AXAFS as a Probe of Charge Redistribution within Organometallic Complexes

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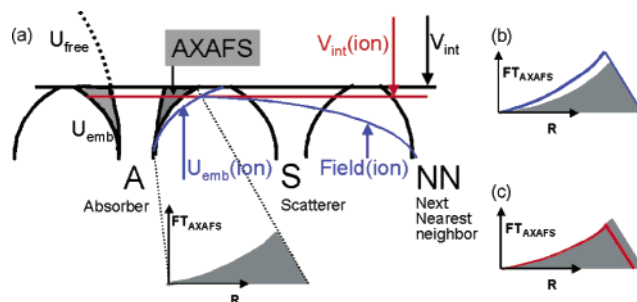Gerard van Koten,‡ David E. Ramaker,§ and Diek C. Koningsberger*,†

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Transition metal complexes with NCN-pincer ligands (NCN = $[2,6-(Me_2NCH_2)_2C_6H_3]^-$) have been prepared for numerous applications in the fields of catalysis, catalyst immobilization, supramolecular assembly, and sensor materials.[1] An important tool to construct larger structures, and to tune the metal center electronically, has been the introduction of substituents at the *para*-position of the pincer ligand. This functionalization has been most successful with pincer complexes from the nickel triad (Ni, Pd, Pt), due to their exceptional stability. Recently, we have been able to synthesize a library of *para*-substituted NCN-pincer platinum complexes [PtCl(NCN)−Z] to study the influence of the substituent on the electronic properties of the metal center.[2]

Further, we have developed a new technique, which directly provides information about the electronic structure of the metal under investigation, so-called atomic X-ray absorption fine structure spectroscopy (AXAFS). For the more common used extended XAFS (EXAFS) technique, it is known that the EXAFS oscillations originate from the scattering of the outgoing electron against the potential of neighboring atoms, creating a backscattered wave that interferes with the outgoing photoelectron. AXAFS represents the change in scattering by the absorber atom itself relative to the free atom. This change is due to bonding of the absorbing atom with its environment. Consequently, any change in the environment that alters the electronic structure of the absorbing atom should be reflected in the AXAFS.

In Figure 1, AXAFS is schematically described using the well-known muffin-tin approximation.[3] The interstitial potential V_{int} determines the zero energy of the system. The free atom potential U_{free} reflects the electron distribution in the free atom, whereas the embedded potential U_{emb} reflects the electron distribution after embedding the free atom into its chemical environment and allowing interaction with neighbors. The Fourier transform (FT) of AXAFS is then shown to be directly proportional to $U_{emb}(R) - U_{free}(R)$, and therefore its shape and intensity directly reflect electronic and chemical bonding information. Due to polarization of the absorbing atom by neighbors, two important effects on the electronic properties can be distinguished with AXAFS: (a) the interatomic potential, that is, space field effect induced by a Coulomb field, correlated to different charges on neighboring substituents (blue lines in Figure 1a and 1b), and (b) the value of the interstitial potential, that is, the bond inductive effect induced by a difference in electronegativity of the substituent (red lines in Figure 1a and 1c). From a more chemical point of view, the placement of a more electronegative element Z (Scheme 1) creates an inductive effect on the benzene

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Figure 1. (a) Schematic potential model, based on the muffin-tin approximation, defining AXAFS as the dark gray area.[3] Changing AXAFS intensity and shape (red and blue lines) due to exclusively (b) space field effect (blue lines) or (c) bond inductive effect (red lines).

Scheme 1. *para*-Substituted NCN-Pincer Platinum Complexes; Z Creates an Inductive Effect on (a) the Benzene Ring and (b) the Pt Atom
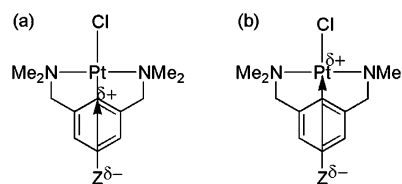
ring. In Scheme 1a, the inductive effect stops at the benzene ring, leaving positive charges at the carbon atoms near Pt. This creates a Coulomb field change on the Pt, which shifts the valence band to higher binding energy, thereby increasing the AXAFS (Figure 1b). In contrast, if the inductive effect proceeds all the way to the Pt (Scheme 1b), the reduced electron density near the Fermi level decreases the AXAFS (Figure 1c). Therefore, the relative change in the AXAFS directly reflects the response of the absorber atom to the placement of that substituent in the molecule.

So far, AXAFS has been demonstrated for mainly electrochemical systems and heterogeneous catalysts[4,5] in which both geometric and electronic effects simultaneously influence the AXAFS signal. This complicates the analysis and interpretation. The electronic properties of the above-described [PtCl(NCN)−Z] pincer complexes can be tuned selectively via the *para*-substituent. The geometry of the coordination environment of the platinum nucleus stays nearly unchanged upon *para*-substitution. Consequently, changes in electron density of the Pt pincer complexes arising from other factors than the *para*-substitution can be neglected, making the system perfect for demonstrating and proving the AXAFS theory.
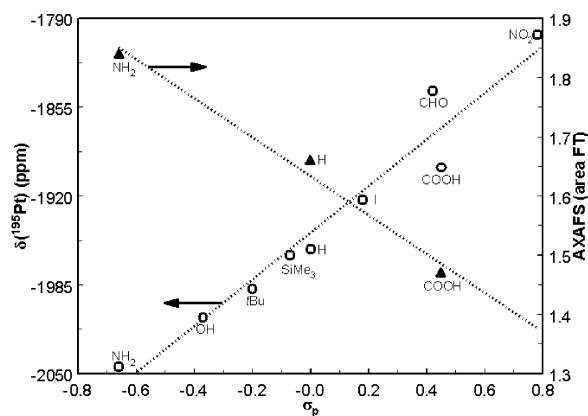
Electronic tuning of pincer complexes has been shown to be a very powerful tool for tuning the reactivity of the catalytically active pincers, for example, NCN-pincer nickel complexes used for the Karasch addition. Electron-donating *para*-substituents decrease the oxidation potential of the Ni(II)/Ni(III) couple, resulting in more

Figure 2. ^{195}Pt chemical shift (○) and AXAFS area (▲) of [PtCl(NCN−Z)] versus the σ_p Hammett substituent constant.

Figure 3. Fourier transforms (k^1, $\Delta k = 3.0-8$ Å^{-1}) of AXAFS of [PtCl-(NCN−NH$_2$)], [PtCl(NCN−H)], and [PtCl(NCN−COOH)] pincer complexes.

active atom transfer catalysts.[6] Therefore, it would be very useful to be able to determine the electron density of the pincers directly. In the case of [PtCl(NCN)−Z] pincer complexes, this is shown to be possible using ^{195}Pt NMR.

The [PtCl(NCN)−Z] pincers were synthesized as described in the literature with a series of different *para*-substituents, that is, from substituents with electron-withdrawing (Z = COOH) to electron-donating properties (Z = NH$_2$) and a neutral substituent H.[2] In ref 2b, the ^{195}Pt NMR study on these [PtCl(NCN)−Z] pincer complexes has been described in detail and shown to be a sensitive probe for the change in electron density on the metal atom. In general, an increase in electron density on the metal leads to an increase in shielding of the nucleus. For these pincer systems, this shielding can be solely attributed to the *para*-substituent, and a linear correlation between the Pt chemical shift and the σ_p Hammett constant of the *para*-substituent was found (with a correlation of $R^2 = 0.981$) as shown in Figure 2.

Pt L$_3$ edge XAFS data were collected on the solid samples at liquid nitrogen temperature. A precise background subtraction is performed, one which optimizes the AXAFS and EXAFS contributions in the XAFS data while leaving the double electron excitations in the background.[7,8] As was recognized in the literature,[3,7,9] the background subtraction procedure is not straightforward. However, a consistent, albeit perhaps not perfect, background subtraction allows the observed trends in the AXAFS signal to still reflect the changes in chemistry.[8] The AXAFS is then isolated from the total XAFS data by subtracting the fitted EXAFS contributions from the experimental XAFS data. The obtained EXAFS data are similar, confirming the similar structure of the complexes in the vicinity of the Pt.[2] This facilitates the AXAFS isolation, making the obtained AXAFS precise to within ±10%.[8]

Figure 3 shows the AXAFS decreasing in magnitude particularly between 0.75 and 1.2 Å and its centroid slightly shifting to lower R. This is strongly suggestive of Figure 1c, reflecting a downward shift in V_{int} with increasing electron-withdrawing properties of the *para*-substituent and, therefore, a decreasing electron density near the Fermi level on the Pt atom (Scheme 1b).

As shown in Figure 2, a linear correlation is found between the AXAFS (quantified by the area) and the Hammett constant (with $R^2 = 0.985$). This correlation between electron-donating and -withdrawing properties and AXAFS as found for these [PtCl-(NCN)−Z] pincer complexes is in good agreement with that for the ^{195}Pt NMR. This shows that AXAFS is a sensitive probe for
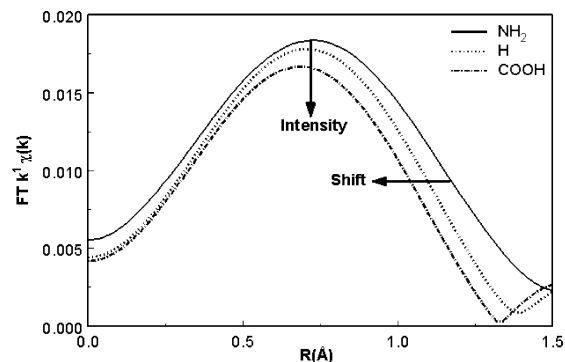
the determination of the electron density on the metal atom, similar yet complementary to NMR.

Additionally, this system perfectly demonstrates the correctness of the AXAFS theory described, because the geometry around the absorber atom remains the same and only one electronic effect is playing a role, thereby facilitating the analysis and interpretation.

In this paper, we have shown that AXAFS can be used to probe the electronic properties of Pt and, principally, of every atom, which is especially interesting for systems that, for example, are not amenable to NMR. Moreover, XAFS measurements can be performed in situ so the changes in electronic properties can be monitored during the reaction and, most interestingly, time-resolved.

Supporting Information Available: Experimental details, EXAFS data, and full analysis results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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