Models for Iron Active Sites of Nitrogenases

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The search for homogeneous nitrogen fixation catalysts which function at ambient temperatures and pressures is one of the enduring chemical challenges. The FeMo cofactor of nitrogenases is proposed to be the site of nitrogen reduction and hydrogen production. Development of discrete homogeneous catalysts capable of reducing dinitrogen may provide insight into the role of the metallocofactor in nitrogen activation. The ability of iron in threefold-symmetric $[PhBP^{iPr}_3]Fe$ scaffoldings (where $[PhBP^{iPr}_3] = PhB(CH_2P(CH(CH_3)_2)_2)_3^-$) to fix dinitrogen in a Chatt-type cycle is examined. This fascinating ligand scaffolding allows access to a wide variety of iron formal oxidations states (ranging from 0-IV). Furthermore this complex has been demonstrated to form an iron(IV) nitride which upon protonation yields ammonia. The specific aim is to utilize low valent iron centers to activate dinitrogen and study the subsequent reactivity of iron dinitrogen adducts with electrophilic reagents or hydrogen equivalents (R^+/e^- or H+/e-). The reactivity of several low valent iron centers will be discussed. A variety of physical methods have been employed to establish the formal oxidation states and spin states of these species.