orbital. The gap between the rising-edge positions of Pd^{II} and Pd^{III} (3 eV) is larger than the gap between the pre-edges (0.7 eV), indicating that the ligand field splitting in for Pd^{III} is greater than Pd^{II} , as expected. Even larger ligand field splitting is observed when moving from complex Pd^{III} to Pd^{IV} as the gap between rising-edge positions (3.4 eV) is again, larger than the gap between the pre-edge intensities (0.0 eV).

Intensity Analysis of Pre-edge Features. The pre-edge of complex II at the Pd L_{III} -edge is located at 3178.1 eV. The total analytical area of the Pd L_{III} - and L_{II} -edge pre-edge features is 12.3 ± 0.2 eV. No transition dipole integral has been established for Pd^{III} oxidation states yet. The method following describes how a transition dipole integral for previous literature⁷⁴ a linear relationship is made between the dipole integrals and the relative edge inflection points (from Pd^0) for complexes $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$ and $[\text{MeN4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$. Using the linear correlation, as seen in Figure 3.14, a transition dipole integral for Pd^{III} is interpolated. The relative rising-edge shift of $[\text{MeN4Pd}^{\text{III}}\text{Cl}_2]^+$ from Pd^0 is 11.1 eV, which correlates to a transition dipole integral of 25.4 eV. The pre-edge intensity therefore correlates to 48.5% total Pd 4d character for the Pd^{III} complex.

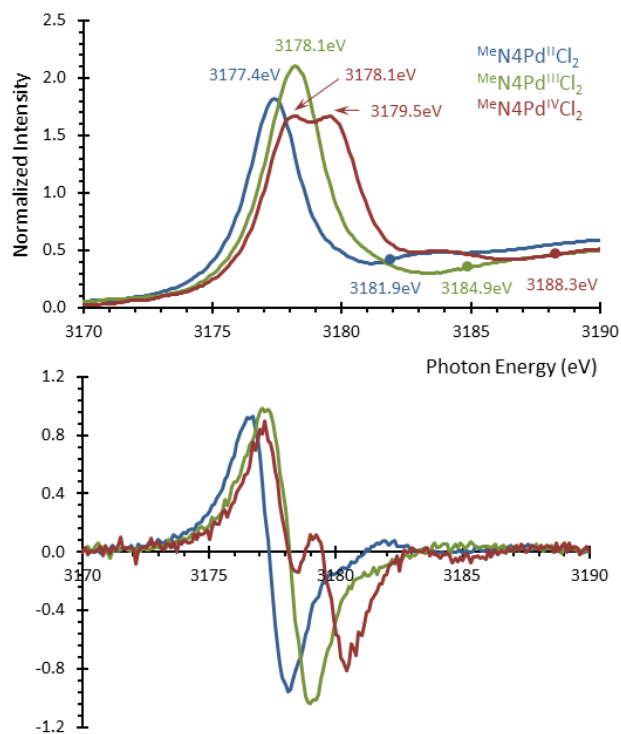


Figure 3.13: (a) Normalized spectra of the Pd^{II} (blue), Pd^{III} (green) and Pd^{IV} (red) analogous complexes. (b) First-derivative plots of respective complexes. the Pd^{III} oxidation state was established. Using methods outline examples from in

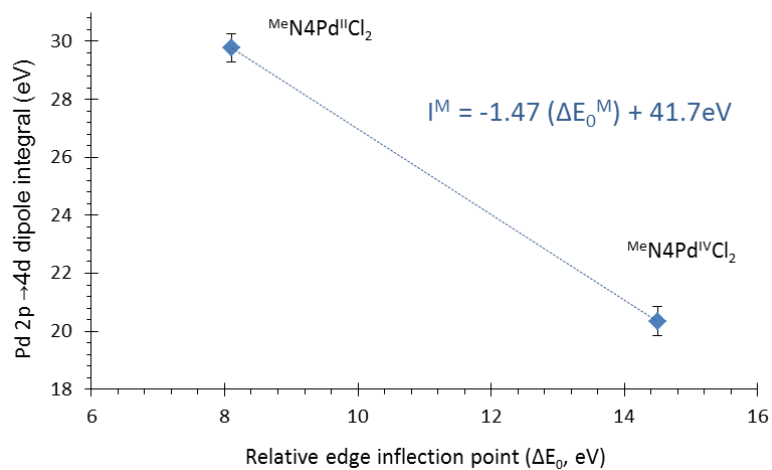


Figure 3.14: Correlation of edge positions relative to Pd^0 rising-edge inflection point (3178.8 eV) and Pd $2p \rightarrow 4d$ dipole integrals

Pd K-edge XANES of Pd^{II}, Pd^{III} and Pd^{IV} Complexes

Energy Position Analysis of the Rising-edge. The Pd K-edge reflects the Z_{eff} of the Pd 1s orbital energy and is a result the transition from Pd 1s $\rightarrow$ 5p orbitals. Intense pre-edge features do not exist at the Pd K-edge due to the weak intensity of quadrupole allowed transitions (Pd 1s $\rightarrow$ 4d). Rising-edge energy positions were obtained using the first maximum in the first derivative spectrum in the energy range of 24,325-24,370 eV. The complexes measured at the Pd K-edge clearly parallel the increase in Z_{eff} based on formal oxidation states of the complexes. Rising-edges increase in the order of Pd powder, Pd^{II}, Pd^{III} then Pd^{IV} with energies of 24,350.5 eV, 24,352.1 eV, 24,354.8 eV and 24,357.4 eV, respectively.

The energy difference between the Pd⁰ the formally Pd^{II} complex is 1.6 eV. The next two consecutive one-electron oxidations result in a 2.7 eV and 2.6 eV shift. A 1.6 eV shift between Pd⁰ and corresponds to a two formal two-electron oxidation. However, the energy gap is 1 eV smaller than the other one-electron oxidations. Considering that Pd⁰ has no coordinating ligands, and the Pd^{II} complex has four good sigma donating ligands, the energy position for Pd^{II} reflects the reduction of the metal center by the ligand environment. Additionally, the energy position of Pd^{II} reflects what the energy position of a formally Pd^I would look like because of the large magnitude of Cl $\rightarrow$ Pd electron donation. The ~2.6 eV shift for the other two complexes can be correlated with the energy shift associated with a one electron oxidation. As seen in the Pd L-edge, the Pd metal center will accept electron density up to about 50%. Therefore, the energy position of the Pd^{III} and Pd^{IV} complexes corresponds to formal Pd^{II} and Pd^{III} Z_{eff} , respectively.

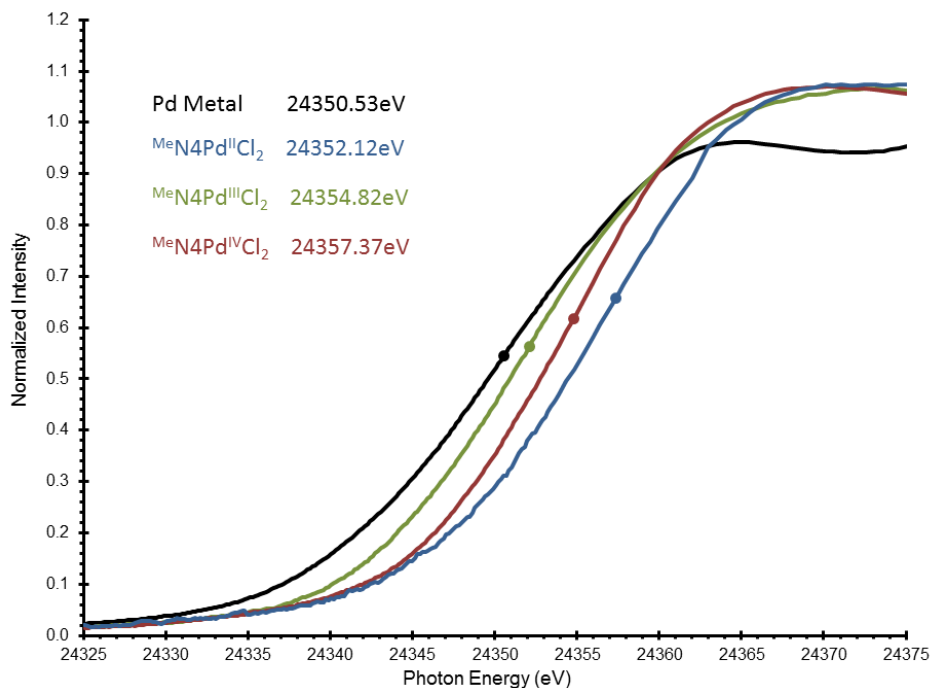


Figure 3.15: Pd K-edge of the heteroleptic Pd^{II} (blue), Pd^{III} (green) and Pd^{IV} (red) complexes plotted against Pd^0 (black) to show relative energy shifts correlated with formal oxidation

Discussion

The multi-edge XAS technique has allowed for a comprehensive analysis of a series of heteroleptic complexes at the Cl K-edge, Pd L-edge and Pd K-edge. By comparing heteroleptic complexes to already defined homoleptic palladium complexes of the same formal oxidation state, insights about the electronic structure of the “N4 ligand” system were made.

Quantitative analysis of Pd^{II} complexes at the Cl K-edge indicated that pyridines donate more than chloride ligands to the palladium metal center. Both chloride and nitrogen-based ligands are good σ -donors, but the combination of better overlap of N 2p

and Pd 4d orbitals at shorter Pd-N bond lengths support the decrease of chlorine character relative to the homoleptic complexes.

Pd^{IV} complex analysis at the Cl K-edge revealed similar results with a decrease in chlorine 3p character from the homoleptic complex to the heteroleptic complex. This decrease of Cl 3p character is attributed to increased donation from the “N4 ligand” to the palladium center. Given the lack of N K-edge data, there is not enough experimental evidence to show which type of coordinated nitrogen ligand is better at donating electron density to the metal center.

Information gained about the N4 ligand’s donating characteristics allowed for the electronic structure analysis to be extended to a Pd^{III} complex. With three electron holes available to accept electron density in the Pd^{III} complex, we observe that total chlorine covalency increases with the shift in the rising-edge. However, on a per hole and per chloride basis, there is no observed difference in Cl 3p character when compared to the Pd^{IV} complex. The design of the N4 ligand allows for electronic structural stabilization through its strained geometric structure. Because the Cl 3p character is maximized in the Pd^{III} complex, it indicates that even with the longer N-Pd bond lengths, the paramagnetic Pd^{III} center is also stabilized by the electronic donation from the N4 ligand.

Detailed information about the ligand environments of the heteroleptic complex mostly stems from analysis at the ligand (Cl) K-edge. However, important electronic structural information was gained from the Pd L-edge. Despite the significant changes in coordinated ligand environments between the chloropalladium complexes and the heteroleptic complexes, the Pd 4d orbital character remains about 50%. The surprisingly

uniform Pd contribution to the frontier unoccupied orbitals shows that, regardless of the given ligand system, the palladium will always accepted electron density up to half of its electron holes via covalent Pd-L bonds.

Conclusion

The comparative study of a redox-series of Pd^{II}, Pd^{III}, and Pd^{IV} complexes demonstrates the power of multi-edge XAS technique in defining the electronic structure of catalytically relevant homoleptic Pd complexes with varied ligand environments. The analysis of multiple edges revealed that the “N4” ligand optimizes electron donation to the metal center, when compared to the monatomic chloride ligand. Importantly, this study revealed that the “N4” ligand stabilizes the Pd^{III} metal center electronically as well as geometrically.

A transition dipole integral was established for the Pd^{III} oxidation state and is applied to quantify the Pd 4d character in the [^{Me}N4Pd^{III}Cl₂]⁺ complex. The intensity analysis of five palladium complexes with oxidation states of II, III and IV reveal that regardless of the ligand environment, the metal center will always accept about 50% of the electron density per electron hole from their ligands.

The XAS technique and corresponding electronic structure analysis used in this study serves as powerful examples for analysis of relevant inorganic complexes in literature. Future research outlook is to extend this technique to catalytically relevant organometallic complexes used from organic literature. Electronic structural analysis will

make structure and activity relationships to advance the understanding of engineered ligand environments and advance their design and optimization.

CHAPTER 4

ELECTRONIC STRUCTURE CALCULATIONS FOR THE $^{\text{Me}}\text{N4PdCl}_2$ COMPLEXES
OF Pd^{II} , Pd^{III} and Pd^{IV} REDOX SERIESIntroduction

The “N4” ligand system coordinates as a bidentate ligand to a Pd^{II} metal center and as a tetradentate ligand to Pd^{III} and Pd^{IV} metal centers.²⁶ Bond lengths and bond angles of the coordinated “N4” ligand are described in Chapter 3. Reactivity studies of $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Me}_2$ have shown oxygen mediated oxidation and carbon-carbon bond forming reactivity via formal $\text{Pd}^{\text{II}}/\text{Pd}^{\text{IV}}$ catalytic cycles.^{26,27} Because the “N4” ligand stabilizes Pd^{III} formal oxidation, it is the first example in organometallic palladium chemistry to be observed and isolated as an important intermediate in these catalytic cycles.²⁷ In order to gain further insights into the electronic structure that make the “N4” ligand environment unique, especially with its ability to stabilize Pd^{III} metal centers, multi-edge X-ray absorption spectroscopic measurements were carried out. Modifications of the ligand environment, by replacing methyl ligands with chlorides, allowed for comprehensive data collection at the Pd K- and L-edges and at the Cl K-edge.

As described in Chapter 3, XAS data collection for the $^{\text{Me}}\text{N4Pd}^{\text{x}}\text{Cl}_2$ complexes was performed at the Stanford Synchrotron Radiation Lightsource on Beamline 4-3. Cl K-edge and Pd L-edge data were used to obtain complimentary data about metal and chloride ligand bonding. Through comparative analysis of energy shifts and peak intensities from similar homoleptic chloropalladium complexes, a detailed analysis of the

palladium and chloride components was performed for the heteroleptic complexes. Further, conclusions were made about the electronic structure of the “N4” ligand with each metal oxidation state.

Experimental results from the Cl K-edge indicate that the nitrogen based ligands, whether coordinated to Pd^{II}, Pd^{III} or Pd^{IV} metal centers are always better electron donors than the monatomic chloride ligands. Peak intensity analysis at the Pd L-edge revealed that regardless of the ligand environment, palladium has nearly 50% 4d character among all three oxidation states, II, III, and IV. The consistency of the Pd 4d covalency paired with smaller than expected Cl 3p donation vs. the N-based ligands indicates that the remaining electron density among the d-manifold holes has to be nitrogen based. To date we do not have direct experimental data at the N K-edge.

To further support the experimental data, theoretical ground state and excited state analysis is reported herein. Ground state calculations can aid in the assignment of spectral features but also, when appropriately calibrated to experimental data can provide experimentally sound metal and ligand covalency values. With the correct level of theory, extension of theoretical methods to predict reactivity can be performed.

Methods

Electronic structure calculations were performed using Gaussian09⁵⁵ and Amsterdam Functional Theory⁵⁶ and ORCA⁷⁴ computational packages. Single point calculations were performed using crystal structures⁵⁰ in gas phase environments. An optimum basis set for palladium metal centers was established previously,³³ with a triple

ζ -basis set reaching basis-set saturation. For simplicity, this level of theory was used to determine metal and ligand character among the $^{Me}N_4PdCl_2$ complexes. The Gaussian-type basis set def2-TZVP⁷⁵ was employed in the Gaussian09 calculations, while the analogous Slater-type TZVP^{76,77} was employed in ADF.

Atomic composition of palladium and chloride from the same LUMOs probed from XAS measurements was examined using different population analysis methods: Mulliken Population Analysis⁵⁷ (MPA), Natural Population Analysis⁵⁸ (NPA) and Bader's Atoms-in-Molecules⁵⁹ (AIM). ADF calculations report MPA values only.

To examine functional dependence, the following density functionals were used: The GGA exchange functionals used were B88⁷⁸ and PW91⁷⁹⁻⁸³ and the GGA correlation functionals used were P86⁸⁴ and PBE.^{85,86} The meta-GGA functional used was M06-L.⁸⁷ Hybrid-GGA functionals used were B3LYP⁸⁸ and BHandHLYP⁸⁹ and the meta-hybrid GGA functional was M06-HF.⁹⁰

Δ SCF and TDDFT calculations were performed using the ADF package using BP86/TZVP. TDDFT calculations contained relativistic corrections using ZORA (zero order regular approximation) and an acetonitrile solvation environment. Excitations originated from Cl 1s orbitals. TDDFT was also performed using the ORCA⁷⁴ computational package using B3LYP/def2-TZVP with ZORA correction to relativistic effects and an acetonitrile solvation environment.

Results and Analysis

Computational Methodology

Gaussian or Slater-type orbitals can be used to describe molecular wave-functions in solving the Schrödinger equation. The dependence of the results on the type of basis set used was examined by using Slater Type Orbitals (STOs) in ADF calculations or Gaussian Type Orbitals (GTOs) in Gaussian09 calculations. These two computational packages are popular in inorganic quantum chemical calculations, where triple ζ -basis sets and a pure or hybrid functionals are typically used to model inorganic or organometallic systems.⁶⁰⁻⁶³ These methods are considered to be acceptable for obtaining molecular orbital contour plots and relative energy shifts of molecular orbitals toward predicting reactivity and understanding the electronic structure. However, in order to use the methodology quantitatively, calibrated basis set and functionals must be determined, which accurately reproduces experimental data. From that point, further theoretical models can be used to predict reactivity.

Table 4.1 reports the population analysis results for Cl 3p and Pd 4d character using the ADF and Gaussian computational packages. The ADF package uses Mulliken population analysis (MPA) to evaluate electron density on each atom in the molecule. MPA assumes that electrons are shared equally between two atoms along a bond. Comparisons of Gaussian based MPA and ADF MPA results indicate that there is no clear advantage for either method.

ADF MPA results show consistently too high in Cl 3p character and too low in Pd 4d character relative to experiment. Gaussian MPA, NPA and AIM results, on average,

overestimate Cl 3p character and underestimate Pd 4d character according to experimental values. Once the density of the complex has been calculated, the NPA method fits core, valence, and Rydberg natural type orbitals to the density. While this method has more chemical relevance, the data shows that it is still poor at replicating

Table 4.1
Summary of electronic structure parameters (covalency α_2 (%); Amsterdam Density Functional Theory, Mulliken Population Analysis (MPA); Gaussian Density Functional Theory: Mulliken Population Analysis, Natural Population Analysis (NPA), and Bader atoms-in-molecule analysis (AIM)) for Pd and Cl in $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$, $^{\text{Me}}\text{N4Pd}^{\text{III}}\text{Cl}_2$, and $^{\text{Me}}\text{N4Pd}^{\text{IV}}\text{Cl}_2$.

Pd 4d						
Exp. α^2 ^c		ADF ^a	Gaussian ^b			
		BP86	BP86	BHandHLYP	M06-L	
^{Me} N4Pd ^{II} Cl ₂	49%	41%	MPA	40%	48%	44%
			NPA	36%	44%	38%
			AIM	39%	49%	46%
^{Me} N4Pd ^{III} Cl ₂	49%	35%	MPA	42%	55%	34%
			NPA	24%	31%	36%
			AIM	44%	35%	44%
^{Me} N4Pd ^{IV} Cl ₂	51%	33%	MPA	36%	42%	38%
			NPA	27%	44%	30%
			AIM	39%	44%	41%
Cl 3p						
Exp. α^2 ^c		ADF ^a	Gaussian ^b			
		BP86	BP86	BHandHLYP	M06-L	
^{Me} N4Pd ^{II} Cl ₂	19%	32%	MPA	29%	24%	30%
			NPA	32%	26%	32%
			AIM	22%	24%	28%
^{Me} N4Pd ^{III} Cl ₂	16%	24%	MPA	16%	10%	3%
			NPA	16%	14%	27%
			AIM	23%	24%	23%
^{Me} N4Pd ^{IV} Cl ₂	16%	24%	MPA	23%	22%	23%
			NPA	26%	21%	27%
			AIM	22%	21%	22%

(a): ADF electronic structure calculations using TZVP basis set. (b) Gaussian electronic structure performed with def2-TZVP basis set. (c) Experimental data extracted from Chapter 3.

experimental bond character. Pd character is drastically underestimated, by about 10-20%, when the population is determined using BP86 or M06-L functionals with def2-TZVP. NPA performs best when paired with the BHandHLYP functional, which incorporates 50% HF exchange in with the local density approximation and Becke88 exchange functional. Pd characters are only 5% off for the diamagnetic complexes, but deviates by 19% for the paramagnetic Pd^{III} complex. While functional dependence is observed, this method shows that it is not the best for modeling both paramagnetic and diamagnetic systems.

The closest theoretical values for Cl and Pd character to experimental data were calculated for the Pd^{II} complexes. Using BHandHLYP/def2-TZVP level of theory and AIM population analysis methods, Cl 3p character was calculated as 24% and Pd 4d character as 49%. Experimental data shows $19 \pm 1\%$ Cl 3p character and $49 \pm 1\%$ Pd 4d character in the bonding description. This functional was used based on previous publications showing that it models Pd-Cl bonds most reasonably for Pd^{II} and Pd^{IV} homoleptic complexes.³³ While this functional is acceptable at matching data for Me₄NPd^{II}Cl₂, it fails to match experimental values for the [Me₄NPd^{IV}Cl₂]²⁺ complex; overestimating Cl character by 5% and underestimating Pd character by 10%. Interestingly, population analysis of the Pd^{III} complex is the worst fit overall, using this method of population analysis. The functional BHandHLYP overestimates Cl 3p character by 8% and underestimates Pd 4d character by 15%.

There is no universal agreement between population analysis methods to make a conclusion for which is the best for determining theoretical metal and chloride covalency.

Neither ADF nor Gaussian computations have matched the XAS experimental covalency values, thus far.

Ground State MO Theory Based Calculations

Functional Dependence A variety of functionals are available in the Gaussian09 package. These functionals differ in how exchange and correlation energies are approximated within DFT calculations. GGA (BP86, PW91PBE), hybrid GGA (B3LYP, BHandHLYP), metaGGA (M06-L) and meta-hybrid GGA (M06-HF) functionals were

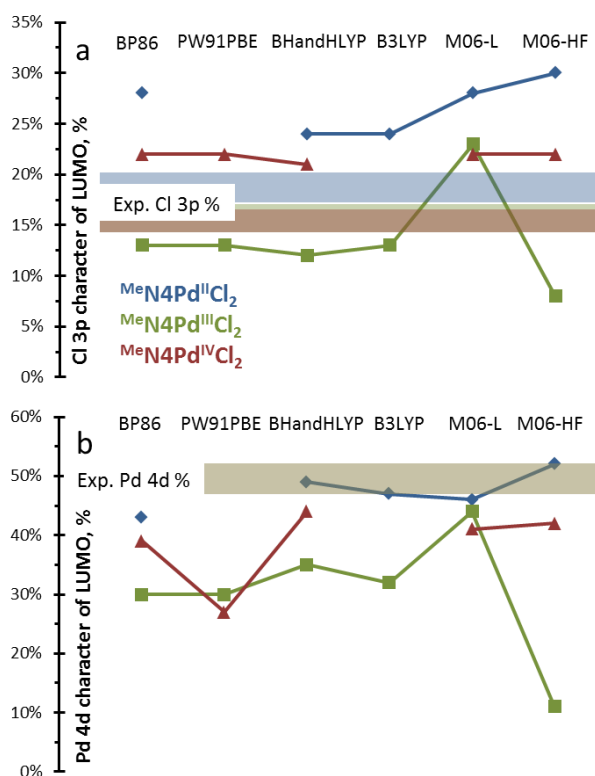


Figure 4.1: Calibration of DFT functionals (dots) to experimental XAS data (shaded regions) for Cl 3p (a) and Pd 4d (b) orbital character in the frontier molecular orbitals using def2-TZVP. Results for $\text{Me}_4\text{N}_4\text{Pd}^{\text{II}}\text{Cl}_2$ are in blue, $[\text{Me}_4\text{N}_4\text{Pd}^{\text{III}}\text{Cl}_2]^+$ in green and $[\text{Me}_4\text{N}_4\text{Pd}^{\text{IV}}\text{Cl}_2]^{2+}$ in red

used to find the most appropriate model for covalent bonding between the chloride ligand and palladium metal in the $^{\text{Me}}\text{N4Pd}^{\text{x}}\text{Cl}_2$ complexes. A graphical representation of the results is shown in Figure 4.1.

The results show no clear correlation of Cl 3p or Pd 4d character among all three oxidation states between theoretical and XAS experimental values. BHandHLYP was expected to be the most accurate functional based on previous literature values for chloropalladium complexes.³³ However, with scattered atomic character between the diamagnetic and paramagnetic systems, it is difficult to make the same conclusion. Nonetheless, BHandHLYP most accurately quantifies the Pd 4d covalency in the Pd^{II} and Pd^{IV} systems when compared to the other five functionals represented.

Only one of the six functionals replicates the trend for Cl 3p covalency values derived from XAS data across the three complexes. Experimentally, Cl 3p character is 19%, 16% and 16% for $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$, $[\text{MeN4Pd}^{\text{III}}\text{Cl}_2]^+$ and $[\text{MeN4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$, respectively. M06-L, a meta-GGA functional, provides theoretical covalency values of 28%, 23% and 22%, respectively. The largest drop in Cl 3p covalency (3% vs. 5% for experimental vs. theoretical) is observed between $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$ and $[\text{MeN4Pd}^{\text{III}}\text{Cl}_2]^+$, while only a slight decrease (0% vs. 1%) is observed between $[\text{MeN4Pd}^{\text{III}}\text{Cl}_2]^+$ and $[\text{MeN4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$. All other functionals underestimate the Cl 3p character in the paramagnetic Pd^{III} species while overestimating for the Pd^{II} and Pd^{IV} species. Pd 4d character is consistently underestimated in bond covalency when compared to experimental values.

M06-L is also the only functional to accurately represent the Pd 4d character with nearly all the values, near 50%. Experimentally, the Pd 4d character is 49%, 49% and

51% for $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$, $[\text{MeN4Pd}^{\text{III}}\text{Cl}_2]^+$ and $[\text{MeN4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$, respectively. M06-L provides Pd 4d character of 46%, 44% and 41% in the same respective order. While these values range from 3-10% deviation from experimental values, it is the only functional to keep palladium character relatively constant across all three oxidation states. Based on current data, M06-L is considered as the most reasonable functional for replicating experimental trends in bond character.

Excited State Calculations

Ground State Description. The ground state picture of orbital energies is a good zero order approximation for assigning transitions between core orbitals and unoccupied frontier orbitals. The energy difference between the donor and acceptor orbitals from single point calculations are relatively good at predicting the order of which transitions can be assigned in an XAS spectrum. Ground state descriptions also aid in determining which LUMO-s will be represented in an XAS spectrum as it describes the orbital composition of anti-bonding orbitals, Figure 4.2. Table 4.2 shows the energy of the transitions as calculated from the ground state SCF energy for each complex.

The Cl K-edge is around 2820 eV as shown in the experimental Cl K-edge data in Figure 4.3. The estimated energies of transitions in the Pd^{III} and Pd^{IV} complexes is ~ 100 eV too low from the experimental values. This is expected since we did not consider in the calculations any relativistic effects due to the presence of the Cl 1s core hole. Three transitions are expected to occur at the Cl K-edge for $[\text{MeN4Pd}^{\text{III}}\text{Cl}_2]^+$ due to the three d-manifold vacancies. While the XAS spectrum only indicates one observable peak at the

Cl K-edge. The ground state description shows three possible transitions for which the energy spacing between them is relatively small, with a 0.6 eV and 0.1 eV gap between

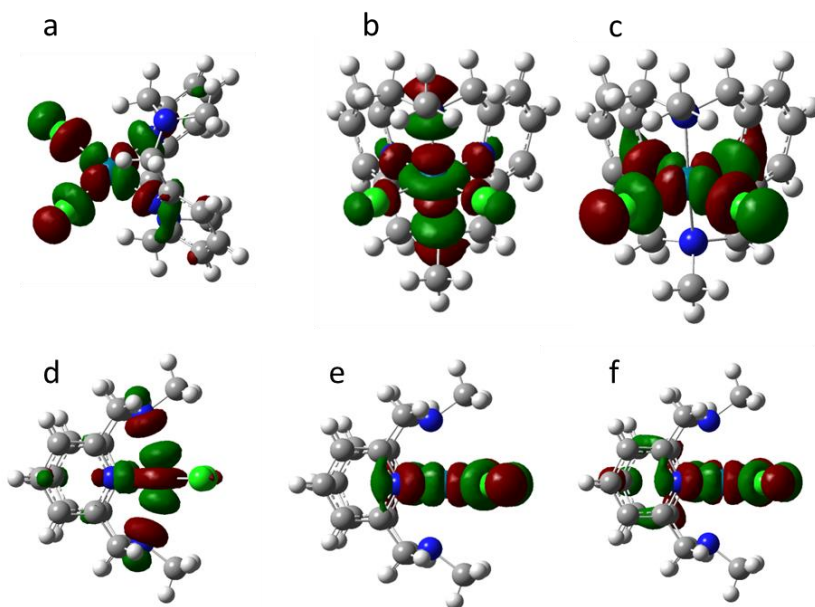


Figure 4.2: Lowest unoccupied molecular orbital contour plots: (a) Pd $4d_{x^2-y^2}$ based LUMO of $^{\text{Me}}\text{N4Pd}^{\text{II}}\text{Cl}_2$; (b) Pd $4d_{z^2}$ and (c) Pd $4d_{x^2-y^2}$ based LUMO of $[\text{MeN4Pd}^{\text{IV}}\text{Cl}_2]^{2+}$; (d) Pd $4d_{z^2}$ based singly occupied molecular β orbital, (e) β and (f) α Pd $4d_{x^2-y^2}$ based LUMOs of $[\text{MeN4Pd}^{\text{III}}\text{Cl}_2]^+$. Transitions from the Cl 1s and Pd 2p core orbitals into these LUMOs give rise to XAS pre-edge features at the Cl K-edge and Pd L-edge, respectively.

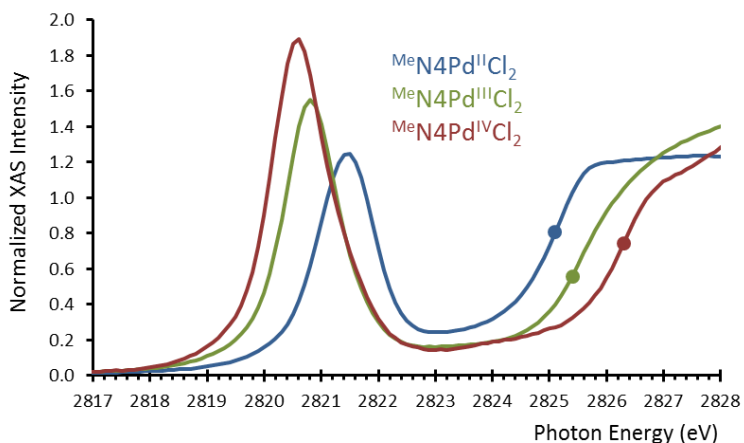


Figure 4.3: Cl K-edge XAS data of the heteroleptic Pd^{II} (blue), Pd^{III} (green) and Pd^{IV} (red)

Table 4.2: ΔE between donor Cl 1s orbital energy and acceptor orbital energies in ground and excited states compared to ΔSCF energies and XAS peak positions.

			G.S.		1st E.S.	2nd E.S.	3rd E.S.	Exp. Peak
	MO	Assignment	ΔE_{MO}^a	ΔSCF^c	ΔE_{MO}^b	ΔE_{MO}	ΔE_{MO}	Position
$^{Me}N4Pd^{II}Cl_2$	LUMO	Cl 1s $\rightarrow$ Pd 4d _{x²-y²} ($\alpha=b$)	2735.0					2821.5
$^{Me}N4Pd^{III}Cl_2$	SOMO	Cl 1s $\rightarrow$ Pd 4 _{z²} (b)	2723.6	2572.4	2860.4			
	LUMO	Cl 1s $\rightarrow$ Pd 4 _{x²-y²} (α)	2724.2	2565.1		2860.6		2820.8
	LUMO	Cl 1s $\rightarrow$ Pd 4 _{x²-y²} (b)	2724.3	2573.5			2860.9	
$^{Me}N4Pd^{IV}Cl_2$	LUMO	Cl 1s $\rightarrow$ Pd 4d _{z²} ($\alpha=b$)	2734.3	2806.5	2860.0	2860.1		2821.4
					2860.5	2861.1		
	LUMO+1	Cl 1s $\rightarrow$ Pd 4d _{x²-y²} ($\alpha=b$)	2735.1	2807.2	2860.0	2860.1		2820.6
					2860.5	2861.1		

(a) Ground state ΔE_{MO} = LUMO energy- Cl 1s orbital energy. (b) Excited state ΔE_{MO} = occupied LUMO energy - vacant Cl 1s orbital energy. (c) Excited state bonding energy - ground state bonding energy.

the unoccupied frontier molecular orbitals. The close spacing of the orbital energies cannot be resolved by XAS due to the limited experimental resolution.

The ground state picture does not, however, predict the correct ordering of the Cl K-edge pre-edge peak ordering for the Pd^{IV} complex. The XAS spectrum contains one intense feature with an unresolvable shoulder on its higher energy side. The main feature is due to the overlap between Cl 3p and Pd $4d_{x^2-y^2}$ orbitals while the second is due to smaller overlap between Cl 3p and Pd $4d_{z^2}$ orbitals. This orbital reordering indicates that excited state effects are influencing the ground state picture and that specifically; the Pd $4d_{x^2-y^2}$ orbital could be relaxing when occupied by a core electron.

Δ SCF Calculations Δ SCF methods were used to model excited state relaxation effects, and are considered a first order approximation to modeling energy positions from experimental data. An electron from the Cl 1s orbital was moved into one of the LUMO's involved in the dipole allowed transitions at the Cl K-edge. This electronic configuration reflects that of the excited state. This excited state configuration was then allowed to relax through the energy minimization while maintaining the orbital occupations. The energy difference between the ground and excited states can be attributed to the amount of energy needed to obtain that excited state energy, or the theoretical peak positions of XAS features.

The Δ SCF results predict peak positions which are ~ 250 eV lower than experimental values for the Pd^{III} complex. Results already indicate that Δ SCF calculations poorly model the Pd^{III} complex in gas phase. Individual Δ SCF peak positions are another indication that the model does not correctly predict XAS features. The energy

position for the α spin transition is ~ 8 eV lower in energy than the two β -spin transitions. And, while the energy difference between the beta transitions is 0.8 eV from the ground state description, Δ SCF energies show this increases to 1.1 eV.

Δ SCF energies for the Pd^{IV} system are in the right energy range for predicting peak positions with ~ 15 eV difference between theoretical and experimental values. However, similar to the ground state description, Δ SCF results fail to represent the reordering of the $4d_{x^2-y^2}$ and $4d_{z^2}$ orbital energies.

While the SCF energies do not indicate reordering, observations were made about the energy difference between the vacant Cl 1s orbital energy and the occupied LUMOs in these excited state calculations, which more accurately show relaxation effects. The calculated orbital energy differences for the Pd^{III} complex are in better agreement with the experimental peak positions at the Cl K-edge. Peaks are now 40 eV above experimental values (instead of 250 eV below). There is also a small contraction of the orbital energies from each of the excited state calculations. The energy gap between the beta transitions went down from 0.7 eV in the ground state description to 0.5 eV.

The orbital energy differences in the Pd^{IV} complex are significant, however. The excited state relaxation changed the orbital compositions of the first and second LUMO's. The ground state depicts the first LUMO as only having Pd $4d_{z^2}$ character and the second LUMO with only $4d_{x^2-y^2}$ character. The excited state shows mixing of the $4d_{z^2}$ and $4d_{x^2-y^2}$ character in both the first and second LUMO's. Mixing of orbital character in the excited state describes relaxation of the $4d_{x^2-y^2}$ orbital, which is while not completely definitive, but it shows the tendency toward reordering of the orbitals.

TDDFT Calculations The second-order approximation for predicting orbital ordering and peak assignments is to use time dependent density functional theory (TDDFT). This method applies a perturbation the ground state electron density of a

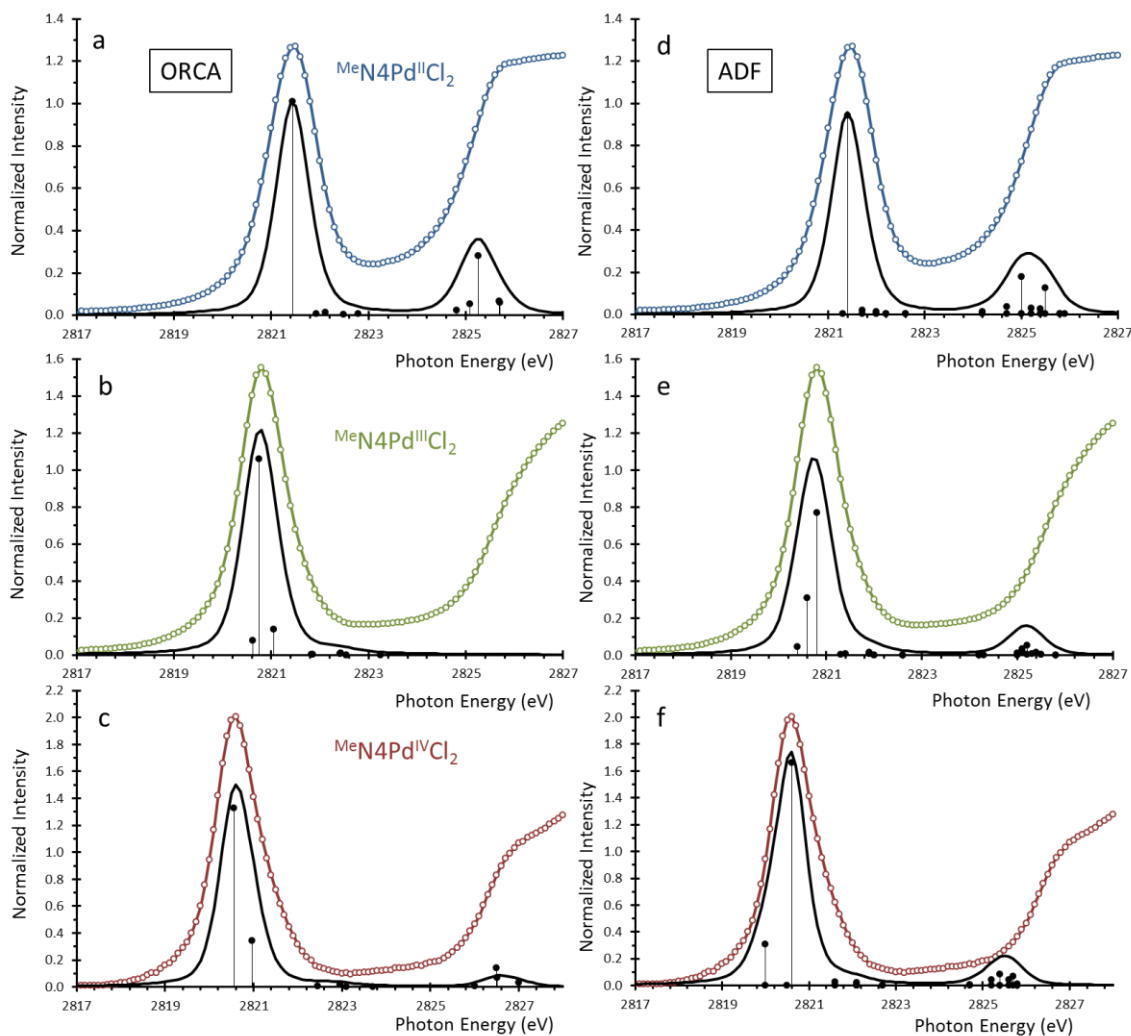


Figure 4.4: TDDFT results from ORCA (a, b and c) and ADF (d, e and f). Spectra with hollow dots are the experimental Cl K-edge XAS data from SSRL, beamline 4-3. Black dots indicate the oscillator strengths of transitions located at that specific energy. Solid black lines are the TDDFT spectra incorporating line broadening due to beamline optics and excited state lifetimes.

molecular system at a given energy, and then observes how the system responds as a function of time. Standing waves formed in response to a given time-dependent perturbation give rise to eigenstates at a given perturbation energy.

TDDFT was performed using ADF and ORCA computational packages. Results from each method are shown in Figure 4.4. Peak assignments of the pre-edge features are listed in Table 4.3. The spectral differences between the pre-edge of the Pd^{II} complex from experiment and TDDFT are reasonably small. One intense feature is present in the TDDFT spectrum from ORCA (Figure 4.4a) and ADF (Figure 4.4d) calculations, as a result of the $\text{Cl } 1s \rightarrow \text{LUMO}$ with $\text{Pd } 4d_{x^2-y^2}$ and $\text{Cl } 3p$ character. As predicted from the ground state picture and ΔSCF calculations, three transitions are present in the pre-edge of the Pd^{III} complex. TDDFT shows that these transitions occur within 0.5 eV and 0.4 eV for ORCA (Figure 4.4b) and ADF (Figure 4.4e) respectively. These results, too, are in good agreement with the orbital energy differences between the vacant $\text{Cl } 1s$ orbital and LUMO energies presented previously. Between ADF and ORCA, the orbital energy and respective transitions have different ordering. However, both assign the most intense feature to the beta $\text{Cl } 1s \rightarrow \text{Pd } 4d_{x^2-y^2}$ transition. The Pd^{IV} TDDFT results are the most different between the two methods used. Orbital reordering is observed from the ORCA (Figure 4.4c) calculations and not from the ADF (Figure 4.4f) calculations. The transitions in the ORCA spectrum are assigned as $\text{Cl } 1s \rightarrow \text{Pd } 4d_{x^2-y^2}$ followed by $\text{Cl } 1s \rightarrow \text{Pd } 4d_{z^2}$ with a 0.4 eV energy gap between them. ADF transitions have the same ordering as seen in the ground state with a 0.6 eV gap between the transitions.

Table 4.3: Cl K-edge pre-edge features as calculated by TDDFT using ORCA and ADF packages

ORCA			
Compound	Assignment	Energy	f
^{Me} N4Pd ^{II} Cl ₂	Cl 1s→Pd 4d _{x²-y²} ($\alpha=b$)	2821.4	1.68E-03
^{Me} N4Pd ^{III} Cl ₂	Cl 1s→Pd 4 _{z²} (b)	2820.6	1.29E-04
	Cl 1s→Pd 4 _{x²-y²} (b)	2820.8	1.76E-03
	Cl 1s→Pd 4 _{x²-y²} (α)	2821.1	2.28E-04
^{Me} N4Pd ^{IV} Cl ₂	Cl 1s→Pd 4d _{x²-y²} ($\alpha=b$)	2820.6	2.21E-03
	Cl 1s → Pd4d _{z²} ($\alpha=b$)	2821.0	5.69E-04
ADF			
Compound	Assignment	Energy	f
^{Me} N4Pd ^{II} Cl ₂	Cl 1s→Pd 4d _{x²-y²} ($\alpha=b$)	2821.4	1.17E-03
^{Me} N4Pd ^{III} Cl ₂	Cl 1s→Pd 4 _{z²} (b)	2820.4	5.62E-05
	Cl 1s→Pd 4 _{x²-y²} (α)	2820.6	3.88E-04
	Cl 1s→Pd 4 _{x²-y²} (b)	2820.8	9.64E-04
^{Me} N4Pd ^{IV} Cl ₂	Cl 1s → Pd4d _{z²} ($\alpha=b$)	2820.0	3.11E-04
	Cl 1s→Pd 4d _{x²-y²} ($\alpha=b$)	2820.6	1.66E-03

Discussion

Ground state orbital energy differences, Δ SCF and TDDFT methods were all used to provide corroborating information about the energy positions and peak assignments of the XAS spectra presented in Figure 4.2. Ground state orbital energy differences are useful for zeroth order approximation to XAS feature assignments and peak positions. The ground state molecular orbital energies agree well with XAS results for the Pd^{II} and Pd^{III} complex. It is only when excited state effects show up in the experimental data, that ground state depictions fail to accurately predict peak energies, as seen in the Pd^{IV} system. However, ground state methods are good at determining orbital character in

LUMOs which would be occupied in an XAS spectrum. With the correct computational model, i.e. solvation environment and point charges to replicate the solid state environment, a more accurate description of the metal and ligand covalency is expected to be observed.

The data presented in the computational methodology section, which attempts to quantify and match experimental Pd and Cl covalency values, indicates a work in progress for the heteroleptic palladium-based coordination compounds. The results currently, do not replicate the XAS data, which is most likely attributed to treating the systems as gas phase molecules especially when the complexes are charged. Once the appropriate methodology is defined, potential energy surfaces can be modeled to provide insights into ligand modifications and their respective reactivity.

Excited state methods show mixed success in their ability to support the peak position assignments in the XAS spectra for the studied heteroleptic complexes. $\square$ SCF calculations poorly replicate the energy of Cl 1s $\rightarrow$ LUMO transitions for the Pd^{III} complexes, yet are satisfactory with the Pd^{IV} complex. The excited state molecular orbital energies of the excited states are better at getting within the range of Cl K-edge transitions. However, neither of these methods was able to definitively show that the Pd 4d_{z²} and 4d_{x²-y²} orbital energies switch in the excited state.

The most unexpected results come from the TDDFT calculations. ORCA shows the excited state reordering as observed in the XAS data for the Pd^{IV} complex. This result indicates that excited state relaxation of the populated LUMOs does take place when the system is perturbed. However, the ADF results fail to replicate the same phenomenon.

Conclusion

While ground state results presented do not accurately replicate experimental results for all the complexes in all oxidation states, it can be concluded the M06-L functional is the most useful method for describing the electronic structure with respect of XAS data. It provides the most insights into electronic structure and is able to model HOMO and LUMO contour plots for predicting reactivity. This is the most viable method for quantifying orbital character of metal and ligand components in order to obtain detailed understanding of electronic structures.

The data presented in the results section indicates that there are still more tasks to complete. Better ground state descriptions can be made to quantify orbital character among the ligands and metal, and improved excited state methods can be employed to understand the excited state effects observed in the XAS spectra.

In order to improve the ground state descriptions, all of the coordination complexes need to be modeled with point charges or high dielectric solvent environments as in their crystal packing environments. With these added parameters, some functionals are expected to raise above the rest in replicating experimental values. While already one of the functionals presented within this chapter (M06-L) could be shown to be the best, a widened search of functionals should be employed.

Once appropriate ground state methods are determined, excited state calculations using the appropriate model should be repeated to model the energy of the XAS features. Investigations into why ORCA shows excited state relaxation and ADF does not, also needs to be explored. There may be an additional correction in the ORCA

implementation of the TDDFT method that allows for a more accurate description of excited state orbital energy ordering.

Finally, to continue examination of excited state effects, multi-reference calculations should be performed to identify what, if any, configuration interactions may influence experimental data. Multi-reference calculations would be especially useful in understanding the homoleptic palladium complex spectrum of $[\text{PdCl}_6]^{2-}$, which isn't discussed in this chapter. None of the excited state methods, thus far, have been able to show the prominent second feature for this octahedral complex.

CHAPTER 5

UTILIZING THE MULTI-EDGE X-RAY ABSORPTION NEAR-EDGE
SPECTROSCOPIC ANALYSIS OF ORGANOMETALLIC PALLADIUM-BASED
PRE-CATALYSTS FOR ESTABLISHING QUANTITATIVE STRUCTURE AND
ACTIVITY RELATIONSHIPS (QSAR)

Introduction

PEPPSI complexes were introduced briefly in Chapter 1 as exemplary examples of ligand design and optimization in organometallic research. These PEPPSI (pyridine-enhanced pre-catalyst preparation stabilization and initiation) complexes are Pd^{II} based pre-catalysts developed by Mike Organ at York University, Canada. They contain an N-heterocyclic ligand, which has two phenyl groups bonded at the N-atoms of the imidazole ring. The simplest NHC backbone is functionalized with iso-propyl ligands at the two ortho positions of the two phenyl rings. The second characteristic of PEPPSI complexes is a pyridine ring coordinated trans to the NHC carbene. The other two coordination sites in these square planar complexes can be occupied with chloride or phenyl thiolate ligands. Chloride and thiolate ligands are removed by a strong base in pre-catalyst activation. Figure 5.1 presents comparative categories for the family of PEPPSI complexes. These categories were established based on types of ligand modifications: functionalization of the NHC backbone, functionalization of the pyridine ligand, or increased steric bulk on the NHC.

PEPPSI complexes as one of the best-selling catalysts by Sigma-Aldrich are actively used in carbon-carbon bond coupling reactions, specifically in coupling secondary carbons. The design features of these complexes are to facilitate branched product formation by increasing the rate of reductive elimination.^{3,17} Without a specialized ligand environment, β -hydride elimination causes rearrangement of secondary carbons and favors linear product formation.¹⁷ NHC ligand modifications, either by increasing steric bulk or adding substituents to the NHC backbone, show remarkable influence on the isomeric ratio of products in Negishi coupling reaction as shown in Figure 5.2.

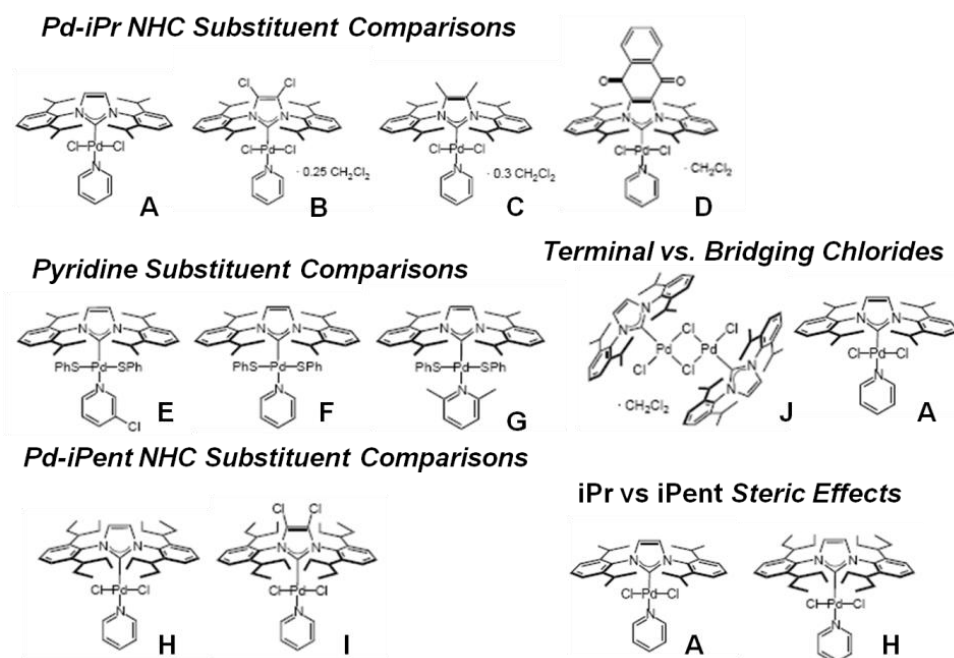


Figure 5.1: PEPPSI complexes categorized by substituent additions to the NHC backbone (A, B, C, D, H and I), substituents on pyridine (E, F and G), bridging and terminal chlorides (J, A) and steric bulk (A and H)

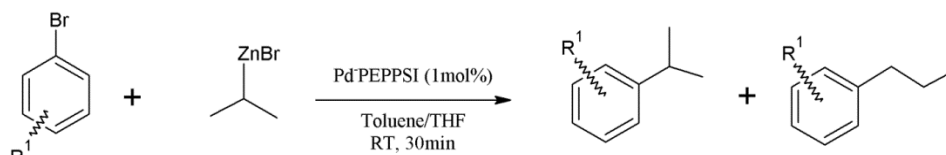


Figure 5.2: Negishi coupling using a PEPPSI pre-catalyst. Products show branched (desired) and linear (rearranged) conformations

Control studies have indicated that substituent effects increase the isomeric ratio, in favor of the branched product, by 15 times.¹⁷ Steric bulk favors branched products by increasing the ratio by about 10 times.¹⁷ The combination of the two NHC ligand modifications has a dramatic influence on the isomeric ratio and favors branched products 61:1, a 60 fold increase.¹⁷ This remarkable change in reactivity is profound; whether electron donating or withdrawing groups are added to the NHC backbone, reactivity is increased. While steric influences are well understood, the electronic effects are not. XAS is proposed as a powerful technique in obtaining detailed electronic structural information for establishing quantitative structure and activity relationships between different types of ligand modifications and observed chemical reactivity.

The multi-edge XAS technique can be utilized to characterize the electronic structure of chloride and sulfur based ligands and the palladium metal centers at the Cl K-edge, S K-edge and Pd L-edges. The rich information content of this technique was explored in Chapter 3 for chloride and palladium edges. Extension of this technique to the S K-edge will continue to validate the utility of the multi-edge XAS technique for probing the electronic structures of organometallic pre-catalysts. Characterization of bond covalency, orbital character and electro- and nucleophilicity of the PEPPSI complexes will aid in understanding the effects of substituent additions and help guide future ligand

optimizations. Data has already been collected by us on all of the complexes highlighted in Figure 5.1. This chapter will qualitatively compare spectral features and rising-edge energy positions for initial analysis of electronic structural differences.

Characterization of the pre-catalysts will open up future research directions toward *in operando* studies of the PEPPSI pre-catalysts. Pre-catalyst activation is not well understood. It is generally accepted that strong bases work in activating Pd^{II} pre-catalysts. *In operando*, the multi-edge approach at the Cl K-edge or S K-edge has the potential to experimentally capture the dissociation of chloride or sulfur ligands in pre-catalyst activations with pre-edge features diminishing or growing in and rising-edge energy positions shifting. Simultaneously, the Pd L-edge will capture the reduction processes in the pre-catalyst activation with pre-edge features disappearing and rising-edge energy positions shifting to lower energies. The Pd K-edge has the potential to

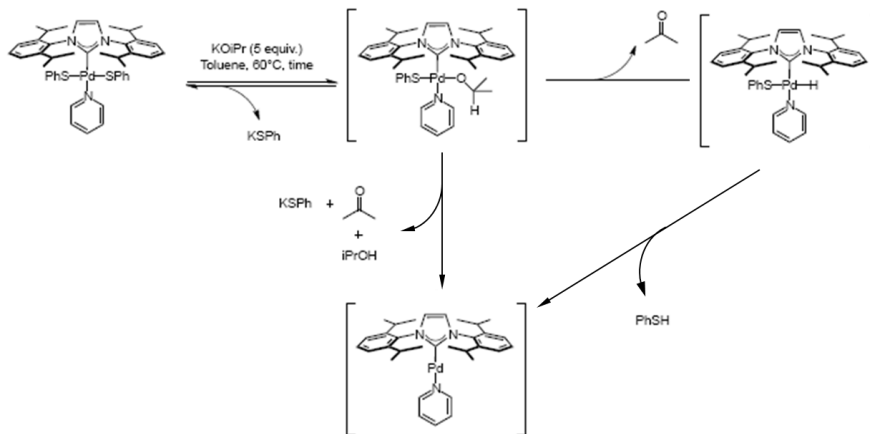


Figure 5.3: Proposed steps and intermediates in pre-catalyst activation with a strong base. Each palladium complex can be differentiated at the S K-edge and Pd L-edge to determine the mechanism of activation to Pd^0 species

identify intermediate species in the activation process and determine their geometric structure from extended X-ray fine structure analysis (EXAFS). Figure 5.3 outlines potential species involved in the activation of a PEPPSI pre-catalyst where XANES features would clearly indicate what metal-ligand bonding is present in solution.

Methods

Samples

The samples shown in Figure 5.1 were provided by the Organ group who are also responsible for their synthesis and characterization.⁶⁷ They were used as provided, as solid powders, and mounted thinly onto Kapton tape for XAS measurement.

Data Collection

All measurements were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) under storage ring (SPEAR 3) conditions of 450 mA current in top off mode and 3G eV energy. The S K-edge, Cl K-edge and Pd L-edge XANES regions were collected on beamline 4-3.

Beamline 4-3 is a 20-pole, 2.0 T Wiggler beamline equipped with a liquid N₂ cooled Si(111) double crystal monochromator. It was optimized in the S K-edge region using Na₂SO₃ and calibrated to the first pre-edge at 2472.02 eV. Cs₂CuCl₄ was used as the calibrant for the Cl K-edge and the pre-edge feature was calibrated to 2820.20 eV. S K-edge, Cl K-edge and Pd L-edge spectra were collected in single sweeps the energy range of 2420-3550 eV using an unfocused beam in a He-purged beam path at room temperature using a Lytle fluorescence detector. All of the samples were mounted onto

contaminant-free Kapton tape. At least three scans were collected and averaged to obtain improved signal-to-noise ratios. Radiation damage was not observed in any of the sample collection processes.

Results

PEPPSI-iPr NHC Substituent Comparisons at the Cl K-edge

Cl K-edge data is shown in Figure 5.4, comparing spectral data of the PEPPSI-iPr complexes with different functionalized NHC backbones. Spectrum B is renormalized since there is twice the number of chloride absorbers. Rising-edge energy positions of all complexes are located at 2824.5 eV. Pre-edge energy positions are 2821.8 eV for complexes A and B, 2821.9 eV for complex C and 2821.7 eV for complex D. The range of pre-edge values is 0.2 eV. Amplitudes of the pre-edges range from 1.4 eV and 1.6 eV.

Rising-edge energy positions indicate the Z_{eff} of the chloride absorber. Since all rising-edge energy positions among the four complexes are the same, the Cl Z_{eff} values are all the same. This data suggests that NHC functionalization does not dramatically influence covalent bonding between chloride ligands and the palladium metal. Pre-edge energy positions only vary by 0.2 eV from one another. Since all of the peaks most likely indicate the same transition between Cl 1s orbitals to Pd $4d_{x^2-y^2}$ based LUMOs, they indicate that the Z_{eff} on the palladium is also relatively constant. All complexes have four coordinate, square planar environments, so it is expected that the energy of the pre-edge remains relatively constant. The slight changes in pre-edge energy position, relative to the rising-edge indicate small variations in ligand field splitting of the d-orbitals.

The amplitude and line shape among these complexes is similar, indicating that the Cl 3p character in the Pd-Cl bonds remains relatively constant. Lack of variation in the pre-edge indicates that chloride-palladium bonding does not change with added substituents on the NHC backbone.

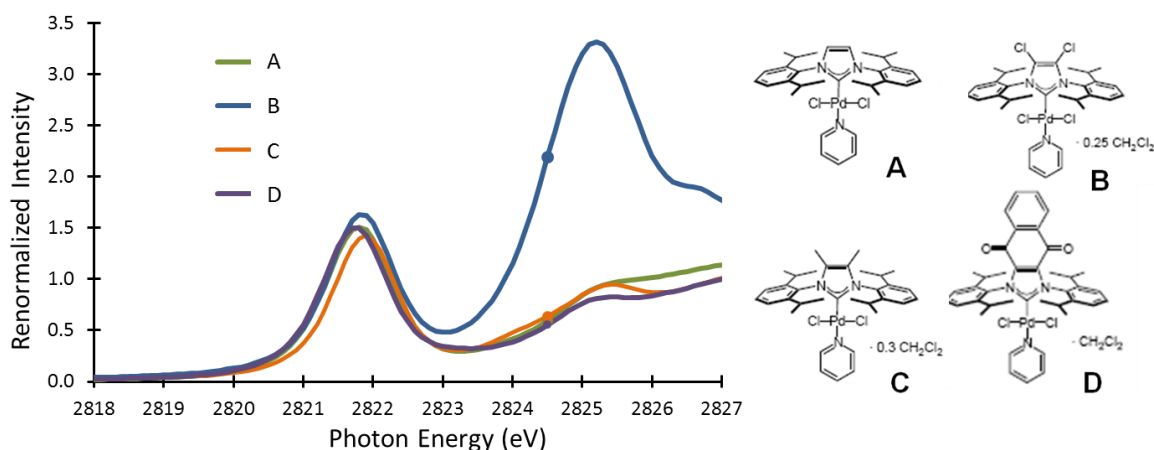


Figure 5.4: Renormalized Cl K-edge data of complexes A (green), B (blue), C (orange) and D (purple) used to compare pre-edge and rising-edge energies among functionalized NHC's

Pyridine Substituent Comparisons at the S K-edge

S K-edge data of the PEPPSI complexes with functionalized pyridine ligands is presented in Figure 5.5. Rising-edge energy positions are located at 2742.1 eV, 2473.0 eV and 2472.0 eV for complexes E, F and G, respectively. Pre-edge energy positions for complexes E and G are located at 2471.1 eV while the resolved pre-edge for complex F is located at 2471.7 eV. There is a shoulder in the complex spectrum of F at what looks like the same energy position as the other two complex pre-edge features.

Rising-edge energy positions of the S K-edge indicate a change in S 1s orbital energies. Complex F, with no pyridine functionalization, has the highest rising-edge

energy position of the three complexes. This rising-edge energy indicates that the phenyl sulfide ligand is more oxidized and has a more covalent bond with palladium. The other two complexes, E and G, both have functionalization on the pyridine ligand and their rising-edge energy positions are the same. Both of these complexes, therefore, have similar covalent bonding interactions with the palladium metal center.

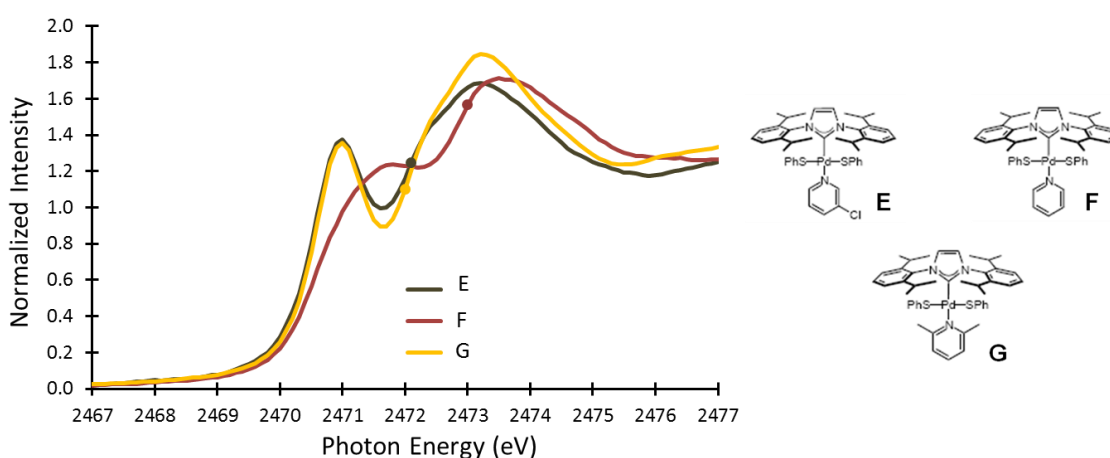


Figure 5.5: Normalized S K-edge spectra of E (brown), F (red) and G (yellow) used to differentiate electronic structural influences from pyridine functionalization

Pre-edge features for complexes E and G are equivalent, both in energy position and amplitude, indicating that bond character remains the same between. The pre-edge of complex F is much broader than the other two complexes. Peak broadening is an indication that multiple bonding interactions with sulfur are present. However, further information from computational work needs to be done in order to assign these features.

First approximation of the electronic structural differences indicates however, that pyridine functionalization, whether with electron donating or withdrawing groups, increases the electron density to the metal, thereby decreasing the strength of the Pd-S covalent bonds.

Terminal vs Bridging Chloride Comparisons at the Cl K-edge

The Cl K-edge comparisons between bridging and terminal chlorides are presented in Figure 5.6. The rising-edge features are located at 2824.5 eV and 2825.0 eV for complex A and J, respectively. The pre-edge for complex A represents the transition from terminal Cl 1s orbitals to the Pd $4d_{x^2-y^2}$ based LUMO and is located at 2821.8 eV. Two features are present in the spectrum of complex J. The first peak represents the transition from terminal Cl 1s orbitals to the Pd $4d_{x^2-y^2}$ based LUMO and is located at 2821.5 eV. The second transition is assigned as the transition between bridging Cl 1s orbitals and the same LUMO, and is located at 2822.5 eV.

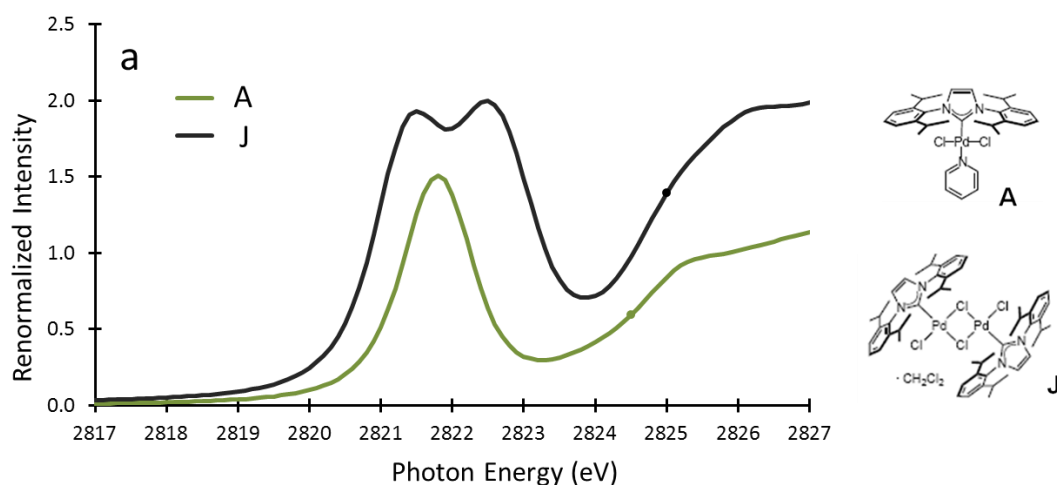


Figure 5.6: Renormalized Cl K-edge spectra of complex A (green) and B (black) used to show electronic structural differences between bridging and chloride environments

The rising-edge energy position of complex J represents a mixture of chlorine environments. It is difficult to justify the rising-edge energy position increase as representing both chloride ligands. However, we know from homoleptic bridging

complexes, that bridging chlorides are effectively less negative than terminal chlorides³³. Thus the rising-edge observed for the dimer is a reflection of only terminal chlorides Z_{eff} .

The spectrum containing both chloride ligand environments was renormalized to account for twice as many chloride absorbers. The amplitude of the pre-edge feature in spectrum A is 1.5 while the two amplitudes of spectrum J are 1.9 and 2.0. Similar to the results presented in Chapter 2, the bridging chlorides have more contribution to each of the Pd-Cl bonds. However, the relative intensity ratio between the terminal chlorides is different. Qualitatively, the bridging chlorides seem much more covalent than terminal chlorides as the intensity is greater than that of the terminal feature. This is reverse from what was reported in the homoleptic complexes. Quantitative analysis of these features will provide notable information about the electron donating strength of the NHC carbene and pyridine ligands.

PEPPSI-iPent Substituent Comparisons at the Cl K-edge

Spectral comparisons of two PEPPSI complexes with iso-pentyl groups and either functionalized (I) or non-functionalized (H) NHC carbenes are compared in Figure 5.7. This comparison is similar to the PEPPSI-iPr series. Rising-edge energy positions are 2824.9 eV and 2824.5 eV with pre-edge energy positions at 2821.9 eV and 2821.8 eV for complexes H and I, respectively.

While there was no change in rising-edge energy position for the PEPPSI-iPr complexes with functionalized NHCs, there is a 0.4 eV energy difference between functionalized and non-functionalized PEPPSI-iPent complexes. The 0.4 eV decrease in

rising-edge energy position is difficult to analyze, since it represents a mixture of chlorine absorbers within the complex. Peak amplitudes and energy positions however, indicate that the amount of Cl 3p character in the Pd-Cl bonds is nearly the same.

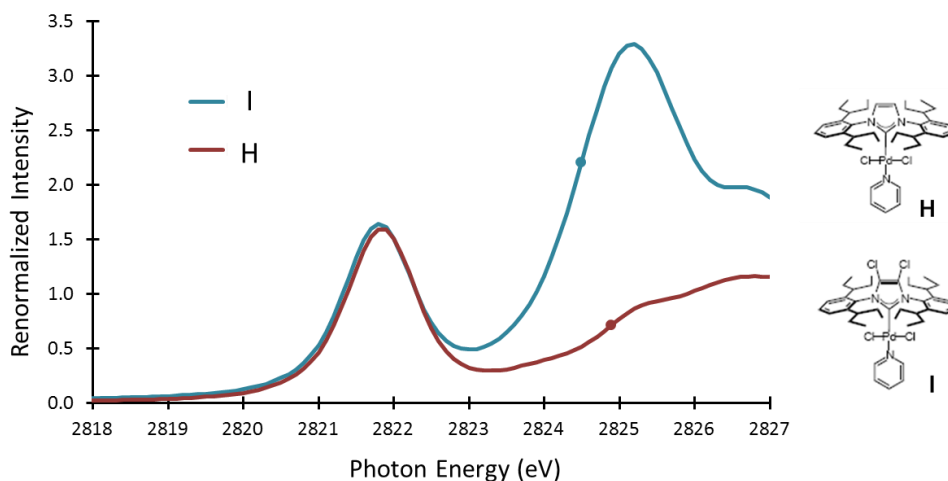


Figure 5.7: Normalized Cl K-edge data for complex I (turquoise) and complex H (red) used to analyze energy position shifts correlated with NHC functionalization of PEPPSI-iPent complexes

PEPPSI-iPr and PEPPSI-iPent Comparison at the Cl K-edge

Comparisons of PEPPSI complexes with different steric bulk around the palladium are presented in Figure 5.8. The rising-edge and pre-edge energy positions for complex A are at 2824.5 eV and 2821.7 eV, respectively. For complex H, the positions are 2824.9 eV and 2821.8 eV, respectively.

The 0.4 eV increase in energy from the PEPPSI-iPr to PEPPSI-iPent complex indicates that steric bulk may be influencing Pd-Cl bonding. Chlorine Z_{eff} is increased in the PEPPSI-iPent complex. Pre-edge features are only 0.1 eV different in their energy position indicating that the palladium Z_{eff} is the same between the two complexes.

However, the amplitude for PEPPSI-iPent is slightly larger than the PEPPSI-iPr complex. The bulk of the iPent ligands could be forcing a more covalent bond between Pd-Cl indicated by the rising-edge feature. The amplitudes support this claim with increased character in the LUMO of the complex.

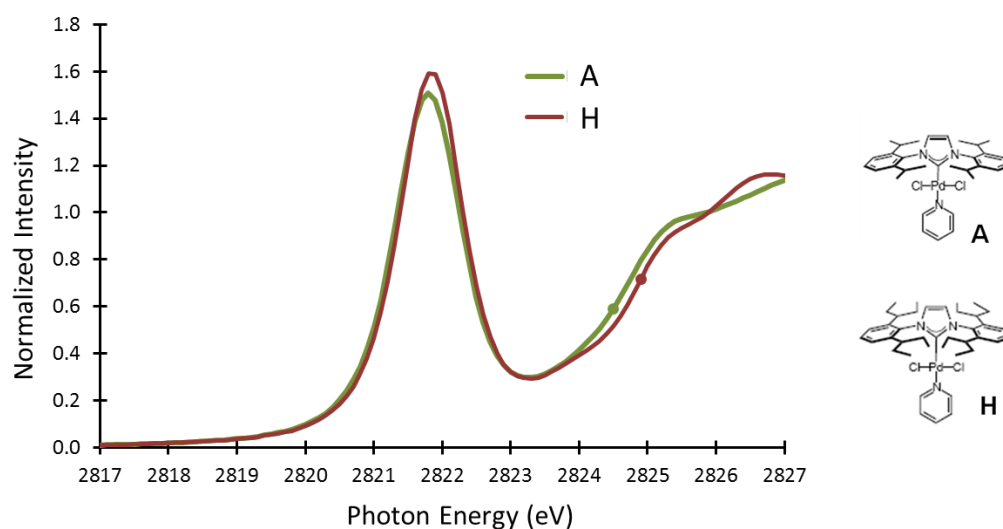


Figure 5.8: Normalized Cl K-edge XAS data of complex A (green) and complex H (red) used correlate energy position shifts associated with increasing steric bulk on the NHC.

Conclusion

As expected, large features at the Cl K-edge and S K-edge are sensitive to slight changes in the electronic structures of the PEPPSI complexes. Analysis of the Pd L-edges will further supplement the ligand K-edge data for making more sound inferences on the bonding of NHC and pyridine ligands. Data has been collected for the Pd L-edge, but it has not been background subtracted and normalized.

A more complete analysis of these pre-edge features will be done with supplemental ground state theoretical calculations. Molecular orbital energy levels and

contour plots will further the understanding of spectral feature origins. Quantitative analysis of these spectra will also provide useful information for the Organ group in understanding the role of NHC and pyridine functionalization for future design and optimizations.

This data has a large impact on future research design and direction. Detailed analysis of the electronic structures of PEPPSI complexes provides the foundation for moving into experimentally validated, theoretical potential energy surface scans and *in operando* studies. Basis set and functional dependence will be evaluated to determine the calibrated functional for modeling PEPPSI pre-catalysts. Once the level of theory is established will, it can be used to predicting reactivity of future ligand designs within the PEPPSI family a priori to chemical synthesis. *In operando* experiments will be designed to capture changes in ligand K-edge and metal L-edge data as the reaction proceeds. With an established reference XAS library for the pre-catalyst electronic structure, in operando activation measurements will track changes in pre-edge intensities and rising-edge positions. By evaluating the changes in ligand and metal Z_{eff} and bond character, mechanistic details pre-catalyst activations can be defined.

CHAPTER 6

SUMMARY OF SCIENTIFIC ACHIEVEMENTS

Palladium-based complexes have profoundly impact on the synthetic tools of organic chemists due to their importance as catalysts in a myriad of chemical transformations. Palladium in the 0, II, III and IV oxidation states have all been experimentally observed to have catalytic activity in carbon-carbon and carbon-heteroatom bond coupling reactions. To understand electronic effects of ligand systems of palladium catalysts and their impact on reactivity, X-ray absorption spectroscopy was used to characterize the electronic structure of the ligand and metal components of a variety of pre-catalysts and palladium model complexes.

This thesis began by verifying that previous Pd L-edge method developments are transferable to palladium complexes with different ligand environments. Due to this transferability, the Pd L-edge was extended to a redox series of palladium based complexes of II, III and IV oxidations states with a unique “N4” ligand. Multi-edge XANES at the Cl K-edge and Pd L-edge were used in a comparative analysis between homoleptic chloropalladium complexes and these heteroleptic palladium based complexes was used to understand the stabilizing effects of the “N4” ligand environment. To support the experimental XAS results of this redox series, theoretical calculations were performed to assign spectral features and evaluate the origin of excited state effects. The thesis concluded with a brief analysis of ligand modification among a family of

palladium based pre-catalysts and their impact on electronic structure and defined the future direction of this XAS technique.

Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University. The SSRL Structural Molecular Biology Program is supported by the DOE Office of Biological and Environmental Research, and by the National Institutes of Health, National Institute of General Medical Sciences (including P41GM103393). The contents of this publication are solely the responsibility of the authors and do not necessarily represent the official views of NIGMS or NIH. Data collection described in this thesis was also carried out at the Canadian Light Source, which is supported by the Natural Sciences and Engineering Research Council of Canada, the National Research Council Canada, the Canadian Institutes of Health Research, the Province of Saskatchewan, Western Economic Diversification Canada, and the University of Saskatchewan. Data collection was also performed at the Advanced Light Source, which is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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