DEVELOPMENT OF PALLADIUM L-EDGE X-RAY ABSORPTION
SPECTROSCOPY AND ITS APPLICATION ON
CHLORO PALLADIUM COMPLEXES

by

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

of

Master of Science

in

Chemistry

MONTANA STATE UNIVERSITY
Bozeman, Montana

December 2005

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ABSTRACT

X-ray Absorption Spectroscopy (XAS) is a synchrotron-based experimental technique that can provide information about geometric and electronic structures of transition metal complexes with unoccupied d orbitals. Combination of metal L-edge and ligand K-edge XAS has the potential to define the experimental ground state electronic structure. We developed a quantitative treatment for Pd L-edge spectroscopy based on the already established Cl K-edge XAS for a series of chloro palladium complexes, which are precatalysts in numerous organic transformations. We found that Pd-Cl bonds are highly covalent (23% per Cl in $[\text{PdCl}_4]^{2-}$, 34% per Cl in $[\text{PdCl}_6]^{2-}$, and 46% in PdCl_2). Dipole integrals for Pd(2p $\rightarrow$ 4d) transitions of 42 eV for Pd(II) and 48 eV for Pd(IV) L_{III} -edges and 39 eV and 35 eV, respectively, at these Pd oxidation states for the L_{II} -edges were determined. Application of the metal-ligand covalencies and transition dipole integrals by describing the ground state bonding in PdCl_2 with bridging Cl ligands was demonstrated. In future studies, a similar approach will be utilized for palladium phosphine, allyl, olefin complexes in order to define their experimental electronic structure and correlate this with their observed reactivity.

INTRODUCTION

Palladium complexes have long been known to be important in the formation of carbon-carbon bonds. The palladium catalyzed Heck reaction, which is widely used in the production of substituted olefins, dienes and other unsaturated compounds^{1,2} is an example of this importance. The general mechanism for the Heck reaction is presented in Scheme 1 and shows the initial pre activation of the Pd(II) species by reduction and multiple ligand exchange equilibria. This species subsequently undergoes oxidative addition with an arylhalide followed by migratory insertion. Reductive elimination is the last step before the recycling of the Pd catalyst. Since Mizoroki³ and Heck's⁴ independent discoveries of the arylation and alkylation of olefins in the early 1970's that was subsequently developed by Heck into a general method for organic chemistry, interest in this general series of reactions has only increased.

Scheme 1. General scheme for Pd catalyzed Heck reaction.

By varying the structure of the ligand (tuning the electronic and geometric structures) in the activated Pd catalyst, such properties as selectivity and reactivity can be adjusted. Recently, ligand tuning of palladium based catalysts has shown to be effective for controlling the regiochemistry of olefins in the intramolecular Heck reactions^{5,6}. Changing the functional group (L) attached to the 1,2-bis(diphenylphosphino) ligand in Scheme 2 from ethane or propane to methane, ferrocene, butane, or binaphthyl will change the α/β selectivity in the product from >99/1 to about 50/50 in the Pd catalyzed arylation of butyl vinyl ether⁶.

Scheme 2. General scheme for the arylation of butyl vinyl ether.

Further, tuning of the diphenylphosphino type ligand electronic structure in the Pd(0) catalyzed allylic substitution polymerization reactions in Scheme 3 has been shown to have an effect on both the reaction pathway (cascade allylation or dissociation) and the catalytic rate⁷.

Scheme 3. General scheme for an allylic substitution polymerization.

Industrial interest in the polymerization of olefins, particularly the vinyl polymerization of norbornene (Scheme 4), has been sparked by the polymers unique properties of extended thermal stability, high optical transparency, low moisture absorption and low birefringence⁸⁻¹⁰. There is still a need for the development of new catalysts that aren't poisoned by the functional groups on the norbornene while maintaining high catalytic activity. Pd based catalysts are of particular interest because they have been shown to have greater functional group tolerance than their Ni analogues. However, slower Pd reaction rates necessitates further development in this area as well^{10,11}.

Scheme 4. Vinyl polymerization of norbornene.

An allyl ligand, a neutral two-electron-donor phosphine ligand, and a weakly coordinating counter ion coordinated to Pd(II) shows high activity and selectivity by producing >1 ton per hour of 5-butylnorbornene and 5-tirethoxysilylnorbornene copolymer¹⁰. Similar results were found for other norbornene polymerization reactions as catalysts of the type $[\text{PdCl}_2\{\text{Ph}_2(\text{CH}_2)_n\text{PPh}_2\}]$ have been shown to give up to 10^7 g norbornene polymer per mol Pd catalyst¹². Ligand tuning is a promising avenue for further development of these Pd catalysts. Our aim is to develop an experimental technique for investigating the electronic structure of Pd compounds. The general strategy for accomplishing this can be broken into three steps. First, palladium chlorine

bonding interactions are studied and quantified using X-ray Absorption Spectroscopy (XAS) and these measurements are used to calibrate electronic structure calculations. Secondly, XAS is performed on PdCl_xP_x complexes to investigate the Pd-P and Pd-Cl bonding interactions. Thirdly, these experimentally determined bonding interactions are utilized in calibrated potential energy surface calculations. The first step in this process has been accomplished and is presented in this study.

XAS can give both electronic and geometric structural information about a transition metal complex. The extended X-ray absorption fine structure (EXAFS) region in Figure 1 shows the spectrum that originates from the excited electrons leaving the core orbital scattering from neighboring atoms. The peaks in this energy range are from constructive interference and the wells are due to destructive interference of the excited electron's wave and back scattered wave. A Fourier transform and subsequent fitting of this region yields a high resolution radial distribution of the atoms within the studied complex. This can be useful for catalytic intermediates or other metal complexes where the geometry is unknown. Because the crystal structures of the complexes measured in this study are known, the region of interest is the X-ray Absorption Near Edge Structure (XANES) in Figure 1 where the pre-edge and rising edge regions are located. The position of the rising edge jump for XAS is determined by the oxidation state of the atom as the effective nuclear charge affects the energy of the core orbitals. XAS utilizes the dipole allowed $s \rightarrow p$ (in the K-edge) or $p \rightarrow d$ (in the L-edges) transitions. The intense features in the L-edges are split due to the two spin orbit coupled states $2p_{3/2}$ and $2p_{1/2}$ corresponding to the L_{III} and L_{II} -edges, respectively ($p_{3/2}$: $l+s=3/2$ and $p_{1/2}$: $l+s=1/2$). The

position of the pre-edge feature of a metal complex is a function of both the oxidation state and d-manifold shift of the metal center. Furthermore, the intensity of the pre-edge feature is a measure of the metal ligand covalency so the experimental electronic structure can be obtained.

Figure 1. PdCl₂ Cl K-edge spectra showing the different regions and features.

Quantitation of metal-ligand covalency utilizing chlorine K-edge XAS was developed in the early 1990's by the Solomon, Hodgson and Hedman groups at Stanford¹³⁻¹⁵. Figure 2 shows a comparison the Cl K-edge NEXAS region of T_d [ZnCl₄]²⁻ and D_{2d} [CuCl₄]²⁻. No pre-edge feature is observed in the closed shell d¹⁰ Zn(II) metal ion complex [ZnCl₄]²⁻ because the lowest energy transition available for a Cl 1s electron is

Figure 2. Cl K-edge spectra of T_d $[\text{ZnCl}_4]^{2-}$ and D_{2d} $[\text{CuCl}_4]^{2-}$ showing the difference in the pre-edge region. The inset is a simplified MO diagram showing the origin of the $[\text{CuCl}_4]^{2-}$ pre-edge feature.

into the Cl 4s or 4p orbitals. The intense rising edge feature between 2823-2827 eV corresponds to Cl $1s \rightarrow 4p$ excitation. In contrast, the Cu(II) in $[\text{CuCl}_4]^{2-}$ is an open shell d^9 metal ion with an electron hole in the antibonding Cu $3d_{x^2-y^2}$ as shown in the inset in Figure 2. The $3d_{x^2-y^2}$ orbital must have a significant amount of Cl 3p character due to the localized nature of the Cl K-edge transition and the presence of a pre-edge feature in the $[\text{CuCl}_4]^{2-}$ spectra. The area under the pre-edge feature ($D_0(\text{eV}) = 2 \text{ half height line width (eV)} \times \text{peak intensity}$) is proportional to the Cl 3p orbital character in the $3d_{x^2-y^2}$, which is the measure of metal-ligand covalency (α^2). Cu-Cl covalency for D_{4h} $[\text{CuCl}_4]^{2-}$ is known to be 9.75% per Cl from EPR data¹⁶ and was used to determine that the transition

dipole integral (I (eV)) for the Cl K-edge in Equation 1 is 21.04 eV^{13} , where N is the number of metal d-manifold holes.

Equation 1.
$$D_0 = \frac{1}{3N} I \alpha^2$$

Using the Cl K-edge as a reference, the quantitation methods for metal ligand bonding can be extended to study the palladium L_{III} - and L_{II} -edges, which in turn can be utilized to analyze the phosphorus K-edge. For example, for a simple PdCl_x compound, the chlorine 3p orbital contribution to the LUMO can be experimentally determined from XAS and Molecular Orbital (MO) theory predicts that the remainder of the palladium-chlorine bonding interaction is comprised primarily of Pd 4d-orbital character with minor contributions from Cl 3s and 3d and Pd 5s and 5p orbitals. Equation 2 shows the formula for the ground state electronic structure of a PdCl_xP_y complex with the assumption that the Pd 5s and 5p and Cl and P 3s and 3d contributions are negligible (less than 3%).

Equation 2.
$$\Psi^* = c_1 \phi(\text{Pd } 4d) - \sqrt{(1 - c_1^2)} (c_2 \phi(\text{Cl } 3p) + c_3 \phi(\text{P } 3p))$$

The remainder of the bonding interaction not present in the Cl K-edge for PdCl_x is Pd 4d orbital character which can be obtained from the Pd L_{III} and L_{II} -pre-edge features and used to develop the Pd(II) and Pd(IV) transition dipole integrals. It then becomes possible to determine the phosphorus 3p orbital character in the palladium-phosphorus bonding interaction in a PdCl_xP_y complex by measuring the Cl K-edge and the Pd L_{III} - and L_{II} -edges. In this manner, the most important metal-ligand interactions in Pd chemistry can be experimentally probed.

In the 1980's the chlorine K-edges and palladium L_{III} -edges of $[\text{PdCl}_4]^{2-}$, PdCl_2 and $[\text{PdCl}_6]^{2-}$ were measured¹⁷⁻²¹. However, only the peak positions were identified and

the covalency was not quantified. In this study the XAS technique was applied in the measurement and interpretation of the pre-edge intensities and energies of the Pd L_{III} - and L_{II} -edges. This was done at the most common palladium oxidation states of 0, II, and IV using the series Pd(0) powder, $[PdCl_4]^{2-}$ and $[PdCl_6]^{2-}$. Ligand-metal covalency for each Pd-Cl bond were determined by measuring the Cl K-edge pre-edge intensities. The remainder of the bonding interaction not accounted for in the Cl K-edge was then used to develop the transition dipole integrals for the Pd L_{III} and L_{II} -edges so that quantization of Pd 4d orbital covalency by XAS in a Pd-ligand bond could be performed. Electronic structure calculations on the Pd series were correlated with experimental XAS data to aid the spectral assignments and to find a calibrated level of theory for accurate computations.

An application of this method is also presented in this study. The new Pd(II) L -edge dipole integrals are applied to the $PdCl_2$ spectra to quantify the Pd 4d orbital covalency. The remainder of the bond is Cl 3p character and was used to develop a new Cl K-edge transition dipole integral for the bridging Cl's of $PdCl_2$.

MATERIALS AND METHODS

Sample Preparation

K_2PdCl_6 , K_2PdCl_4 , PdCl_2 , $\text{Pd}(0)$, CsCl and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were purchased from STREM Chemical and were of the purity >99%, >99%, and >99.9%, >99.99%, and >99.999% respectively. $\text{D}_{2d} \text{Cs}_2\text{CuCl}_4$ was prepared as described in the literature²² and involved dissolving stoichiometric amounts of CsCl and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in methanol and evaporating the solvent to obtain a solid sample.

Samples were ground into a fine powder that was spread on the sticky side of Kapton tape purchased from SHERCON. This procedure has been shown to minimize self absorption¹⁵. The tape with the powder on it was mounted across the window of an aluminum plate and placed in the sample chamber for measurement.

X-ray Absorption Measurements

Palladium L_{III} and L_{II} -edge, and chlorine K-edge X-ray absorption spectra of K_2PdCl_6 , K_2PdCl_4 , PdCl_2 were measured at Advanced Light Source (ALS) on beam line 9.3.1 and at Stanford Synchrotron Radiation Laboratory (SSRL) on beam line 6.2. The $\text{Pd}(0)$ L_{III} -edge and the Cs_2CuCl_4 Cl K-edge were measured at ALS.

Fluorescence data was collected at ALS in an ultra high vacuum (10^{-7} torr) with a Si-photodiode (Hamamatsu model S3584) aligned parallel with the sample cell. The incident beam was approximately 45° relative to the sample and Beamline conditions, such as sample cell position, detector position, beam focus, and beam size, were

Figure 3. Schematic representation of the end station setup at the ALS BL9.3.1

optimized at 3000 eV and 3300 eV for the Cl K-edge and Pd L-edges, respectively, in order to maximize the signal to noise ratio. A schematic representation of the end station is shown in Figure 3. Optimization procedure at this beamline was performed in four steps. First, the beam was focused and upstream jaws were adjusted to obtain maximum flux with minimum beam halo. Clipping the top and bottom portion of the beam was the best way to achieve this. The residual beam halo is due to the irregularities in the focusing mirror because clipping the beam before the focusing cannot completely eliminate the halo. Secondly, the beam was centered on the sample and vertical feedback foils were adjusted to the proper positions. At the time of the measurements, horizontal feedback was not yet implemented and the foils were removed from the beam to maximize flux. Thirdly the sample and detector positions were optimized to achieve the maximum signal. The detector was positioned so that it was nearly clipping the beam. The x axis was then adjusted until maximum detector signal was obtained followed by

slight rotation of the sample cell to further increase the signal. A small amount of horizontal beam motion occurs throughout the scans, so the detector was backed away from the sample by 2 mm. Fourthly, the gains on the detector and I_0 foil amplifiers were adjusted to a level where the signal was in the linear range of the detector without an overload during the scan. This usually occurred at 200 nA for the Pd L-edges and 20 nA for the Cl K-edges. A small amount of the fluorescence signal was detected on the back of the I_0 foil. Therefore, the I_0 foil was rotated 45 degrees so that it presented less area for detection of the fluorescence signal. Resting and dwell times were set to 400ms and 1s respectively while the energy was scanned in 0.1 eV step sizes in the rising edge region and between 0.5 and 2.0 eV step sizes outside the region. A Si(1 1 1) double crystal monochromator was used to scan through the energy range. When the Cl K-edges of K_2PdCl_6 , K_2PdCl_4 , and $PdCl_2$ were collected at room temperature, photoreduction was observed in the K_2PdCl_6 and $PdCl_2$ spectra. Photoreduction is the most common radiation damage in XAS and is caused by free electrons (resulting from ionizing excitation) in the sample reducing the metal center in the complex being measured. In order to prevent radiation damage, the spectra of the Cl K-edge and Pd L_{III} and L_{II} -edges were subsequently collected while the sample rod was cooled with liquid nitrogen. An average of 2 or 3 scans was analyzed for samples that were not photoreduced. The samples that showed radiation damage are treated separately in the data workup.

Figure 4. Schematic representation of the experiment setup at SSRL BL6-2 (ppw: polypropylene window, Alw: aluminized Mylar window, Bew: beryllium window, EY: electron-yield, F: fluorescence). Figure was adapted from reference 80.

SSRL XAS fluorescence spectra were collected at room temperature in helium atmosphere with a N_2 -purged Lytle detector without using a filter or Soller slits. A 127 μm Be window separated the vacuum in the ring from the experimental end station while a He gas path protected this window from oxidation. The gas path was sealed on the downstream side by a 6.35 μm polypropylene window. He gas was again used as atmosphere as the beam passed through vertical and horizontal slits and an ionization chamber to detect the I_0 signal. Another 6.35 μm polypropylene window was used to separate the sample chamber from the ionization chamber. The sample was rotated 45° relative to the incident beam and the detector was parallel to the sample as shown in Figure 4. The X-ray beam and sample chamber positions were optimized at 3150 eV which is the end of the Cl K-edge scan. Because the beam was already focused and the

detector and sample were stationary relative to each other, optimization involved centering the beam on the sample and adjusting the end station slits so that the I_0 and FF detectors were not overloaded by the signal. The beam was first centered in the beampipe, then in the I_0 chamber, by moving the end station table. Lastly, the beam was centered on the sample by moving the sample chamber. The slits were closed to 2 mm vertical and 7 mm horizontal producing a rectangular shaped beam in the end station. A Si(1 1 1) double crystal monochromator was utilized to scan the rising edge region at 0.1 eV steps and 0.5 -2.0 eV steps outside the region with a dwell time of 1s. Minimal radiation damage (<1% change in individual peak intensity) occurred for K_2PdCl_6 and $PdCl_2$ while none was observed for K_2PdCl_4 . For all spectra radiation damage was determined to be negligible and an average of the 2 or 3 scans was analyzed.

Data Workup

The energy of the Cl K-edges and Pd L_{III} and L_{II} -edges were calibrated to the first absorption maximum of the Cl K-edge spectrum of $D_{2d} Cs_2CuCl_4$ which was assigned to 2820.20 eV¹⁴. Figure 5a illustrates how a smooth background was removed from all spectra by fitting a second order polynomial to the pre-edge region and subtracting this from the entire spectra. Data was then normalized to one absorber by fitting a polynomial spline to the region above the edge and normalizing the edge-jump to one at 2840 eV for the chlorine K-edges as shown in Figure 5b. The palladium L_{III} -edges and L_{II} -edges were normalized to one at 3195 eV and 3345 eV respectively. For the Pd L_{III} and L_{II} -edges together, a smooth background was fit to the L_{III} -pre-edge region and

Figure 5. Sample background correction and normalization of Cl K-edge (a,b), and Pd L-edges (c,d).

subtracted from the entire spectra (Figure 5c). This corrected spectra was then normalized to one at 3345 eV (Figure 5d). The Appendix contains a detailed description of the data workup of each spectra used in the analysis.

Photoreduction was observed in the Cl K-edges of PdCl_2 and $[\text{PdCl}_6]^{2-}$ measured at ALS at room temperature. The isobestic points visible in Figure 6 are evidence of this phenomena. A logarithmic extrapolation (also seen in Figure 6) of the first three spectra collected for each compound was performed to yield an extrapolated spectra to zero radiation exposure. This extrapolation was performed by finding the rate of change for each energy position measured within a spectra. The natural logarithmic function was used to extrapolate from the first scanned spectra to find the XAS intensity at each energy at zero radiation exposure. The data workup procedure discussed above was then

performed on the extrapolated spectra. Less than 1% variation in peak intensity was observed if a linear extrapolation of the photoreduced data was used instead of a logarithmic extrapolation.

Figure 6. Three consecutive scans (red, blue, green) of photoreduced XAS spectra with extrapolated to zero radiation exposure (black) showing isobestic points.

Peak positions were obtained from the minima in the second derivative of the spectra and the inflection point of the rising edge or the maxima of the first derivative was used to determine the rising edge positions.

Fitting

Chlorine K-edge

The normalized Cl K-edge spectra of Cs_2ZnCl_4 was used for a rising edge correction. It was shifted to the rising edge of each normalized PdCl spectra and

subtracted from the spectra. This yielded only the pre-edge features which arise from the Cl 3p covalent bonding interaction. The pre-edge features were then fit with pseudo-Voigt lines (1:1 sum of Gaussian and Lorentzian line shapes) over the energy range 2815 eV to 2827 eV. The minimum number of peaks were used to fit the data and this number was determined from the minima seen in the second derivative. All pre-edge peaks in a spectra were fit with linked half-height line widths (HHLW) because these peaks arise from the same state (the Cl 1s orbital electron transitioning into the Cl 3p based orbital) and should have the same core-hole lifetime broadening.

Palladium L-edges

The Pd(0) L-edge spectra does not have any pre-edge features due to its d^{10} electron configuration and simulates the environment of a Pd without any covalent bonding interaction. Similarly to the Cl K-edge, the normalized Pd(0) L_{III} -edge spectra was shifted and subtracted from each renormalized Pd L_{III} -edge spectra to leave only the pre-edge features for fitting. Because the Pd L_{III} and L_{II} -edges for each compound measured look nearly identical when shifted by 150 eV, the Pd(0) L_{III} -edge was also shifted, scaled and subtracted from the normalized Pd L_{II} -edge spectra for fitting. The remaining Pd L_{III} and L_{II} -pre-edge features were fit with 35% Gaussian and 65% Lorentzian lines over the energy ranges 3165-3185 eV and 3325-3345 eV, respectively. Deviation from the established pseudo Voigt line shape was necessary to achieve reasonable fits for these spectra. The pre-edge features were fit with linked HHLW. The number of peaks used to fit each spectra was determined by the minima in the second

derivative. Are under the pre-edge features were determined from the product of the amplitude and HHLW

The Pd(0) L_{III} -edge was shifted to the L_{III} -rising edge of each $L_{III}+L_{II}$ spectra and scaled so that the spectra with Pd(0) subtracted would be zero at 3325 eV. This allowed for both the fitting of the L_{III} -pre-edge features, and the subsequent shift, scaling, and subtraction of the Pd(0) L_{III} -edge from the newly subtracted $L_{III}+L_{II}$ edge for fitting of the L_{II} -pre-edge features. The EDG_FIT²³ program was used for deconvolution and fitting of all spectra.

Error Analysis

The amount of uncertainty in the energy positions of the peaks is a function of the reproducibility of the spectra. It is established¹⁴ and can be seen in the Appendix that the resolution allows for an error of 0.1 eV in peak positions. The absolute uncertainty at the Pd L-edges is 0.5 eV between beamlines due to different Si(1 1 1) double crystal stepping motors at ALS and SSRL and the calibration point being ~300 or 500 eV away from the edges.

Errors in peak intensity and covalency come from several possible sources. The amount of shift applied to Cs_2ZnCl_4 or Pd(0) when subtracting the edge-jump as discussed in the fitting section can introduce up to 1% error for both the Cl K-edge and Pd L-edges. In order to estimate the error in the normalization procedure, normalization parameters were varied and the average normalized spectra was taken. For the Cl K-edges and the Pd L-edges, 3-5% and 4-6% error, respectively, in peak intensity was

introduced from the entire data workup and fitting. For the Pd L_{III} + L_{II}-edges together, 5-7% error in peak intensity was introduced from data workup in addition to the 1% from fitting. Self-absorption could result in artificially low intensities. While it is believed that the samples were thin enough at SSRL to make this effect negligible, samples at ALS had to be thicker in order to get a good signal to noise ratio. Consequently, peak intensities for room temperature ALS measurements are slightly lower than their analogous measurements at SSRL. As discussed in the results section, different transition dipole integrals are used in this study at SSRL and ALS in order to compensate for the different spectral backgrounds under different beamline conditions. Self-absorption is factored into the different dipole integral at ALS. It is then important to note that the transition dipole integral is a semi-empirical value and has limited relevance to theoretically predicted Cl 1s→3p and Pd 2p→4d transitions.

Electronic Structure Calculations

Modeling of Chloro Palladium Complexes

Unless otherwise noted, electronic structure calculations were performed using Gaussian 03²⁴. Single point ab initio MO and gradient-corrected Density Functional Theory (DFT) calculations were employed to quantify Cl 3p character in the LUMO. A calculation was considered converged when the change in energy between cycles was less than 10⁻⁸ a.u. (tight convergence criterion). Exact D_{4h} symmetry for [PdCl₄]²⁻ with Pd-Cl bond distances of 2.30 Å as determined by Takazawa²⁵ was used as input geometry. The converged basis sets for both Pd and Cl were employed while adding

neighboring atoms to the central $[\text{PdCl}_4]^{2-}$ in the crystal structure positions in an increasing sphere to find the smallest model needed for DFT calculations (point where adding additional atoms does not change the Cl p orbital character in the LUMO b_{1g}^*). This is an appropriate method for determining the necessary model size as crystal packing can affect the frontier orbitals and thus the Pd-Cl covalency. The crystal structure of $[\text{PdCl}_6]^{2-}$ shows octahedral symmetry with Pd-Cl bond distances of 2.29 Å²⁵. The necessary size of the model was determined in the same manner as $[\text{PdCl}_4]^{2-}$ except that, due to different symmetry, the Cl p orbital character in the LUMO e_g^* was the criteria used for model convergence.

The chlorines in PdCl_2 are all in the same plane and bridging two Pd atoms placing the molecule in the D_{2h} symmetry group. Within chains the Pd-Cl bond is 2.31 Å and the Pd-Cl-Pd bonds form a 93° angle²⁶. The shortest necessary chain length required for accurate computations was determined by continually increasing the size of the $\text{Pd}_x\text{Cl}_{2x+2}$ chain until the SCF population of the Cl 3p orbital for the central Cl in the LUMO converged. The crystal packing effects were determined by adding neighboring PdCl_2 molecules to the central chain and monitoring the Cl character in the LUMO.

Finding the Theoretically Converged Basis Sets

A basis set was considered converged if additional Gaussian functions did not change the Cl 3p orbital character in the LUMO b_{1g}^* for D_{4h} $[\text{PdCl}_4]^{2-}$. The GGA type Becke88²⁷ exchange and Perdew 86²⁸ correlation functionals (BP86) were employed along with the SDD basis set for Pd using all the Cl basis sets in Table 1 in order to find the converged Cl basis set. This Cl basis set was subsequently employed while

evaluating the Pd basis sets in Table 1 using both BP86 DFT and Hartree Fock²⁹⁻³¹ (HF) ab initio calculations.

Table 1. List of basis sets evaluated in this study and their contraction schemes.

Effective Core Potential Basis Sets				
element	description		contraction scheme	pol.function coefficient ref
Cl	SDD	(4s,5p)	31/311	32
Cl	CEP-31g	(4s,4p)	31/31	33
Pd	SDD	(8s,7p,6d)	311111/22111/411	34
Pd	SDD(f)	(8s,7p,6d,1f)	311111/22111/411/1	f 1.472 34
Pd	LANL1DZ	(5s,6p,4d)	31/321/31	35
Pd	CEP-121g	(8s,8p,5d)	4211/4211/311	36,37
Pd	CEP-121g(f)	(8s,8p,5d,1f)	4211/4211/311/1	f 1.472 36,37
Pd	HAY-WADT ECP	(8s,6p,4d)	341/321/31	35
Gaussian Type All Electron Basis Sets				
element	description		contraction scheme	pol.function coefficient ref
Cl	sto-3g	(9s,6p)	333/33	38
Cl	3-21g	(9s,6p)	3321/321	39
Cl	6-31g	(16s,10p)	6631/631	40
Cl	6-311g	(12s,10p)	63111/52111	41
Cl	6-31g(d)	(16s,10p,1d)	6631/631/1	d 0.75 40
Cl	6-311g(d)	(12s,10p,1d)	63111/52111/1	d 0.75 41
Cl	6-311g(df)	(12s,10p,1d,1f)	63111/52111/1/1	d 0.75, f 70 41
Pd	WTBS	(27s,20p,17d)	25 25 25 25/20 20 20/17 17	42,43
Pd	WTBS-Split	(27s,20p,17d)	12 62221/10 4222/844441	42,43
Pd	DZVP	(18s,12p,9d)	633321/53211/531	44
Pd	STO-3g	(15s,12p,6d)	33333/3333/33	45
Pd	3-21g	(15s,12p,6d)	333321/33321/321	46

Relativistic effects were accounted for by utilizing the Douglas-Kroll-Hess second order scalar relativistic⁴⁷ (DKH) and Relativistic Elimination of Small Components⁴⁸ (RESC) approaches in Gaussian03 and comparing the results to the uncorrected calculations. Amsterdam Density Functional^{49,50} (ADF) was used to evaluate the Zero Order Relativistic Approximation⁵¹ (ZORA) with the TZP all electron basis for Pd and Cl and the BP86 exchange correlation. Because Pt has a greater nuclear charge

than Pd and relativistic effects are expected to be more important in this atom, geometry optimization as well as Cl p orbital SCF population analysis was done on D_{4h} $[\text{PtCl}_4]^{2-}$ to see if the relativistic correction methods at least treat the electrons differently than the non corrected methods.

Calibration of Theory

A basis set and theory is considered calibrated if it reproduces the covalency obtained from Pd L-edge and Cl K-edge XAS. In order to find the calibrated level of theory, the converged basis sets for Cl and Pd were employed while evaluating various DFT and ab initio methods as shown in Table 2 for $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$. The calibrated theory for Pd(II) and optimal basis sets were utilized to verify that computations on the PdCl_2 model reproduce the experimental XAS covalency.

Table 2. List of theories employed in this study.

Density Functional Theory			
description	exchange	correlation	reference
BP86	B88	P86	27,28
PBEPBE	PBE	PBE	52,53
PW91PW91	PW91	PW91	54,55
Density Functional Theory hybrid functionals			
description	exchange	correlation	reference
BHnadHLYP	50% HF 50% B88	50%	56
PB11PBE	25% HF 75% B88	75%	53
B3LYP	20% HF 80% B88	LYP non-local correlation VWN local correlation	56
ab initio MO theory			
description	definition		reference
HF	Hartree Fock		29-31
MP2	Moller-Plesset correlation energy correction truncated at second order		57-59
MP4	Moller-Plesset correlation energy correction truncated at fourth order		60
CCD	Coupled Cluster calculations using double substitutions		61
CCSD	Coupled Cluster calculations using single and double substitutions		62-65
QCISD	Quadratic CI calculation using single and double substitutions		66-68

Atomic charges were calculated with calibrated basis sets and levels of theory utilizing the Atoms In Molecules⁶⁹ (AIM), Natural Population Analysis⁷⁰ (NPA), and Electrostatic Potential⁷¹ (ESP) approaches. The polarized continuum model for the United Atom Topological Model was used to find the radii for Pd to be utilized in the ESP charge calculations⁷². NPA was also performed to determine the amount of Pd 5s/5p. and Cl 3s/3d mixing. This information is essential as it affects covalency, and thus the ground state electronic structure.

RESULTS

Data Quality Dependence on Beamline Setup and Optics

Figure 7a-c shows the Cl K-edge and Pd L_{III}-edge XAS spectra for [PdCl₄]²⁻, PdCl₂, and [PdCl₆]²⁻. The difference in areas under the pre-edge features when the sample is cooled with liquid nitrogen and when the sample is measured at room temperature is due to both self absorption and a different spectral background. Self absorption is the result of the necessary thicker samples needed at ALS. The Pd L_{III}-edge spectra for [PdCl₄]²⁻ (Figure 7d), PdCl₂ (Figure 7e) and [PdCl₆]²⁻ (Figure 7f) look nearly identical to the corresponding Pd L_{II}-edges (in the Appendix pages 88-92) when shifted 150 eV so only the L_{III}-edge is shown. The same background subtraction procedure was done for all spectra and it is apparent that a different procedure is needed for samples measured at ALS while being cooled with liquid nitrogen (see the Appendix pages 77, 79, 81, 83, 85, 86, 88, 90, 92, 94, 96, and 98 for background corrections and raw data). Until more data is collected and a general data workup procedure is established, different dipole integrals are used for both the Cl K-edge and the Pd L-edges at SSRL and ALS if the sample is cooled with LN₂. A new Cl K-edge ALS dipole integral was found to be 19.3 eV and is based on the pre-edge feature of D_{2d} Cs₂CuCl₄. The chlorine covalency is known to be 7.3% per Cl from previous XAS studies¹⁴. The spectra and fit are shown in the supporting information and the peak intensity, half height line widths (HHLW), and integrated areas (D₀) are shown in Table 3 located in the Cl K-edge results section (p27).

Figure 7. The Cl K-edge spectra of a) $[\text{PdCl}_4]^{2-}$, b) PdCl_2 and c) $[\text{PdCl}_6]^{2-}$ measured at SSRL (solid) and ALS (dashed). The Pd L_{III}-edge spectra of d) $[\text{PdCl}_4]^{2-}$, e) PdCl_2 and f) $[\text{PdCl}_6]^{2-}$ measured at SSRL (solid) and ALS (dashed).

Separate dipole integrals at LN₂ temperatures at ALS and at room temperature at SSRL for the Pd L-edge are also calculated and are presented in Tables 4-6 located in the Pd L-edge results section. Experimental Pd-Cl covalencies for $[\text{PdCl}_4]^{2-}$ measured at room temperature at ALS compared to SSRL indicated that ~4% self absorption occurs at ALS due to the necessary thicker samples. This phenomenon most likely occurs during all

measurements at ALS and thus factored into the separate Cl(1s→3p) and Pd(2p→4d) transition dipole integrals.

Figure 8 shows the Cl K-edge spectra of $[\text{PdCl}_4]^{2-}$ measured two separate times at SSRL giving nearly identical pre-edge peak areas (D_0) while having an intensity difference of nearly 9%. This is caused by different upstream beamline setups, which were not accessible for the general users, yielding different spectral resolution. The Cl K-edge linewidths at ALS are between (0.57-0.68) and are slightly smaller than the SSRL linewidths, which are 0.64-0.69 suggesting greater spectral resolution. These linewidths are listed in Tables 3-5.

Figure 8. The Cl K-edge spectra of $[\text{PdCl}_4]^{2-}$ measured at SSRL with beamline setup A (orange) and beamline setup B (blue) showing different resolutions.

Figure 9. Fits and the second derivative fits of the Pd L_{III} -edge of $PdCl_2$ using a) the pseudo Voigt line, b) 0% Gaussian and 100% Lorentzian line shape and c) 35% Gaussian and 65% Lorentzian line shape.

Fits of the Pd L_{III}-edge of PdCl₂ in Figure 9 show that the pseudo Voigt line is reasonable, but not the best fit for the spectra. The 0% Gaussian 100% Lorentzian line shape in Figure 9b appears to be the best fit of the spectra. Because the generally used line shape is pseudo Voigt and there is little theoretical evidence to deviate from this, the line shape with Gaussian/Lorentzian ratio of 0.35/0.65 in Figure 9c was chosen as a compromise to fit all the L-pre-edge features.. The excited state lifetime is represented by the Gaussian line shape and the beamline optics are represented by the Lorentzian line shape.

As discussed in the materials and methods error analysis, the Pd L_{III} and L_{II} pre-edge peaks at the ALS are 0.4-0.5 eV and 0.6-0.7 eV higher in energy than at SSRL (see Figure 7 and Tables 4 and 5). We propose setting the first L_{III}-pre-edge peak of [PdCl₄]²⁻ to 3175.8 eV and using it as a calibration point for both the Pd L_{III} and L_{II}-edges.

Cl K-edge Spectra Results

A comparison of the Cl K-edge spectra of [PdCl₄]²⁻, PdCl₂, [PdCl₆]²⁻, and Cs₂ZnCl₄ is shown in Figure 10. The rising edge-inflection points, peak positions, intensities, HHLW and Cl 3p character in the LUMOs are listed in Table 3 and the Appendix show the fits and data workup. The rising edge-inflection points and pre-edge peak positions for the series are marked in Figure 10. Many of the PdCl₂ results and spectra are included here, but will be analyzed in more detail later (page 47).

Figure 10. Cl K-edge spectra and second derivative or the spectra of $[\text{PdCl}_4]^{2-}$ (blue), PdCl_2 (green), $[\text{PdCl}_6]^{2-}$ (red), and $[\text{ZnCl}_4]^{2+}$ (black) measured at SSRL showing the difference in peak intensities, peak positions and rising edge positions.

As the palladium-chlorine bond becomes more covalent and the effective nuclear charge of the Cl goes up, the rising edge-inflection points shift to higher energy in the order of $[\text{CuCl}_4]^{2-}$, $[\text{PdCl}_4]^{2-}$, $[\text{PdCl}_6]^{2-}$. The pre-edge peaks are assigned to the transitions from the Cl 1s orbitals into the doubly unoccupied LUMO b_{1g}^* for $[\text{PdCl}_4]^{2-}$ and into the quadruply unoccupied LUMO e_g^* for $[\text{PdCl}_6]^{2-}$. The higher energy shoulders on these

peaks are shake-up satellite transitions caused by electron excitation from the Cl 1s orbitals due to core hole induced electronic relaxation into the fixed excited state. (See the electronic structure calculations results section for a more detailed description of the electronic relaxation.) Because these excited states originate from the same ground state, they are both included in D_0 and covalency calculations.

Table 3. The Cl K-edge data measured at ALS and SSRL.

complex	location and setup	rising edge inflection point (eV)	peak position	intensity		D_0	ΣD_0	total Cl 3p covalency	average total Cl 3p covalency
				of peak	HHLW				
$[\text{PdCl}_4]^{2-}$	SSRL setup A	2825.0	2821.5	1.10	0.69	1.5	1.6	92%	92%±3
			2823.4	0.12	0.69	0.2			
	4 absorbers	2825.0	2821.5	1.2	0.62	1.5	1.6	94%	
			2823.3	0.12	0.62	0.1			
	2 electron holes	2825.0	2821.5	1.21	0.60	1.5	1.6	89%	
			2823.3	0.10	0.60	0.1			
	ALS Setup D	2825.0	2821.5	1.21	0.57	1.4	1.5	92%	
			2823.3	0.10	0.57	0.1			
$[\text{PdCl}_6]^{2-}$	SSRL setup B	2826.9	2820.2	1.60	0.64	2.0	2.4	203%	202%±8
			2821.8	0.27	0.64	0.3			
	6 absorbers	ALS setup C [†]	2820.2	1.63	0.62	2.0	2.4	203%	
			2821.7	0.30	0.62	0.4			
	4 electron holes	2827.0	2820.2	1.47	0.62	1.8	2.1	200%*	LN ₂ cooled dipole integral at the ALS
			2821.9	0.23	0.62	0.3			
$[\text{CuCl}_4]^{2-}$	ALS setup D	2825.3	2820.2	0.41	0.54	0.4	0.5	29% [‡]	19.3

4 absorbers and 1 electron hole

*ALS dipole integral while the sample is cooled with LN was used for covalency calculation.

[†]Extrapolated data due to photoreduction radiation damage.

[‡]Covalency was obtained from previous XAS study¹⁴.

Fits of the pre-edge features reveal total areas of 1.6 and 2.4 at the SSRL for $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$, respectively, and 1.4 and 2.1, respectively, at the ALS while

cooled with LN₂. The total Cl covalency per d orbital hole was found to be 46% and 50% for [PdCl₄]²⁻ and [PdCl₆]²⁻, respectively, with an error bar of $\pm 2\%$ for each. Covalency was defined as the total Cl character in the LUMO so that Pd character and thus the Pd L-edge dipole integrals could be calculated.

Pd L-edge Spectra Results

There are three possibilities to define the transition dipole integral for the palladium L-edges. Different methods can be useful when the measurement of both the L_{III}- and L_{II}-edges together is hindered, such as when crystal glitches or other absorbers with overlapping edges are present. The first, method I, is to measure only the L_{III}-edge and use it to define the dipole integral. The second, method II, is to measure only the L_{II}-edge and use it to define the dipole integral. The third, method III, is to measure both edges and use the combination of the two to define a total dipole integral for the Pd L-edges. In addition, multiple quantitation of these data can reduce the statistical error in these data.

Figure 11 compares the Pd L_{III}-edge spectra of [PdCl₄]²⁻, PdCl₂, [PdCl₆]²⁻ and Pd(0). The rising edge positions (listed in Table 2) and pre-edge peak positions are also marked on Figure 11. Although the rising edge positions of the Pd L-edges are not as well resolved as the Cl K-edge, the first derivatives shown in the Appendix (pages 83-87) clearly show maxima at these points. The order of this series reflects the difference in the effective nuclear charge of each palladium as greater charge gives rise to a higher energy

rising edge. Tables 3 and 4 also list the peak positions, intensities, HHLW, and dipole integrals for the Pd L-edges.

Figure 11. The Pd L_{III}-edge spectra and second derivative of the spectra of $[\text{PdCl}_4]^{2-}$ (blue), PdCl_2 (green), $[\text{PdCl}_6]^{2-}$ (red), measured at SSRL and $\text{Pd}(0)$ (black) measured at ALS showing the difference in peak intensities, peak positions and rising edge positions.

Table 4. Pd L_{III}-edge data measured at ALS and SSRL.

complex	location and setup	rising edge inflection point (eV)	peak position	intensity of peak	HHLW	ΣD_0	total Pd d character*	transition dipole integral for L _{III} (eV)
[PdCl ₄] ²⁻	SSRL setup A	3180.2	3175.8	2.57	1.42	7.3	104%	42±4
absorbers (1) electron holes (2)	ALS setup D	3181.0	3176.4	2.29	1.26	5.7	104%	33±3
[PdCl ₆] ²⁻	SSRL setup B	3185.0	3177.8 3175.6	3.25 0.31	1.47 1.47	10.5	176%	48±5
absorbers (1) electron holes (4)	ALS setup D	3186.0	3178.3	2.57	1.55	8.0	176%	36±4

*Pd d character comes from the remainder not measured in the Cl K-edge XAS such as Cl 3s and 3d and Pd 5s and 5p characters from calibrated electronic structure calculations and analysis of rising edge positions.

Table 5. Pd L_{II}-edge data measured at the ALS and SSRL.

complex	location and setup	rising edge inflection point (eV)	peak position	intensity of peak	HHLW	ΣD_0	total Pd d character*	transition dipole integral for L _{II} (eV)
[PdCl ₄] ²⁻	SSRL setup A	3337.4	3332.7	2.47	1.32	6.7	104%	39±4
absorbers (1) electron holes (2)	ALS setup D	3338.1	3334.5	2.45	1.20	5.9	104%	34±3
[PdCl ₆] ²⁻	SSRL setup B	3341.9	3334.7	2.57	1.47	7.7	176%	35±3
absorbers (1) electron holes (4)	ALS setup D	3342.7	3335.4	2.60	1.39	7.2	176%	33±3

*Pd d character comes from the remainder not measured in the Cl K-edge XAS such as Cl 3s and 3d and Pd 5s and 5p characters from calibrated electronic structure calculations and analysis of rising edge positions.

Figure 12 is included to verify that the lower energy shoulder in the [PdCl₆]²⁻ L-edge spectra in Figure 11 and higher energy shoulder in the Cl K-edge spectra of [PdCl₆]²⁻ in Figure 10 was not a result of contamination by one of the chloro-Pd(II)

Figure 12. The second derivative of the Pd L_{III}-edge spectra of $[\text{PdCl}_6]^{2-}$ spectra a) and normalized Cl K-edge spectra of $[\text{PdCl}_6]^{2-}$ b) with 20% of the chloro-Pd(II) spectra removed to verify that the shoulder in the $[\text{PdCl}_6]^{2-}$ spectra was not the result of contamination.

complexes. At least 20% of either PdCl_2 or $[\text{PdCl}_4]^{2-}$ L-edge spectra must be subtracted from the $[\text{PdCl}_6]^{2-}$ spectrum to achieve a second derivative where this shoulder is not present. If this shoulder were due to contamination of the complex by 20% of either of the chloro-Pd(II) complexes, then this contamination would also be evident in the Cl K-

edge. This is not the case as subtracting 20% of each chloro-Pd(II) Cl K-edge spectra from the $[\text{PdCl}_6]^{2-}$ spectra gives an unreasonable XAS spectra with negative absorbance.

The most intense pre-edge features for $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$ L_{III} -edges at ALS are at 3176.4 and 3178.3 eV respectively and, similar to the Cl K-edge, are assigned to the transition into the unoccupied b_{1g}^* for $[\text{PdCl}_4]^{2-}$ and the unoccupied e_g^* for $[\text{PdCl}_6]^{2-}$. As discussed earlier, a distinction must be made between sample measurement locations as the calibration at this energy is different at each beamline. The lower energy shoulder in the $[\text{PdCl}_6]^{2-}$ spectra is a satellite feature. (Further discussion of this occurs in the Electronic Structure Calculations results section). Similar transitions are expected for the $[\text{PdCl}_4]^{2-}$ and PdCl_2 spectra, but are very close to the main peak and thus not resolvable with the current beamline setup. The transition envelop nature of the pre-edge peak was taken into account by a non pseudo-Voigt line shape used in fitting.

Figure 13. The Pd L_{III} + L_{II} -edge spectra of $[\text{PdCl}_4]^{2-}$ (blue), PdCl_2 (green), and $[\text{PdCl}_6]^{2-}$ (red) shows the relative intensities of each edge-jump.

The spectra of the Pd L_{III} and L_{II}-edges measured and normalized together are shown in Figure 13. Table 4 lists the area under the pre-edge features and the ratio of the L_{III} to the L_{II}-edge jump. In all three cases this ratio is about 1.5 to 1.0 while the theoretical value is 2.0 to 1.0⁷³.

Table 6. Pd L_{III}+L_{II}-edge data measured at ALS and SSRL.

complex	location and setup	L _{III}				L _{II}				L _{III} + L _{II}		transition	
		peak positions	intensity of peak	HHLW	L _{III} ΣD ₀	peak positions	intensity of peak	HHLW	L _{II} ΣD ₀	L _{III} + L _{II} ΣD ₀	L _{III} /L _{II} edge jumps	total Pd d character* for L _{III} + L _{II} (eV)	dipole integral
[PdCl ₄] ²⁻	SSRL setup A	3175.8	1.56	1.42	4.4	3332.7	0.99	1.35	2.7	7.1	0.6	104%	41±4
absorbers (1) electron holes (2)	ALS setup D	3176.6	1.23	1.28	3.2	3333.4	0.93	1.19	2.2	5.4	0.6	104%	31±3
[PdCl ₆] ²⁻	SSRL setup B	3177.8	1.86	1.38	5.7	3334.7	1.35	1.39	3.8	9.4	0.6	176%	32±3
		3175.4	0.20	1.38									
absorbers (1) electron holes (4)	ALS setup D	3178.3	1.45	1.36	3.9	3335.4	1.25	1.41	3.5	7.5	0.6	176%	25±3

*Pd 4d character per hole comes from Cl K-edge XAS and Cl 3s and 3d and Pd 5s and 5p character is taken from calibrated electronic structure calculations.

The LUMO is a combination of the Cl 3p orbital and the Pd 4d orbitals with minor contributions from the Pd 5s/5p and Cl 3s/3d orbitals. Consequently, an estimate of the Pd 5s/5p and Cl 3s/3d character in the LUMO is needed to find accurate transition dipole integrals for the Pd L-edges. Results from electronic structure calculations presented below employing the calibrated basis sets and levels of theory reveal a total of 4% Cl 3d and 3s character and 0% Pd 5p and 5s character for [PdCl₄]²⁻. Subtracting this from the remaining 108% from the Cl K-edge yields 104% Pd 4d character that should correspond to the pre-edge intensities in the Pd L-edges. Calibrated electronic structure calculations indicate 11% total Cl 3s and 3d and 0% Pd 5p and 5s character in the LUMO of [PdCl₆]²⁻. However, insights gained from the analysis of the Cl K- and Pd L-edge rising edge positions and covalencies indicate some mixing of Pd 5s/5p orbital character in the bond. Therefore, an additional estimated 11% Pd 5s/5p bond character is added to

$[\text{PdCl}_6]^{2-}$ leaving 175% Pd d orbital character that should be present in the L-pre-edge features.

Electronic Structure Calculations

Electronic structure calculations were performed on the Pd series to find a spectroscopically calibrated level of theory for Pd(II) and Pd(IV) which can accurately describe the potential energy surfaces for catalytic mechanisms of Pd complexes. In order to establish this, it was necessary to find the appropriate basis sets for Cl and Pd. The calibrated computations were subsequently used as an aid in the assignment and interpretation of the XAS spectra.

While Figure 14 shows that the 6-31G(d) basis set for Cl can be considered theoretically converged for Cl 3p orbital character in the LUMO from single point $[\text{PdCl}_4]^{2-}$ calculations, the 6-311G(d) was employed for all further models to ensure that the basis set was converged.

The Pd basis set dependence in Figure 15 shows an increase in the covalency of the Pd-Cl bond as the size of the all electron basis sets increase and the covalency decrease as the size of the basis sets with effective core potentials are increased. This is a similar trend as the one found in $[\text{CuCl}_4]^{2-}$ ⁷⁴. Although the WTBS-Split uses more Gaussians to define the orbitals than the SDD basis set with f orbitals (SDD(f)), the SDD(f) basis was employed for this study because the WTBS basis is too computationally expensive for calculations on larger systems.

Figure 14. Chlorine basis set effect comparing the Cl 3p orbital character in the LUMO b_{1g}^* in $[\text{PdCl}_4]^{2-}$ using the BP86 exchange functional.

Figure 15. Palladium basis set effect on the SCF population. Comparing the Cl 3p orbital character per LUMO b_{1g}^* in $[\text{PdCl}_4]^{2-}$ using both BP86 (dashed) and HF (solid) theories. The red marks the all electron basis sets and the black marks the basis sets with effective core potentials.

Adding external point charges, or counterions around the central $[\text{PdCl}_4]^{2-}$ or $[\text{PdCl}_6]^{2-}$ as in the crystal structure to simulate crystal packing effects had little effect ($<1\%$) on the Cl character in the LUMO σ^* . Therefore, gas phase calculations were employed when calibrating the theory to XAS covalency data. Results of the gas phase

SCF population analysis calculations of $[\text{PdCl}_4]^{2-}$, plotted in Figure 16, show the ab initio calculations with increasing electron correlation converge to 36% Cl 3p orbital character in the LUMO σ^* of $[\text{PdCl}_4]^{2-}$ for the QCISD method. The density functionals converge at 47 % Cl character for the 50/50 exchange BHandHLYP and this most accurately reproduces the 46% experimental Cl character from Cl K-edge XAS.

Figure 16. The calibration of theory to experimental XAS Pd-Cl covalency for $[\text{PdCl}_4]^{2-}$ using the SDD(f) basis set for Pd and the 6-311G(d) basis set for Cl.

A similar trend is observed in the theory calibration calculations of $[\text{PdCl}_6]^{2-}$ in Figure 17. The exchange functionals show a decrease in Cl 3p character in the LUMO as more HF exchange is added and the ab initio electron correlation methods also show a decrease in palladium-chlorine covalency as higher order electron correlation is considered. However, the QCISD level of theory proved to be calibrated for the Pd(IV) complex as it calculates 51% Cl character, which most accurately reproduces the experimental XAS Pd-Cl covalency of 50%. Due to the high computational cost of the

QCISD method on large Pd systems, the BHandHLYP will be considered the most reasonable level of theory for Pd(IV) as well as Pd(II). A discussion of the difference in QCISD calculations on Pd(II) and Pd(IV) occurs in the electronic structure analysis section (page 50).

Figure 17. The calibration of theory to XAS experimental Cl covalence for $[\text{PdCl}_6]^{2-}$ using the SDD(f) basis for Pd and the 6-311g(d) basis for Cl.

As discussed in the materials and methods, the bridging chlorines in PdCl_2 are all in the same plane effectively forming an infinitely long chain. By finding that the calculated Pd 4d character in the palladium-chlorine bond for the central Pd converged to 54% (Table 7) using the theoretically converged basis sets and the BHandHLYP exchange functional, it was observed that this chain can be approximated with a cluster model that is 3 palladium atoms long and terminated with potassium atoms between 2.6-3.4 Å away from the terminal Pd as pictured in Figure 18. This is in reasonable agreement with the experimental XAS value of 52% Pd 4d character. In this case, Pd 4d character in the palladium chlorine bond was used to determine the appropriate model

because Pd character was experimentally quantitated using Pd L-edge XAS. Because $\text{K}_2\text{Pd}_2\text{Cl}_6$ will not effectively model the infinitely long PdCl_2 chain, it was concluded that the terminal chlorides are bonding differently to Pd than bridging chlorides.

Table 7. Models of PdCl_2 with Cl 3p and Pd 4d covalency in Pd-Cl bonds.

complex	distance (Å)		
	terminal alkali metal from Pd	central Cl covalency	central Pd covalency
$\text{K}_2[\text{Pd}_2\text{Cl}_6]$	3.0	27%	39%
$\text{K}_2[\text{Pd}_2\text{Cl}_6]$	3.4	26%	40%
$\text{K}_2[\text{Pd}_2\text{Cl}_6]$	3.8	25%	41%
$\text{K}_2[\text{Pd}_2\text{Cl}_6]$	4.0	24%	41%
$\text{K}_2[\text{Pd}_2\text{Cl}_6]$	4.1	30%	24%
$\text{K}_2[\text{Pd}_2\text{Cl}_6]$	4.2	30%	29%
$\text{K}_2[\text{Pd}_3\text{Cl}_8]$	2.6	22%	53%
$\text{K}_2[\text{Pd}_3\text{Cl}_8]$	3.0	21%	53%
$\text{K}_2[\text{Pd}_3\text{Cl}_8]$	3.4	21%	53%
$\text{Rb}_2[\text{Pd}_3\text{Cl}_8]$	3.2	21%	53%
$\text{Na}_2[\text{Pd}_3\text{Cl}_8]$	2.8	22%	53%
$\text{K}_2[\text{Pd}_4\text{Cl}_{10}]$	3.0	21%	54%

Figure 18. Varying the distance of K from Pd to find an appropriate model for PdCl_2 that simulates an infinitely long chain for the Cl covalency of the central Cl.

Table 8 summarizes the results of calculations with relativistic corrections and indicates that ZORA in ADF changed the Cl 3p orbital character in the LUMO by 5% and 1% for D_{4h} $[\text{PtCl}_4]^{2-}$ and $[\text{PdCl}_4]^{2-}$, respectively, compared to non-relativistic calculations. Gaussian relativistic DKH and RESC revealed $\ll 1\%$ change in covalency for both the 50/50 exchange BHandHLYP and BP86 on both compounds. The results of

the geometry optimization in Table 9 show a larger bond length difference between ZORA correction and uncorrected calculations for $[\text{PtCl}_4]^{2-}$ compared to $[\text{PdCl}_4]^{2-}$. No bond length change was observed for either molecule using the correction implemented in Gaussian. It was concluded that relativistic effects do not have a significant affect on Pd-ligand covalency.

Table 8. Effects of relativistic corrections on Cl p orbital character in the LUMO of $[\text{PdCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ using both ADF ZORA corrections and DKH, and RESC corrections in Gaussian.

complex	theory	Pd basis	relativistic correction	total Cl 3p covalency per d manifold hole
$[\text{PdCl}_4]^{2-}$	BP86	SDD(f)	None	54%
			DKH	54%
			RESC	54%
$[\text{PtCl}_4]^{2-}$	BP86	SDD	None	53%
			DKH	53%
			RESC	53%
$[\text{PdCl}_4]^{2-}$	BP86	TZP	None	55%
			ZORA	55%
$[\text{PtCl}_4]^{2-}$	BP86	TZP	None	58%
			ZORA	53%
$[\text{PdCl}_4]^{2-}$	BHandHLYP	SDD(f)	None	47%
			DKH	47%
			RESC	47%
$[\text{PtCl}_4]^{2-}$	BHandHLYP	SDD	None	47%
			DKH	47%
			RESC	47%

Table 9. Effects of relativistic corrections in ADF and Gaussian on the Pd-Cl and Pt-Cl bond lengths in D_{4h} compounds.

complex	theory	Pd basis	relativistic correction	Metal -Cl bond length (Å)
$[\text{PdCl}_4]^{2-}$	BP86	TZP	None	2.42
			ZORA	2.39
$[\text{PtCl}_4]^{2-}$	BP86	TZP	None	2.44
			ZORA	2.38
$[\text{PdCl}_4]^{2-}$	BHandHLYP	SDD(f)	None	2.39
			DKH	2.39
			RESC	2.39
$[\text{PtCl}_4]^{2-}$	BHandHLYP	SDD(f)	None	2.41
			DKH	2.41
			RESC	2.41

Calibrated electronic structure calculations presented in Table 10 on the Cl orbital characters in the LUMOs of $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$ show that Pd-Cl bond covalency from XAS is reproduced by the calculations. Chlorine 3s and 3d character in the LUMOs of $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$ was found to be 2% and Pd 5s and 5p character was found to be less than 0.5%. Table 11 lists the calculated atomic charges for AIM, NPA, and ESP on each atom using the calibrated theory. While the charges are definitely method dependent, the relative differences in charges between species are consistent from method to method. For the AIM calculations, the chlorines in $[\text{PdCl}_4]^{2-}$ have a charge of -0.66 and the Pd has a charge of +0.64 while the Cl's in $[\text{PdCl}_6]^{2-}$ have a -0.51 charge and Pd has a +1.04 charge. The chlorines and Pd in PdCl_2 have charges of -0.35 and +0.69, respectively.

NPA, summarized in Table 12, of $[\text{PdCl}_4]^{2-}$, PdCl_2 , and $[\text{PdCl}_6]^{2-}$ reveals that orbital occupations of the tetrachloro and dichloro Pd species are nearly the same with populations of Pd $5s^{0.4}$, $4d^9$, and $5p^{0.4}$ and Cl $3s^{1.9}$ and $3p^{5.5}$ and $[\text{PdCl}_6]^{2-}$ has populations of Pd $5s^{0.4}$, $4d^{8.6}$, and $5p^1$ and Cl $3s^{1.9}$ and $3p^{5.4}$ corresponding to an overall more covalent bonding interaction in $[\text{PdCl}_6]^{2-}$ compared to PdCl_2 or $[\text{PdCl}_4]^{2-}$.

Table 10. Atomic orbital character in the LUMO of $[\text{PdCl}_4]^{2-}$, PdCl_2 , and $[\text{PdCl}_6]^{2-}$ using calibrated electronic structure calculations on the experimental crystal structure.

complex	theory used	Cl 3p character in LUMO	Pd 4d character in LUMO	Cl 3s and 3d character in LUMO	Pd 5s and 5p character in LUMO
$[\text{PdCl}_4]^{2-}$	BHandHLYP	47%	51%	2%	0%
$[\text{PdCl}_6]^{2-}$	BHandHLYP	61%	38%	2%	0%
PdCl_2	BHandHLYP	43%	54%	2%	1%

Table 11. NPA, AIM, ESP atomic charges of $[\text{PdCl}_4]^{2-}$, PdCl_2 , and $[\text{PdCl}_6]^{2-}$ using the calibrated level and theory and basis sets.

complex	theory used	atom	ESP	AIM	NPA
$[\text{PdCl}_4]^{2-}$	BHandHLYP	Pd	0.60	0.64	0.67
		Cl	-0.65	-0.66	-0.67
$[\text{PdCl}_6]^{2-}$	BHandHLYP	Pd	0.56	1.04	0.86
		Cl	-0.43	-0.51	-0.48
PdCl_2	BHandHLYP	Pd	0.25	0.69	0.68
		Cl	-0.13	-0.35	-0.36

Table 12. NPA showing the electron configuration of the valence orbitals in $[\text{PdCl}_4]^{2-}$, PdCl_2 , and $[\text{PdCl}_6]^{2-}$ with the calibrated level of theory. Orbitals with ≤ 0.02 electron occupation are omitted.

Compound	Theory	Atom	valence orbital (occupation)		
$[\text{PdCl}_4]^{2-}$	BHandHLYP	Pd	5S(0.43)	4d(9.09)	5p(0.47)
		Cl	3S(1.90)	3p(5.59)	
$[\text{PdCl}_6]^{2-}$	BHandHLYP	Pd	5S(0.43)	4d(8.64)	5p(0.98)
		Cl	3S(1.87)	3p(5.44)	3d(0.01)
PdCl_2	BHandHLYP	Pd	5S(0.35)	4d(8.91)	5p(0.41)
		Bridging Cl	3S(1.83)	3p(5.32)	3d(0.01)

Specifying the electron occupations in ADF, a Cl 1s electron was excited to the appropriate LUMO to simulate the Cl K-edge pre-edge transition for $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$. Figure 19 illustrate that in both compounds these electron transitions resulted in the LUMO orbital, along with it's bonding combination, rising in energy relative to the unoccupied Pd 5s orbital. In addition, for $[\text{PdCl}_4]^{2-}$, the Pd d-orbital character in the antibonding combination increases while the Cl p orbital character decreases. The

reverse trend is true for $[\text{PdCl}_6]^{2-}$ as the Pd d-orbital character decreases while the Cl p orbital character increases in the LUMO.

Figure 19. Excitation of an electron from the Cl 1s orbital to the a) LUMO b_{1g}^* in $[\text{PdCl}_4]^{2-}$ and b) LUMO e_g^* in $[\text{PdCl}_6]^{2-}$ using the TZP all electron basis set for both Pd and Cl and the BP86 exchange function in ADF. The occupied orbitals between the bonding and antibonding b_{1g} and e_g orbitals are omitted for clarity.

An excitation of a Pd 2p electron into the LUMO b_{1g}^* of $[\text{PdCl}_4]^{2-}$ or LUMO e_g^* for $[\text{PdCl}_6]^{2-}$ designed to simulate the Pd L-edge pre-edge excitation is seen in Figure 20. The core vacancy results in both the anti-bonding LUMO b_{1g}^* and e_g^* and their bonding counterparts lowering in energy relative to the Pd 5s orbital. Concurrent with the orbital energy drop in $[\text{PdCl}_4]^{2-}$, the Cl 3p orbital character in the LUMO increases while the Pd 4d orbital character decreases. Once again, the reverse trend is observed in $[\text{PdCl}_6]^{2-}$. Upon electronic relaxation after excitation, the Cl 3p orbital character decreases while the Pd 4d orbital character increases in the LUMO.

Figure 20. Excitation of an electron from the Pd 2p orbital to the a) LUMO b_{1g}^* in $[\text{PdCl}_4]^{2-}$ and b) LUMO e_g^* in $[\text{PdCl}_6]^{2-}$ using the TZP all electron basis set for both Pd and Cl and the BP86 exchange function in ADF. The occupied orbitals between the bonding and antibonding b_{1g} and e_g orbitals are omitted for clarity

ANALYSIS

Analysis of the Cl K-edge

The rising edge position is a measure of the transition energy from the Cl 1s to the 4p orbitals. Because the Cl 4p orbitals are involved in bonding only to a limited extent, a change in the rising edge-inflection point is indicative of a change in the energy of the Cl 1s orbital, which directly correlates with the effective nuclear charge of the Cl. The Cl K-edge rising edge position of D_{4h} $[\text{PdCl}_4]^{2-}$ at 2825.0 eV compared to 2824.0 eV for the Cl ligands in $[\text{ZnCl}_4]^{2-}$ and 2826.9 eV for $[\text{PdCl}_6]^{2-}$. To explain this trend, it is noted that each Cl in the hexachloro complex has 4 Pd 4d orbital holes to donate into while the chlorines in the tetrachloro complex only has 2 electron holes for donation. The Zn in the $[\text{ZnCl}_4]^{2-}$ is d^{10} and doesn't have any d orbital holes to donate into. Further discussion of the rising edge positions occurs throughout the analysis.

The most intense pre-edge peak positions were located at 2821.5 and 2820.2 eV for $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$, respectively. The difference between the locations of the pre-edge peaks is due to both the energies of the Pd d manifolds as well as the energies of the core Cl 1s orbitals. The d manifold shift is quite pronounced when comparing an O_h Pd(IV) species to a square planar Pd(II). Although the $[\text{PdCl}_6]^{2-}$ chlorines have a greater charge than the square planar chlorines in $[\text{PdCl}_4]^{2-}$, the pre-edge feature is 1.6 eV lower in energy in the hexachloro complex indicating that the d manifold is lower in the O_h complex. This is expected for $[\text{PdCl}_6]^{2-}$ as the Pd has a greater Z_{eff} .

Assuming that there is a linear relationship between nuclear charge and the Cl K-edge rising edge inflection point as reported in the literature¹⁴, then experimental information can be obtained about Pd 5s/5p and Cl 4s/3d/4p mixing by the comparison of the Cl K-edge rising edge inflection points and Pd-Cl covalencies. Observing that Pd-Cl covalencies of 23% and 33% Cl character per bond were found in $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$, respectively, and that the rising edge position of $[\text{PdCl}_6]^{2-}$ is 1.9 eV greater than $[\text{PdCl}_4]^{2-}$ points to additional mixing of the Cl and Pd orbitals in $[\text{PdCl}_6]^{2-}$. The calculated AIM charges in Table 11 confirm that the difference in the rising edge positions is not due to the effective nuclear charges as the chlorines on $[\text{PdCl}_6]^{2-}$ have a charge of -0.55 compared to -0.66 on $[\text{PdCl}_4]^{2-}$. This mixing means that the Pd 4d character in the Pd-Cl bond of $[\text{PdCl}_6]^{2-}$ can not be assumed to be the remainder not accounted for in the Cl K-edge pre-edge peak intensity and must be considered when developing the Pd L-edge transition dipole integral. This is discussed further in the Pd L-edge section.

The most intense pre-edge peaks in Figure 11 are assigned to transitions into the doubly unoccupied LUMO b_{1g}^* for $[\text{PdCl}_4]^{2-}$ and quadruply unoccupied LUMO e_g^* for $[\text{PdCl}_6]^{2-}$. The b_{1g}^* orbital (pictured in Figure 21a) is a combination of the Pd based $4d_{x^2-y^2}$ and Cl based 3p orbitals while the e_g^* orbital (pictured in Figure 21b,c) is a combination of the Pd based $4d_{x^2-y^2}$, $4d_{z^2}$, and Cl based 3p orbitals. The shoulders at the higher energy side of the pre-edge peaks in Figure 4 were assigned to excited state satellite transitions. Excited state calculations performed in ADF on $[\text{PdCl}_4]^{2-}$ shown in Figure 19a support this assertion by revealing the collapse of the Cl orbitals upon an excitation from the Cl 1s to the LUMO b_{1g}^* leading to new orbitals available to accept the

excitation from the core. The resulting higher energy LUMO gives rise to a higher energy satellite peak. Likewise, similar phenomena occurs in $[\text{PdCl}_6]^{2-}$ as calculations on the excitation of a Cl 1s electron into the LUMO e_g^* , illustrated in Figure 19b, show similar energy changes.

Figure 21. Molecular orbital contour plots of the a) LUMO b_{1g}^* for D_{4h} $[\text{PdCl}_4]^{2-}$, b) LUMO Pd d_{z^2} and Cl 3p of degenerate e_g^* set and c) LUMO Pd $d_{x^2-y^2}$ and Cl 3p of degenerate e_g^* set for O_h $[\text{PdCl}_6]^{2-}$. Transitions from the Cl 1s and Pd 2p orbitals into these LUMO's gives rise to the XAS pre-edge features seen in the Cl K, Pd L_{III} and L_{II} -edges.

Analysis of the Pd L-edge Spectra

The rising edge position of the Pd L-edges should be complimentary to the Cl K-edge as a greater effective nuclear charge on the Cl means a lower effective nuclear charge on the Pd and lower energy Pd 2p to 4d transition. The relatively high energy rising edge position of 3185.0 eV for the hexachloro complex compared to 3180.0 eV for the tetrachloro complex is evidence of Pd 5s/5p orbital mixing in $[\text{PdCl}_6]^{2-}$. This information is vital as an experimental tool for determining the minor contributions that the other orbitals make to the palladium-chlorine bond has not yet been developed.

As with the Cl K-edge, the effective nuclear charge and the Pd 4d manifold shift must be considered when analyzing the Pd L_{III} pre-edge peak positions. The pre-edge peaks are located at 3175.8 and 3177.8 eV for [PdCl₄]²⁻ and [PdCl₆]²⁻, respectively. Noticing that the rising-edge position of [PdCl₆]²⁻ is nearly 5 eV greater than [PdCl₄]²⁻ and that the pre-edge feature is only 3 eV greater points to a lower energy Pd d manifold in the hexachloro complex. This is expected when comparing an O_h d⁶ metal to a D_{4h} d⁸ metal.

The most intense pre-edge features for the [PdCl₄]²⁻ L-edges are assigned to a transition from the Pd 2p to the LUMO b_{1g}* while the same feature is assigned to the transition into the LUMO e_g* for [PdCl₆]²⁻. Lower energy satellite peaks are thought to be present in the [PdCl₄]²⁻ L-edges but hidden due to its proximity to the primary pre-edge feature. As an electron is removed from the [PdCl₄]²⁻ Pd 2p orbital and placed in the LUMO b_{1g}* the Pd d manifold collapses due to a greater effective nuclear charge lowering the energy of the LUMO b_{1g}*. The second derivative of the hexachloro complexes L-edge spectra in Figure 12 reveals that this lower energy satellite is resolved. The reason for the appearance of this satellite in the [PdCl₆]²⁻ L-edge spectra and not in the spectra of the Pd(II) complexes is probably due to the greater effective nuclear charge on the Pd(IV) center causing the d-orbitals, and therefore, the electronic states to have greater energy separation. The satellite peak switches from a higher energy shoulder to a lower energy shoulder moving from the Cl K-edge to the Pd L-edge. The Cl 1s core hole lowers the energy of higher unoccupied orbitals. These lower lying unoccupied orbitals then mix with the LUMO giving rise to higher energy satellite peak. Conversely, the

electronic relaxation caused by the 2p core hole in Pd is faster than the excited state recombination to ground state and thus a lower energy satellite feature arises.

Application of the Calibrated Level of Theory and Pd L-edge Dipole Integrals on PdCl₂

The MO contour plots of the LUMO and LUMO+1 in Figure 22a and b show the anti-bonding orbitals being probed by XAS for a model of PdCl₂. Although this model does not reproduce the experimental XAS Pd-Cl covalency, it is useful for visualization of the molecular orbitals. The orientation of the Cl 3p orbital lobes is different in the bridging and terminal Cl's with the terminal Cl 3p orbital lobes pointing directly at the Pd to form a σ bond with the Pd d_{xy} (or $d_{x^2-y^2}$ depending on the coordinate definition) orbital and the bridging Cl $3p_x$ and $3p_y$ orbital lobes rotated 45° relative to the terminal Cl p orbitals. The bridging Cl p_x forms a sigma bond with the +,- combination of 2 Pd d_{xy} orbitals (LUMO) and the Cl p_y forms a second σ bond with the +,+ combination of 2 Pd d_{xy} orbitals (LUMO+1). A Pd-Pd bonding interaction would cause the LUMO+1 in Figure 22 to be much higher in energy than the LUMO. Clearly this is not the case as this energy separation is <0.05 eV for all the models in Table 9.

Figure 22. The LUMO (a) and LUMO+1 (b) MO contour plots of Pd₂Cl₆ showing the different overlap of the terminal and bridging Cl's with the Pd centers.

Because the L-pre-edge peak positions and rising edge positions of PdCl_2 and $[\text{PdCl}_4]^{2-}$ shown in Figure 12 are at nearly the same energy, the Pd's have the same effective nuclear charge and thus the same Pd L-edge dipole integrals apply. Tables 13 and 14 list the peak positions, intensities, HHLW, ΣD_0 's, and Pd covalency for PdCl_2 using the dipole integrals for the three separate methods developed on $[\text{PdCl}_4]^{2-}$ at both the ALS and the SSRL. The average Pd covalency was found to be 50% per Pd 4d orbital hole. It is believed that similar satellite transitions to the $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$ spectra are occurring in PdCl_2 because of the similarity of the complexes and the presence of the satellites in the Cl K-edge spectra. However, these satellite transitions are not resolvable in the Pd L-edges due to its proximity to the main pre-edge feature.

Table 13. PdCl_2 L_{III} - and L_{II} -edge data measured at the ALS and SSRL and its quantitative analysis.

PdCl_2 edge	location and setup	rising edge		intensity of peak	HHLW (eV)	Pd d	
		inflection point (eV)	peak position (eV)			ΣD_0 (eV)	character using $[\text{PdCl}_4]^{2-}$ integrals
L_{III}	SSRL setup B	3181.1	3175.7	2.49	1.46	7.3	104%
absorbers (1) electron holes (2)	ALS setup D	3181.2	3176.2	1.88	1.59	6.0	109%
L_{II}	SSRL setup B	3338.1	3332.6	2.14	1.38	5.9	91%
absorbers (1) electron holes (2)	ALS setup D	3338.7	3333.2	2.46	1.17	5.8	102%

Table 14. PdCl_2 Pd $L_{\text{III}}+L_{\text{II}}$ -edge data measured at the ALS and SSRL. The number of absorbers is one and the number of electron holes is two.

PdCl_2 location and setup	L_{III}				L_{II}				Pd d		
	peak positions (eV)	intensity of peak	HHLW (eV)	ΣD_0 (eV)	peak positions (eV)	intensity of peak	HHLW (eV)	ΣD_0 (eV)	$L_{\text{III}} + L_{\text{II}}$ ΣD_0 (eV)	$L_{\text{III}}/L_{\text{II}}$ -edge jumps	character using $[\text{PdCl}_4]^{2-}$ integrals
SSRL setup B	3175.7	1.40	1.45	4.1	3332.6	0.81	1.35	2.2	6.3	0.6	91%
ALS setup D	3176.2	1.03	1.47	3.0	3333.2	0.82	1.38	2.3	5.3	0.6	103%

Table 15. PdCl₂ Cl K-edge data measured at ALS and SSRL.

complex	location and setup	rising edge inflection point (eV)	peak position (eV)	intensity of peak	HHLW (eV)	D ₀ (eV)	ΣD ₀ (eV)	total Cl 3p covalence per d manifold hole	transition dipole integral (eV) for bridging Cl	average transition dipole integral (eV) for bridging Cl
PdCl ₂	SSRL	2826.6	2821.8	1.81	0.67	2.4	2.73	94%	35	34
	setup B		2823.2	0.23	0.67	0.3				
absorbers 4	ALS	2826.6	2821.8	1.67	0.68	2.3	2.60	94%	33	
	Setup C [†]		2823.3	0.23	0.68	0.3				
electron holes 2	ALS	2826.6	2821.8	1.56	0.68	2.1	2.4	94%	31	31
	Setup D		2823.2	0.22	0.68	0.3				

[†]Extrapolated data due to photo reduction radiation damage.

The greater effective nuclear charge on the bridging Cl in PdCl₂ directly affects the Cl 1s orbital and thus the Cl (1s→3p) dipole integral. This requires a new Cl K-edge dipole integral for the bridging Cl. The LUMO and LUMO+1 of PdCl₂ are a combination of the Pd d_{xy} orbital, which was quantitated in the Pd L-edge, and the Cl 3p orbitals with minor contributions from the Pd 5s, 5p and Cl 3s, 3d orbitals. Results of electronic structure calculation presented above provide an estimate of the Cl 3s and 3d and Pd 5s and 5p contributions to the ground state electronic structure. They reveal 4% total Cl 3d and 3s character and 2% Pd 5p and 5s character for PdCl₂. Subtracting this from the remaining 100% from the Pd L-edges yields 94% Pd d character that should correspond to the pre-edge intensities in the Cl K-edge. The number of Cl absorbers is defined to be the number of Cl p orbitals that form a σ bond because each σ bond must be accounted for in the renormalization process. In PdCl₂ the Cl 3p_x and 3p_y orbitals in each Cl form sigma bonds with a Pd resulting in four Cl absorbers in PdCl₂. Similar the Cl K-edge of the other Pd complexes measured, PdCl₂ has a higher energy satellite peak. Because the peak arises from the same state as the primary pre-edge feature, it is also included in D₀ and thus dipole integral calculations. Cl K-edge dipole integrals of 34 eV at ALS with LN₂ cooling and 31 eV at SSRL were found for the bridging Cl's in PdCl₂.

Electronic structure calculations

It is clear in Tables 8 and 9 that the relativistic corrections in Gaussian had little effect on the geometry and covalency of both $[\text{PdCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ while ZORA calculations in ADF showed minor geometric and covalency effects on $[\text{PdCl}_4]^{2-}$ and greater effects in these areas on $[\text{PtCl}_4]^{2-}$. This indicates that ZORA at least treats relativistic electrons differently than non-relativistic electrons. Although the 50/50 BHandHLYP functional for Pd(II), the QCISD ab initio energy correction for Pd(IV), or the SDD(f) basis set cannot be applied in ADF, it is very likely that ZORA relativistic corrections are not method dependent and would not have a significant effect on the Pd-Cl covalency of $[\text{PdCl}_4]^{2-}$ if these methods were employed. Further evidence that relativistic effects are insignificant in covalency calculations on Pd complexes comes from the literature⁷⁵. The RESC method has been shown to explain the difference in reactivity between Pd and Pt monorganic complexes with two trimethylphosphine ligands for reactivity toward CO insertion. Experimental data shows Pd complexes to be highly reactive as catalysts in carbonylation reactions in contrast to the lack of reactivity for the Pt complexes. Table 10 shows that the RESC relativistic correction has a large effect on the activation energy and heat of formation for the CO insertion reaction in the Pt complex indicating that the relativistic effects caused by the greater nuclear charge in Pt compared to Pd are responsible for the difference in reactivity toward CO insertion in these complexes. Relativistic corrections showed only minor changes in the transition state and product energy for the Pd analogue⁷⁵.

Table 16. Comparison of non-relativistic and relativistic (RESC) corrections of activation energy and heat of formation in the CO insertion to Pt complex⁷⁵.

Relativistic Corretion	Reactant Energy (kcal/mol)	Transition State Energy (kcal/mol)	Product Energy (kcal/mol)
None	0.0	20.6	-1.5
RESC	0.0	33.2	10.9

While QCISD has been shown to both reproduce experimental XAS covalency for third row transition metal chlorides and calculate Cl character in a metal-chlorine bond that is greater than HF, but less than the BP86 theories, it is apparent that this trend breaks down in fourth row transition metal chlorides because it shows neither of these behaviors for $[\text{PdCl}_4]^{2-}$. The calculated Cl ovalency for Group VIIIB $[\text{MCl}_4]^{2-}$ complexes in Figure 15 shows that Pt falls in line with the Pd for relative Cl covalencies of each theory while experimental XAS experimental covalency is unavailable. Noting that QCISD reproduced the experimental XAS Pd-Cl covalency of $[\text{PdCl}_6]^{2-}$ indicates that the main difference between third and fourth or fifth row transition metals is that electron correlation methods increase the covalency compared to HF for the third row and decrease the covalency for fourth and fifth row metal complexes. Complete Active Space Multiconfiguration^{76,77} (CASSCF) calculations showed only a small amount of mixing for all of the Group VIIIB chloride complexes. The irregularity of the MP2 calculation (see Figure 10) is further evidence of the unusual behavior of ab initio electron correlation calculations on chloro palladium complexes. Regardless of the reason for the inadequacy of first and second order quadratic CI calculations on these planar complexes, an accurate, computationally efficient, hybrid functional method exists for computations.

Figure 23. Calculated metal-Cl covalencies using different theories to show the difference in trends in third, fourth and fifth row transition metal chloride complexes.

DISCUSSION

This study is an extension of the bonding description of the chlorocuprate complexes to fourth row chloro palladium complexes. The most natural and straightforward link is between D_{4h} $[\text{CuCl}_4]^{2-}$ and D_{4h} $[\text{PdCl}_4]^{2-}$ because it is a comparison of d^9 to d^8 electron configuration and third to fourth row transition metals. These spectra are shown in Figure 24. The Cl K-edge rising edge position is at 0.1 eV greater energy in the Pd compared to Cu suggesting that the Cl has a higher effective nuclear charge due to more Cl covalency. In fact, XAS shows that the individual Cl covalency is 9.7%¹⁴ for D_{4h} $[\text{CuCl}_4]^{2-}$ compared to 23% for $[\text{PdCl}_4]^{2-}$. In addition to the higher Cl covalency in $[\text{PdCl}_4]^{2-}$ causing the Cl 1s orbital to be lower in energy, the higher energy Pd 4d manifold compared to the Cu 3d manifold leads to a 0.9 eV higher energy pre-edge feature in $[\text{PdCl}_4]^{2-}$.

Figure 24. Cl K-edge spectra of $[\text{CuCl}_4]^{2-}$ and $[\text{PdCl}_4]^{2-}$.

Each terminal Cl in the Pd(II) species $[\text{PdCl}_4]^{2-}$ shows donation of 23% Cl p orbital to the Pd-Cl bond. The chlorines are arranged on the x and y axis about the Pd with a lobe of the Pd $4d_{x^2-y^2}$ orbital pointing directly at each Cl. These lobes combine with the Cl 3p orbitals on the axis to form a σ bond. Minor contributions to this bond come from Cl 3s and 3d orbitals through mixing.

Comparing this bonding picture to the PdCl_2 species with bridging Cl's, the individual Cl covalency goes up to 46% while the total Cl covalency per Pd stays constant. This is due to both the p_x and p_y orbitals on a Cl forming two σ bonds with pairs of Pd(II) ions. Each Cl is rotated 45° relative to the terminal chlorines so that orbital lobes of Cl $3p_x$ and $3p_y$ orbitals form σ bonding pairs with the two respective lobes of two Pd $4d_{xy}$ orbitals. Because these two orbitals are within 0.05 eV of each other, there is no direct Pd-Pd bonding interaction.

The bonding picture of $[\text{PdCl}_6]^{2-}$ is simplified as each Cl is aligned along the axis with a lobe of a p orbital pointing directly at the Pd center yielding 34% Cl 3p character in a Pd-Cl bond. With no distortion from O_h symmetry, the Pd $4d_{x^2-y^2}$ and d_{z^2} orbitals mix to give bonding lobes that point directly at each Cl forming 6 σ bonds.

The spectra of $[\text{PdCl}_4]^{2-}$, PdCl_2 , and $[\text{PdCl}_6]^{2-}$ were measured by Sugiura in the 1980's¹⁷⁻²¹. A few comments are made about the differences in both the spectra and spectra interpretation. Although the spectra was not previously quantitatively analyzed, it is evident that the most recent measurements have increased resolution probably due to the better instrumentation at the newer beamlines allowing for more information to be obtained from the XAS spectra. Previously, the shoulder in the $[\text{PdCl}_6]^{2-}$ Cl K-pre-edge

region was assigned to contamination of $[\text{PdCl}_4]^{2-}$ due to photoreduction of the hexachloride. If this was the case, isobestic points would be present when comparing consecutive scans, given the intensity of the shoulder in the $[\text{PdCl}_6]^{2-}$ spectra, the rising edge of $[\text{PdCl}_4]^{2-}$ would also be seen. Clearly, neither of these are visible in the measurements presented here. The same comment about the shoulder and rising edge position of the hexachloride L-edge spectra can also be made.

Because there are three different methods for determining the $\text{Pd}(2p \rightarrow 4d)$ transition dipole integrals, comments on the accuracy of each and the necessity for more than one method are made. The accuracy depends on a couple of factors. Firstly, when the length of the region that is splined is longer, two very different background subtractions that are both equally valid can be found causing the error bar for measuring both L-edges together to be greater than the error bar for measuring them separately. Secondly, both the greater intensity of the L_{III} -edge transition, which leads to a larger signal to noise ratio, and the lack of an EXAFS scattering pattern from a previous edge interfering with the spectra contribute to the L_{III} -edge having a smoother background than the L_{II} -edge. This translates to a more reliable background subtraction and normalization for the L_{III} -edge. In all three Pd complexes measured, the $\text{L}_{\text{III}}:\text{L}_{\text{II}}$ -edge ratio is about 1.5 to 1.0, while Ligand-Field Multiplet Theory⁷³ and Atomic Multiplet Theory⁷³ predict the ratio to be 2 to 1. These theoretical predictions have previously been shown to differ from experimental results as vanadium and titanium $\text{L}_{\text{III}}:\text{L}_{\text{II}}$ edge ratios are close to 1:1^{78,79}. The consistency of this measurement on Pd complexes indicates that the edge ratio is neither chloride complex nor oxidation state dependent. Therefore, the intensity

of the L_{II}-edge intensity can be predicted from the L_{III}-edge intensity and vica versa eliminating the need to collect both edges. It is still recommended that both edges are measured and, if possible, the covalency is calculated with all of the before mentioned methods and averaged to reduce the error bars of a covalency measurement. The importance of having three separate dipole integrals for the Pd L-edges becomes apparent when there are other absorbers present in the system causing interference with the Pd L-edge spectra. Figure 25 shows several absorbers that would interfere with the measurement of the Pd L-edges. Measuring a sample with a significant amount of one or more of these absorbers present would prevent an accurate background and/or normalization of the Pd L-edge spectra due to overlapping edges necessitating the use of the method I or method II dipole integral depending on the absorber present.

Figure 25. Energy positions of the Pd L_{III}- and L_{II}-edges along with other absorbers that could interfere with Pd XAS measurements.

Applying the Pd(II) L-edge dipole integrals developed for $[\text{PdCl}_4]^{2-}$ on the PdCl_2 L-edge spectra, the Pd 4d orbital covalency was determined to be 52%. These new dipole integrals can be applied to PdCl_2 as both complexes have the same pre-edge peak

position indicating the same effective nuclear charge (Z_{eff}). The calculated charges verify this assertion. This remainder of the palladium-chlorine bond not accounted for in the Pd L-edge (along with minor Pd 5s/5p and Cl 3s/3d character) was then used to determine a new dipole integral for the more positively charged bridging Cl's. Precedence for a new dipole integral based on Z_{eff} was established at the S K-edge as sulfide, thiolate, and enedithiolate all have unique S K-edge dipole integrals⁸⁰. A shift in the S rising edge positions to higher energy in the order sulfide, thiolate, and enedithiolate indicates a greater Z_{eff} on the S in the same order. Dipole integrals of 6.54 eV, 8.05 eV, and 9.15 eV for sulfide, thiolate, and enedithiolate, respectively, have been shown to linearly reflect the S Z_{eff} and thus the rising edge shifts going from sulfide to thiolate (+1.1 eV) and thiolate to enedithiolate(+0.8 eV). Figure 26 illustrates that the new Cl K-edge and Pd L-edge dipole integrals and rising edge positions fit with this linear trend established at the S K-edge.

Figure 26. Plot of XAS transition dipole integrals and rising edge positions for a series at the S K-edge, Cl K-edge, and Pd L-edge.

The calculated relative orbital energies and ordering of $[\text{PdCl}_4]^{2-}$ are inconsistent with the assignments made from polarized single crystal UV/Vis absorption data⁸¹. Deeth provides an explanation of this discrepancy⁸². DFT uses the full molecular symmetry to generate a different set of d function for each d state. This leads to six electrons with amplitudes along the + and -z axis and two electrons in the xy plane in a low-spin planar d^8 complex such as $[\text{PdCl}_4]^{2-}$. The d_{xy} orbital then experiences less interelectron repulsion and thus has lower energy relative to the d_{xz} and d_{yz} orbitals. This reasoning is verified by the reproduction of the experimental orbital sequence when 0.6 electrons is shifted from the d_{z^2} into the $d_{x^2-y^2}$ orbital. This caveat to the functionality of DFT does not detract from its utility for assessing the electronic structure of these complexes. The DFT orbital ordering for the O_h Pd remains consistent with experiment.

CONCLUSIONS AND FUTURE WORK

The description of the experimental ground state electronic structure of $[\text{PdCl}_6]^{2-}$ and $[\text{PdCl}_4]^{2-}$ presented Scheme 5 has immediate application in the spectroscopic calibration of DFT calculations. Ligand covalency is a key indicator of reactivity providing validity to this calibration method. While the 50/50 density functional and HF exchange is an effective computational method for treating Pd(II) complexes, only the highest level ab initio calculations can reproduce Pd(IV) XAS covalency. Clearly a new computational method is needed for Pd(IV) complexes as QCISD is too expensive to perform potential energy surface calculations for larger systems. The BHandHLYP functional is relatively close to the $[\text{PdCl}_6]^{2-}$ experimental XAS Pd-Cl covalency and is recommended for use on all Pd complexes.

Scheme 5. The experimental ground state electronic structure of $[\text{PdCl}_4]^{2-}$ and $[\text{PdCl}_6]^{2-}$. Calibrated electronic structure calculations estimated the minor Cl 3s/3d contributions. Pd 5s/5d contributions were estimated from their relative rising L-edge positions.

Figure 27. XAS Cl K-edge (red), Pd L_{III}-edge (green) and Pd L_{II}-edge (blue) spectra of $(\text{PCy}_3)_2\text{PdCl}_2$ showing the pre-edge features as insets that can be used to quantitate the covalency in Pd-ligand bonds.

This study developed the quantitation of Pd d orbital covalency in a Pd-Ligand bond from Pd L-edge XAS. The first application of this method was performed on PdCl_2 . After the Pd 4d character in the Pd-Cl bond was quantitated, the dipole integral for the bridging Cl in Pd-Cl was calculated. XAS can now be extended to study the electronic structure of chloro phosphino palladium complexes. The raw data in Figure 27 for the Pd L-edges and Cl K-edge of $(\text{PCy}_3)_2\text{PdCl}_2$ show pre-edge features at each edge that can be used to quantitate the Cl and Pd character in the ground state electronic structure. In a similar fashion to the development of the Pd L-edge dipole integrals and the bridging Cl K-edge dipole integral, the P K-edge dipole integral can be obtained from the pre-edge features of the $(\text{PCy}_3)_2\text{PdCl}_2$ Pd L- Cl K- and P K-edge spectra in Figure 27

and 28. This technique could then be extended to study the bonding in catalytically active palladium phosphine, allyl, and olefin complexes.

Figure 28. Phosphorus K-edge spectra of $(\text{PCy}_3)_2\text{PdCl}_2$ showing pre-edge features that can be used in the development of the P K-edge dipole integral and to quantitate the covalency in Pd-P bonds.

Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences. The SSRL Structural Molecular Biology Program is supported by the Department of Energy, Office of Biological and Environmental Research, and by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program. Portions of this research was carried out at the Advanced Light Source. The Advanced Light Source is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the US Department of Energy undercontract No. DE-AC03-76SF00098.S.

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APPENDIX A

DATA WORKUP AND FITTING

Part 1: Chlorine K-edge spectra	75
$[\text{PdCl}_4]^{2-}$	75
Beamline setup A	75
Beamline setup B	75
Beamline setup C	76
Beamline setup D	77
PdCl_2	78
Beamline setup B	78
Beamline setup C	78
Beamline setup D	79
$[\text{PdCl}_6]^{2-}$	80
Beamline setup B	80
Beamline setup C	81
Beamline setup D	81
$[\text{CuCl}_4]^{2-}$	82
Beamline setup D	82
Part 2: Palladium L_{III} -edge spectra	83
$[\text{PdCl}_4]^{2-}$	83
Beamline setup A	83
Beamline setup D	83
PdCl_2	84
Beamline setup B	84
Beamline setup D	85
$[\text{PdCl}_6]^{2-}$	86
Beamline setup B	86
Beamline setup D	86
$\text{Pd}(0)$	87
Beamline setup C	87
Part 3: Palladium L_{II} -edge spectra	88
$[\text{PdCl}_4]^{2-}$	88
Beamline setup A	88
Beamline setup D	88

PdCl ₂	89
Beamline setup B	89
Beamline setup D	90
[PdCl ₆] ²⁻	91
Beamline setup B	91
Beamline setup D	92
Part 4: Palladium L _{III} -L _{II} -edge spectra.....	93
[PdCl ₄] ²⁻	93
Beamline setup A	93
Beamline setup D	94
PdCl ₂	95
Beamline setup B	95
Beamline setup D	96
[PdCl ₆] ²⁻	97
Beamline setup B	97
Beamline setup D	98

Beamline setup A: The data were collected at SSRL beamline 6.2 July 19-22, 2004.

Beamline setup B: The data were collected at SSRL beamline 6.2 March 27-April 4, 2005

Beamline setup C: The data were collected at ALS beamline 9.3.1 March 4-7, 2004 at room temperature

Beamline setup D: The data were collected at ALS beamline 9.3.1 November 8-13, 2004 while being cooled with liquid nitrogen.

[PdCl₄]²⁻ Cl K-edge measure at SSRL (beamline setup A)

[PdCl₄]²⁻ Cl K-edge measure at SSRL (beamline setup B)

$[\text{PdCl}_4]^{2-}$ Cl K-edge measure at ALS (Beamline setup C)

$[\text{PdCl}_4]^{2-}$ Cl K-edge measure at ALS (Beamline setup D)

PdCl_2 Cl K-edge measure at SSRL (Beamline setup B)

PdCl_2 Cl K-edge measured at ALS (Beamline setup C)

PdCl₂ Cl K-edge measured at ALS (Beamline setup D)

$[\text{PdCl}_6]^{2-}$ Cl K-edge measure at SSRL (Beamline setup B)

[PdCl₆]²⁻ Cl K-edge measure at ALS (Beamline setup C)

[PdCl₆]²⁻ Cl K-edge measure at ALS (Beamline setup D)

$[\text{CuCl}_4]^{2-}$ Cl K-edge measured at ALS (Beamline setup D)

$[\text{PdCl}_4]^{2-}$ Pd L_{III}-edge measured at SSRL (Beamline setup A)

$[\text{PdCl}_4]^{2-}$ Pd L_{III}-edge measured at ALS (Beamline setup D)

PdCl_2 Pd L_{III} -edge measured at SSRL (Beamline setup B)

PdCl_2 Pd L_{III} -edge measured at ALS (Beamline setup D)

$[\text{PdCl}_6]^{2-}$ Pd L_{III}-edge measured at SSRL (Beamline setup B)

$[\text{PdCl}_6]^{2-}$ Pd L_{III}-edge measured at ALS (Beamline setup D)

Pd(0) Pd L_{III} -edge measure at ALS (Beamline setup C)

$[\text{PdCl}_4]^{2-}$ Pd L_{II}-edge measured at SSRL (Beamline setup A)

$[\text{PdCl}_4]^{2-}$ Pd L_{II}-edge measured at ALS (Beamline setup D)

PdCl_2 Pd L_{II} -edge measured at SSRL (Beamline setup B)

PdCl_2 Pd L_{II} -edge measured at ALS (Beamline setup D)

$[\text{PdCl}_6]^{2-}$ Pd L_{II} -edge measured at SSRL (Beamline setup B)

$[\text{PdCl}_6]^{2-}$ Pd L_{II} -edge measure at ALS (Beamline setup D)

$[\text{PdCl}_4]^{2-}$ Pd L_{III} + L_{II}-edges measured together at SSRL (Beamline setup A)

$[\text{PdCl}_4]^{2-}$ Pd L_{III} + L_{II}-edges measured at ALS (Beamline setup D)

PdCl_2 Pd L_{III} + L_{II} -edges measured together at SSRL (Beamline setup B)

PdCl_2 Pd L_{III} + L_{II} -edges measured at ALS (Beamline setup D)

$[\text{PdCl}_6]^{2-}$ Pd L_{III} + L_{II}-edges measured together at SSRL (Beamline setup B)

$[\text{PdCl}_6]^{2-}$ Pd L_{III} + L_{II}-edges measured at ALS (Beamline setup D)