Manganese-catalyzed oxidative conversion of ammonia into dinitrogen

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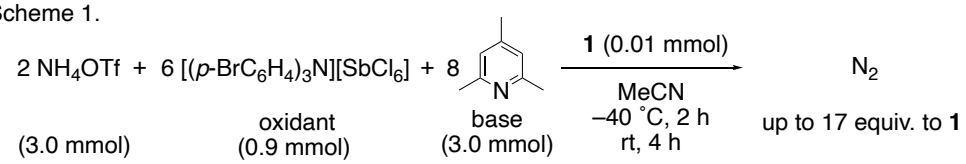
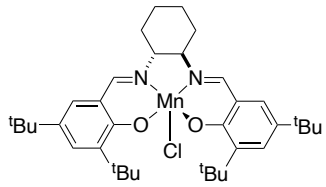
Ammonia is a desirable candidate as an energy carrier toward a sustainable society because of its advantages such as easiness of handling, high energy density, and a carbon-free fuel.[1] Recently, for extraction of energy from ammonia, a few examples of catalytic oxidation of ammonia into dinitrogen using transition metal complexes have been reported.[2] To utilize ammonia as an energy carrier, oxidative conversion of ammonia into dinitrogen by base metal catalyst is an important transformation. Toward this goal, we have focused on manganese complexes bearing salen ligand (salen: *N,N'*-ethylene-bis(salicyldeneamine)) because these complexes have catalytic activity for several oxidation reactions such as epoxidation of olefins, benzylic oxidation, and sulfide oxidation.[3]

Herein, we report catalytic ammonia oxidation into dinitrogen by Mn(salen) complexes under chemical and electrochemical oxidation conditions (Scheme 1). A detailed reaction mechanism was investigated by the synthesis of intermediates and stoichiometric reactions using manganese intermediates, which suggests the formation of hydrazine complexes via attack of ammonia on monometallic imide complexes as key reactive intermediates. In addition, we also confirmed that proton-coupled electron transfer (PCET) occurs in the first oxidation step from electrochemical study.

Scheme 1.





1

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