Ammonia Formation Catalyzed by Dinitrogen-Bridged Dirhenium Complex Bearing PNP-Pincer Ligands under Mild Reaction Conditions

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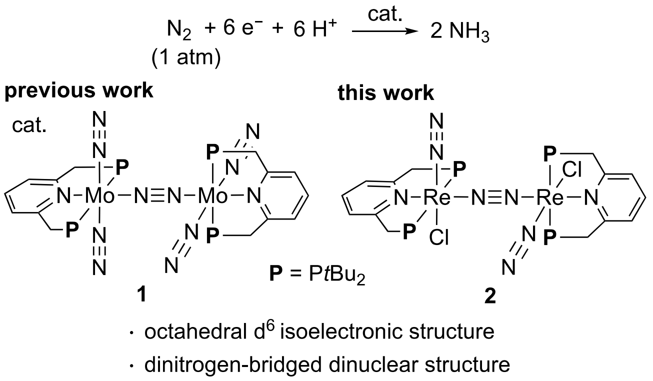
Abstract: A series of rhenium complexes bearing a pyridine-based PNP-type pincer ligand are synthesized from rhenium phosphine complexes as precursors. A dinitrogen-bridged dirhenium complex bearing the PNP-type pincer ligands catalytically converts dinitrogen into ammonia in the reaction with KC_8 as a reductant and $[HPCy_3]BAr^F_4$ (Cy = cyclohexyl, Ar^F = $3,5\text{-}(CF_3)_2C_6H_3$) as a proton source at –78 °C to afford 8.4 equiv of ammonia based on the rhenium atom of the catalyst. The rhenium-dinitrogen complex also catalyzes silylation of dinitrogen in the reaction with KC_8 as a reductant and Me_3SiCl as a silylating reagent under ambient reaction conditions to afford 11.3 equiv of tris(trimethylsilyl)amine based on the rhenium atom of the catalyst. These results demonstrate the first successful example of catalytic nitrogen fixation under mild reaction conditions by using rhenium-dinitrogen complexes as catalysts.

The reduction of dinitrogen into ammonia and its equivalents under ambient reaction conditions has been a challenging task in chemistry. Recently, much attention has been paid to the development of homogeneous molecular catalysis capable of nitrogen fixation under mild reaction conditions.[1,2] Currently, well-defined transition metal complexes such as Ti-, V-, Mo-, Fe-, Ru-, Os-, and Co-complexes have been known to work as effective catalysts toward transformation of dinitrogen into ammonia and/or hydrazine under mild reaction conditions.[3-8] Besides, catalytic reduction of dinitrogen into tris(trialkylsilyl)amines has been achieved by the use of Ti-, V-, Cr-, Mo-, W-, Mn, Fe-, Co-, Rh-, and Ni-complexes as catalysts.[9-16]

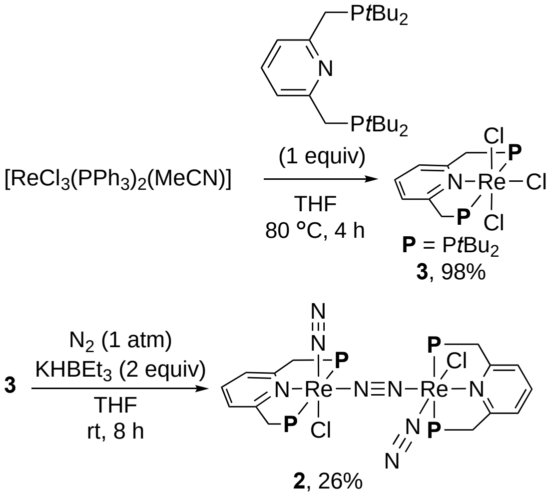
Significant progress has been made in study on the preparation and reactivity of rhenium-dinitrogen complexes for the last decade.[17-20] Typical examples are as follows. An anionic rhenium(I) complex reduced dinitrogen to form a rhenium(III)-silyldiazenide complex upon silylation.[17] Rhenium(II) species cleaved the N-N triple bond of dinitrogen to afford the corresponding rhenium(IV)-nitride complexes, which were converted into nitrogen-containing organic compounds and ammonia.[18,19] However, unfortunately, all of these transformations are stoichiometric reactions using rhenium-dinitrogen complexes. In contrast to the stoichiometric reactions, no successful example of catalytic reduction of dinitrogen using rhenium-dinitrogen complexes as catalysts has been reported until now.



Scheme 1. Catalytic formation of ammonia from dinitrogen using dinitrogen-bridged d^6 metal complexes bearing PNP-type pincer ligands.

In 2011, we reported that a dinitrogen-bridged dimolybdenum complex bearing the PNP-type pincer ligands $[Mo(N_2)_2(PNP)]_2(\mu\text{-}N_2)$ (**1**; PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) worked as an effective catalyst for the formation of ammonia from dinitrogen under ambient reaction conditions (Scheme 1).[5b,21] Considering that Mo(0) and Re(I) are isoelectronic, we have envisaged that a dinitrogen-bridged dirhenium(I) complex bearing the same PNP-type pincer ligands $[ReCl(N_2)(PNP)]_2(\mu\text{-}N_2)$ (**2**) has a catalytic activity toward the formation of ammonia from dinitrogen (Scheme 1). Herein, we report the preparation of **2** and its catalytic activity toward reduction of dinitrogen into ammonia and tris(trimethylsilyl)amine ($N(SiMe_3)_3$) under mild reaction conditions.

The reaction of $[ReCl_3(PPh_3)_2(MeCN)]$ with 1 equiv of PNP-pincer ligand in THF at 80 °C for 4 h gave a rhenium-trichloride complex bearing the PNP-type ligand $[ReCl_3(PNP)]$ (**3**) in 98% yield (Scheme 2). We confirmed the molecular structure of **3** by X-ray analysis, and an ORTEP drawing of **3** is shown in Figure 1a.[22] Complex **3** shows a strongly shifted signal at –1587 ppm in $^{31}P\{^1H\}$ NMR spectrum. Solution magnetic moment of **3** is estimated as 1.5 μ_B by Evans' method, being much smaller than a spin-only value for a triplet state. These observations indicate that an energetically well-separated ground state causes temperature-independent paramagnetism (TIP). Magnetic susceptibility measurement of solid-state in the temperature range from 300 to 5 K also suggests TIP behavior (Figure S1). Large contributions from TIP are often observed in various Re complexes including a Re(III) state.[17c,17d,19,23]



Scheme 2. Synthesis of rhenium complexes bearing the PNP-pincer ligand

The reaction of **3** with 2 equiv of $KHBEt_3$ in THF at room temperature for 8 h under an atmospheric pressure of dinitrogen afforded the dinitrogen-bridged dirhenium(I) complex **2** in 26% yield (Scheme 2).[24] The molecular structure of **2** confirmed by X-ray analysis reveals that each rhenium center has an octahedral geometry with end-on dinitrogen and chloride ligands in axial positions.[22] An ORTEP drawing of **2** is shown in Figure 1b. The two rhenium fragments are bridged by one end-on dinitrogen ligand and twisted around the Re-N-N-Re axis with each other. The dihedral angle between the planes defined by P1-Re1-P1*-N1 and P1**-Re1*-P1***-N1* of **2** is 80.79(3)°, being larger than that of **1** (61.41(9)°).[5b]

The IR spectrum of **2** in a solid-state (KBr) shows two strong ν_{NN} bands at 1888 and 1949 cm^{-1}. A similar dirhenium-dinitrogen complex $[Re(N_2)(NNN)]_2$ (NNN = $CH_3N(CH_2CH_2NC_6F_5)^{2-}$) exhibited the same pattern in the IR spectra (ν_{NN} = 2031 and 2015 cm^{-1}).[25] IR spectrum in a solution state (THF) of **2** shows two absorptions of the terminal dinitrogen ligands at 1892 and 1956 cm^{-1}. Raman spectrum of a THF solution of **2** exhibits a strong band assignable to the bridging dinitrogen ligand at 1890 cm^{-1}. These results suggest that the dinuclear structure of **2** maintains in solution.

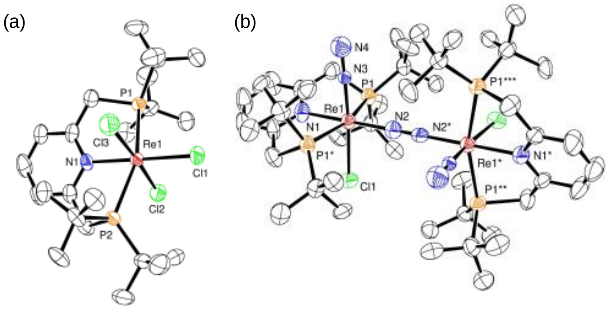


Figure 1. ORTEP drawings of **3** (a) and **2** (b). Thermal epllipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity.

To get more information on the property of **2**, we carried out DFT calculations. The calculated ν_{NN} values of the terminal (2010 and 2013 cm^{-1}) and bridged dinitrogen ligands (2053 cm^{-1}) are closed to the experiment values. Due to the low π-accepting ability of Cl ligands *trans* to the axial N_2 ligand, NPA charge of the terminal dinitrogen ligands of **2** (–0.18) are larger than that of **1** (–0.09).[26] The bond dissociation free energy for a Re–N bond between the Re atom and the bridging dinitrogen ligand is high enough (25.6 kcal/mol) to maintain the dinuclear structure in solution.

We examined the stoichiometric reactivity of **2** toward the formation of ammonia. Protonation of **2** with an excess amount of sulfuric acid in THF at room temperature for 24 h produced 0.2 equiv of ammonia and no hydrazine based on the Re atom [Eq. (1)]. The obtained amounts of ammonia and hydrazine are smaller than those from protonation of dinitrogen-bridged dimolybdenum complex **1**.[27] This result suggests the lower reactivity of the dinitrogen ligands in **2** toward protonation than that in **1**.

$$\underset{\text{complex}}{\text{M-N}_2} + \underset{\text{(excess)}}{H_2SO_4} \xrightarrow[\text{rt, 24 h}]{\text{THF}} \underset{\substack{\textbf{2}\text{, 0.18 equiv/Re}\\ \text{(c.f. }\textbf{1}\text{, 0.61 equiv/Mo}}}{NH_3} + \underset{\substack{\text{0 equiv/Re}\\ \text{0.06 equiv/Mo)}}}{NH_2NH_2} \qquad (1)$$

Next, the catalytic transformation of dinitrogen into ammonia using **2** as a catalyst was investigated under our previous reaction conditions, where dinitrogen-bridged dimolybdenum complex **1** worked as an efficient catalyst toward the formation of ammonia.[5b,5e,5f,21] However, the reaction of N_2 (1 atm) with 36 equiv of $CoCp_2$ (Cp = η^5-C_5H_5) as a reductant and 48 equiv of [LutH]OTf (Lut = 2,6-lutidine, OTf = OSO_2CF_3) as a proton source in the presence of a catalytic amount of **2** in toluene at room temperature for 20 h afforded neither ammonia nor hydrazine at all (Table 1, entry 1). The use of the combination of $CoCp^*_2$ (Cp* = η^5-C_5Me_5) and [ColH]OTf (Col = 2,4,6-collidine) did not produce ammonia (Table 1, entry 2). The use of SmI_2-H_2O produced only a small amount of ammonia (Table 1, entry 3). Then we investigated the catalytic reaction at low temperature.[3,6a,6h] The reaction of N_2 (1 atm) with 400 equiv of KC_8 and 400 equiv of $[HPCy_3]BAr^F_4$ (Cy = cyclohexyl, Ar^F = 3,5-$(CF_3)_2C_6H_3$) in the presence of **2** in Et_2O at –78 °C afforded 4.0 equiv of ammonia based on the rhenium atom of **2** (Table 1, entry 4). No formation of hydrazine was observed in this reaction, while 50 equiv of dihydrogen were produced as a byproduct. The use of $CoCp^*_2$ (400 equiv/Re) as a reductant instead of KC_8 afforded only a trace amount of ammonia (Table 1, entry 5). The use of $[H(OEt_2)_2]BAr^F_4$ (400 equiv/Re) produced a comparable amount of ammonia to that of $[HPCy_3]BAr^F_4$ (Table 1, entry 6). When larger amounts (800 equiv/Re) of the reductants and the proton sources were used, $[HPCy_3]BAr^F_4$ worked better than $[H(OEt_2)_2]BAr^F_4$ as a proton source, giving 8.4 equiv of ammonia based on the Re atom of **2** (Table 1, entries 7 and 8). To the best of our knowledge, rhenium-dinitrogen complex **2** represents the first successful example of the rhenium-catalyzed reduction of dinitrogen into ammonia under mild reaction conditions. We also confirmed that the formation of ammonia was derived from dinitrogen by using $^{15}N_2$ gas instead of $^{14}N_2$ gas (see the Supporting Information in details).

Table 1. Catalytic formation of ammonia from dinitrogen by **2**.

$$\underset{(1\ \text{atm})}{N_2} + \underset{(X\ \text{equiv/Re})}{6\ \text{reductant}} + \underset{(Y\ \text{equiv/Re})}{6\ \text{proton source}} \xrightarrow[\text{solvent, T}]{\text{cat. } \mathbf{2}} 2\ NH_3$$

entry	reductant (X)	proton source (Y)	solvent	T	NH_3[a]
1[b]	$CoCp_2$ (36)	[LutH]OTf (48)	toluene	rt	0
2[b]	$CoCp^*_2$ (36)	[ColH]OTf (48)	toluene	rt	0
3[c]	SmI_2 (36)	H_2O (36)	THF	rt	0.4
4[d]	KC_8 (400)	$[HPCy_3]BAr^F_4$ (400)	Et_2O	–78 °C	4.0±0.0[e]
5[d]	$CoCp^*_2$ (400)	$[HPCy_3]BAr^F_4$ (400)	Et_2O	–78 °C	0.1
6[d]	KC_8 (400)	$[H(OEt_2)_2]BAr^F_4$ (400)	Et_2O	–78 °C	4.1±0.4[e]
7[d]	KC_8 (800)	$[HPCy_3]BAr^F_4$ (800)	Et_2O	–78 °C	8.4±0.9[f]
8[d]	KC_8 (800)	$[H(OEt_2)_2]BAr^F_4$ (800)	Et_2O	–78 °C	4.8

[a] Equiv based on the Re atom of **2**. [b] For 20 h. [c] For 18 h. [d] At –78 °C for 2 h then at room temperature for 15 h. [e] An average of two runs. [f] An average of four runs.

Next, we examined other rhenium complexes as catalysts for the reduction of dinitrogen under the optimized reaction conditions (Table 2). The use of $[ReCl_3(PNP)]$ **3** afforded more than a stoichiometric amount of ammonia (Table 2, entry 2), while only 1.2 equiv of ammonia were produced of the reaction using $[ReCl_3(PPh_3)_2(MeCN)]$ as a catalyst (Table 1, entry 3). Simple rhenium complexes such as $[ReCl(CO)_5]$, and $[ReI_3]$ did not exhibited the catalytic activity under the same reaction conditions (Table 1, entries 4 and 5).

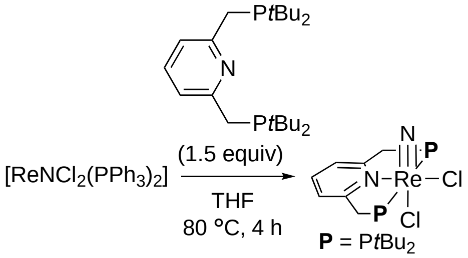
To get information on the reaction mechanism, we investigated the reactivity of **2**. No reaction was observed upon treatment of **2** with 1 equiv (based on the Re atom) of $[HPCy_3]BAr^F_4$ in Et_2O at –78 °C for 2 h. According to DFT calculations, the protonation of the terminal dinitrogen ligand of **2** by $[HPCy_3]^+$ is highly endergonic by 17.2 kcal/mol at 195 K in Et_2O (see Figure S10). Due to the low reactivity of **2** toward protonation and the weak acidity of $[HPCy_3]^+$,[3,28] we consider that the N-H bond formation by the reaction of **2** with $[HPCy_3]BAr^F_4$ may not proceed smoothly. The cyclic voltammogram of **2** in THF shows an irreversible reduction wave at –2.10 V vs. $FeCp_2^{0/+}$ (Figure S2). The free energy change at 195 K (ΔG_{195}) for the reduction of **2** is calculated to be –37.6 kcal/mol based on reaction **2** + e^- → $[\mathbf{2}]^-$. The reaction of **2** with 1 equiv (based on the Re atom) of KC_8 in Et_2O at –78 °C for 1 h consumed **2** completely to form new species, which showed ν_{NN} bands at 2038 and 1951 cm^{-1}, although we have not yet identified this species because of its instability. However, these results suggest that **2** may be reduced during the catalytic cycle. DFT calculations predict that the one-electron reduction of **2** can facilitate the protonation of its dinitrogen ligand. The protonation of the reduced species $[\mathbf{2}]^-$ by $[HPCy_3]^+$ is *exergonic* by 2.0 kcal/mol with a low activation free energy of 8.8 kcal/mol at 195 K (see Figure S11).

Table 2: Catalytic formation of ammonia from dinitrogen by rhenium complexes.[a]

$$\underset{(1\ \text{atm})}{N_2} + \underset{(800\ \text{equiv/M})}{6\ KC_8} + \underset{(800\ \text{equiv/M})}{6\ [HPCy_3]BAr^F_4} \xrightarrow[\substack{Et_2O \\ -78\ ^\circ C,\ 2\ h \\ \text{then rt, 15 h}}]{\text{cat.}} 2\ NH_3$$

entry	cat	NH_3[b]
1	$[ReCl(N_2)(PNP)]_2(\mu\text{-}N_2)$ (**2**)	8.4±0.9[c]
2	$[ReCl_3(PNP)]$ (**3**)	4.1±0.7[d]
3	$[ReCl_3(PPh_3)_2(MeCN)]$	1.2
4	$[ReCl(CO)_5]$	0.4
5	$[ReI_3]$	0
6	$[Re(\equiv N)Cl_2(PNP)]$ (**4**)	3.7±0.7[d]
7	$[Mo(N_2)_2(PNP)]_2(\mu\text{-}N_2)$ (**1**)	8.1±0.1[d]

[a] A mixture of catalyst (1.0 μmol/M), KC_8 (0.80 mmol, 800 equiv/M) and $[HPCy_3]BAr^F_4$ (0.80 mmol, 800 equiv/M) in Et_2O (5 mL) was stirred at –78 °C for 2 h then at room temperature for 15 h under 1 atm of N_2. [b] Equiv based on the metal atom of the catalyst. [c] An average of four runs. [d] An average of two runs.



4, 14%

Scheme 3. Synthesis of rhenium-nitride complex **4**.

Because rhenium-nitride complexes have been considered as key intermediates in nitrogen fixation,[18,19] we newly synthesized a rhenium-nitride complex $[Re(\equiv N)Cl_2(PNP)]$ (**4**) in 14% yield from the reaction of $[Re(\equiv N)Cl_2(PPh_3)_2]$ with the PNP-type pincer ligand to investigate the catalytic activity (Scheme 3).[22] The catalytic reaction using **4** as a catalyst afforded 3.7 equiv of ammonia based on the Re atom of **4** (Table 1, entry 6). Although the coordination of the two chloride ligands to the rhenium atom may decrease the activity of **4**, the more than a stoichiometric amount of ammonia suggests that a similar rhenium-nitride complex is involved in the catalytic cycle. We consider that the rhenium-catalyzed formation of ammonia from dinitrogen proceeds via a similar distal pathway as our previously proposed one for **1**.[26] However, we currently do not exclude the possibility of the formation of ammonia via other pathway such as a N_2 splitting pathway in which the direct cleavage of the nitrogen-nitrogen triple bond occurs at a dirhenium structure.[5e,18,19]

As described in the present manuscript, rhenium-dinitrogen complex **2** catalyzes the formation of ammonia from dinitrogen only at low temperature. This result is in sharp contrast to the catalytic reactivity of molybdenum-dinitrogen complex **1**, where the formation of ammonia from dinitrogen proceeded even at room temperature. For comparison, we carried out the catalytic reaction at low temperature using **1** as a catalyst to afford 8.1 equiv of ammonia produced based on the Mo atom of **1** (Table 1, entry 9). Unfortunately, we have not yet clarified the exact role of the PNP-pincer ligand toward the central metal during the catalytic process. However, we believe that the PNP-pincer ligand may stabilize the dinitrogen-bridged structure during the catalytic cycle by its appropriate steric and electronic properties.

The catalytic reduction of dinitrogen into $N(SiMe_3)_3$ was also investigated under ambient reaction conditions.[29] We carried out the reaction of atmospheric pressure of dinitrogen with 600 equiv of KC_8 as a reductant and 600 equiv of Me_3SiCl as a silylating reagent in the presence of **2** in THF at room temperature for 20 h to afford 11.3 equiv of $N(SiMe_3)_3$ based on the Re atom of **2** [Eq. 2]. This result represents the first successful example of the rhenium-catalyzed formation of $N(SiMe_3)_3$ from dinitrogen under mild reaction conditions. According to the time profiles of the formation of $N(SiMe_3)_3$ (Figure S4), we observed no induction period and the formation of $N(SiMe_3)_3$ almost finished within 8 h. The addition of Hg to the reaction mixture did not inhibit the catalytic activity. This result suggests that homogeneous rhenium species promotes the silylation of dinitrogen under ambient reaction conditions.

$$\underset{(1\ \text{atm})}{N_2} \; + \; \underset{(600\ \text{equiv/Re})}{6\ KC_8} \; + \; \underset{(600\ \text{equiv/Re})}{6\ Me_3SiCl} \; \xrightarrow[\substack{\text{THF} \\ \text{rt, 20 h}}]{\text{cat. } \mathbf{2}} \; \underset{11.3\ \text{equiv/Re}}{2\ N(SiMe)_3} \qquad (2)$$

In summary, we have found the first successful example of the rhenium-catalyzed formation of ammonia and $N(SiMe_3)_3$ from dinitrogen under mild reaction conditions. The current results show the potential that group 7 metals work as efficient catalysts for nitrogen fixation. Further studies for the elucidation of the reaction mechanism and the development of more efficient catalytic nitrogen fixation system by rhenium-dinitrogen complexes are ongoing in our laboratory.

Acknowledgements

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Keywords: Ammonia • Nitrogen fixation • Rhenium • Homogeneous catalysis • Pincer ligand

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[24] No characteristic peak was observed in ^{1}H NMR spectrum of **2.** The solution magnetic moment of **2** (1.6 μ_B) suggests TIP behavior. However, the measurement of magnetic susceptibility of **2** by SQUID was failed due to the air-sensitive nature of **2**.

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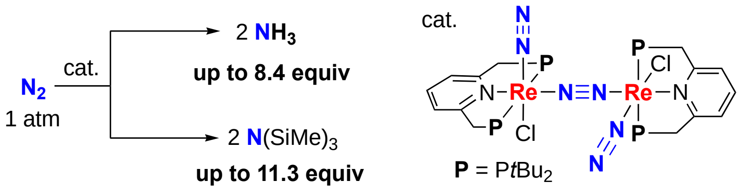
[29] We investigated the catalytic activity of other rhenium complexes such as **3**, **4**, [$ReCl_3(PPh_3)_2(MeCN)$], and [$Re_2(CO)_{10}$] toward the formation of silylamine. See Supporting Information for details.

Entry for the Table of Contents



The first successful example of catalytic nitrogen fixation using a rhenium-dinitrogen complex as a catalyst under mild reaction conditions is described here. A dinitrogen-bridged dirhenium complex worked as an effective catalyst toward formation of ammonia and silylamine, where up to 8.4 equiv of ammonia and 11.3 equiv of silylamine were produced based on the Re atom of the catalyst.