Mechanistic Study on Rhenium-Catalyzed Ammonia Formation from Dinitrogen under Mild Reaction Conditions

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Catalytic reduction of dinitrogen under mild conditions represents a green and efficient methodological possibility for future ammonia production. To date, several transition metal-complexes have shown catalytic activities toward nitrogen fixation under mild reaction conditions.[1] Recently, we have reported that a dinitrogen-bridged dirhenium complex bearing PNP-type pincer ligands [{$ReCl(N_2)(PNP)\}_2(\mu\text{-}N_2)$] (**1**, PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) worked as a catalyst for the reaction of dinitrogen (1 atm) with KC_8 as a reductant and $[HPCy_3]BAr^F{}_4$ (Ar^F = 3, 5-bis(trifluoromethyl)phenyl) as a proton source at −78 °C to produce 8.4 equiv of ammonia based on the rhenium atom of the catalyst (Scheme 1A).[2] Here, we have carried out extensive studies to get mechanistic information for this catalytic system.

When complex **1** was treated with KC_8 and triflic acid at −78 °C, the formation of a rhenium nitride complex bearing a dinitrogen-bridged dirhenium structure was observed but the dinuclear rhenium nitride complex was not isolated as a pure form. On the other hand, a mononuclear nitride complex [$Re(N)Cl_2(PNP)$] (**2**), which was prepared from the reaction of [$ReCl_3(PPh_3)_2(MeCN)$] with PNP at 80 °C, also catalyzed the formation of ammonia at −78 °C (Scheme 1A). These results suggest a rhenium-nitride species as a key intermediate in the rhenium-catalyzed nitrogen fixation. We also found that dinitrogen (1 atm) reacted with SmI_2 as a reductant and water as a proton source in the presence of **2** at room temperature for 18 h to give 5.8 equiv of ammonia based on the rhenium atom of the catalyst (Scheme 1B).

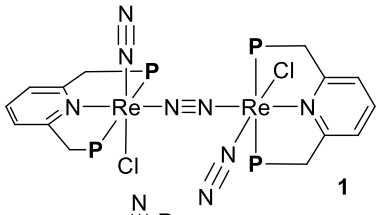
Scheme 1

(A)

N_2 + 6 KC_8 + 6 $[HPCy_3]BAr^F{}_4$ —(cat. **1** or **2**, Et_2O, −78 °C, 2 h)→ 2 NH_3

(1 atm)(800 equiv/Re) (800 equiv/Re)

1: 8.4 equiv/Re
2: 3.6 equiv/Re

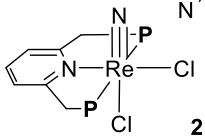


1

(B)

N_2 + 6 SmI_2 + 6 H_2O —(cat. **2**, THF, rt, 18 h)→ 2 NH_3

(1 atm)(180 equiv/Re)(180 equiv/Re) 5.8 equiv/Re



2 **P** = P^{t}Bu$_2$

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