Overcoming Kinetic Barriers to Metal-Hydride Formation using Ligand-Cooperativity

Metal hydrides are key intermediates in fuel-forming catalytic reactions, and the kinetics and mechanisms involved with forming these metal hydrides can dictate the efficiency, selectivity, and durability of fuel-formation. Oftentimes, there are high kinetic barriers to metal-based protonation of transition metal complexes. Coordination complexes can overcome these high kinetic barriers to metal-based proton transfer by leveraging ligand-cooperativity in PCET reactions, even when ligand protonation is thermodynamically less favorable than metal protonation. Therefore, this work aims to understand how pendant bases impact the proton-coupled electron transfer (PCET) pathways in metal hydride formation.

To accomplish this goal, the cobalt pre-catalyst containing pendant amines in the ligand backbone, $[CoCp(P_2^{Ph}N_2^{Ph})(CH_3CN)][PF_6]_2$, was synthesized. Using cyclic voltammetry experiments with acids with varying pK_a values, we unraveled the mechanism and kinetics associated with the PCET steps involved in hydride formation for this system. Overall, this work lays groundwork to understand how to use ligand-based proton transfer in transition metal catalysts to optimize the efficiency of fuel forming reactions.