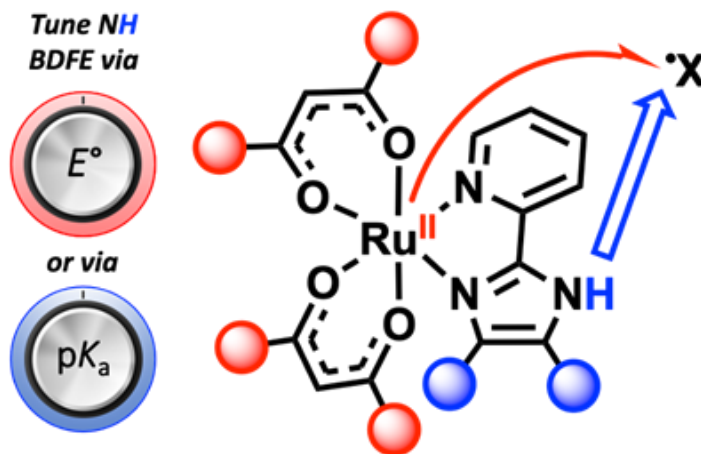


Steering the selectivity of hydrogen atom transfer reactions: bond strengths and polar effects

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Hydrogen atom transfer (HAT) is critical to a host of processes, ranging from biological and industrial nitrogen fixation to the functionalization of strong C–H bonds in the synthesis of pharmaceuticals. The kinetics (and therefore selectivity) of these reactions is important and predominantly dictated by the strengths of the X–H bonds being cleaved and formed: generally, it is more favorable, and therefore *faster*, to break a weak bond than a strong one. *Selective* cleavage of *strong* bonds is therefore an ongoing challenge in synthetic chemistry. Yet, there is a growing body of literature that suggests that the kinetics of an HAT reaction are also affected by how *acidic* (pK_a) or *reducing* (E°) the X–H bond is, in addition to its bond strength. The origin of this effect and its magnitude, however, are still poorly understood.

In the present work, we have developed a series of ruthenium bis(acetylacetonate) pyridine-imidazole complexes which undergo HAT to a variety of H \cdot acceptors. These complexes are unique in that their pK_a and E° can be tuned independently of one another, through modifications of separate ligands. This decoupling of the pK_a and E° allows us to study the effect of each individually on the HAT kinetics, and to compare these effects to that of changing the bond strengths of the Ru complexes. Synthesis, characterization, and the origin of the pK_a/E° decoupling in these complexes will be presented, followed by a discussion on the HAT reactivity of the pK_a - and E° -tuned series of complexes. The results indicate that the effect of the pK_a/E° on the kinetics is subtle, but significant.



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Ben was born and raised in Lancaster, PA, and then attended the University of Virginia, where he majored in mathematics and chemistry. During his time there, he worked in the lab of Prof. Rebecca Pompano, researching immune response in lymph node tissue. Interested in pursuing research further, Ben began a PhD program at Yale after graduating in 2018. He is currently in his 5th year, studying inorganic chemistry in the lab of Prof. James Mayer. Ben is studying the kinetics and thermodynamics of multi-site concerted proton-electron transfer (MS-CPET) reactions in ruthenium(II) complexes.