Catalytic Reduction of Dinitrogen into Ammonia and Hydrazine Using Chromium Complexes Bearing PCP-Type Pincer Ligand

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Supporting Information Placeholder

A series of chromium–halide, –nitride, and –dinitrogen complexes bearing a carbene- and phosphine-based PCP-type pincer ligand is newly prepared and some of them are found to work as effective catalysts to reduce dinitrogen under atmospheric pressure, whereby up to 8.40 equiv of ammonia and 2.46 equiv of hydrazine (13.32 equiv of fixed N atom) are produced based on the chromium atom. To the best of our knowledge, this is the first successful example of chromium-catalyzed conversion of dinitrogen to ammonia and hydrazine under mild reaction conditions.

Nitrogen is an essential element for living organisms although 78% of atmospheric air consists of dinitrogen gas, use of this gas as a nitrogen source in the synthesis of nitrogen-containing compounds is difficult, given the high stability of the nitrogen–nitrogen triple bond in dinitrogen. Therefore, the fixation of nitrogen from dinitrogen is one of the most interesting chemical reactions. Today, artificial nitrogen fixation is performed *via* the Haber–Bosch process, whereby ammonia is produced starting from dinitrogen and dihydrogen under harsh conditions, leading to much energy expenditure and substantial CO_2 emissions.[1] On the other hand, in nature, nitrogenase, an enzyme comprising molybdenum–iron multinuclear clusters as its active site, presides to a catalytic nitrogen fixation reaction occurring under ambient conditions.[2] Therefore, transition metal complexes inspired by the active site of nitrogenase have been widely investigated with the goal of achieving artificial catalytic nitrogen fixation under mild reaction conditions.[3,4] Various transition metal complexes containing molybdenum,[5-7] iron,[8-10] cobalt,[11] vanadium,[12] titanium,[13] ruthenium,[14] osmium,[14] and rhenium[15] have been reported to catalyze nitrogen fixation to produce ammonia and/or hydrazine. Quite recently, we have found that SmI_2 and simple alcohols or water used in combination acted as reductant and proton sources, respectively, to afford the high-performance formation of ammonia catalyzed by molybdenum trihalide complexes bearing pincer ligands under ambient conditions.[6d]

Nitrogen fixation catalyzed by chromium complexes has also attracted much attention, because chromium is a group-6 metal, much like molybdenum, which has displayed high catalytic activity in nitrogen fixation.[5-7] However, in contrast to molybdenum complexes, only few examples exist of chromium complexes catalyzing nitrogen fixation.[16-20] In 1972, Shiina reported the first chromium-catalyzed nitrogen fixation reaction, whereby $CrCl_3$ catalyzed the conversion of dinitrogen to $N(SiMe_3)_3$ known as the equivalent of ammonia.[17] After the publication of Shiina's report, no chromium-catalyzed nitrogen fixation reactions were reported until 2018, when Mock and co-workers reported the catalytic $N(SiMe_3)_3$ formation achieved using chromium–dinitrogen complexes as catalysts.[19a] Recently, Xi's[19b] and Murray's[19c] groups also reported that multinuclear chromium–dinitrogen complexes displayed catalytic activity in the formation of $N(SiMe_3)_3$. Although catalytic reduction of dinitrogen to $N(SiMe_3)_3$ using chromium complexes has been reported, examples whereby dinitrogen was reduced to ammonia have been limited only to stoichiometric reactions.[19a,20]

In the present study, we have achieved the chromium-catalyzed formation of ammonia and hydrazine from dinitrogen under mild reaction conditions. In this reaction course, chromium complexes bearing a phosphine- and carbene-based PCP-type pincer ligand (PCP = 1,3-bis((di-*tert*-butylphosphino)methyl)benzimidazol-2-ylidene) worked as efficient catalysts in the presence of KC_8 acting as reductant and phosphonium salts as proton sources. To the best of our knowledge, this is the first reported example of the chromium-catalyzed conversion of dinitrogen at atmospheric pressure to ammonia.

First, we synthesized chromium complexes bearing the PCP-type pincer ligand, which proved the most effective ligand in the molybdenum-catalyzed conversion of dinitrogen to ammonia.[6d] The reaction of $CrCl_2$ with the benzimidazolium salt of PCP in tetrahydrofuran (THF) at room temperature over the course of 20 h produced [$CrCl_2(PCP)$] (**1a**) in 59% yield (Scheme 1). We then transformed **1a** into a range of different complexes. Ligand exchange in **1a** in the presence of an excess amount of NaI proceeded smoothly to afford [$CrI_2(PCP)$] (**1b**
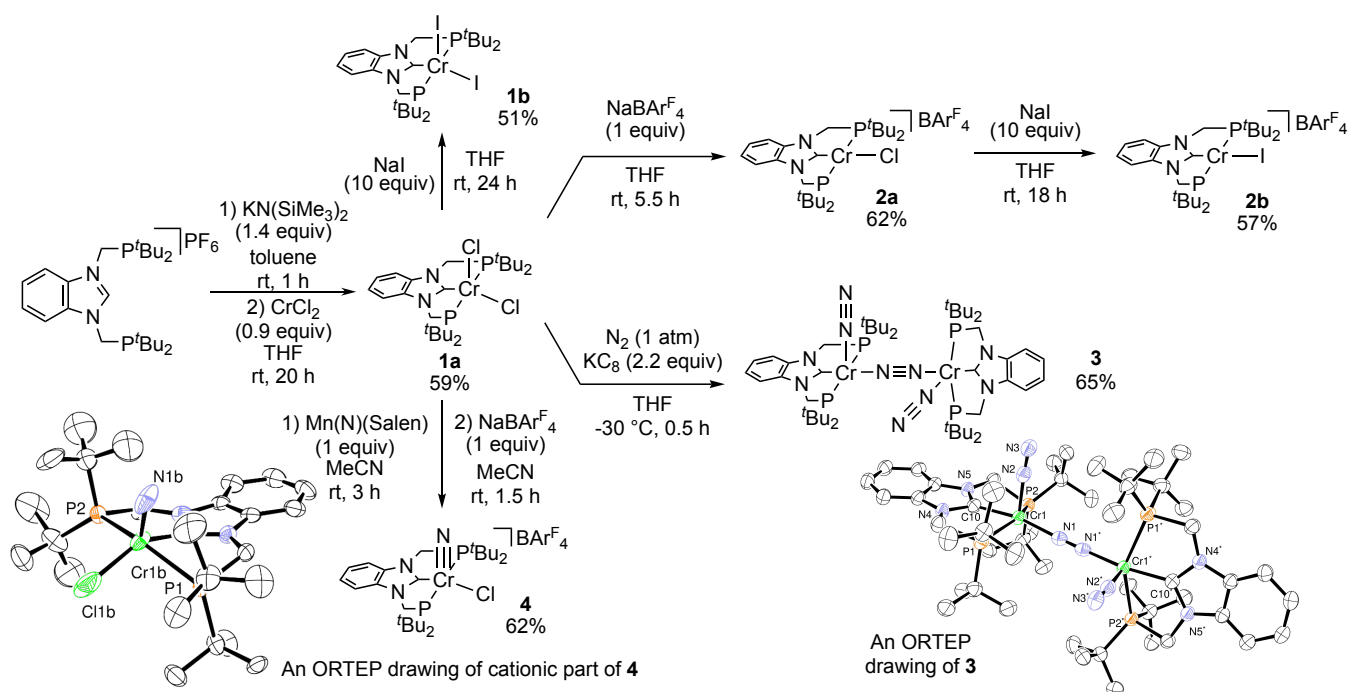
Scheme 1. Synthesis of Chromium Complexes and ORTEP Drawings.

in 51% yield. By contrast, the reaction of **1a** with 1 equiv of NaBAr$^F_4$ (Ar^F = 3,5-bis(trifluoromethyl)phenyl) gave the corresponding cationic chromium complex [CrCl(PCP)]BAr$^F_4$ (**2a**). Notably, the crystal structure of **2a** is characterized with a distorted square-planar geometry around the chromium atom; the value of the geometry index τ_4 for this structure was 0.18; indeed, τ_4 ranges from 0.00, corresponding to an ideal square-planar geometry, to 1.00, corresponding to an ideal tetrahedral geometry.[21] The chloride ligand of **2a** could be exchanged with an iodide ligand as a result of the reaction of **2a** with an excess amount of NaI to give the corresponding iodide complex [CrI(PCP)]BAr$^F_4$ (**2b**). **1a**, **1b**, **2a**, and **2b** were observed to have values for the solution magnetic moments of 4.5 μ_B, 5.1 μ_B, 5.4 μ_B, and 4.8 μ_B (as measured by Evans method[22]), respectively, which indicate that these complexes are characterized by a S = 2 spin state (4.9 μ_B) (see Supporting Information).

In order to obtain the corresponding chromium–dinitrogen complex, we carried out reduction of **1a** under dinitrogen. The reaction of **1a** with 2 equiv of KC$_8$ in THF at -30 °C for 0.5 h under 1 atm of dinitrogen gave a dark purple solution. After recrystallization from THF-pentane at -30 °C, the corresponding dinitrogen-bridged dichromium complex [Cr(N$_2$)(PCP)]$_2$(μ-N$_2$) (**3**) was obtained as a brown crystalline solid in 65% yield (Scheme 1). IR spectrum of **3** showed a strong absorption attributable to ν(NN) band at 1897 cm^{-1}. The detailed structure of **3** was unambiguously determined by X-ray crystallography. An ORTEP drawing is shown in Scheme 1. The chromium centers in **3** have a square pyramidal geometry with PCP, terminal dinitrogen, and bridging dinitrogen ligands. The [Cr(N$_2$)(PCP)] fragments are bridged by a dinitrogen ligand with an end-on fashion.

Next, the corresponding chromium–nitride complex was prepared from **1a** (Scheme 1). The reaction of **1a** with the manganese–nitride complex [Mn(N)(salen)] (salen = *N,N*'-bis(2-hydroxybenzylidene)ethylenediamine) proceeded *via* a nitride

transfer reaction,[23] which was followed by an anion exchange with NaBAr$^F_4$, resulting in the formation of the cationic chromium–nitride complex [CrCl(N)(PCP)]BAr$^F_4$ (**4**) in 62% yield. The detailed structure of **4** was unambiguously determined by X-ray crystallography (Scheme 1).

The catalytic reduction of dinitrogen to produce ammonia using these chromium complexes was carried out under the reported conditions of catalytic nitrogen fixation.[6d,8,10,13] The reaction with 36 equiv of SmI$_2$ and 36 equiv of water with respect to the chromium-based catalyst in the presence of **4** under atmospheric pressure of dinitrogen in THF at room temperature for 20 h afforded 0.52 equiv of ammonia based on the chromium atom (Table 1, run 1). The analogous reaction conducted with 40 equiv of CoCp*$_2$ (Cp* = η^5-C$_5$(CH$_3$)$_5$), acting as a reductant, and 36 equiv of [Ph$_2$NH$_2$]OTf (OTf = OS(O)$_2$CF$_3$), acting as a proton source, at −78 °C for 2 h afforded 0.61 equivalents of ammonia based on the chromium atom (Table 1, run 2). The combination of KC$_8$ and [H(Et$_2$O)$_2$]BAr$^F_4$ as a reductant and proton source, respectively, also yielded a stoichiometric amount of ammonia and a small amount of hydrazine as a minor product (Table 1, run 3). On the other hand, the reaction conducted under the conditions reported by Liddle,[13] whereby KC$_8$ and [PCy$_3$H]I were used as reagents, afforded 4.15 equiv of ammonia and 0.09 equiv of hydrazine (4.33 equiv of fixed N atom) based on the chromium atom, respectively (Table 1, run 4). Notably, the efficiency of the catalytic reaction was observed to depend on the counter-anion of the phosphonium salt. Although [PCy$_3$H]Cl did not work as an effective proton source, [PCy$_3$H]OTf, [PCy$_3$H]BAr$^F_4$, and [PCy$_3$H]BF$_4$ performed well the said role. In fact, use of [PCy$_3$H]BF$_4$ as a proton source gave the best results, with 5.26 equiv of ammonia and 0.04 equiv of hydrazine (5.34 equiv of fixed N atom) produced based on the chromium atom (Table 1, runs 5–8).

Table 1. Catalytic Reduction of N₂ to NH₃ and N₂H₄ Using Chromium Complexes.[a]

$$N_2 \ + \ e^- \ + \ H^+ \xrightarrow[\substack{Et_2O \\ -78\,°C\ to\ rt \\ 1\ h\ to\ 1\ h}]{Cr\ catalyst} NH_3 \ + \ N_2H_4 \quad \left(+\ H_2\right)$$

1 atm   reductant   proton source

40 equiv/Cr   36 equiv/Cr

run	Cr catalyst	reductant	proton source	NH₃ (equiv/Cr)	N₂H₄ (equiv/Cr)	fixed nitrogen atom (equiv/Cr)	H₂ (equiv/Cr)
1[b]	**4**	SmI₂	H₂O	0.52	0	0.52	0.92
2[c]	**4**	CoCp*₂	[Ph₂NH₂]OTf	0.61	0	0.61	5.98
3	**4**	KC₈	[H(Et₂O)₂]BAr$^F_4$	1.68	0.08	1.84	5.95
4	**4**	KC₈	[PCy₃H]I	4.15	0.09	4.33	3.36
5	**4**	KC₈	[PCy₃H]Cl	1.24	0.2	1.64	2.09
6	**4**	KC₈	[PCy₃H]OTf	3.84	0.01	3.86	4.87
7	**4**	KC₈	[PCy₃H]BAr$^F_4$	2.98	0.21	3.4	5.42
8	**4**	KC₈	[PCy₃H]BF₄	5.26	0.04	5.34	1.57
9	**1a**	KC₈	[PCy₃H]I	0.77	0.13	1.03	1.75
10	**1b**	KC₈	[PCy₃H]I	0.95	0.18	1.31	2.01
11	**2a**	KC₈	[PCy₃H]I	1.06	0.09	1.24	3.45
12	**3**	KC₈	[PCy₃H]I	0.66	0	0.66	0.6
13	**2b**	KC₈	[PCy₃H]I	5.12	0.9	6.92	1.18
14	**2b**	KC₈	[PCy₃H]BF₄	4.87 ± 0.39^d	1.07 ± 0.50^d	7.01	2.01 ± 0.27^d
15[e]	**2b**	KC₈	[PCy₃H]BF₄	8.40 ± 3.25^d	2.46 ± 1.21^d	13.3	16.3 ± 4.5^d

[a]A mixture of Cr complex (0.01 mmol), reductant (0.40 mmol, 40 equiv based on the Cr atom) and proton source (0.36 mmol, 36 equiv based on the Cr atom) in Et₂O (5 mL) at −78 °C was stirred for 1 h under 1 atm of dinitrogen, followed by stirring at room temperature for another 1 h. [b]To a mixture of Cr complex (0.01 mmol) and SmI₂(THF)₂ (0.36 mmol, 36 equiv based on the Cr atom) in the THF (5.0 mL) was added the THF solution (1 mL) containing water (0.36 mmol, 36 equiv based on the Cr atom) in one portion at room temperature, followed by stirring at room temperature for 20 h under 1 atm of dinitrogen. [c]The reaction time is 1 h at −78 °C and 19 h at room temperature. [d]The values were determined as the mean of multiple individual experiments (at least two) with error bars (s.d.). [e]The larger amounts of KC₈ (200 equiv based on the Cr atom) and [PCy₃H]BF₄ (180 equiv based on the Cr atom) were used.

Next, reactions conducted in the presence KC₈ and [PCy₃H]I using various chromium complexes were investigated. The neutral chromium(II) dihalide complexes **1a** and **1b**, the cationic chromium(II) chloride complex **2a**, and the dinitrogen-bridged dichromium(0) complex **3** did not work well as catalysts (Table 1 runs 9–12). We consider that no catalytic activity of **3** is due to the low solubility of **3** in diethyl ether (Et₂O). However, the reaction whereby the cationic chromium(II) iodide complex **2b** was used as a catalyst yielded 5.12 equiv of ammonia based on the chromium atom and 0.90 equiv of hydrazine (6.92 equiv of fixed N atom) (Table 1, run 13). Finally, the amount of nitrogen atoms undergoing fixation reached a value of 7.01 equiv based on the chromium atom in the reaction conducted in the presence of KC₈ and [PCy₃H]BF₄, using **2b** as catalyst; in this case, 4.87 equiv of ammonia and 1.07 equiv of hydrazine were produced, based on the catalyst (Table 1, run 14). Notably, by conducting the catalytic reaction in the presence of larger amounts of KC₈ and [PCy₃H]BF₄ using **2b** as a catalyst, up to 8.40 equiv of ammonia and 2.46 equiv of hydrazine

(13.32 equiv of fixed N atom) were obtained based on the chromium atom (Table 1, run 15). Separately, we confirmed the direct conversion of molecular dinitrogen to ammonia and hydrazine when **2b** was used a catalyst in a reaction conducted under atmospheric pressure of ¹⁵N₂ gas, in place of the regular ¹⁴N₂ gas (see Supporting Information).

In order to gain insight into the reaction mechanism, a stoichiometric reaction of **4** was carried out. The reaction of **4** with 6 equiv of KC₈ and 5 equiv of [PCy₃H]BF₄ in Et₂O at −78 °C for 2 h under argon atmosphere produced ammonia in 83% yield based on the nitride ligand in **4** without the formation of hydrazine (Scheme 2). Although ammonia may form from the chromium–nitride complexes acting as reactive intermediates in the catalytic reactions, hydrazine detected in the catalytic reactions is confirmed not to be produced via chromium–nitride complexes.

4 + KC$_8$ + [PCy$_3$H]BF$_4$ $\xrightarrow[\substack{\text{Et}_2\text{O} \\ -78\,°\text{C to rt} \\ \text{1 h to 1 h}}]{\text{Ar (1 atm)}}$ NH$_3$ + N$_2$H$_4$

6 equiv/Cr   5 equiv/Cr   83%   0%

Scheme 2. Stoichiometric Reaction of Chromium–Nitride Complex.

The isolation of chromium-dinitrogen complex such as **3** and the conversion of dinitrogen to ammonia and hydrazine catalyzed by **2b** might be reminiscent of the reactivity of planar four-coordinate Fe and Co complexes bearing a pyrrole-based PNP-pincer ligand (Scheme 3).[9a,11] We previously reported

cat.	[Fe(N$_2$)(PNP)]	[Co(N$_2$)(PNP)]	**5**
NH$_3$ (equiv/cat.)	14.3	15.9	8.40
N$_2$H$_4$ (equiv/cat.)	1.8	1.0	2.46

Scheme 3. Catalytic Activity of M–N$_2$ Complexes (M = Fe,[9a] Co[11]) and a Possible Cr–N$_2$ Complex.

that these metal–N$_2$ complexes served as catalysts for the conversion of dinitrogen to ammonia and hydrazine.[9a,11] Based on previously reported findings, we would like to propose the planar four-coordinate Cr–N$_2$ complex [Cr(N$_2$)(PCP)] (**5**) as an active dinitrogen species and discuss possible reaction pathways for the formation of **5** from **2b** with the aid of DFT calculations at the B3LYP-D3 level of theory (see Supporting Information). The ΔG_{195} value of the reaction **2b** + N$_2$ + 2e$^-$ → **5** + I$^-$ is calculated to be +0.3 kcal/mol in Et$_2$O, indicating that, from a thermodynamic standpoint, the formation of **5** is likely to occur.

Figure 1 shows free energy profiles of three possible pathways for the transformation of **2b** into **5** involving two-electron reduction, coordination of N$_2$, and release of I$^-$. In **Path A**, a dinitrogen molecule coordinates to [Cr^{II}(I)]$^+$ **2b** (**Cr** = [Cr(PCP)]), and then the five-coordinate Cr^{II}–N$_2$ complex **6** is reduced by two electrons. However, a large positive value of ΔG_{195} for **2b** → **6** (+30.7 kcal/mol) indicates that the N$_2$ coordination to the

Figure 1. Free Energy Profiles (ΔG_{195} in kcal/mol) of Three Possible Reaction Pathways for Transformation of 2b to 5.

Cr^{II} center is thermodynamically unfavorable. In **Paths B** and **C**, reduction of **2b** is exergonic by 10.1 kcal/mol. The four-coordinate Cr^I complex [Cr^I(I)] **7** undergoes N$_2$ coordination and reduction to afford the five-coordinate Cr^0 complex [Cr^0(N$_2$)(I)]$^-$ **10**. These two steps are totally endergonic by 18.1 kcal/mol. In the final step, the release of I$^-$ from **10** yields the Cr^0–N$_2$ complex **5** ($\Delta G_{195} = -7.7$ kcal/mol). Protonation of **5** by [PCy$_3$H]$^+$ will smoothly proceed at 195 K ($\Delta G_{195} = -4.8$ kcal/mol and $\Delta G^{\ddagger} = 0.8$ kcal/mol (see Figure S14 in Supporting Information). At present, **Path B** could be the most probable pathway, because it comprises no highly endergonic reaction steps.

We also theoretically examined the possibility of direct N≡N bond cleavage of N$_2$ by two Cr cores. In our previous works on catalytic ammonia formation using molybdenum complexes bearing the same pincer-type ligand,[6c,6d,24] the direct N≡N bond cleavage of [Mo^I(PNP)]$_2$(μ-N$_2$) (PNP = 2,6-bis((di-*tert*-butylphosphinomethyl)pyridine) was proposed as a key reaction step. Figure 2 presents a free energy profile at 195 K calculated for the direct N≡N bond cleavage of a dinitrogen-bridged dichromium complex [Cr^I(I)(PCP)]$_2$(μ-N$_2$) **11**, a structural analog of [Mo^I(PNP)]$_2$(μ-N$_2$). The ground spin state of complex **11** is a high-spin septet, while both the resulting Cr–nitride complex [Cr^{IV}I(N)(PCP)] **12** and the transition state **TS$_{11/12}$** connecting **11** and **12** favor the lowest spin state. We were not able to optimize **TS$_{11/12}$** at the quintet and septet states. As a result, the direct N≡N cleavage of **11** is highly endergonic ($\Delta G_{195} = 46.9$ kcal/mol) with an extremely high activation free energy (at least 81.2 kcal/mol). Thus, we can exclude the reaction mechanism via the direct N≡N bond cleavage of N$_2$ in the Cr-catalytic system (see Supporting Information for a proposed reaction pathway in Scheme S1).

Figure 2. Free Energy Changes (ΔG_{195} in kcal/mol) in the N≡N Bond Cleavage of 11 Yielding a Couple of 12.

In summary, we have found the chromium-catalyzed reduction of dinitrogen into ammonia and hydrazine under mild reaction conditions. The use of the chromium complexes bearing a PCP-type pincer ligand provides the first successful example of the catalytic and direct conversion of dinitrogen into ammonia and hydrazine, in contrast to well studies on the catalytic formation of silylamine using chromium-dinitrogen complexes bearing other ligands. Further investigation on the mechanistic study to elucidate the reaction pathway and the development of more effective chromium catalysts is now in progress.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

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Notes
The authors declare no competing financial interest.

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$$N_2 \; + \; KC_8 \; + \; [PCy_3H]BF_4 \xrightarrow[-78\ °C]{\text{cat. Cr}} NH_3 \; + \; N_2H_4$$

1 atm · reducing reagent · proton source · up to 13.3 equiv/Cr fixed nitrogen atom

cat. Cr

$[\text{Cr}-\text{I}]\ BAr^F_4$ (benzimidazole-diphosphine P^tBu_2 / P^tBu_2 Cr–I complex)

$[\text{N}\equiv\text{Cr}-\text{Cl}]\ BAr^F_4$ (benzimidazole-diphosphine P^tBu_2 / P^tBu_2 Cr–Cl complex)