

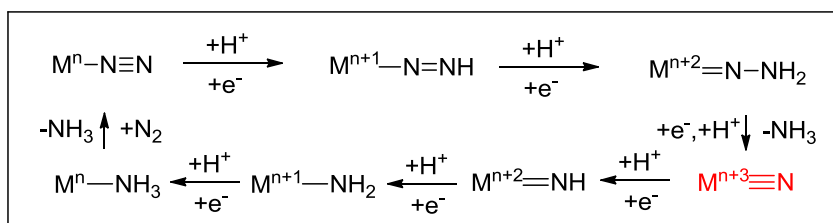
Isolation of High Valent Iron Nitrides Stabilized by Tripodal NHC Ligands

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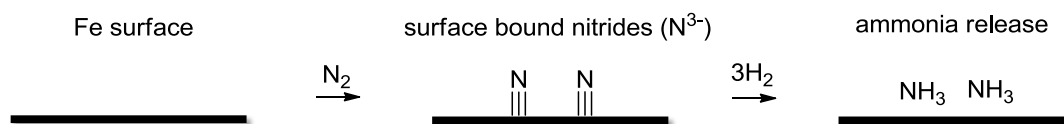
Literature seminar

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Ammonia is produced from atmospheric dinitrogen in Nature by bacterial nitrogenases. Though the conditions are mild, nitrogenases require at least 16 ATP molecules to produce ammonia and also give dihydrogen as a byproduct. In comparison, the industrial method for ammonia production, the Haber-Bosch process, demands high pressures and high temperatures that consume up to 1.4% of all anthropogenic power each year, but does not yield byproducts.¹ It is desired to perform catalysis under mild conditions in an energy efficient process that generates ammonia cleanly. The search for a catalyst that combines useful features of both nitrogenase and the Haber-Bosch process has led researchers to investigate both mechanisms. For nitrogenases, one possible mechanism is the Chatt-type nitrogen reduction cycle mediated by a single iron center. Through this route, release of the first equivalent of ammonia gives an iron nitride species (Scheme 1).^{2,3} Recent studies on the Haber-Bosch process also reveal surface bound nitrides are involved (Scheme 2).⁴



Scheme 1. Chatt-type nitrogen reduction cycle



Scheme 2. Ammonia production in the Haber-Bosch process

The above observations indicate iron nitrides to be important intermediates in ammonia production, motivating the syntheses of such compounds. For complexes of iron(V) or lower oxidation states, the usual 5-coordinate and 6-coordinate geometry around the iron center is destabilized by the π -donating interaction from the nitride ligand. Rather, a low coordinate pseudotetrahedral environment is preferred for these nitrido complexes.^{5,6} Employing ligands that will enforce this geometry is crucial for the successful synthesis.

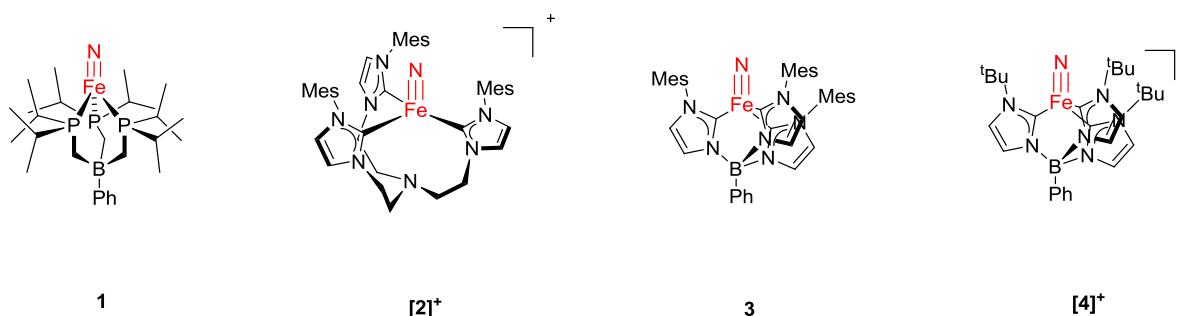
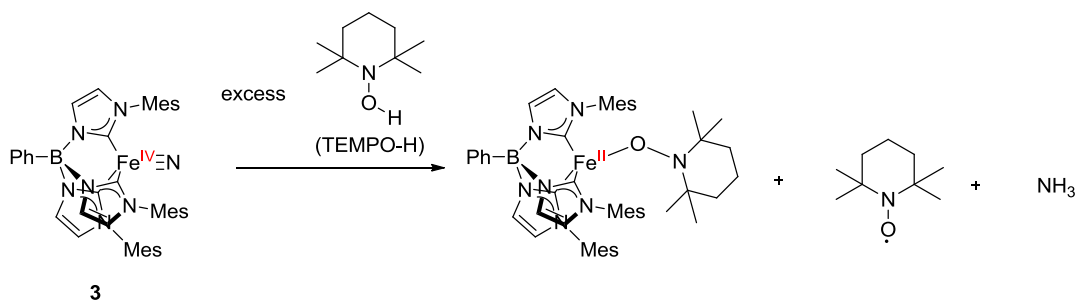


Figure 1. High valent iron nitrides

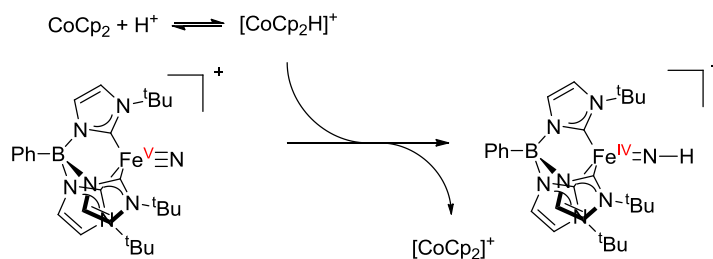
Based on this concept, Peters and coworkers were able to synthesize iron nitride **1** by utilizing a tris(phosphino)borate ligand.⁷ Compound **1** is prone to dimerization and can only be isolated as the $\text{Fe}^{\text{I}}\text{-N}\equiv\text{N-Fe}^{\text{I}}$ dimer. The instability of **1** can be attributed to one or more of the following factors: 1) the lack of steric bulk on the ligand 2) insufficient σ -basicity of the ligand to stabilize the high oxidation state.⁸

Incorporation of *N*-heterocyclic carbene (NHC) ligand provided marked improvement to the stability of iron nitrides relative to **1**. The unique properties of tris(NHC) ligands are best demonstrated by the successful isolation of an air-stable iron nitride **2** by Meyer and coworkers.⁹ Bulky substituents on the NHC form a cylindrical cavity which protect the terminal nitrido functionality from dimerizing and reaction with small molecules. The enhanced σ -basicity of the ligand relative to tris(phosphino)borates further stabilizes the high oxidation state of the iron center. However, compound **2** is not competent towards ammonia production. By switching to a tris(NHC)borate ligand,¹⁰ Smith and coworkers isolated iron nitride **3** which exhibits reactivity towards ammonia production.¹¹ Reaction of **3** with a hydrogen atom source, 1-hydroxy-2,2,6,6-tetramethyl-piperidine (TEMPO-H), yields ammonia in a near quantitative fashion based on **3** (Scheme 3).



Scheme 3. Ammonia production of 3

In 2011, the iron(V) nitride **4** was synthesized by oxidation of an iron(IV) compound similar to **3**.¹² Compound **4** reacts with water in the presence of cobaltocene to give high yields of ammonia with concomitant formation of an iron(II) species. One possible mechanism is ammonia formation via a hydrogen atom transfer route with protonated cobaltocene as the hydrogen atom source (Scheme 4).¹³ Another possibility would be subsequent protonation followed by electron transfer.^{14,15}



Scheme 4. First step of proposed hydrogen atom transfer reaction of [4]⁺

The focus of this talk will be on the unique properties of tris(NHC) ligands and their corresponding iron nitrides. Though none of these iron nitrides exhibit catalytic activities towards ammonia formation, mechanisms of the stoichiometric reactions will be discussed. The successful isolation of these compounds further supports the possibility of iron nitrides participating in both natural and industrial ammonia production processes.

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