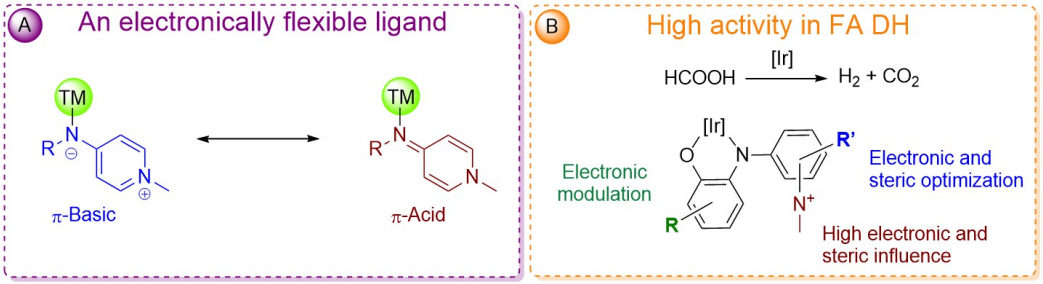
Investigation and optimization of iridium complexes bearing O-functionalized PYE ligands for efficient formic acid dehydrogenation

S. Reuge[1], N. Lentz[1], M. Albrecht[1]

[1]Department of Chemisrty, Biochemistry and Pharmaceutical Sciences

The long-term storage of renewable energies is a matter of urgency to accommodate seasonal variations. Hydrogen is a promising energy carrier for fuel, but its storage as a compressed gas is still problematic. Chemicals such as formic acid (FA) can act as liquid organic hydrogen carriers through hydrogenation and dehydrogenation cycles. The catalytic dehydrogenation of FA has found a growing interest during the past decade and several homogeneous complexes based on iridium, ruthenium, and iron have been reported as catalysts for this reaction.[1-3]

Our group recently propelled FA dehydrogenation using an iridium complex containing a simple and inexpensive O-functionalized pyridylidene-amine (PYE).[4] The PYE moiety features unique donor flexibility (Fig. 1a) known to stabilize transition metals resulting in high catalytic activity, *e.g.* olefin oxidation.[5] Here I will present our efforts to understand electronic and steric influence of the ligand on the catalyst performance. We will demonstrate that structurally similar iridium complexes lacking donor flexibility are inactive in FA dehydrogenation. Moreover, simple ligand modifications led to a library of complexes with varied steric and electronic properties arising from (i) positional PYE isomers, (ii) PYE functionalization, and (iii) the phenolate functionalization (Fig. 1b). We will discuss the catalytic impact of these modifications and disclose some useful correlations.



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