Abstract
Nitrogen reduction to NH₃ is a requisite transformation for life. While it is widely appreciated that the Fe-rich cofactors of nitrogenase enzymes facilitate this transformation, how they do so remains poorly understood. A central element of debate has been the site(s) of dinitrogen coordination and reduction. The synthetic inorganic community placed an early emphasis on Mo because Mo was thought to be an essential element of nitrogenases, and because pioneering work by Chatt and his coworkers established that well-defined Mo model complexes could mediate the stoichiometric conversion of coordinated N₂ to NH₃. Catalytic N₂-to-NH₃ conversion was later demonstrated using a molecular Mo catalyst by Schrock.

It is known, however, that Fe is the only transition metal essential to all nitrogenases, and recent biochemical and spectroscopic data have implicated Fe as the likely site of N₂ binding in FeMo-co. These observations motivate our search for functional Fe catalysts. In this lecture, I will discuss a tris(phosphine)borane supported Fe complex that catalyzes the reduction of N₂ to NH₃. This catalytically functional model system established for the first time that a single Fe site is capable of stabilizing the various NₓHᵧ ligands generated en route to NH₃ formation. Recent efforts have targeted improving the efficiency of these synthetic iron nitrogenases via exploring alternative conditions and catalyst scaffolds, and using both experiment and theory to better understand the mechanisms by which these catalysts function.