Organic Seminar

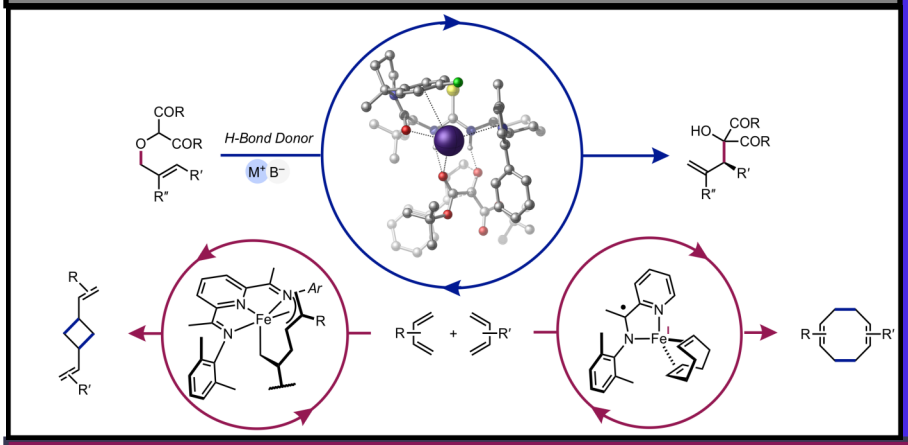
"Leveraging Mechanistic Insight to Enable Regio- and Stereoselective C–C Bond Formation through Ion-Pairing Organocatalysis and Ligand-Controlled Iron Catalysis"

Guest Speaker:

Dr. C. Rose Kennedy

Princeton University

Department of Chemistry



Friday, March 30th, 9:00am

Hutchison Hall 473

University of Rochester

Department of Chemistry

Abstract:

Insights gleaned from mechanistic elucidation are potent tools enabling the design of efficient and selective catalytic transformations. Select examples of mechanism-guided method development to enable regio- and stereoselective C–C bond formation are described, drawing on the complementary strengths of either (i) dual hydrogen-bond-donor organocatalysts or (ii) well-defined organometallic iron precatalysts.

In the former case, experimental and computational analyses delineate the precise mode of substrate activation in amido-thiourea-catalyzed transformations representative of enantioselective anion-abstraction catalysis and enantioselective Brønsted acid co-catalysis. These insights lead to (i) the rational design of systems that impart enhanced reactivity while retaining high enantioselectivity and (ii) the development of a synergistic ion-binding approach for engaging highly diffuse transition structures.

In the latter case, reduced iron complexes bearing redox-active ligands are examined as powerful catalysts for intermolecular hydrovinylation and cycloaddition reactions of unactivated alkenes and 1,3-dienes. Structural studies and mechanistic experiments provide evidence for the formation of metallacyclic intermediates, from which catalyst control over competing pathways for reductive elimination dictates reaction outcome. Mechanistically informed ligand designs are leveraged to modulate catalyst–substrate interactions in order to effect chemo-, regio-, and stereoselective valorization of olefinic coupling partners. Applications of the resulting cycloadducts for the synthesis of fuels, polymers, and fine chemicals are discussed.

Host: Alison Frontier ● Email: Alison.Frontier@rochester.edu