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

Fanqiang Meng, Shogo Kuriyama, Hiromasa Tanaka, Akihito Egi, Kazunari Yoshizawa, and Yoshiaki Nishibayashi**

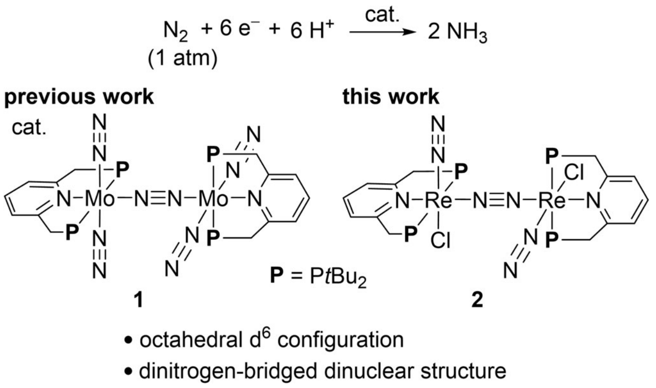
Abstract: *A series of rhenium complexes bearing a pyridine-based PNP-type pincer ligand are synthesized from rhenium phosphine complexes as precursors. A dinitrogen-bridged dirhenium complex bearing the PNP-type pincer ligands catalytically converts dinitrogen into ammonia during the reaction with* 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 11.7 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 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, considerable attention has been paid to the development of homogeneous molecular catalysis that is capable of nitrogen fixation under mild reaction conditions.[1,2] Currently, well-defined transition metal complexes (e.g., Ti-, V-, Mo-, Fe-, Ru-, Os-, and Co-complexes) worked as effective catalysts for the transformation of dinitrogen into ammonia and/or hydrazine under mild reaction conditions.[3–8] Furthermore, the catalytic reduction of dinitrogen into silylamines was achieved using Ti-, V-, Cr-, Mo-, W-, Mn-, Fe-, Co-, Rh-, Ni-, and U-complexes as catalysts.[9–17]

During the last decade, substantial progress has been made in the study on the preparation and reactivity of rhenium-dinitrogen complexes.[18–21] The typical examples are as follows. An anionic rhenium(I) complex reduced dinitrogen to form a rhenium(III)-silyldiazenide complex upon silylation.[18] Rhenium(II) species cleaved the N-N triple bond of dinitrogen to afford the corresponding rhenium(V)-nitride complexes, which were converted into nitrogen-containing organic compounds and ammonia.[19,20] Unfortunately, all of these transformations are stoichiometric reactions that use rhenium-dinitrogen complexes. Compared to stoichiometric reactions, until now, there have been no successful examples of catalytic reduction of dinitrogen using rhenium-dinitrogen complexes as catalysts.

In 2011, we reported that a dinitrogen-bridged dimolybdenum complex bearing 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,22] Considering that Mo^0 and Re^I adopt a d^6 configuration, we speculated that a dinitrogen-bridged dirhenium(I) complex bearing the same PNP-type pincer ligands $[ReCl(N_2)(PNP)]_2(\mu\text{-}N_2)$ (**2**) would have catalytic activity toward the formation of ammonia from dinitrogen (Scheme 1). Herein, we report the preparation of **2** and its catalytic activity for the 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-



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

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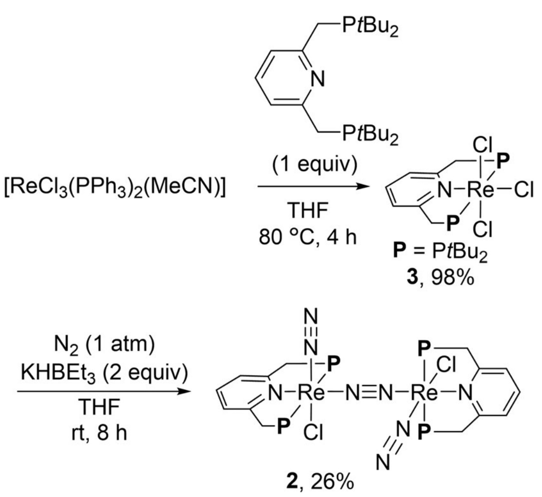


Scheme 2. Synthesis of rhenium complexes bearing the PNP-pincer ligand.

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.[23] Complex **3** shows a strongly shifted signal at −1587 ppm in a $^{31}P\{^1H\}$ NMR spectrum. The solution magnetic moment of **3** is estimated to be 1.5 μ_B by Evans' method, which is much smaller than a spin-only value for the triplet state. These observations indicate that an energetically well-separated ground state causes temperature-independent paramagnetism (TIP). The magnetic susceptibility measurement of solid-state in the temperature range from 300 K to 5 K also suggests the TIP behavior (Supporting Information, Figure S1). Large contributions from TIP are often observed in various Re complexes including a Re^{III} state.[19c,d,20,24]

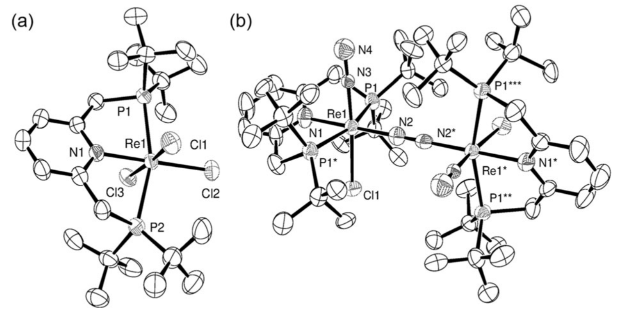


Figure 1. ORTEP drawings of **3** (a) and **2** (b). Ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

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). The molecular structure of **2**, which was confirmed by X-ray analysis, reveals that each rhenium center has an octahedral geometry with end-on dinitrogen and chloride ligands in axial positions.[23] 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)°, which is larger than that of **1** [61.41(9)°].[5b]

A ^1H NMR spectrum of **2** exhibits peaks consistent with its dinuclear structure in paramagnetic region, suggesting paramagnetic nature of **2**. The measurement of magnetic susceptibility of **2** at variable temperature (5 K to 300 K) may suggest the TIP behavior as observed in **3** and other reported rhenium complexes (Figure S2).[19c,d,20,24,25]

The IR spectrum of a solid sample in KBr of **2** (Figure 2) exhibits two strong N_2 stretching absorptions (1888 and 1949 cm^{-1}) and a weak N_2 stretching absorption (1993 cm^{-1}). We consider that these three absorptions of **2** are derived from conformers of **2** in the crystals. The crystallographic data of **2** indicates that the two conformers coexist in the crystals of **2** due to the disorder of the terminal dinitrogen (N3-N4) and the chloride ligands (Cl1), which is caused by the rotation of [$ReCl(N_2)(PNP)$] units about the bridging dinitrogen ligand (N2-N2*). Because the dihedral angles between the planes defined by N2-Re1-N3 and N2*-Re1*-N3* of the two isomers are different, each isomer is expected to have two N_2 stretching absorptions (symmetric and asymmetric stretches), like a similar dirhenium-dinitrogen complex $[Re(N_2)(NNN)]_2$ ($NNN = CH_3N(CH_2CH_2NC_6F_5)^{2-}$) exhibited ($\nu_{NN}$ = 2031 cm^{-1} and 2015 cm^{-1}).[26] The partial overlap of absorptions is considered to result in the observed three N_2 stretching bands. In fact, Harman and co-workers reported that a dinitrogen-bridged dirhenium complex $[TpRe(CO)_2]$-(μ-N_2) (Tp = hydridotris(pyrazolyl)borate) showed three CO stretching absorptions derived from the rotational conformers.[27] DFT calculations also suggest that **2** can access two energetically-degenerated rotational conformers and that the conformers show different patterns of N_2 absorptions in IR (Figure S20). The IR spectrum in a solution state (THF) of **2** shows only two absorptions of dinitrogen ligands at 1892 cm^{-1} and 1956 cm^{-1} (Figure 2). The Raman spectrum of a THF solution of **2** exhibits a strong band at 1890 cm^{-1} (Figure S6). The spectroscopic data in solution suggest that only one of the two conformers exist in solution. When the solution of **2** in THF was exposed to $^{15}N_2$ (1 atm) at 50 °C for 2 h, no ligand

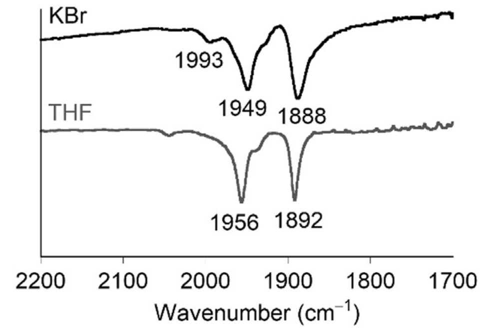


Figure 2. IR spectra of **2** in KBr (black) and THF (gray). Absorptions observed around 1930 and 2030 cm^{-1} were machinery noise.

exchange of the original $^{14}N_2$ in **2** for $^{15}N_2$ was observed. This reactivity of **2** is in sharp contrast to that of **1**, which underwent ligand exchange of coordinated $^{14}N_2$ for $^{15}N_2$.[5b] Instead, the reduction of **3** with $KHBEt_3$ under $^{15}N_2$ atmosphere produced $^{15}N_2$-labeled complex **2**-$^{15}N_2$, which shows shifted dinitrogen stretching absorptions in IR spectrum as expected (Figure S8).

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	3.9 ± 0.2[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	3.7 ± 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	4.9 ± 0.1[e]
9[d]	KC_8 (800)	$[HPtBu_3]BAr^F_4$ (800)	Et_2O	−78 °C	7.5 ± 0.6[g]
10[d]	KC_8 (800)	$[HPnBu_3]BAr^F_4$ (800)	Et_2O	−78 °C	6.0 ± 1.2[g]
11[d,h]	KC_8 (800)	$[HPCy_3]BAr^F_4$ (800)	Et_2O	−78 °C	8.2 ± 0.4[e]

[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 three runs. [f] An average of four runs. [g] An average of two runs. [h] Molybdenum complex **1** was used as a catalyst instead of **2**.

To obtain more information on the properties of **2**, we carried out density functional theory (DFT) calculations at the B3LYP-D3 level of theory. For geometry optimization calculations, we employed the SDD basis set for rhenium and chlorine atoms and the 6-31G(d) basis set for other atoms (see Supporting Information for details). Calculated ν_{NN} values are 1963 cm^{-1} and 1970 cm^{-1} for the terminal dinitrogen ligands, and 2023 cm^{-1} for the bridging dinitrogen ligands. The asymmetric and symmetric vibrational modes of the terminal dinitrogen ligands are IR active, while the symmetric vibrational modes of both the terminal and bridged dinitrogen ligands are Raman active. Owing to the low π-accepting ability of Cl ligands *trans* to the axial N_2 ligand,[28] the NPA charge of terminal dinitrogen ligands of **2** (−0.18) is larger than that of **1** (−0.09). Because the NPA charge of terminal dinitrogen ligand is more negative than that of the bridging one (−0.02), terminal dinitrogen ligands are more activated. The bond dissociation free energy for a Re−N bond between the Re atom and bridging dinitrogen ligand is sufficiently high (24.7 $kcal\,mol^{-1}$) to maintain the dinuclear structure in solution.

We examined the stoichiometric reactivity of **2** toward the formation of ammonia. The 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**.[29] This result suggests the lower reactivity of dinitrogen ligands in **2** toward protonation than that in **1**.

$$\underset{\text{complex}}{\text{M-}N_2} + \underset{\text{(excess)}}{H_2SO_4} \xrightarrow[\text{rt, 24 h}]{\text{THF}} \underset{\substack{\mathbf{2},\ 0.18\ \text{equiv/Re} \\ (\text{c.f. } \mathbf{1},\ 0.61\ \text{equiv/Mo}}}{NH_3} + \underset{\substack{0\ \text{equiv/Re} \\ 0.06\ \text{equiv/Mo})}}{NH_2NH_2} \qquad (1)$$

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,e,f,22] 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 (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,h] 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 3.9 equiv of ammonia based on the rhenium atom of **2** (Table 1, entry 4). The formation of hydrazine was not observed in this reaction, while 50 equiv of dihydrogen were produced as a byproduct. Separately, we confirmed that $[NH_2NH_3]BAr^F_4$ was partially converted into ammonia in the presence of KC_8 and $[HPCy_3]BAr^F_4$ without catalyst in Et_2O at −78 °C. This result indicates that hydrazine can be converted to ammonia under the catalytic reaction conditions even if hydrazine is produced during the catalytic reaction.

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 an amount of ammonia that was comparable to that of $[HPCy_3]BAr^F_4$ (Table 1, entry 6). When larger amounts (800 equiv/Re) of the reductants and 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). Similar amounts of ammonia were obtained by using $[HPtBu_3]BAr^F_4$ and $[HPnBu_3]BAr^F_4$ as weaker and stronger proton sources, respectively (Table 1, entries 9 and 10).[3,30] To our knowledge, rhenium-dinitrogen complex **2** represents the first successful example of the rhenium-catalyzed reduction of dinitrogen into ammonia under mild reaction conditions. Additionally, we confirmed that the formation of ammonia was derived from dinitrogen using $^{15}N_2$ gas instead of $^{14}N_2$ gas and $^{15}N_2$-

labeld complex **2**-^{15}N$_2$ as a catalyst (see the Supporting Information for detail).

Next, we examined other rhenium complexes as catalysts for the reduction of dinitrogen under 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 2, entry 3). Simple rhenium complexes, such as [ReCl(CO)$_5$] and [ReI$_3$], did not exhibit catalytic activity under the same reaction conditions (Table 2, entries 4 and 5).

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

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

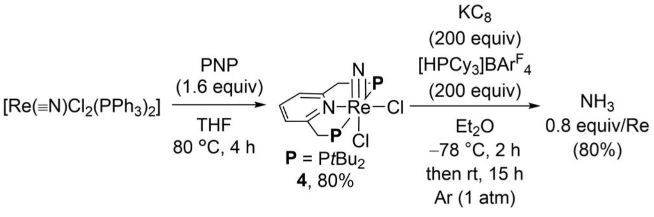
Entry	Cat.	NH$_3$[b]
1	[ReCl(N$_2$)(PNP)]$_2$(μ-N$_2$) (**2**)	8.4 ± 0.9[c]
2	[ReCl$_3$(PNP)] (**3**)	3.9 ± 0.6[d]
3	[ReCl$_3$(PPh$_3$)$_2$(MeCN)]	1.2
4	[ReCl(CO)$_5$]	0.4
5	[ReI$_3$]	0
6	[Re(≡N)Cl$_2$(PNP)] (**4**)	3.6 ± 0.7[d]

[a] A mixture of catalyst (1.0 μmol/Re), KC$_8$ (0.80 mmol, 800 equiv/Re), and [HPCy$_3$]BAr$^F_4$ (0.80 mmol, 800 equiv/Re) in Et$_2$O (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 rhenium atom of the catalyst. [c] An average of four runs. [d] An average of three runs.

To obtain information on the reaction mechanism, we investigated the reactivity of **2**. No reaction was observed upon the treatment of **2** with 1 equiv (based on the Re atom) of [HPCy$_3$]BAr$^F_4$ in Et$_2$O 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^{-1} at 195 K in Et$_2$O (see Figure S22). Owing to the low reactivity of **2** toward protonation and the weak acidity of [HPCy$_3$]$^+$,[3,30] 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 S11). The reaction of **2** with 1 equiv (based on the Re atom) of KC$_8$ in Et$_2$O at −78 °C for 1 h completely consumed **2** to form new species, which showed ν_{NN} bands at 2038 cm^{-1} 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.

When **2** was treated with 10 equiv (based on the Re atom) of KC$_8$ and 10 equiv of HOTf (based on the Re atom) in Et$_2$O at −78 °C for 2 h, a dinuclear-nitride complex bearing the dinitrogen-bridged dirhenium core was observed by mass spectrometry (Figure S15). We have carried out DFT calculations to discuss possible structures of the dirhenium core (Figure S24). In the most probable candidate of the dirhenium core, a Re^{III}-nitride unit is connected with a Re^{I}(N$_2$)(OTf) unit through the bridging dinitrogen ligand. Thus, the structure of the dirhenium core can be described as [Re(≡N)(PNP)](μ-N$_2$)[Re(N$_2$)(OTf)(PNP)]. Interestingly, in the Re-nitride unit, the nitride ligand occupies the coordination site opposite to the N atom of PNP. As a result, the dinitrogen ligand of *cis*-[Re(≡N)(N$_2$)(PNP)] bridges to *trans*-[Re(N$_2$)(OTf)(PNP)] in an end-on fashion. We previously reported dinitrogen-bridged dinuclear molybdenum dinitrogen complexes which have similar *cis*,*trans*-structures.[22a,31] The bond dissociation free energy for Re-N(bridging) bonds is estimated to be at least 27 kcal mol^{-1} at 195 K in Et$_2$O, which is high enough to maintain the dinuclear structure. These results suggest that complex **2** is converted into a dinitrogen-bridged dinuclear rhenium-nitride complex upon successive protonation and reduction during the catalytic reaction.

Because the rhenium nitride complex was detected by mass spectroscopy, we synthesized a mononuclear rhenium-nitride complex [Re(≡N)Cl$_2$(PNP)] (**4**) in 80 % yield from the reaction of [Re(≡N)Cl$_2$(PPh$_3$)$_2$] with the PNP-type pincer ligand (Scheme 3).[23] The catalytic reaction using **4** as a catalyst afforded 3.6 equiv of ammonia based on the Re atom of **4** (Table 2, entry 6). The reaction of **4** with KC$_8$ (200 equiv/Re) and [HPCy$_3$]BAr$^F_4$ (200 equiv/Re) in Et$_2$O at −78 °C for 2 h and rt for 15 h under Ar atmosphere (1 atm) gave 0.8 equiv of ammonia based on the Re atom (Scheme 3). This result indicates that the nitride ligand of **4** was converted into ammonia under the catalytic conditions.



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

We consider that the rhenium-catalyzed formation of ammonia from dinitrogen proceeds via a similar distal pathway as our previously proposed one for **1**.[28] Based on the stoichiometric reaction of **2** with the reductant and the acid, we propose that complex **2** maintains its dinitrogen-bridged dinuclear structure during the catalytic reaction. The stepwise reduction and protonation will lead to the formation of a dinuclear nitride complex as an intermediate. The nitride complex will produce ammonia by multiple reduction and protonation together with a dinuclear dinitrogen complex. We do not exclude the possibility of the reaction pathway where monomeric species works as reactive intermediates. Because some research groups have reported that the direct cleavage of the nitrogen–nitrogen triple bond occurs at a dirhenium structure,[5e,19,20] the formation of ammonia via an N$_2$ splitting pathway should be considered.

As described herein, 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. To compare the catalytic activity of **2** at low temperature, we carried out the catalytic reaction at −78 °C using **1** as a catalyst to afford 8.2 equiv of ammonia based on the Mo atom of **1** (Table 1, entry 11). This amount of ammonia produced by **1** is comparable to that produced by **2**.

We would like to discuss the difference in the catalytic activity of dimolybdenum complex **1** and dirhenium complex **2** on the basis of the reactivity toward the protonation of coordinated dinitrogen. As described in the former section, the protonation of **2** by $[HPCy_3]^+$ is highly endergonic. Figure 3 shows the MO energies of HOMO−1, HOMO, and LUMO of **1** and **2**, together with spatial distributions of these MOs of **2** (see Supporting Information for the corresponding MOs of **1**). The HOMO and HOMO−1 consisting of d orbitals of the metal atoms and π* orbitals of dinitrogen ligands play a role in the protonation step because a proton donor attacks the distal nitrogen atom of coordinated dinitrogen. Of note, the HOMO energy of **2** (−3.99 eV) is much lower than that of **1** (−3.13 eV). The low energy level of HOMO of **2** results in the large HOMO–LUMO energy gap of **2** (2.69 eV) compared to that of **1** (2.13 eV). Currently, we believe that the stabilization of HOMO of **2** can be associated with the low reactivity toward the protonation of dinitrogen coordinated to rhenium centers.

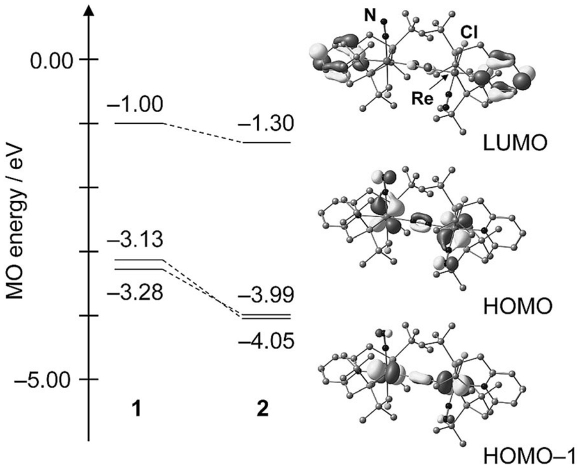


Figure 3. MO energy diagrams of the frontier orbitals of **1** and **2**.

The catalytic reduction of dinitrogen into $N(SiMe_3)_3$ was also investigated under ambient reaction conditions. We carried out the reaction 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 atmospheric pressure at room temperature for 20 h. After hydrolysis of the reaction mixture, 11.7 equiv of ammonia based on the Re atom of **2** were obtained (Table 3, entry 1). Separately, the formation of 10.3 equiv of $N(SiMe_3)_3$ based on the Re atom of **2** was confirmed by GC. 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 S16), approximately 5 equiv of $N(SiMe_3)_3$ were produced during the first 30 min, 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.

Table 3: Catalytic silylation of dinitrogen by rhenium complexes.[a]

$$\underset{(1\ \text{atm})}{N_2} + \underset{(600\ \text{equiv/M})}{6\ KC_8} + \underset{(600\ \text{equiv/M})}{6\ Me_3SiCl} \xrightarrow[\text{THF, rt, 20 h}]{\text{cat.}} 2\ N(SiMe_3)_3 \xrightarrow{H_3O^+} 2\ NH_3$$

Entry	Cat.	NH_3[b]
1	$[ReCl(N_2)(PNP)]_2(\mu\text{-}N_2)$ (**2**)	11.7 ± 1.0[c] (10.3[d])
2	$[ReCl_3(PNP)]$ (**3**)	5.7 ± 0.3[e]
3	$[Re(\equiv N)Cl_2(PNP)]$ (**4**)	5.1 ± 1.0[e]
4	$[ReCl_3(PPh_3)_2(MeCN)]$	2.7 ± 0.5[e]
5	$[ReOCl_3(PPh_3)_2]$	3.7
6	$[Re(\equiv N)Cl_2(PPh_3)_2]$	4.7
7	$[NaReO_4]$	2.4
8	$[MeReO_3]$	5.4
9	$[Re_2(CO)_{10}]$	5.0
10	$[ReI_3]$	1.9
11	Re powder	0
12	$[Mo(N_2)_2(PNP)]_2(\mu\text{-}N_2)$ (**1**)	8.4 ± 1.0[e]

[a] A mixture of catalyst (4.0 μmol/M), KC_8 (2.4 mmol, 600 equiv/M), and Me_3SiCl (2.4 mmol, 600 equiv/M) in THF (10 mL) was stirred at room temperature for 20 h under 1 atm of N_2. [b] Equiv based on the metal atom of the catalyst after acid hydrolysis of the reaction mixture. [c] An average of three runs. [d] GC yield of $N(SiMe_3)_3$. [e] An average of two runs.

Next, we examined other rhenium complexes as catalysts for the silylation of dinitrogen. Yield of $N(SiMe_3)_3$ was determined as ammonia after acid hydrolysis. Re^{III} complex **3** and Re^{V}-nitride complex **4** worked as a less efficient catalyst than **2**, producing 5.7 equiv and 5.1 equiv of ammonia, respectively (Table 3, entries 2–3). Rhenium complexes supported by PPh_3 such as $[ReCl_3(PPh_3)_2(MeCN)]$, $[ReOCl_3(PPh_3)_2]$, and $[Re(\equiv N)Cl_2(PPh_3)_2]$ afforded 2.7–4.7 equiv of ammonia (Table 3, entries 4–6). Commercially available rhenium complexes such as $Na[ReO_4]$, $[MeReO_4]$, $[Re_2(CO)_{10}]$, and $[ReI_3]$ exhibited moderate activities for nitrogen silylation (Table 3, entries 7–10), while use of Re powder as a catalyst afforded no ammonia (Table 3, entry 11). These results indicate that the PNP pincer ligand plays an important role in the catalytic activity for the reduction of dinitrogen into silylamine. Molybdenum complex **1** also worked as an efficient catalyst for the formation of silylamine (Table 3, entry 12).

In summary, we have achieved 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 a more efficient catalytic nitrogen fixation system by rhenium-dinitrogen complexes are ongoing in our laboratory.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: ammonia · homogeneous catalysis · nitrogen fixation · pincer ligands · rhenium

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[1] a) R. J. Burford, M. D. Fryzuk, *Nat. Rev. Chem.* **2017**, *1*, 26; b) Y. Nishibayashi, *Dalton Trans.* **2018**, *47*, 11290–11297; c) N. Stucke, B. M. Flöser, T. Weyrich, F. Tuczek, *Eur. J. Inorg. Chem.* **2018**, 1337–1355; d) Y. Tanabe, Y. Nishibayashi, *Coord. Chem. Rev.* **2019**, *389*, 73–93; e) M. J. Chalkley, M. W. Drover, J. C. Peters, *Chem. Rev.* **2020**, *120*, 5582–5636; f) S. Kim, F. Loose, P. J. Chirik, *Chem. Rev.* **2020**, *120*, 5637–5681; g) F. Masero, M. A. Perrin, S. Dey, V. Mougel, *Chem. Eur. J.* **2021**, *27*, 3892–3928; h) Y. Ashida, Y. Nishibayashi, *Chem. Commun.* **2021**, *57*, 1176–1189; i) S. Kuriyama, Y. Nishibayashi, *Tetrahedron* **2021**, *83*, 131986; j) Y. Tanabe, Y. Nishibayashi, *Chem. Soc. Rev.* **2021**, *50*, 5201–5242.

[2] a) T. A. Bazhenova, A. E. Shilov, *Coord. Chem. Rev.* **1995**, *144*, 69–145; b) A. E. Shilov, *Russ. Chem. Bull.* **2003**, *52*, 2555–2562.

[3] L. R. Doyle, A. J. Wooles, L. C. Jenkins, F. Tuna, E. J. L. McInnes, S. T. Liddle, *Angew. Chem. Int. Ed.* **2018**, *57*, 6314–6318; *Angew. Chem.* **2018**, *130*, 6422–6426.

[4] Y. Sekiguchi, K. Arashiba, H. Tanaka, A. Eizawa, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Angew. Chem. Int. Ed.* **2018**, *57*, 9064–9068; *Angew. Chem.* **2018**, *130*, 9202–9206.

[5] a) D. V. Yandulov, R. R. Schrock, *Science* **2003**, *301*, 76–78; b) K. Arashiba, Y. Miyake, Y. Nishibayashi, *Nat. Chem.* **2011**, *3*, 120–125; c) K. Arashiba, E. Kinoshita, S. Kuriyama, A. Eizawa, K. Nakajima, H. Tanaka, K. Yoshizawa, Y. Nishibayashi, *J. Am. Chem. Soc.* **2015**, *137*, 5666–5669; d) A. Eizawa, K. Arashiba, H. Tanaka, S. Kuriyama, Y. Matsuo, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* **2017**, *8*, 14874; e) K. Arashiba, A. Eizawa, H. Tanaka, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Bull. Chem. Soc. Jpn.* **2017**, *90*, 1111–1118; f) Y. Ashida, K. Arashiba, K. Nakajima, Y. Nishibayashi, *Nature* **2019**, *568*, 536–540; g) Y. Ashida, S. Kondo, K. Arashiba, T. Kikuchi, K. Nakajima, S. Kakimoto, Y. Nishibayashi, *Synthesis* **2019**, *51*, 3792–3795; h) Y. Ashida, K. Arashiba, H. Tanaka, A. Egi, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Inorg. Chem.* **2019**, *58*, 8927–8932.

[6] a) J. S. Anderson, J. Rittle, J. C. Peters, *Nature* **2013**, *501*, 84–87; b) S. E. Creutz, J. C. Peters, *J. Am. Chem. Soc.* **2014**, *136*, 1105–1115; c) G. Ung, J. C. Peters, *Angew. Chem. Int. Ed.* **2015**, *54*, 532–535; *Angew. Chem.* **2015**, *127*, 542–545; d) T. J. Del Castillo, N. B. Thompson, J. C. Peters, *J. Am. Chem. Soc.* **2016**, *138*, 5341–5350; e) M. J. Chalkley, T. J. Del Castillo, B. D. Matson, J. P. Roddy, J. C. Peters, *ACS Cent. Sci.* **2017**, *3*, 217–223; f) T. M. Buscagan, P. H. Oyala, J. C. Peters, *Angew. Chem. Int. Ed.* **2017**, *56*, 6921–6926; *Angew. Chem.* **2017**, *129*, 7025–7030; g) M. J. Chalkley, T. J. Del Castillo, B. D. Matson, J. C. Peters, *J. Am. Chem. Soc.* **2018**, *140*, 6122–6129; h) J. Fajardo, Jr., J. C. Peters, *Inorg. Chem.* **2021**, *60*, 1220–1227; i) S. Kuriyama, K. Arashiba, K. Nakajima, Y. Matsuo, H. Tanaka, K. Ishii, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* **2016**, *7*, 12181; j) P. J. Hill, L. R. Doyle, A. D. Crawford, W. K. Myers, A. E. Ashley, *J. Am. Chem. Soc.* **2016**, *138*, 13521–13524; k) M. J. Dorantes, J. T. Moore, E. Bill, B. Mienert, C. C. Lu, *Chem. Commun.* **2020**, *56*, 11030–11033.

[7] J. Fajardo, Jr., J. C. Peters, *J. Am. Chem. Soc.* **2017**, *139*, 16105–16108.

[8] a) T. J. Del Castillo, N. B. Thompson, D. L. M. Suess, G. Ung, J. C. Peters, *Inorg. Chem.* **2015**, *54*, 9256–9262; b) S. Kuriyama, K. Arashiba, H. Tanaka, Y. Matsuo, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Angew. Chem. Int. Ed.* **2016**, *55*, 14291–14293; *Angew. Chem.* **2016**, *128*, 14503–14507.

[9] P. Ghana, F. D. van Krüchten, T. P. Spaniol, J. van Leusen, P. Kögerler, J. Okuda, *Chem. Commun.* **2019**, *55*, 3231–3234.

[10] R. Imayoshi, K. Nakajima, Y. Nishibayashi, *Chem. Lett.* **2017**, *46*, 466–468.

[11] a) K. Shiina, *J. Am. Chem. Soc.* **1972**, *94*, 9266–9267; b) A. J. Kendall, S. I. Johnson, R. M. Bullock, M. T. Mock, *J. Am. Chem. Soc.* **2018**, *140*, 2528–2536; c) J. Yin, J. Li, G.-X. Wang, Z.-B. Yin, W.-X. Zhang, Z. Xi, *J. Am. Chem. Soc.* **2019**, *141*, 4241–4247.

[12] a) K. Komori, H. Oshita, Y. Mizobe, M. Hidai, *J. Am. Chem. Soc.* **1989**, *111*, 1939–1940; b) H. Tanaka, A. Sasada, T. Kouno, M. Yuki, Y. Miyake, H. Nakanishi, Y. Nishibayashi, K. Yoshizawa, *J. Am. Chem. Soc.* **2011**, *133*, 3498–3506; c) T. Ogawa, Y. Kajita, Y. Wasada-Tsutsui, H. Wasada, H. Masuda, *Inorg. Chem.* **2013**, *52*, 182–195; d) Q. Liao, N. Saffon-Merceron, N. Mézailles, *Angew. Chem. Int. Ed.* **2014**, *53*, 14206–14210; *Angew. Chem.* **2014**, *126*, 14430–14434; e) Q. Liao, N. Saffon-Merceron, N. Mézailles, *ACS Catal.* **2015**, *5*, 6902–6906.

[13] a) M. Yuki, H. Tanaka, K. Sasaki, Y. Miyake, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* **2012**, *3*, 1254; b) D. E. Prokopchuk, E. S. Wiedner, E. D. Walter, C. V. Popescu, N. A. Piro, W. S. Kassel, R. M. Bullock, M. T. Mock, *J. Am. Chem. Soc.* **2017**, *139*, 9291–9301; c) R. Araake, K. Sakadani, M. Tada, Y. Sakai, Y. Ohki, *J. Am. Chem. Soc.* **2017**, *139*, 5596–5606; d) Y. Ohki, Y. Araki, M. Tada, Y. Sakai, *Chem. Eur. J.* **2017**, *23*, 13240–13248; e) R. Imayoshi, K. Nakajima, J. Takaya, N. Iwasawa, Y. Nishibayashi, *Eur. J. Inorg. Chem.* **2017**, 3769–3778; f) R. B. Ferreira, B. J. Cook, B. J. Knight, V. J. Catalano, R. García-Serres, L. J. Murray, *ACS Catal.* **2018**, *8*, 7208–7212; g) A. D. Piascik, R. Li, H. J. Wilkinson, J. C. Green, A. E. Ashley, *J. Am. Chem. Soc.* **2018**, *140*, 10691–10694; h) Y. Bai, J. Zhang, C. Cui, *Chem. Commun.* **2018**, *54*, 8124–8127; i) A. Cavaillé, B. Joyeux, N. Saffon-Merceron, N. Nebra, M. Fustier-Boutignon, N. Mézailles, *Chem. Commun.* **2018**, *54*, 11953–11956; j) S. Arata, Y. Sunada, *Dalton Trans.* **2019**, *48*, 2891–2895; k) S. Li, Y. Wang, W. Yang, K. Li, H. Sun, X. Li, O. Fuhr, D. Fenske, *Organometallics* **2020**, *39*, 757–766.

[14] a) R. B. Siedschlag, V. Bernales, K. D. Vogiatzis, N. Planas, L. J. Clouston, E. Bill, L. Gagliardi, C. C. Lu, *J. Am. Chem. Soc.* **2015**, *137*, 4638–4641; b) R. Imayoshi, H. Tanaka, Y. Matsuo, M. Yuki, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Chem. Eur. J.* **2015**, *21*, 8905–8909; c) Y. Gao, G. Li, L. Deng, *J. Am. Chem. Soc.* **2018**, *140*, 2239–2250; d) T. Suzuki, K. Fujimoto, Y. Takemoto, Y. Wasada-Tsutsui, T. Ozawa, T. Inomata, M. D. Fryzuk, H. Masuda, *ACS Catal.* **2018**, *8*, 3011–3015; e) C. Sanz, C. A. M. Stein, M. D. Fryzuk, *Eur. J. Inorg. Chem.* **2020**, 1465–1471.

[15] R. Kawakami, S. Kuriyama, H. Tanaka, K. Arashiba, A. Konomi, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Chem. Commun.* **2019**, *55*, 14886–14889.

[16] M. C. Eaton, B. J. Knight, V. J. Catalano, L. J. Murray, *Eur. J. Inorg. Chem.* **2020**, 1519–1524.

[17] P. L. Arnold, T. Ochiai, F. Y. T. Lam, R. P. Kelly, M. L. Seymour, L. Maron, *Nat. Chem.* **2020**, *12*, 654–659.

[18] T. D. Lohrey, R. G. Bergman, J. Arnold, *Dalton Trans.* **2019**, *48*, 17936–17944.

[19] a) I. Klopsch, M. Finger, C. Würtele, B. Milde, D. B. Werz, S. Schneider, *J. Am. Chem. Soc.* **2014**, *136*, 6881–6883; b) I. Klopsch, M. Kinauer, M. Finger, C. Würtele, S. Schneider, *Angew. Chem. Int. Ed.* **2016**, *55*, 4786–4789; *Angew. Chem.*

2016, *128*, 4864 – 4867; c) B. M. Lindley, R. S. van Alten, M. Finger, F. Schendzielorz, C. Würtele, A. J. M. Miller, I. Siewert, S. Schneider, *J. Am. Chem. Soc.* **2018**, *140*, 7922 – 7935; d) F. Schendzielorz, M. Finger, J. Abbenseth, C. Würtele, V. Krewald, S. Schneider, *Angew. Chem. Int. Ed.* **2019**, *58*, 830 – 834; *Angew. Chem.* **2019**, *131*, 840 – 844; e) R. S. van Alten, F. Wätjen, S. Demeshko, A. J. M. Miller, C. Würtele, I. Siewert, S. Schneider, *Eur. J. Inorg. Chem.* **2020**, 1402 – 1410.

[20] Q. J. Bruch, G. P. Connor, C.-H. Chen, P. L. Holland, J. M. Mayer, F. Hasanayn, A. J. M. Miller, *J. Am. Chem. Soc.* **2019**, *141*, 20198 – 20208.

[21] J. P. Shanahan, N. K. Szymczak, *J. Am. Chem. Soc.* **2019**, *141*, 8550 – 8556.

[22] a) E. Kinoshita, K. Arashiba, S. Kuriyama, Y. Miyake, R. Shimazaki, H. Nakanishi, Y. Nishibayashi, *Organometallics* **2012**, *31*, 8437 – 8443; b) S. Kuriyama, K. Arashiba, K. Nakajima, H. Tanaka, N. Kamaru, K. Yoshizawa, Y. Nishibayashi, *J. Am. Chem. Soc.* **2014**, *136*, 9719 – 9731; c) S. Kuriyama, K. Arashiba, K. Nakajima, H. Tanaka, K. Yoshizawa, Y. Nishibayashi, *Chem. Sci.* **2015**, *6*, 3940 – 3951.

[23] Deposition Numbers 1993182 (for **2**), 1993183 (for **3**), and 1993184 (for **4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

[24] a) H. P. Gunz, G. J. Leigh, *J. Chem. Soc. A* **1971**, 2229 – 2233; b) S. L. Bartley, M. J. Bazile, Jr., R. Clérac, H. Zhao, X. Ouyang, K. R. Dunbar, *Dalton Trans.* **2003**, 2937 – 2944; c) B. Machura, M. Wolff, I. Gryca, J. Mroziński, *Polyhedron* **2011**, *30*, 354 – 363; d) D. A. Kalofolias, M. Weselski, M. Siczek, T. Lis, A. C. Tsipis, V. Tangoulis, C. J. Milios, *Inorg. Chem.* **2019**, *58*, 8596 – 8606.

[25] One of reviewers pointed out that the detailed investigation on the magnetic property of **2** is necessary. Further study on the magnetic property of **2** is on the way in our laboratory.

[26] J. L. Smeltz, P. D. Boyle, E. A. Ison, *Organometallics* **2012**, *31*, 5994 – 5997.

[27] T. B. Gunnoe, M. Sabat, W. D. Harman, *J. Am. Chem. Soc.* **1998**, *120*, 8747 – 8754.

[28] A. Egi, H. Tanaka, A. Konomi, Y. Nishibayashi, Y. Kazunari, *Eur. J. Inorg. Chem.* **2020**, 1490 – 1498.

[29] K. Arashiba, K. Sasaki, S. Kuriyama, Y. Miyake, H. Nakanishi, Y. Nishibayashi, *Organometallics* **2012**, *31*, 2035 – 2041.

[30] C. A. Streuli, *Anal. Chem.* **1960**, *32*, 985 – 987.

[31] Y. Tanabe, S. Kuriyama, K. Arashiba, Y. Miyake, K. Nakajima, Y. Nishibayashi, *Chem. Commun.* **2013**, *49*, 9290 – 9292.

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Communications

Homogeneous Catalysis

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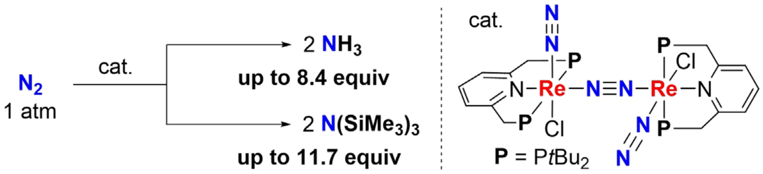
Ammonia Formation Catalyzed by a Dinitrogen-Bridged Dirhenium Complex Bearing PNP-Pincer Ligands under Mild Reaction Conditions



The first successful example of catalytic nitrogen fixation using a rhenium-dinitrogen complex as a catalyst under mild reaction conditions is described in this paper. The dinitrogen-bridged dirhenium complex worked as an effective catalyst for the formation of ammonia and silylamine, where up to 8.4 equiv of ammonia and 11.7 equiv of silylamine were produced based on the Re atom of the catalyst.