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### Measurement of Diphosphine $\sigma$ -Donor and $\pi$ -Acceptor Properties in d<sup>0</sup> Titanium Complexes Using Ligand K-Edge XAS and TDDFT

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Supporting Information

**ABSTRACT:** Diphosphines are highly versatile ancillary ligands in coordination chemistry and catalysis because their structures and donor-acceptor properties can vary widely depending on the substituents attached to phosphorus. Experimental and theoretical methods have been developed to quantify differences in phosphine and diphosphine ligand field strength, but experimentally measuring individual  $\sigma$ -donor and  $\pi$ -acceptor contributions to metal-phosphorus bonding remains a formidable challenge. Here we report P and Cl K-edge X-ray absorption spectroscopy (XAS), density functional theory (DFT), and time-dependent density functional theory (TDDFT)



studies of a series of  $[Ph_2P(CH_2)_nPPh_2]TiCl_4$  complexes, where n = 1, 2, or 3. The d<sup>0</sup> metal complexes  $(Ti^{4+})$  revealed both P 1s  $\rightarrow$  Ti-P  $\pi$  and P 1s  $\rightarrow$  Ti-P  $\sigma^*$  transitions in the P K-edge XAS spectra, which allowed spectral changes associated with Ti-P  $\sigma$ -bonding and  $\pi$ -backbonding to be evaluated as a function of diphosphine alkane length. DFT and TDDFT calculations were used to assign and quantify changes in Ti-P  $\sigma$ -bonding and  $\pi$ -backbonding. The calculated results for [Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>]- $TiCl_4$  were subsequently compared to electronic structure calculations and simulated spectra for  $[R_2P(CH_2)_2PR_2]TiCl_4$ , where R = cyclohexyl or CF<sub>3</sub>, to evaluate spectral changes as a function of diphosphine ligand field strength. Collectively, our results demonstrate how P K-edge XAS can be used to experimentally measure M-P  $\pi$ -backbonding with a d<sup>0</sup> metal and corroborate earlier studies showing that relative changes in covalent M-P  $\sigma$  bonding do not depend solely on changes in diphosphine bite angle.

#### INTRODUCTION

Phosphines and diphosphines are important ancillary ligands in inorganic and organometallic chemistry.<sup>1</sup> They form coordination complexes with all transition metals (as well as some lanthanides and actinides)<sup>2-19</sup> and show remarkable versatility due to the large number of ways in which their substituents and structures can be modified. As such, these ligands figure prominently in homogeneous catalysis,  $2^{0-22}$  and there have been many experimental and theoretical studies aimed at determining how changes to phosphorus substituents give rise to differences in ligand field strength.<sup>23–36</sup> Phosphines can range from strong  $\sigma$ -donors to strong  $\pi$ -acceptors depending on the attached substituents, and changes in donor-acceptor properties have been empirically ranked using a variety of experimental methods. Among the earliest and most prominent of these studies were Tolman's formative investigations of Ni(CO)<sub>3</sub>L complexes (where L = phosphine), which used CO stretching frequencies as a spectroscopic reporter of changes in phosphine field strength.<sup>37</sup>

Although methods to rank phosphine and diphosphine field strength are known, experimentally isolating and measuring individual  $\sigma$  and  $\pi$  contributions to M-P bonding remains a significant challenge.<sup>38</sup> Theoretical methods have shown the most success in quantifying individual  $\sigma$  and  $\pi$  contributions,  $^{26,36,39-41}$ and in some cases have been combined with experimental

results to establish predictive models. For example, it was recently shown by Rampino and co-workers that experimental CO stretching frequencies in square planar Rh diphosphine complexes could be combined with calculated charge distribution profiles to tease out  $\sigma$  and  $\pi$  contributions using spectroscopic data.<sup>42</sup> In an earlier study, Carlton et al. showed that comparison of <sup>57</sup>Fe NMR shifts and CO stretches in Fe( $\eta^{5}$ - $Cp)(SnPh_3)(CO)(PR_3)$  complexes could be used to experimentally distinguish between electronic  $\sigma$  and  $\pi$  effects in phosphines and phosphites.<sup>43</sup> As exemplified in these reports, as well as the influential Tolman studies, CO stretching frequencies are often used as indirect reporters of phosphine field strength. However, great care must be taken when using CO as a reporter because CO stretching frequencies are influenced by electrostatic effects and coupling of molecular vibrations, which can lead to erroneous conclusions about phosphine field strength.<sup>44–47</sup> In this context, a direct measure of orbital-mixing in M-P bonds would be more reliable.

We postulated that an experimental method known as ligand K-edge X-ray absorption spectroscopy (XAS) could selectively quantify  $\sigma$  and  $\pi$  contributions to M-P bonding. Ligand K-edge

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XAS – formally an X-ray absorption near edge structure (XANES) spectroscopy where ligand refers to the atom bound or in close proximity to the metal-uses synchrotron-generated X-rays to excite 1s electrons localized on the ligand into unoccupied molecular orbitals (MOs) containing ligand p and metal d character.<sup>48-50</sup> As a consequence of metal-ligand orbital-mixing, forbidden  $1s \rightarrow$  nd transitions become dipole-allowed (i.e.,  $1s \rightarrow np$ ) and the corresponding XAS transition intensity is governed by the amount of ligand p-character present in the antibonding wave function. As a result, transition intensity can be used to quantify metal-ligand orbital-mixing in unoccupied molecular orbitals. Ligand K-edge XAS was developed and has been used most extensively for third-row ligand elements Cl and S, but has emerged more recently for analysis of M-P bonding. A review of ligand K-edge XAS studies of M-P bonding, along with opportunities and challenges, was recently reported by some of the authors.<sup>51</sup>

In this report, we describe ligand K-edge XAS, DFT, and TDDFT studies of  $[Ph_2P(CH_2)_nPPh_2]TiCl_4$ , where n = 1 (dppm), 2 (dppe), or 3 (dppp) (Chart 1). Ti<sup>4+</sup> complexes were

Chart 1. Ti(IV) Compounds Studied with Ligand K-Edge XAS and DFT (left) and a Simplified Orbital Depiction of M-P  $\sigma$  and  $\pi$  Bonding (right)



targeted to investigate  $\sigma$  and  $\pi$  contributions to M-P bonding using P K-edge XAS because we needed d<sup>0</sup> metal complexes with unoccupied M-P  $\sigma$  and  $\pi$  molecular orbitals available for P K-edge transitions. This requirement appears at odds with the function of  $\pi$ -acceptor orbitals in metal phosphine complexes, which typically participate in M  $\rightarrow$  P  $\pi$ -backbonding with electron-rich metals. M  $\rightarrow$  P  $\pi$ -backbonding requires d-electrons so that the metal can donate electron density into low-lying  $\sigma^*$ orbitals on phosphorus that arise from bonding between phosphorus and the attached substituents. However, virtual  $M \rightarrow P$ MOs involved in  $\pi$ -backbonding are still present even when no d-electrons are available on the metal. Although less relevant to our investigation here, it should be noted that positioning  $\pi$ -donor ligands (such as chloride) trans to  $\pi$ -acceptor ligands is proposed to result in appreciable  $\pi$ -backdonation in d<sup>0</sup> metal complexes.52-55

In addition to our desire to explore M-P donor-acceptor properties, the bis(diphenylphosphino)alkanes shown in Chart 1 were selected because we were interested in comparing the P K-edge XAS results to those collected on square planar PdCl<sub>2</sub> complexes containing the same diphosphine ligands. We previously showed that Pd-P  $\sigma$  covalency did not track as expected with the diphosphine bite angle ( $\beta$ ; P-M-P),<sup>56,57</sup> which is notable because  $\beta$  is a structural parameter that is often used in structure/reactivity correlations in transition metal catalysis with diphosphine ligands.<sup>58-66</sup> The Ti complexes 1 - 3have very different bite angles compared to the PdCl<sub>2</sub> complexes studied previously despite having the same diphosphine ligands. These differences arise because the Ti<sup>4+</sup> complexes have "non-VSEPR" structures that distort from idealized octahedral geometry, which is a phenomenon commonly observed for d<sup>0</sup> metal complexes.<sup>67</sup> As previously described, DFT and TDDFT calculations were performed on 1 - 3, as well as Ti(dcpe)Cl<sub>4</sub> (4) and Ti(dtfpe)Cl<sub>4</sub> (5) (where dtfpe = 1,2-bis[bis-(trifluoromethylphosphino)]ethane) for comparison to the XAS results and to determine how diphosphines with different field strengths affect Ti-P  $\sigma$  and  $\pi$  bonding.

#### RESULTS AND DISCUSSION

Synthesis and Structural Characterization. The Ti complexes 1 - 3 were prepared as described previously by treating TiCl<sub>4</sub> with the corresponding diphosphine (dppm, dppe, or dppp, respectively) in toluene.<sup>68</sup> Ti(dcpe)Cl<sub>4</sub> (4), where dcpe = bis(dicyclohexylphosphino)ethane, was prepared similarly and is described for the first time. The molecular structures of 1 and 3 have yet to be reported, so we collected their single-crystal X-ray diffraction data so that their experimental structures could be compared to the XAS and DFT results (Figure 1). Selected bond distances and angles are



Figure 1. Molecular structures of Ti(dppm)Cl<sub>4</sub> (1; left) and Ti(dppp)Cl<sub>4</sub> (3; right). Ellipsoids are drawn at a 35% probability level. The second molecule of Ti(dppm)Cl<sub>4</sub> in the asymmetric unit cell, cocrystallized solvent molecules, and hydrogen atoms have been omitted from the figure.

provided in Table 1 along with those obtained from DFT calculations (vide infra). Not surprisingly, the biggest structural change across the series is observed in the P-Ti-P and Ti-P-C angles. The diphosphine bite angle increased sequentially in a stepwise fashion from 65.09(3) in 1 to  $76.66(5)^{\circ}$  in 2 to  $80.66(2)^{\circ}$  in 3 as the number of methylene units in the diphosphine backbone increased. These are significantly smaller than those in [Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>]PdCl<sub>2</sub> complexes with the same diphosphine ligands at 72.68(3)° (dppm), 85.82(7)° (dppe), and  $90.58(5)^{\circ}$  (dppp) due to the d<sup>0</sup> configuration and the associated distortions from octahedral geometry.<sup>53,67</sup> Likewise, the Ti-P-C angles increased from  $95.1(1)^{\circ}$  in 1 to 111.76(7)° in 3. Only subtle differences were observed in the experimental Ti-P and Ti-Cl bond distances and the Cl-Ti-Cl angles. XRD data collected on twinned crystals of 4 confirmed chelation of dcpe to  $TiCl_4$  (Figure S1), but the twinning could not be modeled to produce an acceptable R-factor for more thorough structural comparisons.

**P** and Cl K-Edge XAS Studies. To investigate the electronic structure of the Ti complexes, we collected their P and Cl K-edge XAS data at the Stanford Synchrotron Radiation Lightsource (SSRL) in Menlo Park, CA. The Ti complexes are all highly air-sensitive, which required special measures to avoid exposing the samples to air during loading. In past experiments, we and others have shown that moderately air-sensitive samples can be protected from air during sample loading by

	Ti–P (Å)		Ti–Cl (Å)		P-Ti-P (deg)		Ti-P-C (deg)		$Cl_{eq}$ -Ti- $Cl_{eq}$ (deg)	
compd	expt	calcd	expt	calcd	expt	calcd	expt	calcd	expt	calcd
Ti(dppm)Cl4	2.662(1)	2.690	2.2749(8)	2.306	65.09(3)	65.2	95.1(1)	96.6	106.56(4)	110.1
(1)	2.664(1)	2.690	2.2895(8)	2.306			95.3(1)	96.6		
(molecule 1)			2.249(1)	2.246						
			2.244(1)	2.246						
Ti(dppm)Cl4	2.6435(9)		2.2723(9)		65.27(3)		95.2(1)		108.51(4)	
(1)	2.646(1)		2.294(1)				95.5(1)			
(molecule 2)			2.2560(8)							
			2.262(1)							
Ti(dppe)Cl4	2.660(2)	2.715	2.265(2)	2.307	76.66(5)	76.7	106.8(2)	106.2	107.74(7)	105.8
(2)	2.640(2)	2.712	2.296(2)	2.307			106.1(2)	106.2		
			2.265(2)	2.251						
			2.251(2)	2.251						
Ti(dppp)Cl4	2.6832(6)	2.733	2.3013(6)	2.313	80.66(2)	80.8	111.09(7)	110.1	105.19(2)	106.6
(3)	2.6888(7)	2.733	2.2799(6)	2.312			111.76(7)	110.0		
			2.2619(7)	2.242						
			2.2324(7)	2.242						

Table 1. Experimental (XRD) and Calculated (DFT) Bond Distances and Angles for 1-3<sup>a</sup>

"Bond distances and angles for 2 are reported in ref 68. A polymorph of 2 with similar structural metrics is reported in the Supporting Information.

(1) sealing them behind a layer of thin polypropylene in a glovebox, (2) transporting them to the beamline in a sealed container, and (3) quickly transferring them to the sample chamber, sometimes using a glovebag for additional protection.<sup>69</sup> However, this method did not work for the more airsensitive Ti complexes 1-3. The problem is that the protecting layer of polypropylene must be thin to avoid attenuation of the X-rays at the P K-edges (the attenuation length of polypropylene is ca. 53  $\mu$ m at 2150 eV),<sup>70</sup> but such thin barriers allow small amounts of air to effuse through the material fast enough to decompose the complexes described here. To overcome this challenge, we prepared a custom gas flow cell designed to keep the samples under a continuous flow of UHP He during transfer to the sample chamber and data collection (Figure S4). The continuous flow of He quickly removes any air that passes through the polypropylene window before it can decompose the sample. This allowed us to collect reproducible data for 1–3. In contrast, repeated attempts to collect XAS data on the cyclohexyl-substituted 4 were unsuccessful; only peaks attributed to decomposition were observed. We were unable to determine if the decomposition was photoinduced or due to small amounts gas impurities during handling at SSRL. However, we note that 4 is more air-sensitive than 1-3, consistent with the well-known increased air-sensitivity of alkyl vs phenyl substituted phosphines.

The Cl K-edge XAS spectra for 1-3 each revealed two resolved pre-edge features that closely match those reported for the octahedral dianion in (PPh<sub>4</sub>)<sub>2</sub>TiCl<sub>6</sub> (Figure 2).<sup>71</sup> Analysis of the second derivative traces revealed that the two peak positions were almost identical for all three complexes and shifted *ca*. 0.4–0.5 higher energy relative to those observed in the Cl K-edge XAS spectrum of (PPh<sub>4</sub>)<sub>2</sub>TiCl<sub>6</sub> at 2820.80 and 2822.25 eV (Table 2).<sup>71</sup> The first pre-edge features in the spectra of 1–3 were located at 2821.2 eV, whereas the second features were located at 2822.7–2822.8 eV. On the basis of peak assignments made for (PPh<sub>4</sub>)<sub>2</sub>TiCl<sub>6</sub> and our TDDFT calculations presented in the following section,<sup>71</sup> the first pre-edge feature in each spectrum was assigned as 1s  $\rightarrow$  Ti–Cl  $\pi^*$ , and the second higher energy feature was assigned as 1s  $\rightarrow$  Ti–Cl  $\sigma^*$ .

The Cl K-edge pre-edge peaks were modeled with curves containing a 1:1 mixture of Lorentzian and Gaussian lineshapes



Figure 2. Normalized and background-subtracted fluorescence yield P K-edge (top) and Cl K-edge (bottom) XAS data for  $Ti(dppm)Cl_4$  (1; black trace),  $Ti(dppe)Cl_4$  (2; red trace), and  $Ti(dppp)Cl_4$  (3; blue trace).

(as described previously),<sup>49,56,57,69,72</sup> to quantify their relative intensities (Figure 3). The postedge was modeled with a step function containing a 1:1 mixture of arctan and error functions. The relative intensities of the first peak assigned to  $1s \rightarrow Ti-$ Cl  $\pi^*$  were 1.07(5) (1), 1.21(6) (2), and 1.09(5) (3), whereas those for the  $1s \rightarrow Ti-$ Cl  $\sigma^*$  transitions at higher energy were 0.94(5), 0.83(4), and 0.91(5) for 1–3, respectively. Although there appears to be a statistically significant intensity difference between the  $\sigma$  and  $\pi$  transitions for 2 compared to 1 and 3, we attribute this to the decreased resolution in the spectra of 1 and 3.

Table 2. Experimental and Calculated P and Cl K-Edge XAS Peak Positions (eV), Calculated Oscillator Strengths (f; Uncorrected from TDDFT Calculations), and Pre-edge Peak Assignments for Ti(dppm)Cl<sub>4</sub> (1), Ti(dppe)Cl<sub>4</sub> (2), and Ti(dppp)Cl<sub>4</sub> (3)

	$Ti(dppm)Cl_4$ (1)				Ti(dppe)Cl <sub>4</sub> (2)				Ti(dppp)Cl <sub>4</sub> (3)			
	expt	calcd	f	assignment	expt	calcd	f	assignment	expt	calcd	f	assignment
РК	2144.1	2144.1	0.0007	1s $\rightarrow$ Ti–P $\pi$	2143.9	2144.0	0.0004	1s $\rightarrow$ Ti–P $\pi$	2144.0	2144.0	0.0003	1s $\rightarrow$ Ti–P $\pi$
	2145.2	2145.3	0.0013	1s $\rightarrow$ Ti–P $\sigma^*$	2145.1	2145.2	0.0016	1s $\rightarrow$ Ti–P $\sigma^*$	2145.2	2145.2	0.0013	1s $\rightarrow$ Ti–P $\sigma^*$
	2145.7	2145.6			2146	2145.7			2145.9	2145.8		
	2146.8	2146.1			2147	2146.2			2146.8	2146.3		
	2147.5	2147.5			2147.8	2147.4			2147.5	2146.6		
	2147.8				2148.8				2148.8			
	2149.3								2149.2			
Cl K	2821.2	2821.3	0.0067	1s $\rightarrow$ Ti $-$ Cl $\pi^*$	2821.2	2821.2	0.0065	1s $\rightarrow$ Ti $-$ Cl $\pi^*$	2821.2	2821.2	0.0064	1s $\rightarrow$ Ti $-$ Cl $\pi^*$
	2822.8	2822.7	0.0039	1s $\rightarrow$ Ti $-$ Cl $\sigma^*$	2822.8	2822.7	0.0041	1s $\rightarrow$ Ti $-$ Cl $\sigma^*$	2822.7	2822.7	0.0041	1s $\rightarrow$ Ti $-$ Cl $\sigma^*$
	2824.6				2824.6				2824.8			



**Figure 3.** P K-edge (left) and Cl K-edge (right) XAS curve fit models for  $Ti(dppm)Cl_4(1)$ ,  $Ti(dppe)Cl_4(2)$ , and  $Ti(dppp)Cl_4(3)$ . Experimental data points are depicted as open circles and the model fit is shown as a red trace. Total residual data equal to the experimental data minus the curve fit is offset below the trace and depicted in orange.

The lower resolution allows the second curve in each spectra to broaden and capture some of the area under the first curve. We were able to fit both curves reproducibly, as evident from the small standard deviations in the peak areas shown in parentheses in Figure 3, but summing the two peak areas yielded practically identical values for 1-3 (2.01, 2.04, and 2.00, respectively). The calculated oscillator strengths from our TDDFT calculations also suggest only small differences in the intensity of Ti-Cl  $\sigma$  and  $\pi$  transitions for 1-3 (vide infra).

Although the overlapping pre-edge features limited analysis of separate  $\sigma$  and  $\pi$  contributions to covalent Ti–Cl bonds, we were able to quantify how they combined for comparison to other Ti complexes. The sum of the two Cl pre-edge peak intensities were converted into percent Cl 3p character per bond using the  $D_{2d}$ -Cs<sub>2</sub>CuCl<sub>4</sub> intensity standard developed by Solomon and co-workers.<sup>49</sup> The three values derived for 1–3 were identical within error at 28(1)% Cl 3p per Ti–Cl bond. These fall within the range of summed values reported previously for (PPh<sub>4</sub>)<sub>2</sub>TiCl<sub>6</sub> (22%),<sup>71</sup> (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiCl<sub>2</sub> (25%),<sup>73,74</sup> (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiCl<sub>2</sub> (25%),<sup>75</sup> (C<sub>5</sub>H<sub>5</sub>)TiCl<sub>3</sub> (32%),<sup>73</sup> and TiCl<sub>4</sub> (37%).<sup>73</sup>

The P K-edge XAS data collected for 1-3 all revealed spectra with a small pre-edge shoulder at ca. 2144 eV and unresolved features merged into the rising edge. Analysis of the second derivative trace for 1 allowed us to identify several minima at 2145.2, 2145.7, and 2146.8 eV prior to the white line (the most intense peak), and similar features were observed in the P K-edge spectra of 2 and 3. The P K-edge data was modeled with curve fits, as described for the Cl K-edge data, but the low peak-to-peak resolution led to relatively large uncertainties in the pre-edge intensities (>10%; Figure 3). Also, unlike the Cl K-edge XAS data, which are relatively well-understood and more easily interpreted for octahedral Group IV metal complexes,<sup>71</sup> interpretation of the P K-edge data for 1-3 required DFT and time-dependent density functional theory TDDFT calculations to help assign and corroborate our analysis of the spectral features.

**DFT and TDDFT Studies.** Dispersion-corrected groundstate DFT calculations were performed as previously described by us on optimized gas-phase structures of 1-3 (see the Supporting Information for details). The B3LYP functional was used because it has been shown to be remarkably accurate in the simulation of experimental XAS spectra via TDDFT for transition metal, <sup>56,69,71,74–76</sup> main group, <sup>72,77,78</sup> lanthanide, <sup>79</sup> and actinide complexes. <sup>17,71,75,76</sup> Although some of the bond distances are slightly overestimated, which is common for DFT even when correcting for dispersion, the calculated structural metrics for 1-3 were in good agreement with the experimental data (Table 1). Even though we were unable to collect XAS data on 4, we performed calculations on 4 and the hypothetical complex 5 with CF<sub>3</sub> substituents attached to P so that their electronic structures could be compared to 1-3.

Data obtained from the DFT calculations were used to construct the MO correlation diagram provided in Figure 4. Labels and Mulliken symbols were assigned by analyzing the individual virtual Kohn–Sham orbitals for 1 in  $C_{2\nu}$  point group symmetry, whereas 2 and 3 were assigned using  $C_2$  symmetry due to the staggered ethylene and propylene phosphine linkers that eliminate the  $C_{2\nu}$  mirror planes. As expected, all three Ti

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**Figure 4.** Calculated molecular orbital correlation diagram for 1–5. Symmetry labels correspond to those used in Table 3.

complexes have five unoccupied MOs derived from the Ti 3dorbitals mixing with frontier orbitals on P and Cl. MOs assigned as 1a<sub>1</sub>, 1a<sub>2</sub>, and 1b<sub>2</sub> are  $\pi$ -type MOs derived from the nondegenerate  $3d_{x^2-y^2}$ ,  $3d_{xz}$ , and  $3d_{yz}$  orbitals and the complementary  $\sigma$ -type MOs 2b<sub>1</sub> and 2a<sub>1</sub> derived from the  $3d_{xy}$  and  $3d_z^2$  are higher in energy. Analysis of the virtual Kohn–Sham orbitals revealed that the  $\pi$ -type orbitals are best described as Ti–P  $\pi$  and Ti–Cl  $\pi^*$ , whereas the  $\sigma$ -type orbitals are antibonding Ti–P and Ti–Cl  $\sigma^*$  (Figure 5).



**Figure 5.** Representative virtual Kohn–Sham orbitals calculated for 1.  $C_{2\nu}$  and  $C_2$  point group symmetry labels correspond to those used in Table 3. The *y*-axis was used as the principal  $C_2$  axis to keep the calculated  $d_{z^2}$  MOs (2a<sub>1</sub> or 3a) aligned with the *z*-axis.

Analysis of the calculated MO compositions revealed that the first five MOs in 1–3 have significant Cl 3p character with values ranging from 15.6–25.4% (Table 3). In contrast, only the LUMO and  $\sigma$ -type MOs (2b<sub>1</sub> and 2a<sub>1</sub> for 1; 3b and 3a for 2 and 3) have appreciable amounts of P 3p character. The LUMO in 1 (Ti–P  $\pi$ ) has more P 3p character (3.6%) than the LUMO in 2 and 3 (1.6 and 1.4%, respectively). A similar reduction in Ti–P  $\sigma^*$  orbital mixing is observed in the 2a<sub>1</sub> or 3a MOs derived from in-phase P lone pair mixing with the torus of the Ti  $3d_{z2}$  orbital, as shown in Figure 6. In contrast, P 3p character in the Ti–P  $\sigma^*$  MO derived from out-of-phase P lone pair mixing with the lobes of the Ti  $3d_{xy}$  ( $2b_1$  or 3b) was slightly higher in 2 (10.4%) vs 1 (9.0%) and 3 (8.8%). This is notable because  $2b_1$  for 1 and 3b for 2 and 3 are the same MOs that were previously interrogated in P K-edge XAS and DFT studies of d<sup>8</sup> square-planar PdCl<sub>2</sub> complexes with bis(diphenylphosphino)alkanes and bis(dicyclohexylphosphino)-alkanes.<sup>56,57</sup> Remarkably, despite significant differences in metal-type, P-M-P bite angles, coordination geometry, and oxidation state, the Ti complexes 1-3 show the same relative trend in P 3p orbital mixing (Figure 6), albeit with lower amounts of P 3p character overall compared to the Pd complexes.

TDDFT calculations were in excellent agreement with the ligand K-edge XAS data collected for 1-3 and corroborated the influence of Cl and P 3p mixing in the MOs on the observed transition intensities (Figure 7). The simulated Cl K-edge spectra each revealed two pre-edge peaks arising from collections of clustered Cl  $1s \rightarrow \text{Ti}-\text{Cl } \pi^*$  and Cl  $1s \rightarrow \text{Ti}-\text{Cl } \sigma^*$  transitions, respectively. The sum of the calculated oscillator strengths for the first pre-edge peak were larger than the second pre-edge peak, consistent with the modeled Cl K-edge peak intensities (Table 2). Only small differences in the calculated oscillator strengths were observed for 1-3, consistent with our assessment based on curve fits of the experimental data (vide supra).

In contrast to the Cl K-edge results, the simulated P K-edge XAS spectra revealed a broader distribution of transitions, which accounted for the overlapping peaks and lower peak resolution in the experimental P K-edge XAS data. The simulated P K-edge spectra for 1-3 from TDDFT calculations were also remarkably accurate and allowed us to assign the spectral features. The lowest energy pre-edge feature was P 1s  $\rightarrow$  LUMO (Ti–P  $\pi$ ), whereas closely spaced transitions assigned to P 1s  $\rightarrow$ Ti-P  $\sigma^*$  and P 1s  $\rightarrow$  ligand were observed at higher energy. The calculated oscillator strengths from TDDFT closely mirrored the relative changes in P 3p orbital-mixing in the associated MOs mixing in the excited state (as provided in Table 3 and Figure 6). The calculated spectra also allowed us to determine the origin of the white line feature, which is assigned to Ti-P  $\pi^*$  transitions involving the higher energy Ti 4p orbitals. These Ti-P  $\pi^*$  orbitals have small amounts of Cl p character that give rise to higher energy features in the Cl K-edge XAS spectra (>2824.5 eV), as captured in the experimental curve fit models (Figure 3) and simulated spectra from TDDFT (see below).

DFT and TDDFT calculations performed on 4 revealed how changing the phosphorus substituents from phenyl to alkyl affected the metal-ligand bonding and the simulated XAS spectra. Calculations on the hypothetical molecule Ti(dtfpe)-Cl<sub>4</sub> (**5**), where dtfpe = 1,2-bis[bis(trifluoromethylphosphino)]ethane, were also performed to investigate the nature of the Ti-P  $\sigma$  and  $\pi$  bonding with a stronger-field diphosphine ligand. It is well-known that electron-withdrawing fluorine substituents increase metal-phosphine  $\pi$ -backbonding by lowering the energy of the  $\pi$ -acceptor orbitals. Indeed, the calculated MOs in **5** are shifted lower in energy relative to those in **1** – **4** due to the electron-withdrawing CF<sub>3</sub> groups. The calculated MO diagrams for **4** and **5** show the same d-orbital splitting and assignments as **1**–**3**. One other notable distinction for **4** is the lack of low-lying phenyl  $\pi$  orbitals

## Table 3. Calculated MO Energies, Compositions, And Symmetry Labels for $Ti(dppm)Cl_4$ (1), $Ti(dppe)Cl_4$ (2), $Ti(dppp)Cl_4$ (3), $Ti(dcpe)Cl_4$ (4), and $Ti(dtfpe)Cl_4$ (5)

			MO Compositions (%)							
		energies (eV)	Ti <sup>a</sup>		Р				Cl <sup>a</sup>	
compd	MO # and assignment		р	d	s	р	d	р	d	
$1 - C_{2\nu}$	146 (2a <sub>1</sub> )	-1.22	0.9	43.4	0.6	10.4	1.2	18.8	0.8	
	145 $(2b_1)$	-1.68	1.8	54.8	3.2	9.0	0.8	14.0	0.6	
	144 $(1b_2)$	-2.78	0.7	80.8			0.2	17.6	0.6	
	143 $(1a_2)$	-2.79		80.8			0.2	17.5	0.8	
LUMO	$142 (1a_1)$	-2.88		76.8	1.0	3.6	0.6	15.6	0.6	
НОМО	141 $(1b_1)$	-6.87	0.1	4.9	5.2	22.6	0.6	28.6		
<b>2</b> - $C_2$	150 (3a)	-1.24	1.5	60.6	1.4	3.6	0.4	25.4	1.2	
	149 (3b)	-1.60	1.7	56.0	3.3	10.4	0.8	15.0	0.6	
	148 (2b)	-2.76	0.7	81.2			0.2	17.4	0.6	
	147 (2a)	-2.82		80.8			0.2	17.4	0.8	
LUMO	146 (1a)	-2.95	0.2	78.5	0.8	1.6	0.6	15.8	0.6	
НОМО	145 (1b)	-6.66	0.2	5.6	2.8	16.4	0.4	20.6		
$3-C_2$	154 (3a)	-1.21	1.4	56.4	1.0	3.0	0.6	24.0	1.0	
	153 (3b)	-1.58	1.8	52.8	2.6	8.8	0.8	14.8	0.6	
	152 (2b)	-2.70	0.9	81.4			0.2	16.6	0.6	
	151 (2a)	-2.73		80.4	0.2	0.4	0.2	17.2	0.8	
LUMO	150 (1a)	-2.85	0.4	78.2	0.4	1.4	0.4	15.6	0.6	
НОМО	149 (1b)	-6.53	0.1	7.4	3.4	17.6	0.4	15.0		
$4-C_2$	162 (3a)	-1.19	1.5	64.0	1.8	3.8	0.2	26.0	1.2	
	161 (3b)	-1.36	1.8	59.5	4.2	12.4	0.4	15.6	0.6	
	160 (2b)	-2.72	0.9	81.8			0.2	16.1	0.6	
	159 (2a)	-2.75		81.2	0.2	0.6	0.2	15.9	0.8	
LUMO	158 (1a)	-2.84	0.4	79.0	0.4	1.4	0.4	15.8	0.8	
НОМО	157 (1b)	-6.56	0.3	7.6	3.4	31.8	0.2	35.2		
<b>5</b> - <i>C</i> <sub>2</sub>	134 (3a)	-2.20	1.0	63.2	1.6	2.5	0.5	27.8	1.1	
	133 (3b)	-2.67	1.1	64.2	2.9	5.3	0.8	20.5	0.8	
	132 (2b)	-3.62	0.6	78.9				19.5	0.8	
	131 (2a)	-3.67		79.3				19.4	0.8	
LUMO	130 (1a)	-3.89	0.4	75.3	1.0	2.1	0.7	17.5	0.6	
НОМО	129 (1b)	-8.09	0.5	1.2	4.9	24.9		57.4		

<sup>*a*</sup>Ti and Cl s-orbital character  $\leq 0.5\%$  in the MOs provided.



**Figure 6.** Left, comparison of calculated %P 3p character in the Ti–P  $\sigma^*$  and Ti–P  $\pi$  derived from the Ti  $3d_{z2}$  ( $2a_1$  or 3a) and  $3d_{x^2-y^2}$  ( $1a_1$  or 1a), respectively, for 1–3. Right, comparison of %P 3p character in the M-P  $\sigma^*$  derived from the  $d_{xy}$  ( $2b_1$  or 3b) in 1–3 and PdCl<sub>2</sub> bis(diphosphino)alkane complexes as a function of methylene units in the diphosphine backbone. The P-M-P angles for each series of compounds are provided in the figure for reference.<sup>56,57</sup>

that extend just beyond the d-manifold (as observed in 1-3; Figure 4).

We compared the P 3p character mixing in the Ti–P  $\pi$  and  $\sigma$  MOs as a function of ligand field strength. A plot of the %P 3p character revealed that Ti–P  $\pi$  orbital mixing increases as expected with increasing ligand field strength in the order of

4 (alkyl) < 2 (phenyl) < 5 (CF<sub>3</sub>), whereas P 3p character in the Ti–P  $\sigma^*$  MO (3b) decreases (Figure 8). Simulated P K-edge XAS spectra from TDDFT calculations on 2, 4, and 5 show the same trend (Figure 9). The calculated oscillator strength for P 1s  $\rightarrow$  1a (Ti–P  $\pi$ ) increases only slightly in the order 4  $\sim$  2 < 5 (f = 0.0004-0.0005), whereas P 1s  $\rightarrow$  3b (Ti–P  $\sigma^*$ )



**Figure 7.** Comparison of experimental (solid line) and calculated (dashed line) P and Cl K-edge XAS spectra for  $Ti(dppm)Cl_4$  (1),  $Ti(dppe)Cl_4$  (2), and  $Ti(dppp)Cl_4$  (3). Calculated transitions are represented as red bars and their heights represent relative differences in oscillator strength. Labels indicate the dominant MO mixing in the excited state and correspond to those provided in Table 3 and Figure 4.



**Figure 8.** Comparison of %P 3p character in the 1a (Ti-P  $\pi$ ; blue) and 3b (Ti-P  $\sigma^*$ ; red) MOs of phosphorus substituents in Ti(dcpe)Cl<sub>4</sub> (4), Ti(dppe)Cl<sub>4</sub> (2), and Ti(dtfpe)Cl<sub>4</sub> (5).

decreases across the same series (f = 0.0019, 0.0016, and 0.0010 for **4**, **2**, and **5**, respectively). Collectively, these results demonstrate the expected changes in diphosphine  $\sigma$ -donor and  $\pi$ -acceptor ability as a function of ligand field strength, as reported previously in DFT studies of other diphosphine complexes.<sup>26</sup>

#### CONCLUSIONS

In summary, we have demonstrated how analyzing diphosphine complexes containing a d<sup>0</sup> metal ion such as Ti<sup>4+</sup> can be used to investigate orbital mixing in M-P  $\sigma$  and  $\pi$  bonds. Our P K-edge XAS results revealed small, but spectroscopically



**Figure 9.** Simulated P K-edge XAS data for  $Ti(dcpe)Cl_4$  (4; top),  $Ti(dppe)Cl_4$  (2; middle), and  $Ti(dtfpe)Cl_4$  (5; bottom). Individual TDDFT transitions are represented as red bars. Calculated transitions are represented as red bars and their heights represent relative differences in oscillator strength. Labels indicate the dominant MO mixing in the excited state and correspond to those provided in Table 3 and Figure 4.

measurable Ti-P  $\pi$ -bonding in all three phenyl-substituted Ti diphosphine complexes. Simulated spectra obtained from TDDFT calculations reproduced the experimental spectra and allowed us to determine how Ti-P  $\sigma$ -bonding changes as a function of alkane length in the diphosphine backbone. Our analysis revealed that orbital-mixing in the Ti-P  $\pi$  and Ti-P  $\sigma^*$  derived from the Ti  $3d_{x^2-y^2}$  and  $3d_{z^2}$ , decreases as the diphosphine alkane linker length is increased. In contrast, a unique increase in Ti–P  $\sigma^*$  orbital-mixing between the Ti  $3d_{xy}$ and the phosphine lone pairs for the dppe complex 2 compared to 1 and 3 with dppm and dppp, respectively. Despite large differences in metal-type (early vs late transition metal), oxidation state, coordination geometry, and P-M-P bite angle, the relative differences in Ti–P  $\sigma$  bonding are identical to the 10% relative increase in Pd-P  $\sigma^*$  orbital-mixing previously reported for Pd(dppe)Cl<sub>2</sub> and Pd(dcpe)Cl<sub>2</sub> vs PdCl<sub>2</sub> complexes with one or three methylene groups in the diphosphine backbone.<sup>56,57</sup> Collectively, these results corroborate our previous reports that changes in M-P  $\sigma$  bonding cannot be explained by only accounting for changes in diphosphine bite angle.

Comparison of DFT and TDDFT calculations on bis-(diphosphino)ethane complexes with cyclohexyl and trifluoromethyl substituents (dcpe and dtfpe, respectively) with Ti(dppe)Cl<sub>4</sub> revealed the expected changes in diphosphine  $\sigma$  donor and  $\pi$  acceptor strength as a function of ligand field strength. Notably, Ti–P  $\pi$ -bonding increased slightly in the order dcpe < dtfpe, whereas phosphine  $\sigma$ -donor strength decreased across the same series. Even though the Ti complexes are d<sup>0</sup>, the results revealed that the vacant Ti–P  $\pi$ -backbonding MOs are present and ready to participate in  $\pi$ -backbonding once d-electrons are provided. Notable in this respect is the fact that formally reduced Ti<sup>2+</sup>, Ti<sup>0</sup>, and Ti<sup>2–</sup> complexes are known to form with strong  $\pi$ -acceptor ligands such as CO and PF<sub>3</sub>.<sup>80–83</sup>

Although our P K-edge XAS studies demonstrated how  $\sigma$  and  $\pi$  contributions to M-P bonds can be distinguished, the pre-edge features lacked sufficient resolution to experimentally quantify differences in M-P orbital-mixing using curve fit models. This is a common issue in P K-edge data of transition metal complexes with phosphorus ligands,<sup>51</sup> but as shown here, TDDFT calculations can be used in tandem to help extract rich electronic structure information from the spectra. We anticipate that the calculations can be used to more rapidly identify metal–ligand combinations that yield highly resolved pre-edge features for comparative analysis of phosphine and diphosphine donor–acceptor properties using P K-edge XAS.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b01511.

Experimental details and NMR spectra for 4, photos of XAS cell, complete XAS spectra, atomic coordinates, and Mulliken charges from DFT (PDF)

#### **Accession Codes**

CCDC 1846146–1846148 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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