E p i l o g u e

A BRIEF DESCRIPTION OF ONGOING WORK

Throughout the work presented in this thesis, I've attempted to discern the character of one-electron oxidized Ir(III) corroles with a battery of techniques and theoretical treatments. This might seem like the foolhardy overemphasis of the blinkered specialist, but there are plenty of broad reasons to continually revisit the issue of electronic structure in non-innocent systems. The ongoing work of scientists like Karl Wieghardt[1] and Edward Solomon[2] has slowly painted a picture of the bonding and electronic structure of coordination compounds wherein the "formal" and "physical" oxidation states of the metal (and of the ligands) can be vastly different. A good example is the neutral, hexacoordinate metal complex $V(pdt)_3$,[3] where pdt = $[cis\text{-}1,2\text{-diphenylethene-}1,2\text{-dithiolate}]^{2-}$. This is formally a V(VI) compound, but of course vanadium is a d^5 metal, and in fact this complex has been assigned as having a V(IV) center with two additional holes distributed across the highly redox-active ligands. In a natural extension of this work to the realm of catalysis, Paul Chirik,[4] Pat Holland,[5] Craig Grapperhaus,[6] and many other chemists have sought to use non-innocent ligands to temporarily dock holes or electrons, so ligand redox activity, once thought of primarily as a difficulty to be surmounted by clever design, has been co-opted into practical catalyst design.

With my increasingly detailed work on the electronic structure of the formal iridium(IV) corrole systems, I have sought to find out if the incorporation of 5d metals, with the high electropositivity and relativistic effects they bring to the table, could allow for clean oxidation of neutral metallocorroles to metal-based radicals by stabilizing the state with

spin on the metal more effectively than has been seen in the past with lighter metals. Corroles are famously non-innocent, and extreme metal-ligand covalency has been well-documented for iron[7] and copper[8] corroles. At first, I felt certain this was the case based on our early EPR and UV-vis experiments.[9]   However, the computational work I did in collaboration with Sijia, Smith, and Bill Goddard gave me significant pause, as it seemed to suggest that ligand-based oxidation would be favored in a simple model case.[10] Additionally, XAS data from SSRL (collected in collaboration with Serena DeBeer, now of Cornell University) also suggested that oxidation was mostly ligand-based.

We have recently run a series of highly sophisticated DFT calculations that include spin-orbit effects and utilize large basis sets as well as a number of perturbative correction factors, and that I believe give a fairly accurate picture of the "true" electronic structure of my one-electron oxidized, formally Ir(IV) iridium corrole complexes.   Remarkably accurate EPR parameters have been calculated based on these ground state electronic structures, suggesting as strongly as possible that the calculated spin density mimics the real distribution of electron spin in the oxidized molecules. Perhaps unsurprisingly, the calculated ground states of the "Ir(IV)" corroles are highly delocalized, with spin both on the iridium and on the ligand. These computed electronic states appear to correspond accurately to the experimental parameters of the complexes; therefore, I postulate that, after extensive experimental and theoretical studies on the subject of iridium corrole non-innocence, we have finally zeroed in on the real electronic structure of the one-electron oxidized $[Ir(tpfc)L_2]^+$ family of complexes.

My original outline of this thesis included a chapter presenting these calculations, comparing them to our experimental EPR spectra, and discussing the XAS parameters as well. Unfortunately, both experimental and computational data were still being collected in the final days of thesis composition, and I don't feel that the project is yet quite at the stage where I can do it justice here. That said, it currently appears that when spin-orbit coupling is explicitly included in the calculations of the iridium(IV) ground state, a small amount of spin density, between 10 and 19% depending on the axial ligand, is transferred from the ring (where all of it resides in our earlier calculations) to the metal. What is more, we can then use these calculated ground states to model the EPR parameters of the oxidized corroles, and we receive very accurate numbers. We have found that the amount of anisotropy (Δg) in the experimental g tensor components scales with the electron-donating strength of the ligand, such that **[1-Ir(meopy)$_2$]$^+$** and **[1-Ir(dmap)$_2$]$^+$** have broad EPR spectra with highly anisotropic signal, and **[1-Ir(cfpy)$_2$]$^+$** has a relatively narrow spectrum with a Δg that is not nearly as large as in the cases where the ligands are electronically rich.

The theoretical calculations we have done model this trend in Δg accurately, and also suggest an explanation for the experimental results. As the axial ligands become more electron-donating, the percentage of spin on the metal increases from 10% in the case of **[1-Ir(cfpy)$_2$]$^+$** to 19% for **[1-Ir(dmap)$_2$]$^+$**, suggesting that the anisotropy of the EPR signal is owing to mixing of small amounts of d$_{xy}$ (C$_{2v}$ symmetry) into an orbital that is of primarily corrole ligand character. The calculated spin on the iridium d$_{xy}$ orbital in **[1-Ir(py)$_2$]$^+$** is 14%, whereas the d$_{xy}$ spin in **[1-Ir(tma)$_2$]$^+$** is 20%, so these results also help to explain the extremely rhombic EPR spectrum observed for the tma-ligated complex. I hope to expand

on these results in an article very shortly, but there a few loose ends to wrap up, such as modeling and interpretation of my XAS data, before that can happen.

Two years on from my initial publication of the iridium corroles, there has been no further examination of third-row metallocorrole complexes, leaving our iridium and the oxorhenium corrole of K. S. Chan as the only examples in the literature.[11] I am currently in the process of finishing the characterization of a platinum corrole dimer which I hope can remedy this sad situation. Additionally, I plan to finish my study of the iridium azaporphyrins described in Chapter 5, which should add a new chapter to the increasingly lengthy tome of corrole reactivity.

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