

Catalytic Nitrogen Fixation by Using Rhenium Complexes

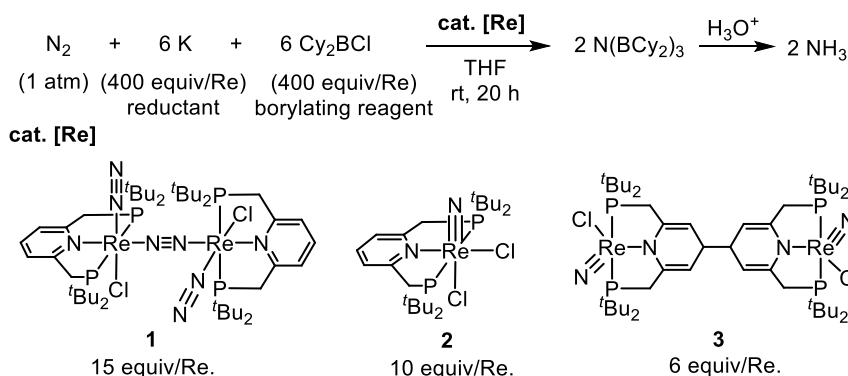
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Very recently, Mézailles reported the first and the only successful example of catalytic conversion of dinitrogen to borylamine by using a molybdenum complex as a catalyst under mild reaction conditions.¹ Previously, we reported the first example of rhenium-catalyzed dinitrogen reduction to ammonia and silylamine under mild reaction conditions by using a dinitrogen-bridged dirhenium(I) complex bearing PNP-type pincer ligands (**1**, PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine).² Based on these works, we have studied the rhenium catalyzed borylamine formation from dinitrogen under mild reaction conditions.

In the presence of catalytic amount of **1**, an atmospheric pressure of dinitrogen reacted with potassium (400 equiv/Re) as a reductant and Cy₂BCl (400 equiv/Re) as a borylating reagent in THF at room temperature for 20 h to afford 15.3 equiv of borylamine based on the rhenium atom of catalyst, which was quantified as ammonia after hydrolysis. This is the first example of rhenium catalyzed borylamine formation under mild reaction conditions. Catalytic activities of other rhenium complexes such as a mononuclear nitride complex **2** and a dinuclear nitride complex **3**, which was synthesized by reduction of **2**, will also be discussed in the presentation.

Scheme 1 Rhenium Catalyzed Borylamine Formation



1) Bennaamane, S.; Espada, F. M.; Mulas, A.; Personeni, T.; SaffonMerceron, N.; Fustier-Boutignon, M.; Bucher, C.; Mézailles, N. *Angew. Chem. Int. Ed.* **2021**, *60*, 20210. 2) Meng, F.; Kuriyama, S.; Tanaka, H.; Egi, A.; Yoshizawa, K.; Nishibayashi, Y. *Angew. Chem. Int. Ed.* **2021**, *60*, 13906.