Homogeneous Catalysis

Cobalt-Catalyzed Transformation of Molecular Dinitrogen into Silylamine under Ambient Reaction Conditions

Ryuji Imayoshi,^[a] Hiromasa Tanaka,^[b] Yuki Matsuo,^[c] Masahiro Yuki,^[a] Kazunari Nakajima,^[a] Kazunari Yoshizawa,^{*[b, c]} and Yoshiaki Nishibayashi^{*[a]}

Abstract: The first successful example of cobalt-catalyzed reduction of N_2 with Me₃SiCl and Na as a reductant, under ambient reaction conditions, gives $N(SiMe_3)_3$, which can be readily converted into NH₃. In this reaction system, 2,2'-bipyridine (bpy) is found to work as an effective additive to

Introduction

Various transition metal–dinitrogen complexes have been synthesized and the stoichiometric transformation of coordinated N₂ has been intensively studied over the past few decades. However, there are only limited examples of the catalytic conversion of N₂ into NH₃.^[1,2] In 2003, Schrock and Yandulov reported the first example of the catalytic formation of NH₃ from N₂ under ambient reaction conditions using a Mo–N₂ complex bearing a triamidoamine ligand.^[3] In 2010, our group reported that N₂-bridged Mo₂—N₂ complexes bearing PNP-type pincer ligands worked as the most effective catalysts for the catalytic formation of NH₃ from N₂.^[4] More recently, Peters and co-workers reported Fe-catalyzed conversion of N₂ into NH₃ at an extremely low reaction temperature.^[5-7]

Transition metal-catalyzed transformation of N_2 into $N(SiMe_3)_3$ (1) has been known as an alternative nitrogen fixation method, because 1 can be quantitatively converted into NH_3 upon hydrolysis. In 1972, Shiina discovered that 1 was formed from N_2 , Me_3SiCl , and Li in the presence of transition metal chlorides such as CrCl₃ as catalysts at room temperature.^[8] However, in this reaction system, the possibility of generating Li₃N, which serves as a reactive intermediate, cannot be ruled out completely. In 1989, Hidai and co-workers developed Mo-catalyzed conversion of N_2 into 1 using Na as a reduc-

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 - Supporting information for this article is available on the WWW under

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201501088. improve substantially the catalytic activity. $Co-N_2$ complexes bearing three Me₃Si groups as ancillary ligands are considered to work as key reactive species based on DFT calculations. The DFT results also allow the proposal of a detailed reaction pathway for the transformation of N₂ into N(SiMe₃)₃.

tant and $[Mo(N_2)_2(PMe_2Ph)_4]$ as a catalyst.^[9] More recently, we reported that *trans*- $[Mo(N_2)_2(depf)_2]$ (depf = 1,1'-bis(diethyl-phosphino)ferrocene) exhibited an unusually high catalytic activity,^[10] and that even some simple Fe complexes, such as $[Fe(CO)_5]$ and ferrocenes, worked as effective catalysts.^[11] In both Mo and Fe reaction systems, we have elucidated the detailed reaction pathway by DFT calculations. Quite recently, other Mo–N₂ or Fe–N₂ complexes were found to promote the transformation of N₂ into 1.^[7,12-14]

Almost all of the aforementioned catalytic systems for the formation of NH₃ and **1** depend on the use of either Mo or Fe complexes as catalysts. Furthermore, Shilov and co-workers previously reported the catalytic reduction of N₂ into NH₂NH₂ by using a polynuclear Mo complex as a catalyst.^[15] It is well known that MoFe nitrogenase promotes the reduction of N₂ into NH₃ under ambient reaction conditions, where the active site of the nitrogenase contains Fe and Mo atoms as a FeMo cofactor.^[16] These findings indicate that the reaction systems to convert N₂ catalytically into NH₃ under mild reaction conditions are limited to the use of Mo or Fe complexes as catalysts.

As an attractive alternative to Fe and Mo, we have studied the use of Co complexes because Co is a widely and cheaply available earth-abundant first-row transition metal.^[17] Notably, $[COH(N_2)(PPh_3)_3]$ was the first transition metal–dinitrogen complex to be directly derived from N₂.^[18] Despite this successful early preparation of a Co–N₂ complex, few examples of the transformation of Co-coordinated N₂ have since been reported.^[19,20] We report herein the Co-catalyzed transformation of N₂ into 1 under ambient reaction conditions. To our knowledge, this is the first successful example of Co-catalyzed transformation of N₂ under mild reaction conditions.

Results and Discussion

During our study on the development of transition metal-catalyzed reduction of N_2 under mild reaction conditions, we found that some cobalt complexes worked as effective cata-

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Table 1. Cobalt-catalyzed transformation of N_2 into $N(SiMe_3)_3$ (1)								
1 atm N ₂ + 6 M + 6 Me ₃ SiCI (30 mmol) (30 mmol) DME (20 mL) temp,time 1 1 N(SiMe ₃) ₃ +6 MCI								
Entry	Catalyst ^[a]	Reductant M	Т	t [h]	1 [mmol] ^[b]	1 [equiv] ^[c]		
1	[Co ₂ (CO) ₈]	Na	RT	20	1.12	22 ^[d]		
2	[Co ₂ (CO) ₈]	Na	RT	40	1.78	36		
3	$[Co_2(CO)_8]$	Na	60 °C	20	0.57	11		
4	[Co ₂ (CO) ₈]	Li	RT	20	0.35	7		
5 ^[e]	[Co ₂ (CO) ₈]	Na	RT	20	0	0		
6	none	Na	RT	20	0	0		
7	[Co(SiMe ₃)(CO) ₄]	Na	RT	20	1.71	34		
8	[Co(SiMe ₃)(CO) ₄]	Na	RT	48	1.81	36		
9	[CpCo(CO) ₂]	Na	RT	40	1.45	29		
10	[Cp ₂ Co]	Na	RT	40	0.39	8		
11	CoCl ₂	Na	RT	20	0	0		
12	$[(Co{N(SiMe_3)_2}_2)_2]$	Na	RT	20	0	0		
[a] 0.050 mmol of catalyst (based on Co atom) was used. [b] Determined by GC. [c] Per Co atom of the catalyst. [d] 21 equivalents of ammonia per Co atom were produced after acid hydrolysis of the reaction mixture								

under the same reaction conditions. [e] Under Ar (1 atm).

lysts for the transformation of N₂ into 1 under ambient reaction conditions. Typical results are summarized in Table 1. A mixture of [Co₂(CO)₈] (0.025 mmol; 0.050 mmol based on Co), Na (30 mmol), Me₃SiCl (30 mmol), and 1,2-dimethoxyethane (DME; 20 mL) was stirred at room temperature under an atmospheric pressure of N₂ for 20 h and the formation of 22 equivalents of 1, based on Co, was observed (11% yield based on Na and Me₃SiCl; Table 1, entry 1). Separately, we confirmed the formation of 21 equivalents of NH₃ based on the Co atom of the catalyst after acid hydrolysis of the reaction mixture under the same reaction conditions. When the reaction was carried out for a longer time (t=40 h), an increased amount of 1 was obtained (36 equivalents of 1 based on Co; 18% yield based on Na and Me₃SiCl; Table 1, entry 2).^[21] The reaction at a higher temperature ($T = 60 \degree C$), gave a lower amount of 1 (Table 1, entry 3). Replacement of Na with Li resulted in a decreased amount of 1 (Table 1, entry 4). We confirmed that 1 was not formed in the absence of either N_2 or [Co₂(CO)₈] (Table 1, entries 5 and 6). These results indicate that the use of both N₂ and the cobalt catalyst is essential to promote the catalytic reaction.

When $[Co(SiMe_3)(CO)_4]$ was employed in place of $[Co_2(CO)_8]$, the reaction took place more smoothly (Table 1, entries 7 and 8). Other Co complexes, such as $[CpCo(CO)_2]$ and $[Cp_2Co]$, also worked as catalysts (Table 1, entries 9 and 10). No formation of 1 took place when $CoCl_2$ was used as a catalyst (Table 1, entry 11), and $[(Co{N(SiMe_3)_2}_2)_2]$ did not work as an effective catalyst either (Table 1, entry 12). The nature of the solvent is another important factor to promote the catalytic reaction. Tetrahydrofuran (THF) was found to be less effective than DME, whereas no formation of 1 was observed in other solvents, such as diethyl ether, 1,4-dioxane, benzene, and hexane (see the Supporting Information for details).

Although we have attempted to identify experimentally the reactive species in the present reaction, we have not succeeded in isolating or observing any $Co-N_2$ species from the reac-

tion mixture. To rule out the possibility that Co nanoparticles generated in situ from Co complexes worked as heterogeneous catalysts in the present reaction, we carried out the following Hg- and guantitative-poisoning tests. Both poisoning tests have been widely used to distinguish homogeneous catalysis from heterogeneous.^[22] Generally, Hg is considered to inhibit heterogeneous metal catalysis by forming an amalgam. Although cobalt is not known to form the corresponding stable amalgam with Hg, heterogeneous cobalt catalysis can be inhibited by the addition of Hg in some reaction systems.^[23,24] In the present reaction, the addition of an excess amount of Hg did not inhibit the conversion of N_2 into **1** in the reaction using a catalytic amount of $[Co_2(CO)_8]$. On the other hand, in the quantitative poisoning test, using PMe₂Ph as a poison, the addition of 2 equivalents of PMe₂Ph for each Co atom of the catalyst was required to significantly suppress the formation of 1 under the same reaction conditions.^[25] Results of both poisoning tests strongly show that homogeneous cobalt complexes worked as the true active catalysts in the present reaction.

Previously, we proposed that Fe-N2 complexes bearing two Me₃Si groups are generated in situ from [Fe(CO)₅], Na, and Me₃SiCl as key reactive intermediates in the Fe-catalyzed transformation of N₂ into 1.^[11] In fact, two Fe–N₂ complexes [Fe(Si- $Me_{3}_{2}(N_{2})(thf)$] (A) and $[Fe(SiMe_{3})_{2}(N_{2})CI]$ (B) were proposed, based on DFT calculations. By comparing the present Co-catalyzed reaction with the Fe-catalyzed one, some similarities between Fe and Co catalysts are present. First, simple metal carbonyl complexes ([Fe(CO)₅] and [Co₂(CO)₈]) and metallocenes ([Cp₂Fe] and [Cp₂Co]) worked as effective catalysts. Second, metal chlorides MCl₂ and metal silylamide complexes $[(M{N(SiMe_3)_2}_2)_2]$ (M = Fe or Co) did not show any catalytic activity. From these experimental results, we consider that the reactive species in the present Co-catalyzed reaction may have a similar structure to **A** and **B**; namely, Co–N₂ complexes bearing SiMe₃ groups as ligands. In fact, after careful DFT calculations of a variety of possible Co-N₂ complexes, we found that a Co^{II}-N₂ complex bearing two SiMe₃ groups and a DME



Figure 1. Molecular structures of C and D based on DFT calculations. BE=Bond energy (Co- N_2).

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ligand, five-coordinated complex [Co(SiMe₃)₂(dme)(N₂)] (**C**; Figure 1) was most plausible. The N–N stretching frequency (ν_{NN}) of **C** was calculated to be 2104 cm⁻¹. The coordinated N₂ on the Co atom is weakly activated compared to a free N₂ molecule (ν_{NN} = 2325 cm⁻¹).

Taking into account the result of DFT calculations, we next tried to design more reactive Co–N₂ complexes. We chose 2,2'bipyridine (bpy) as a possible ligand because bpy is considered to work as a more electron-donating bidentate ligand than DME. The most plausible structure based on DFT calculations was found to be a Co^{III} –N₂ complex bearing three SiMe₃ groups and a bpy ligand, six-coordinated [Co(SiMe₃)₃(bpy)(N₂)] (**D**; Figure 1). Complex **D** has a larger Co–N₂ bond energy (13.6 kcal mol⁻¹) than the five-coordinated [Co(SiMe₃)₂(bpy)(N₂)] (9.3 kcal mol⁻¹). In the presence of bpy as an ancillary ligand, the Co center ligates three SiMe₃ groups. The N₂ ligand coordinating to the Co^{III} center in **D** is also weakly activated (v_{NN} = 2117 cm⁻¹). These results indicate that **D** may work as a more effective catalyst than **C** or [Co(SiMe₃)₂(bpy)(N₂)] in the present catalytic reaction.

Since the Co^{III} complex bearing three silyl groups as ancillary ligands had not to date been reported, we attempted to pre-



Scheme 1. Preparation and ORTEP representation of 2.

pare this complex by the reaction shown in Scheme 1 and succeeded in isolating the new complex $2^{[26]}$ A detailed structure of the six-coordinate complex 2 was confirmed by X-ray analysis.^[27] We believe that the isolation of this Co^{III} complex bearing three silyl groups may support the proposal that a Co^{III}–N₂ complex such as **D** may work as a more efficient catalyst, although we have not yet isolated the corresponding Co–N₂ complex.

With this assumption in mind, we investigated the effect of bpy additive to $[Co_2(CO)_8]$ under the same reaction conditions. Addition of 1 equivalent of bpy per Co atom led to an increased yield of 1; 49 equivalents of 1 were produced per Co atom of the catalyst (25% yield based on Na and Me₃SiCl;

1 atm N ₂ + 6 Na + 6 Me ₃ SiCl (30 mmol) (30 mmol)	[Co ₂ (CO) ₈] (0.025 mmol) bpy (0.050 mmol) DME (20 mL) RT, 40 h	2 N(SiMe ₃) ₃ + 6 NaCl 1 (2.45 mmol; 49 equiv based on Co)
		based on Co)

Scheme 2. Cobalt-catalyzed transformation of $N_{\rm 2}$ into 1 in the presence of bpy.

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Figure 2. Time profiles of the formation of $N(SiMe_3)_3$ (1) from N₂ in the presence of bpy (0.050 mmol; solid line) and in the absence of bpy (dashed line).

Scheme 2), and this was revealed to be the most effective reaction system for the formation of 1 from N₂ by using a cobalt complex as a catalyst.^[28] Time profiles of the catalytic formation of 1 in the presence or absence of bpy are shown in Figure 2. The result indicates that the reaction in the presence of bpy as an additive proceeded more smoothly for the formation of 1. In both cases, there was an induction period of approximately 1 h, probably due to the time for the formation of reactive species such as **C** and **D** under the present reaction conditions. To obtain further evidence for the proposed Co complexes bearing bpy as an ancillary ligand, we carried out the catalytic reaction by using some Co–bpy complexes as catalysts. [Co(bpy)₃] [{Co(CO)₄}₂] (**3**), prepared from the reaction of [Co₂(CO)₈] with 2 equivalents of bpy,^[29] [Co(bpy)₃]Cl₂ (**4**), and [Co(bpy)Cl₂] (**5**) were all found to have similar catalytic activities in the forma-

Table 2. Catalytic transformation of N_2 into $N(SiMe_3)_3$ (1) by using cobalt complexes bearing bpy ligand							
1 atm N ₂ + 6 Na + 6 Me ₃ SiCl (30 mmol) (30 mmol) RT, 20 h 1 ct. [Co] 2 N(SiMe ₃) ₃ + 6 NaCl 1 ct. [Co] 2 N(SiMe ₃) ₃ + 6 NaCl							
Cobalt catalyst ^[a]	1 [mmol] ^[b]	1 [equiv] ^[c]					
$[Co_2(CO)_8] + 2 bpy$ $[Co(bpy)_2][{Co(CO)_4}] (3)$	2.01	40 34					
$[Co(bpy)_3]Cl_2 (4)$ $[Co(bpy)Cl_2] (5)$	1.13 1.29	23 26					
[a] 0.050 mmol of catalyst (based on Co atom) was used. [b] Determined by GC. [c] Per Co atom of the catalyst.							

tion of 1 from N_2 (Table 2). These results show that Co complexes bearing bpy ligands may be involved as key reactive species in the reaction shown in Scheme 2.

A proposed catalytic cycle for the Co-catalyzed transformation of N₂ into **1** in the presence of bpy is shown in Scheme 3. At first, a Co^{III} –N₂ complex **D**, bearing three Me₃Si groups and



Scheme 3. Proposed reaction pathway for the formation of 1 from $N_{\rm 2}$ using D as a catalyst, based on DFT calculations.

bpy, is generated in situ from Na, Me₃SiCl, bpy, and Co complexes. On the assumption that the active silyl species is a Me₃Si radical, the catalytic cycle starts with the silylation of the coordinated N₂ ligand by a Me₃Si radical to afford diazenide intermediate E.^[10,11] A Me₃Si radical adds to E followed by the migration of a $\ensuremath{\mathsf{Me}_3\mathsf{Si}}$ group from the Co atom to the nitrogenous ligand to yield a hydrazide (1-) intermediate F. Then, one of the two Me₃Si ligands on the Co atom moves to the proximal N atom to form a hydrazine group. The temporarily generated hydrazine intermediate G spontaneously separates into monosilyl intermediate H and tetrasilylhydrazine. The hydrazine molecule can be readily transformed into two molecules of 1 in the reaction solution. Finally, the introduction of two Me₃Si radicals and N_2 to **H** results in the regeneration of the initial complex **D**. Throughout the catalytic cycle, the bpy ligand is strongly bound to the Co atom of the complexes. We have theoretically confirmed that the proposed reaction pathway is reasonable by assuming **D** as a catalyst, including the corresponding transition states in all steps of the catalytic cycle (see the Supporting Information for details).

Conclusion

In summary, we have found that some Co complexes, such as $[Co_2(CO)_8]$, are effective catalysts for the formation of $N(SiMe_3)_3$, which can be readily converted into NH_3 after acid hydrolysis, from the reaction of N_2 with Me_3SiCl and Na as a reductant. In this reaction system, up to 49 equivalents of $N(SiMe_3)_3$ were produced per Co atom of the catalyst when bpy was used as an additive. This is the first report of a successful Co-catalyzed transformation of N_2 under ambient conditions.^[30] With the aid of DFT calculations, a Co– N_2 complex bearing three Me₃Si groups and bpy was proposed as a key reactive intermediate in the present catalytic reaction. Further study is currently underway to develop more effective transition metal-catalyzed systems for N_2 fixation under mild reaction conditions.^[31]

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Keywords: cobalt \cdot density functional calculations \cdot nitrogen fixation \cdot reduction \cdot silylation

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- [27] CCDC 1050051(2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.
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Homogeneous Catalysis

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Cobalt-Catalyzed Transformation of Molecular Dinitrogen into Silylamine under Ambient Reaction Conditions alternative nitrogen fixation



Don't pass Co: Cobalt-catalyzed reduction of N_2 with Me_3SiCl and Na as a reductant gives $N(SiMe_3)_3$, which can be readily converted into NH_3 . Based on DFT calculations, $Co-N_2$ complexes bearing three Me_3Si groups as ancillary ligands are considered to work as key reactive species and a detailed reaction pathway of the transformation is also proposed.

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