Synthesis and Reactivity of Vanadium Complexes Bearing Anionic PCP-type Pincer Ligand toward Nitrogen Fixation

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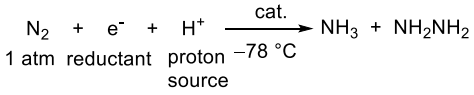
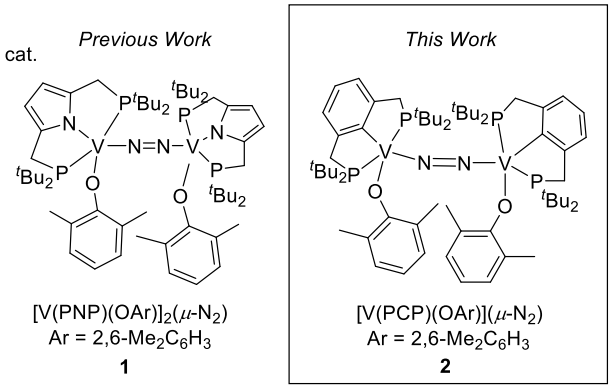
The synthesis of ammonia from dinitrogen in the air, known as nitrogen fixation, has been one of the most essential chemical processes in both industry and biology. In contrast to the traditional Haber-Bosch process which requires harsh reaction conditions, the nitrogen-fixing enzyme nitrogenase has the ability to convert dinitrogen into ammonia at room temperature under an atmospheric pressure. Since vanadium works as one of the key elements in nitrogenase, vanadium-catalyzed nitrogen fixation is interesting for understanding the mechanisms of biological nitrogen fixation and for the possibility of developing an efficient catalytic system under ambient conditions.

So far, we reported a series of vanadium complexes bearing an anionic pyrrole-based PNP-type pincer ligand, represented by a vanadium-dinitrogen complex (**1**) as the first example of vanadium-catalyzed ammonia and hydrazine formation from dinitrogen.[1] Recently, we found that an iron-dinitrogen complex bearing an anionic benzene-based PCP-type pincer ligand also works as an effective catalyst for ammonia and hydrazine formation.[2] Based on these studies, we have newly designed and synthesized a vanadium-dinitrogen complex bearing the anionic benzene-based PCP-type pincer ligand (**2**). X-ray analysis revealed the dinitrogen-bridged structure of **2**. The length of the bridging N–N bond in **2** is 1.244(2) Å, which is close to that in **1**, indicating a typical N=N bond coordinated to the two V atoms. The catalytic activity of **2** toward the formation of ammonia and hydrazine will be presented.





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