

Geometric Influence on Metal-Ligand Covalency in Diphosphine Complexed of Pd and Ti

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Density functional theory(DFT) has been combined with X-ray absorption spectroscopy(XAS) to obtain K-edge behaviors of transition metal diphosphine compounds, and to demonstrate the connection between coordination geometry and metal-ligand bonding. The impact of coordination chemistry, diphosphine bite angle, and the phosphine trans influence on covalency were studied on NiCl_2 and PdCl_2 complexes that contain PPh_3 or $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$. In this project, we use Gaussian DFT and time-dependent DFT to study the K-edge features of TiCl_4 and other PdCl_2 species containing $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ or $\text{C}_6\text{H}_{11}\text{P}(\text{CH}_2)_n\text{PC}_6\text{H}_{11}$. The geometric properties of these species are analyzed mathematically to suggest quantification of Ti- or Pd-phosphorous covalency in terms of the metal-P-C angles, instead of bite or twist angles.

The Ti or Pd species were optimized by Gaussian DFT to first be compared with crystallography results. Optimized geometries and wave functions were entered into TDDFT to calculate K-edge X-ray absorption spectra. Predicted peaks and intensities were matched with data from X-ray absorption spectroscopy. Given the degree of agreement between XRD and DFT on geometry, and between XAS and DFT results on spectroscopy, we seek to extend our calculation in an attempt to establish more evidences on how the metal-ligand molecular orbitals can be quantitatively linked to metal-P-C angles.

