

Titanium Hydride Clusters: Catching and Functionalizing N₂

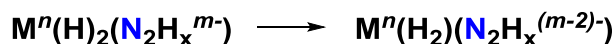
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Literature Seminar

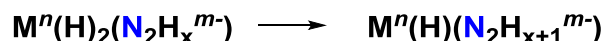
February 24, 2015

Since the isolation of the first dinitrogen complex, [Ru(NH₃)₅N₂]²⁺, by Senoff and Allen¹ in 1965, there have been numerous dinitrogen compounds investigating the coordination, activation and functionalization of the inert gas reported in the literature.² More recently, examples by Schrock,³ Nishibayashi,⁴ and Peters⁵ show the catalytic reduction of dinitrogen into ammonia using different transition metal complexes supplemented by a large excess of reducing agents and proton sources. In Nature, the conversion of dinitrogen to ammonia is mediated by the metalloenzyme nitrogenase at ambient temperature and pressure. While industrially, the Haber-Bosch process accomplishes this task by activating and functionalizing dinitrogen on a solid catalyst surface under harsh conditions with dihydrogen serving as both the source of electrons and protons.⁶ In Nature and industry, the cooperation of multimetallic sites is understood to mediate ammonia formation.

The involvement of hydrogen gas, as observed in the Haber-Bosch process,⁶ has led to transition metal complexes bearing hydrides as ligands in hopes to accomplish a similar task.⁷ The metal hydride route towards dinitrogen activation can deliver two electrons to reduce dinitrogen (**eq. 1**), or the metal hydride can then transfer protons to dinitrogen through heterolytic splitting of dihydrogen (**eq. 2**), with metal hydride acting more like a metal dihydrogen adduct.⁷ A binuclear tantalum tetrahydride, using the metal



Equation 1: Reductive coupling enabling 2 electron transfer



Equation 2: Heterolytic splitting mediating proton transfer

hydride, approach has shown to activate the dinitrogen bond to 1.319(6) Å, but not completely cleave it.⁸ More recently, a diniobium tetrahydride complex has shown to completely cleave the dinitrogen bond, but without N-H functionalization.⁹

Drawing inspiration from Nature, the Haber-Bosch process and previous work with metal hydride complexes¹⁰, the Hou group developed a titanium hydride cluster consisting of three titanium atoms and seven hydride ligands (**Figure 1**).¹¹ Upon reaction of **1** with 1 atm of dinitrogen, the formation of one bridging imide bound to two titanium centers and one nitride bound to three titanium centers was observed, **2**.¹¹ The process was accompanied by the release of two molecules of hydrogen gas and an electrophilic migration of a hydride ligand, which has also been suggested to take place on the solid catalyst surface during Haber-Bosch process,⁶ along with no change in the oxidation state of the titanium center.¹¹ Utilizing low temperature ¹H and ¹⁵N NMR studies along with computational data, a previously unprecedented μ-η¹:η²:η²-end-on side-on coordination mode of dinitrogen was observed.¹¹ Heating **2** at elevated temperatures under a dinitrogen

atmosphere results in **3**, a mixed triimido-nitrido species, accompanied by the oxidation of two titanium centers and intramolecular hydrogen migration.¹¹

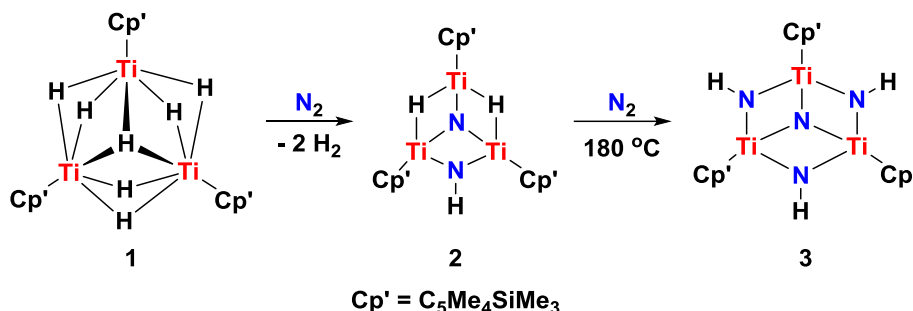


Figure 1: Reaction of trinuclear titanium heptahydride with dinitrogen

In addition to activating and functionalizing dinitrogen, **1** has also been shown to react with benzene (**Figure 2**).¹² The reaction involves various events, including carbon-carbon double bond hydrometallation accompanied by the release of dihydrogen, carbon-hydrogen and carbon-carbon bond cleavage and formation.¹² The cooperation of the titanium hydride cluster promotes these events, but specific details about the mechanism remains unclear.

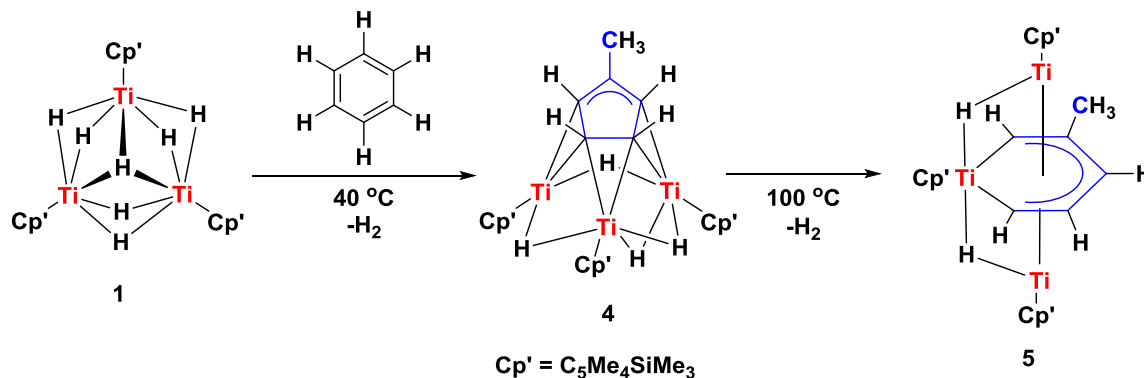


Figure 2: Cleavage of carbon-carbon bond in benzene by 1

Complex **1** can clearly activate and functionalize dinitrogen, however further improvements are still necessary, as this process is not catalytic. In addition, **1** could also serve as a basis for functionalization or transformation of relatively inactive aromatics.

References:

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