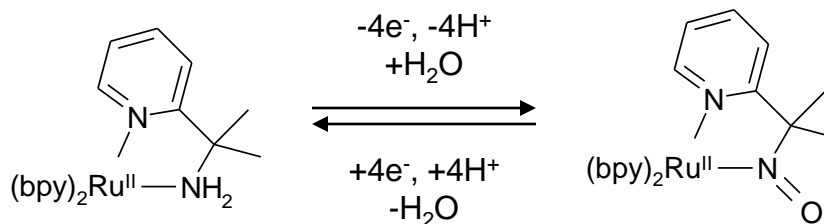
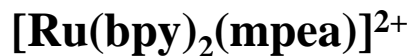


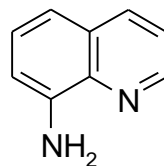
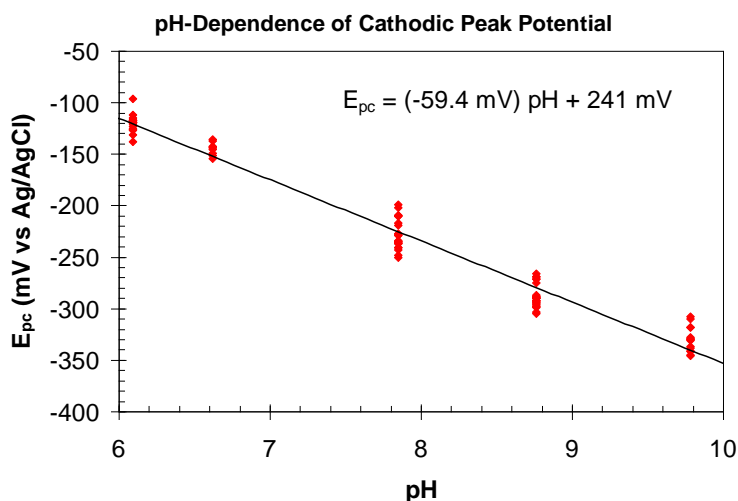
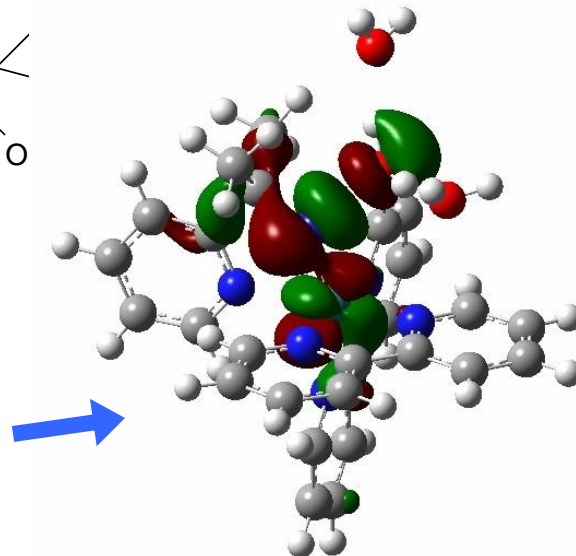
Investigation of the Reactivity of Imidoruthenium Complexes

David N. Blauch, Department of Chemistry, Davidson College, Davidson, NC 28035



- Initial oxidation of $[\text{Ru}(\text{bpy})_2(\text{mpea})]^{2+}$ occurs through a series of one-electron metal-centered oxidations accompanied by deprotonation of the amine site.
- An imidoruthenium(V) species is the key intermediate that is subject to attack by water, which is coupled with oxidation of the nitrogen by the metal.

The image at the right illustrates the b3lyp/cpcm/cep-31g isosurfaces for interaction of the occupied water b_1 orbital with the unoccupied $\text{Ru}^{\text{V}}=\text{N}^{2-}$ d_{xz} and d_{yz} π^* orbitals.



8-aminoquinoline (AQ)

- Poly- $[\text{Ru}(\text{AQ})_3]^{2+}$ exhibits a broad cyclic voltammetric wave.
- Coulometry shows 0.96 ± 0.04 electron per ruthenium, suggesting a one-electron process for which essentially all metal centers are electroactive.
- Variation of anodic peak potential with sweep rate suggests an EC mechanism. Upon oxidation, the polymer may change conformation, perhaps aligning quinoline rings, to delocalize the unpaired electron.
- Variation of cathodic peak potential with pH indicates a one-electron, one-proton process, consistent with reduction of an amidoruthenium(III) center to an aminoruthenium(II) center.