Nitrogen Reduction by Multimetallic Uranium Complexes

Xinyi Chen Literature Seminar Nov. 14, 2017

Nitrogen is a key element for making proteins, DNA, RNA, and many other biomolecules. In agriculture, plants continually remove nitrogen from the soil in the form of nitrate.[1] To replace this lost nitrogen, farmers in preindustrial societies usually fertilized their fields with animal and human wastes or with crop residues.[2] These materials contain relatively low concentrations of nitrogen, however, and so farmers had to apply very large amounts to sustain plant growth. Even so, such methods typically added only up to about 200 kg of nitrogen per hectare per year, an amount that can provide food for only about 15 people per hectare. The limitation availability of nitrogen in the soil also placed a severe limit on human population growth.

A real breakthrough came in the early 20th century, when methods were discovered for the artificial synthesis of ammonia, a key ingredient in synthetic fertilizers. Today, the Haber-Bosch process, which employs an iron-based catalyst under relatively harsh conditions, is used for the large-scale production of ammonia from atmospheric nitrogen, as shown in **Figure 1**.[3]

$$N_2 + 3H_2 \xrightarrow[Fe-based\ catalyst]{300\ bar,\ \ 450\ ^\circ C} 2NH_3$$

Figure 1. The industrial Haber-Bosch process.

The harsh nature of these conditions, which are a consequence of the unreactive nature of dinitrogen, have stimulated many efforts find milder ways to bind, activate, and reduce N_2. In some of the earliest patents on artificial ammonia synthesis, Haber noted that uranium and uranium nitride are just as effective as iron in their ability catalyze ammonia production.[4] This result is somewhat surprising, because the contracted nature of the 5f orbitals of uranium might be expected to lead to a poor ability to bind N_2. But in fact, several uranium complexes are now known that can bind N_2.[5-10]

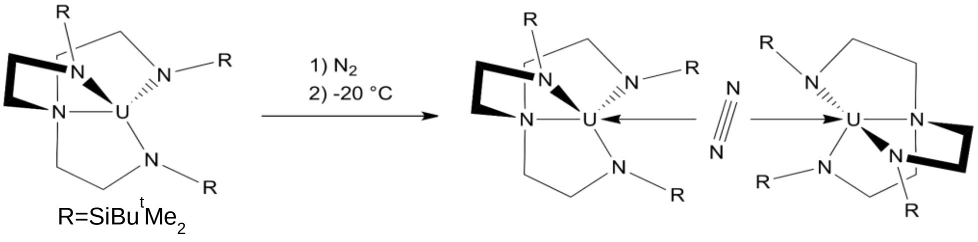

Figure 2. The first dinitrogen complex of uranium.[5]

In 1998, Scott reported the first isolable dinitrogen complex of uranium (or of any actinide element).[5] Exposure of a saturated pentane solution of a uranium(III) tris(amido) complex to 1 atm of dinitrogen at -20 °C gives a new binuclear complex (**Figure 2**). The crystal structure shows that the dinitrogen ligand is bound in a side-on bridging mode between the two uranium centers. The N-N bond distance of 1.109(7) Å, which is essentially the same as that found in the free nitrogen molecule (1.0975 Å), suggests that the binding does not significantly weaken the triple bond and that the N_2 unit has not been reduced.

In 2002, Cloke found that a uranium(III) complex containing substituted cyclopentadienyl ligands also can bind dinitrogen (**Figure 3**).[6] Unlike Scott's compound, however, the N-N bond length of 1.232(10) Å is consistent with an N-N double bond (1.259(4) Å). Therefore, the formation of this binuclear complex involves a formal oxidation of the two U^{III} centers to U^{IV} with concomitant reduction of N_2 to N_2^{2-}. Interestingly, despite the electron transfer, the binding is reversible and the product loses nitrogen easily.

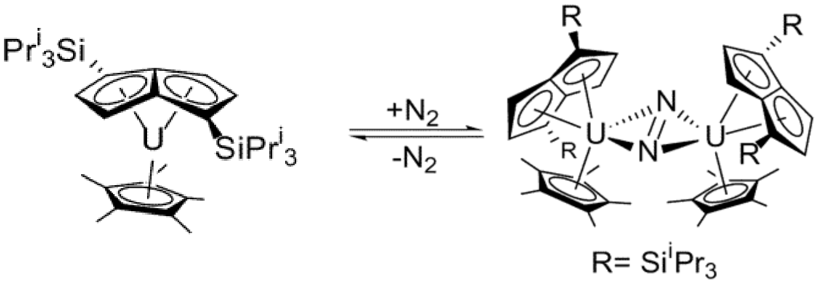

Figure 3. The 2-electron reduction of dinitrogen.

In 2017, Mazzanti reported the 4-electron reduction of N_2 under ambient conditions by the potassium salt of an anionic diuranium(III) nitride complex bearing siloxide ligands, ***1*** (**Figure 4**).[7] Exposure of ***1*** to N_2 at room temperature affords the N_2 complex ***2*** in 68% isolated yield. In ***2***, the original nitride atom and the two atoms of the N_2 unit are all bound to a siloxide-ligated potassium cations. The N-N bond length of 1.521 Å falls in the 1.3 to 1.6 Å range reported for N_2^{4-} species.

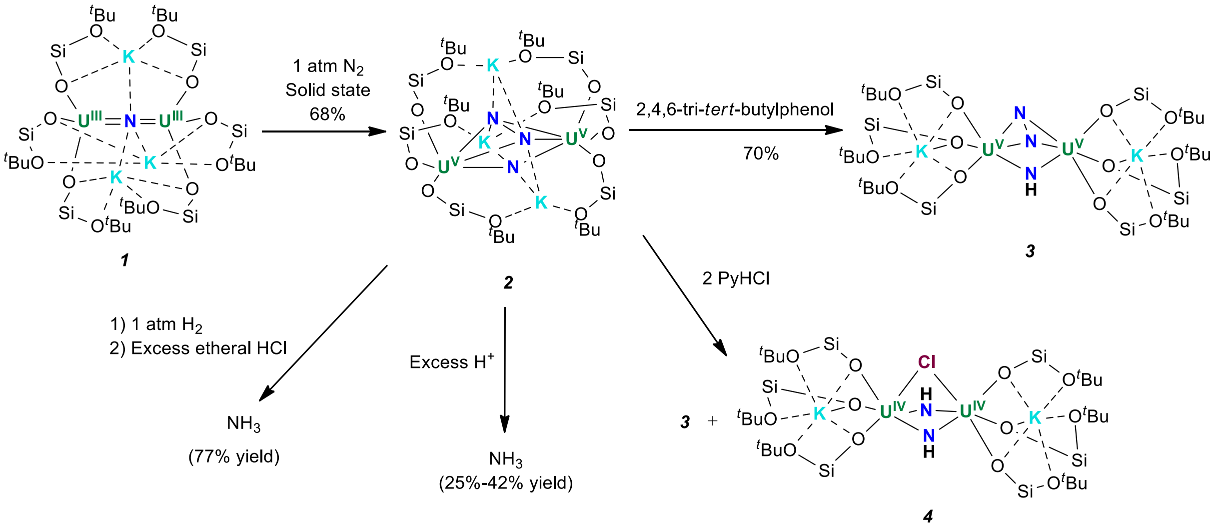

Figure 4. The 4-electron reduction of dinitrogen

Treating ***2*** with 1 equiv. of 2,4,6-tri-tert-butylphenol gives the mono-protonated product ***3*** in 70% yield. The molecular structure of ***3*** shows that the nitride atom has been protonated to afford an imido ligand (NH^{2-}). Treatment of ***2*** with two equiv. of a stronger acid, pyridinium chloride, results formation of the di-imido product ***4***. Adding excess PyHCl leads to the formation of ammonium chloride in ~35% yield. The most interesting result is that treatment of ***2*** with 1 atm H_2 at room temperature for three weeks, following by addition of a solution of HCl in ether, affords ammonia in 77% yield.

These observations prove that uranium complexes can promote the stoichiometric transformation of N_2 into NH_3. However, this approach is still far away from being applied industrially. The re-reduction of uranium(IV) back to a uranium(III) species is thermodynamically difficult, and makes it challenging to construct a catalytic cycle. However the design principles could be extended to other metals and thereby aid the development of new molecular systems for the catalytic fixation of N_2.

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