



A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

Accepted Article

Title: Catalytic Reduction of Molecular Dinitrogen into Ammonia and Hydrazine Using Vanadium Complexes

Authors: Yoshiaki Nishibayashi, Yoshiya Sekiguchi, Kazuya Arashiba, Hiromasa Tanaka, Aya Eizawa, Kazunari Nakajima, and Kazunari Yoshizawa

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201802310
Angew. Chem. 10.1002/ange.201802310

Link to VoR: <http://dx.doi.org/10.1002/anie.201802310>
<http://dx.doi.org/10.1002/ange.201802310>

Catalytic Reduction of Molecular Dinitrogen into Ammonia and Hydrazine Using Vanadium Complexes

Yoshiya Sekiguchi, Kazuya Arashiba, Hiromasa Tanaka, Aya Eizawa, Kazunari Nakajima, Kazunari Yoshizawa,* and Yoshiaki Nishibayashi*

Abstract: Newly designed and prepared vanadium complexes bearing anionic pyrrole-based PNP-type pincer and aryloxy ligands are found to work as effective catalysts toward the direct conversion of molecular dinitrogen into ammonia and hydrazine under mild reaction conditions. This is the first successful example of vanadium-catalyzed dinitrogen reduction under mild reaction conditions.

Development of transition metal-catalyzed dinitrogen reduction under mild reaction conditions is one of the most important and essential issues for human beings. Based on the intensive study of the preparation of various transition metal–dinitrogen complexes and their detailed reactivity,^[1] Schrock and co-workers found the direct and catalytic transformation of molecular dinitrogen into ammonia under ambient reaction conditions using a mononuclear molybdenum–dinitrogen complex as a catalyst.^[2] Since the report of the first successful example of the molybdenum–catalyzed dinitrogen reduction,² some successful examples of catalytic dinitrogen reduction systems using other mid-to-late transition metal–dinitrogen complexes as catalysts have been reported by other research groups.^[3,4] After the seminal report of more effective molybdenum–catalyzed dinitrogen reduction under ambient reaction conditions,^[5] iron–,^[6–8] cobalt–,^[9,10] osmium–,^[11] and ruthenium^[11]–catalyzed dinitrogen reduction under mild reaction conditions has been developed, where a very low reaction temperature such as -78 °C is necessary to avoid the direct reaction of reducing reagents with proton sources. The produced amounts of ammonia and hydrazine depend on the nature of metals, ligands, and solvents. As described here, successful examples are limited to the use of mid-to-late transition metal complexes as catalysts. Thus, early transition metal-catalyzed dinitrogen reduction under mild reaction conditions has not yet been reported until now.

In sharp contrast to the Haber-Bosch process under harsh reaction conditions,^[12] biological nitrogen fixation proceeds

smoothly under ambient reaction conditions. Detailed investigations revealed that FeMo nitrogenase has a sulfur-bridged polynuclear complex containing molybdenum, iron, and carbon atoms although the exact reaction mechanism has not yet been understood.^[13,14] A recent study has disclosed that the molecular structure of FeV nitrogenase is quite similar to that of FeMo nitrogenase.^[15]

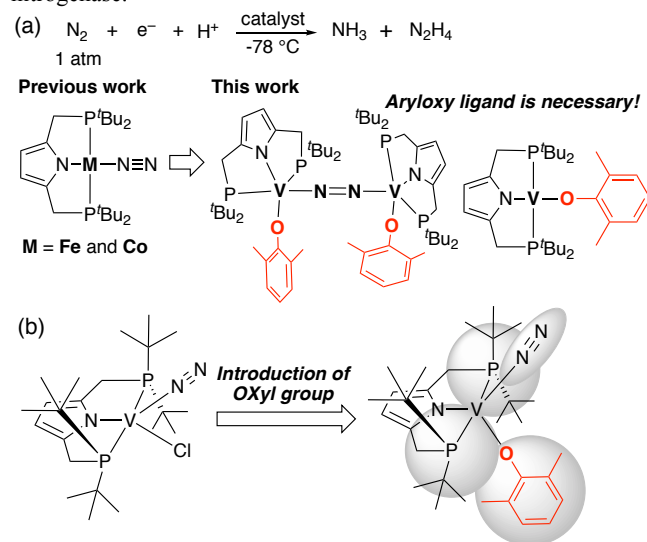


Chart 1. (a) Development of transition metal-catalyzed nitrogen fixation under mild reaction conditions. (b) Change of the configuration around the vanadium center by the introduction of a bulky ligand on the vanadium atom leads to the formation of the corresponding vanadium(II)–dinitrogen complexes.

Structural similarity between FeMo- and FeV-nitrogenases inspired inorganic chemists to prepare a variety of vanadium–dinitrogen complexes and investigate their stoichiometric reactivity in detail.^[16,17] In contrast to the stoichiometric reactions of vanadium–dinitrogen complexes, the vanadium-catalyzed dinitrogen reduction under mild reaction conditions has not yet been achieved until now. Schrock and co-workers previously tried to develop the catalytic conversion of molecular dinitrogen into ammonia by using their vanadium complexes as catalysts; however, no ammonia was observed from dinitrogen gas.^[18] Based on these research backgrounds,^[19] we have found that newly designed and prepared vanadium complexes bearing anionic pyrrole-based PNP-type pincer and aryloxy ligands (PNP = 2,5-bis(dialkylphosphinomethyl)pyrrolide) worked as effective catalysts toward the direct conversion of molecular dinitrogen into ammonia and hydrazine under mild reaction conditions (Chart 1(a)). This is the first successful example of early transition metal-catalyzed dinitrogen reduction under mild reaction conditions. Herein, we report preliminary results.

According to our previous procedure,^[7,10] we newly prepared a vanadium dichloride complex bearing an anionic pyrrole-based PNP-type pincer ligand [VCl₂(PNP)] (1). Treatment of [VCl₃(thf)₃] (thf = tetrahydrofuran) with lithium 2,5-bis(dialkylphosphinomethyl)pyrrolides, generated from 2,5-bis(dialkylphosphinomethyl)pyrroles and ^tBuLi, in THF

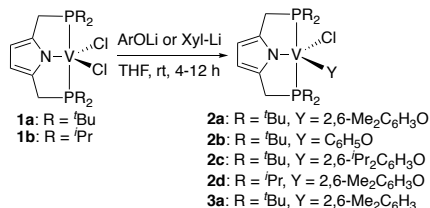
[*] Y. Sekiguchi, Dr. K. Arashiba, A. Eizawa, Dr. K. Nakajima, Prof. Dr. Y. Nishibayashi
Department of Systems Innovation, School of Engineering
University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan
E-mail: ynishiba@sys.t.u-tokyo.ac.jp
Associate Prof. Dr. H. Tanaka, Prof. Dr. K. Yoshizawa
Institute for Materials Chemistry and Engineering,
Kyushu University, Nishi-ku, Fukuoka 819-0395, Japan
E-mail: kazunari@ms.ifoc.kyushu-u.ac.jp

[**] The present project is supported by CREST, JST (JPMJCR1541) and Mitsubishi Foundation. We thank Grants-in-Aid for Scientific Research (Nos. JP17H01201 and JP15H05798) from JSPS and MEXT. A.E. is a recipient of the JSPS Predoctoral Fellowships for Young Scientists. We also thank Dr. Shogo Kuriyama in The University of Tokyo for his experiments at the early stage of this project.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.XXXX>.

(tetrahydrofuran) at room temperature for 6-9 h gave [VCl₂(R-PNP)] (**1a**: R = ^tBu, **1b**: R = ⁱPr) in 95% and 64% yields, respectively. At first, we tried to prepare the corresponding dinitrogen complexes from reactions of **1** with reducing reagents such as KC₈ and Na under 1 atm of N₂; however, only unidentified mixtures were obtained after reduction of **1**. Next, we designed new vanadium complexes by the introduction of one bulky ligand such as aryloxy or aryl group to the vanadium center in **1** because the presence of a bulky ligand on the vanadium atom changes the configuration around the vanadium center to lead the formation of the corresponding vanadium(II)-dinitrogen complexes (Chart 1(b)). Reactions of **1** with some ArOLi in THF at room temperature for 8-12 h gave the corresponding vanadium aryloxy complexes [VCl(OAr)(^tBu-PNP)] (**2a**: Ar = 2,6-dimethylphenyl (Xyl), **2b**: Ar = phenyl, **2c**: Ar = 2,6-di-*iso*-propylphenyl), and [VCl(OXyl)(ⁱPr-PNP)] (**2d**) in 79, 44, 64, and 51% yields, respectively (Scheme 1). On the other hand, the reaction of **1a** with XylLi under the same conditions gave the corresponding vanadium 2,6-xylyl complex [VCl(Xyl)(^tBu-PNP)] (**3a**) in 21% yield (Scheme 1).

Molecular structures of **1**, **2**, and **3** were confirmed by X-ray analysis. ORTEP drawings of **1a** and **2a** are shown in Figure 1 (see ORTEP drawings of **1b**, **2b-2d**, and **3a** in Figure S5 and S7-S10).^[20] Crystal structures of **1a** and **2a** have distorted square pyramidal geometries around the vanadium atoms (the geometry index $\tau_5 = 0.24$ for **1a** and 0.18 for **2a**, where $\tau_5 = 0.00$ for a perfect square pyramidal and $\tau_5 = 1.00$ for a trigonal bipyramidal geometry).^[21] Complexes **1a**, **2a**, and **3a** have solution magnetic moments of 2.7±0.1 μ_B , 2.6±0.1 μ_B , and 2.7±0.1 μ_B at 296K, respectively, which are consistent with the spin-only value for an $S = 1$ spin state (2.83 μ_B).



Scheme 1. Preparation of vanadium complexes bearing anionic PNP-pincer ligands.

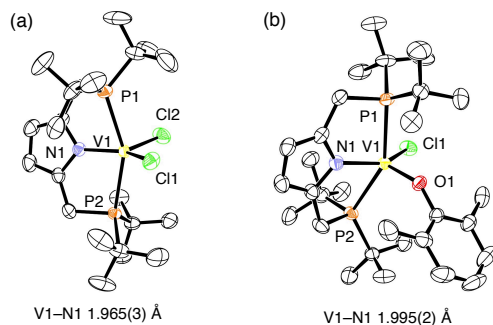
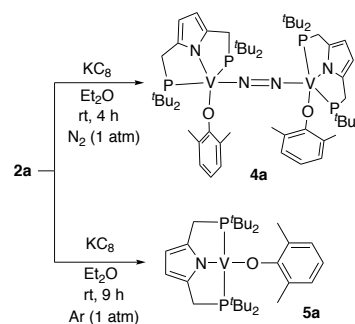


Figure 1. ORTEP drawings of **1a** (a) and **2a** (b). Hydrogen atoms are omitted for clarity.

Reduction of **2a** with KC₈ in Et₂O at room temperature for 4 h under 1 atm of N₂ gave a dinitrogen-bridged divanadium complex [V(OXyl)(^tBu-PNP)]₂(μ -N₂) (**4a**) in 44% yield after recrystallization (Scheme 2). On the other hand, reduction of **2a** with KC₈ in Et₂O at room temperature for 9 h under 1 atm of Ar gas gave a mononuclear vanadium complex [V(OXyl)(^tBu-PNP)] (**5a**) in 56% (Scheme 2). Raman and IR spectra of **4a** in Et₂O under 1 atm of N₂ showed no peak assignable to bridging and terminal dinitrogen ligands. Unfortunately, no Raman band attributable to the bridging-dinitrogen ligand was observed in the solid state of **4a** due to the instability of **4a**. These results suggest that the dinitrogen-bridged dinuclear structure does not remain in solution and the complex may



Scheme 2. Reduction of vanadium complexes.

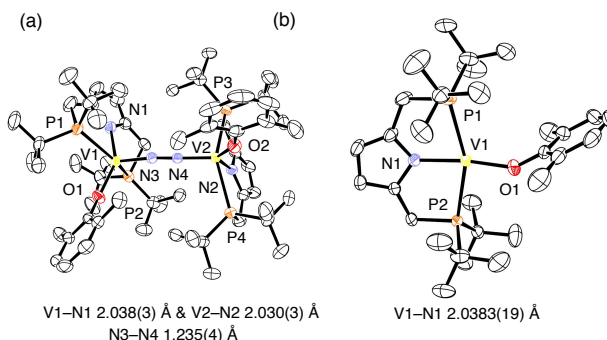


Figure 2. ORTEP drawings of **4a** (a) and **5a** (b). Hydrogen atoms are omitted for clarity.

exist as a mononuclear vanadium complex bearing no terminal dinitrogen ligand such as **5a**. UV spectra of **4a** and **5a** in Et₂O under 1 atm of Ar show that **4a** may be converted into **5a** quite rapidly (see UV spectra of **4a** in Et₂O under 1 atm of Ar in Figure S3). These results also suggest that an equilibrium mixture of **5a** and a mononuclear vanadium-dinitrogen complex such as [V(N₂)(OXyl)(^tBu-PNP)] (**A**) may be formed in a Et₂O solution of **4a**, where **5a** exists with priority. Separately, we confirmed that the conversion of **4a** into **5a** proceeded smoothly in Et₂O under 1 atm of N₂.

Detailed molecular structures of **4a** and **5a** were confirmed by X-ray analysis. ORTEP drawings of **4a** and **5a** are shown in Figure 2. Crystal structures of **4a** and **5a** have distorted square pyramidal and square-planar geometries around the vanadium atoms, respectively (the geometry index $\tau_5^{[21]} = 0.02$ and 0.29 for **4a** and $\tau_4^{[22]} = 0.21$ and 0.30 for **5a**). The bridging N-N bond distance in **4a** is 1.235(4) Å, which signals two-electron reduction with a typical N=N bond coordinated to the V atoms.^[23] The bond lengths between V and N atoms of the pyrrolide group in **4a** and **5a** (2.038(3), 2.030(3), and 2.0383(19) Å) are longer than those in **1a** and **2a** (1.965(3) and 1.995(2) Å). These results indicate that **4a** and **5a** have a poor π -donor ability of the pyrrolide group than **1a** and **2a**. Complex **5a** has a solution magnetic moment of 3.6±0.1 μ_B at 296K, which are consistent with the spin-only value for an $S = 3/2$ spin state (3.87 μ_B).

Next, we investigated catalytic dinitrogen reduction in a modified experimental procedure of the previous method investigated by our group,^[7] originally reported by Peters and co-workers.^[6] The reaction of atmospheric pressure of dinitrogen gas with 40 equiv of KC₈ as a reductant and 38 equiv of [H(OEt₂)₂][BAR^F₄] as a proton source in the presence of a catalytic amount of **2a** in Et₂O at -78 °C for 1 h gave 4.0 equiv of ammonia and 0.8 equiv of hydrazine (5.6 equiv of fixed N atom) based on the vanadium atom of the catalyst together with 4.4 equiv of hydrogen gas (Table 1, Entry 1).^[24,25] No formation of ammonia and hydrazine was observed at all in other solvents such as THF and toluene. When other vanadium complexes **2b-2d** were used as catalysts in place of **2a**, lower amounts of ammonia and hydrazine were produced based on the vanadium atom (Table 1, Entries 2-4). In all cases, the formation

Table 1. Vanadium-catalyzed reduction of dinitrogen to ammonia and hydrazine^[a]

		$\text{N}_2 + \text{KC}_8 + [\text{H}(\text{OEt}_2)_2][\text{BAR}^{\text{F}}_4] \xrightarrow[\text{Et}_2\text{O}, -78^\circ\text{C}, 1\text{h}]{\text{catalyst}} \text{NH}_3 + \text{N}_2\text{H}_4 (+ \text{H}_2)$					
Entry	Cat.	KC ₈ (Equiv) ^[b]	[H(OEt ₂) ₂][BAR ^F ₄] (Equiv) ^[b]	NH ₃ (Equiv) ^[b]	N ₂ H ₄ (Equiv) ^[b]	fixed N atom (Equiv) ^[b]	H ₂ (Equiv) ^[b]
1	2a	40	38	4.0±0.5 ^[c]	0.8±0.2 ^[c]	5.6	4.4±0.6 ^[c]
2	2b	40	38	3.6±0.1 ^[c]	0.5±0.1 ^[c]	4.6	4.3±0.4 ^[c]
3	2c	40	38	3.2±0.1 ^[c]	0.3±0.1 ^[c]	3.8	4.3±1.1 ^[c]
4	2d	40	38	1.9	0	1.9	5.8
5	3a	40	38	3.0±0.4 ^[c]	0.6±0.2 ^[c]	4.2	3.4±0.4 ^[c]
6	1a	40	38	1.3	0.2	1.7	7.4
7	7	40	38	1.8	0	1.8	8.9
8	8	40	38	0.9	0	0.9	3.0
9	2a	200	184	3.5±0.4 ^[c]	1.7±0.2 ^[c]	6.9	39±1 ^[c]
10	5a	40	38	6.8±0.2 ^[c]	0.3±0.1 ^[c]	7.4	1.3±0.0 ^[c]
11	5a	200	184	12±0 ^[c]	1.8±0.7 ^[c]	16	30±2 ^[c]
12	4a	40	38	4.6±0.1 ^[c]	0 ^[c]	4.6	2.4±0.4 ^[c]
13	6a	40	38	6.6±0.1 ^[c]	0.4±0.1 ^[c]	7.4	3.0±0.1 ^[c]

^[a]To a mixture of catalysts, KC₈, and [H(OEt₂)₂][BAR^F₄] was added Et₂O at -78 °C, and then the resultant mixture was stirred at -78 °C for 1 h. ^[b]Equiv based on the V atom. ^[c]Average of multiple runs (≥2 times) are shown.

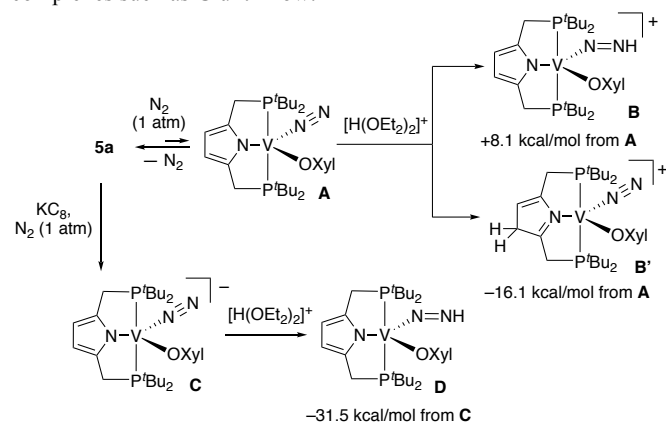
of hydrogen gas was observed as a side-product. The use of **3a** gave 3.0 equiv of ammonia and 0.6 equiv of hydrazine (4.2 equiv of fixed N atom) based on the vanadium atom of the catalyst (Table 1, Entry 5). For comparison, other vanadium complexes such as [VCl₂(^tBu-PNP)] **1a**, *trans*-[Na(thf)][V(N₂)₂(dppe)₂] (**7**, dppe = 1,2-bis(diphenylphosphino)ethane) and K[V{(Me₃SiNCH₂CH₂)₂NSiMe₃}(μ-N)] (**8**) did not work as catalysts under the same reaction conditions (Table 1, Entries 6–8). These results indicate that only vanadium complexes bearing anionic pyrrole-based PNP-type pincer and aryloxy ligands worked as effective catalysts. The result of control experiments supports that the combination of **2a**, dinitrogen gas, KC₈, and [H(OEt₂)₂][BAR^F₄] is necessary for the catalytic formation of ammonia and hydrazine.^[28]

In contrast to **2a** (Table 1, Entries 1 and 9), the largest amounts of ammonia and hydrazine in the present catalytic system were obtained when 200 equiv of KC₈ and 184 equiv of [H(OEt₂)₂][BAR^F₄] were used in the presence of **5a** under the same reaction conditions, where a mixture of ammonia (12 equiv) and hydrazine (1.8 equiv) was obtained based on the vanadium atom of the catalyst (16 equiv of fixed N atom) (Table 1, Entries 10, and 11). The catalytic activity of **5a** is almost the same with those of iron- and cobalt-dinitrogen complexes [M(N₂)(^tBu-PNP)] (M = Fe^[7a] and Co^[10]) under the same reaction conditions (up to 18 equiv of fixed N atom). Unfortunately, **4a** has a slightly lower catalytic activity than **5a** under the same reaction conditions (Table 1, Entry 12). At present, we consider that the low solubility of **4a** in Et₂O at -78 °C may prohibit the catalytic reaction effectively.

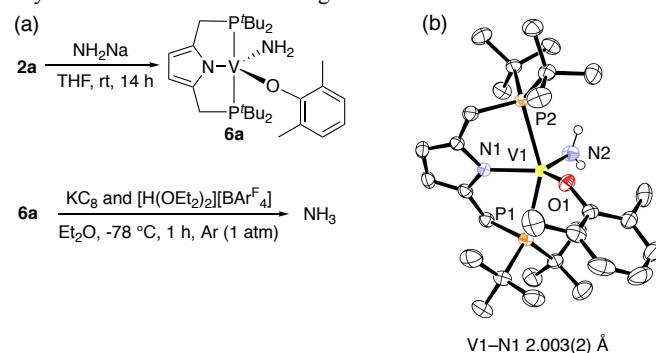
We have not yet observed the formation of mononuclear vanadium–dinitrogen complexes such as **A** from the reaction of **5a** with dinitrogen gas although **4a** was isolated from recrystallization of **5a** under 1 atm of N₂ (Figure 3). This result indicates that the formation of **4a** proceeds smoothly from an equilibrium mixture of **A** and **5a** under 1 atm of N₂. DFT calculations demonstrate that protonation of **A** with [H(OEt₂)₂]⁺ is not likely to occur at the N₂ ligand but at a β-carbon atom of the pyrrole moiety of the PNP ligand. At 195 K, the formation of [V(N=NH)(OXyl)(^tBu-PNP)]⁺ (**B**) is endergonic by 8.1 kcal/mol, while the formation of [V(N₂)(OXyl)(^tBu-PNP^H)]⁺ (**B'**) is exergonic by 16.1 kcal/mol (Figure 3). In fact, we previously isolated and characterized an analogous iron complex [Fe(N₂)(^tBu-PNP^H)]⁺[BAR^F₄]⁻ (**7a**)^[7a]

As a key intermediate toward the catalytic nitrogen fixation in the present system, we would like to propose an anionic vanadium–dinitrogen complex such as [V(N₂)(OXyl)(^tBu-PNP)]⁻ (**C**), which may be generated by reduction of **5a** under 1 atm of N₂ (Figure 3).

The cyclic voltammetry of **5a** revealed one reduction wave at -2.1 V in the reverse cathodic scan under 1 atm of N₂, supporting the possibility of the formation of anionic vanadium complexes. DFT calculations show that the free energy changes at 195 K (ΔG₁₉₅) for the binding of N₂ to neutral and anionic **5a** are -2.6 and -18.1 kcal/mol, respectively. Furthermore, protonation of the N₂ ligand in **C** to form [V(N=NH)(OXyl)(^tBu-PNP)] (**D**) is calculated to be highly exergonic by 31.5 kcal/mol. The enhanced reactivity of the N₂ ligand in **C** can be associated with the increase of the negative atomic charges on N₂ (-0.63 in total) compared with that in **A** (-0.13), in a similar manner as protonation of [Fe(N₂)(^tBu-PNP)]⁺ (**7a**). Unfortunately, despite the reaction of **5a** with various reducing reagents like KC₈, we have not obtained reduced vanadium complexes such as **C** until now.^[29,30]

**Figure 3.** Possible reaction pathway for ammonia from **5a**.

To get more information on the reaction pathway, we prepared a vanadium–amide complex and investigated its reactivity. The reaction of **2a** with NH₂Na in THF at room temperature for 14 h gave the corresponding vanadium amide complex [V(NH₂)(OXyl)(^tBu-PNP)] (**6a**) in 36% yield (Scheme 3(a)). The detailed molecular structure of **6a** was confirmed by X-ray analysis. An ORTEP drawing of **6a** is shown in Scheme 3(b). When the reaction of **6a** with 10 equiv of KC₈ and 10 equiv of [H(OEt₂)₂][BAR^F₄] was carried out in Et₂O at -78 °C for 1 h under 1 atm of Ar, ammonia was obtained in 37% yield based on the vanadium atom. In addition to the stoichiometric reactivity, **6a** has a similar catalytic activity with **5a** (Table 1, Entry 13). Based on these experimental results, we consider that **6a** may be involved as a key reactive intermediate leading to the formation of ammonia.

**Scheme 3.** (a) Preparation and reactivity of vanadium–amide complex. (b) ORTEP drawing of **6a**. Hydrogen atoms are omitted for clarity.

In summary, we have found that newly designed and prepared vanadium complexes bearing anionic pyrrole-based PNP-type pincer and aryloxy ligands worked as effective catalysts toward the direct conversion of molecular dinitrogen into ammonia and hydrazine under mild reaction conditions, where up to 14 equiv of ammonia and 2 equiv of hydrazine (16 equiv of fixed N atom) are produced

based on the vanadium atom. The result described in this paper provides the first successful example of the vanadium-catalyzed direct conversion of molecular dinitrogen into ammonia and hydrazine under mild reaction conditions.^[31] In sharp contrast to the previous reports using mid-to-late transition metal complexes as catalysts, this is the first successful example of early transition metal-catalyzed dinitrogen reduction under mild reaction conditions. At present, we consider that the present dinitrogen reduction proceeds via a similar reaction pathway using $[M(N_2)(PNP)]$ ($M = Fe$ and Co) as catalysts, where not nitride complexes but hydrazine complexes worked as key reactive intermediates.^[7a,10] We believe that the present findings provide a valuable opportunity to elucidate the reaction mechanism in FeV nitrogenase. Further study^[32] is currently in progress to develop more effective vanadium complexes and to elucidate the reaction mechanism.

Received: ((will be filled in by the editorial staff))

Published online on ((will be filled in by the editorial staff))

Keywords: ammonia · catalytic reaction · dinitrogen · pincer ligand · vanadium

- [1] For selected recent reviews, see: (a) C. Köthe, C. Z. Limberg, *Anorg. Allg. Chem.* **2015**, *641*, 18. (b) N. Khoenkhoen, B. de Bruin, J. N. H. Reek, W. I. Dzik, *Eur. J. Inorg. Chem.* **2015**, 567. (c) M. J. Bezdek, P. J. Chirik, *Angew. Chem., Int. Ed.* **2016**, *55*, 7892. (d) I. Čorić, P. L. Holland, *J. Am. Chem. Soc.* **2016**, *138*, 7200. (e) R. J. Burford; M. D. Fryzuk, *Nat. Rev. Chem.* **2017**, *1*, 0026. (f) Y. Roux, C. Duboc, M. Gennari, *ChemPhysChem* **2017**, *18*, 2606. (g) *Nitrogen Fixation; Topics in Organometallic Chemistry* 60, Ed: Y. Nishibayashi, Springer, 2017. (h) N. Stucke, B. M. Flöser, T. Weyrich, F. Tuczec, *Eur. J. Inorg. Chem.* **2018**, DOI: 10.1002/ejic.201701326.
- [2] (a) D. V. Yandulov, R. R. Schrock, *Science* **2003**, *301*, 76. (b) R. R. Schrock, *Angew. Chem., Int. Ed.* **2008**, *47*, 5512. (c) L. A. Wickramasinghe, T. Ogawa, R. R. Schrock, P. Müller, *J. Am. Chem. Soc.* **2017**, *139*, 9132.
- [3] (a) Y. Nishibayashi, *Inorg. Chem.* **2015**, *54*, 9234. (b) Y. Tanabe, Y. Nishibayashi, *Y. Chem. Rec.* **2016**, *16*, 1549. (c) Tanaka, H.; Nishibayashi, K. Yoshizawa, *Acc. Chem. Res.* **2016**, *49*, 987.
- [4] (a) T. A. Bazhenova, A. E. Shilov, *Coord. Chem. Rev.* **1995**, *144*, 69. (b) A. E. Shilov, *Russ. Chem. Bull.* **2003**, *52*, 2555.
- [5] (a) K. Arashiba, Y. Miyake, Y. Nishibayashi, *Nat. Chem.* **2011**, *3*, 120. (b) H. Tanaka, K. Arashiba, S. Kuriyama, A. Sasada, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* **2014**, *5*, 3737. (c) K. Arashiba, E. Kinoshita, S. Kuriyama, A. Eizawa, K. Nakajima, H. Tanaka, K. Yoshizawa, Y. Nishibayashi, *J. Am. Chem. Soc.* **2015**, *137*, 5666. (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.
- [6] (a) J. S. Anderson, J. Rittle, J. C. Peters, *Nature* **2013**, *501*, 84. (b) T. J. Castillo, N. B. Thompson, J. C. Peters, *J. Am. Chem. Soc.* **2016**, *138*, 5341. (c) M. J. Chalkley, T. J. Castillo, B. D. Matson, J. P. Roddy, J. C. Peters, *ACS Cent. Sci.* **2017**, *3*, 217. (d) T. M. Buscagan, P. H. Oyala, J. C. Peters, *Angew. Chem., Int. Ed.* **2017**, *56*, 6921.
- [7] (a) S. Kuriyama, K. Arashiba, K. Nakajima, Y. Matsuo, H. Tanaka, K. Ishii, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* **2016**, *7*, 12181. (b) Y. Sekiguchi, S. Kuriyama, A. Eizawa, K. Arashiba, K. Nakajima, Y. Nishibayashi, *Chem. Commun.* **2017**, 53, 12040. (c) J. Higuchi, S. Kuriyama, A. Eizawa, K. Arashiba, K. Nakajima, Y. Nishibayashi, *Dalton Trans.* **2018**, *47*, 1117.
- [8] P. J. Hill, L. R. Doyle, A. D. Crawford, W. K. Myers, A. E. Ashley, *J. Am. Chem. Soc.* **2016**, *138*, 13521.
- [9] T. J. D. Castillo, N. E. Thompson, D. L. M. Suess, G. Ung, J. C. Peters, *Inorg. Chem.* **2015**, *54*, 9256.
- [10] S. Kuriyama, K. Arashiba, H. Tanaka, Y. Matsuo, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Angew. Chem., Int. Ed.* **2016**, *55*, 14291.
- [11] J. Fajardo, J. C. Peters, *J. Am. Chem. Soc.* **2017**, *139*, 16105.
- [12] H. Liu, *Ammonia Synthesis Catalysts*; Chemical Industry Press & World Scientific; Singapore & Beijing, 2013.
- [13] (a) T. Spatzal, M. Aksoyoglu, L. Zhang, S. L. A. Andrade, E. Schleicher, S. Weber, D. C. Rees, O. Einsle, *Science* **2011**, *334*, 940. (b) K. M. Lancaster, M. Roemelt, P. Ettenhuber, Y. Hu, M. W. Ribbe, F. Neese, U. Bergmann, S. DeBeer, *Science* **2011**, *334*, 974.
- [14] (a) B. M. Hoffman, D. Lukoyanov, Z.-Y. Yang, D. R. Dean, L. C. Seefeldt, *Acc. Chem. Res.* **2013**, *46*, 587. (b) B. M. Hoffman, D. Lukoyanov, Z.-Y. Yang, D. R. Dean, L. C. Seefeldt, *Chem. Rev.* **2014**, *114*, 4041.
- [15] D. Sippel, O. Einsle, *Nat. Chem. Biol.* **2017**, *13*, 956.
- [16] Selected examples of the preparation and reactivity of vanadium-dinitrogen and related complexes, see: (a) J. J. H. Edema, A. Meetsma, S. Gambarotta, *J. Am. Chem. Soc.* **1989**, *111*, 6878. (b) P. Berno, S. Hao, R. Minhas, S. Gambarotta, *J. Am. Chem. Soc.* **1994**, *116*, 7417. (c) P. Berno, S. Gambarotta, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 822. (d) D. Reardon, F. Conan, S. Gambarotta, G. Yap, Q. Wang, *J. Am. Chem. Soc.* **1999**, *121*, 9318. (e) A. J. Keane, B. L. Yonke, M. Hirotsu, P. Y. Zavalij, L. R. Sita, *J. Am. Chem. Soc.* **2014**, *136*, 9906. (f) Y. Ishida, H. Kawaguchi, *J. Am. Chem. Soc.* **2014**, *136*, 16990.
- [17] Shilov tried to develop the catalytic reduction of molecular dinitrogen; however, only a stoichiometric amount of ammonia was produced based on the vanadium atom of the catalyst: A. E. Shilov, *J. Mol. Catal.* **1987**, *41*, 221.
- [18] (a) N. C. Smythe, R. R. Schrock, P. Müller, W. W. Weare, *Inorg. Chem.* **2006**, *45*, 9197. (b) A. K. Guha, A. K. Phukan, *Inorg. Chem.* **2011**, *50*, 8826.
- [19] (a) Recently, we have found the vanadium-catalyzed conversion of molecular dinitrogen into silylamine^[19b,c] as an ammonia equivalent under ambient reaction conditions: R. Imayoshi, K. Nakajima, Y. Nishibayashi, *Chem. Lett.* **2017**, *46*, 466. For recent examples, see: (b) R. Araake, K. Sakadani, M. Tada, Y. Sakai, Y. Ohki, *J. Am. Chem. Soc.* **2017**, *139*, 5596. (c) A. J. Kendall, S. I. Johnson, R. M. Bullock, T. Mock, *J. Am. Chem. Soc.* **2018**, *140*, 2528.
- [20] CCDC 1822776 (**1a**), 1822777 (**1b**), 1822778 (**2a**), 1822779 (**2b**), 1822780 (**2c**), 1822781 (**2d**), 1822782 (**3a**), 1822783 (**4a**), 1822784 (**5a**), 1822785 (**5b**), 1822786 (**5c**), and 1822787 (**6a**) contain 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.
- [21] A. W. Addison, N. Rao, *J. Chem. Soc. Dalton Trans.* **1984**, 1349.
- [22] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955.
- [23] (a) I. Vidyaratne, S. Gambarotta, I. Korobkov, P. H. M. Budzelaar, *Inorg. Chem.* **2005**, *44*, 1187. (b) C. Milsmann, Z. R. Turner, S. P. Semproni, P. J. Chirik, *Angew. Chem., Int. Ed.* **2012**, *51*, 5386.
- [24] We also confirmed by using ¹⁵N₂ gas instead of ¹⁴N₂ gas that molecular dinitrogen was certainly converted into ammonia (see the Supporting Information for details).
- [25] After the catalytic reaction, no vanadium complexes were observed by NMR, where only free PNP-H ligand and phenols were observed from a reaction mixture.
- [26] D. Rehder, C. Woitha, W. Priebsch, H. Gailus, *J. Chem. Soc., Chem. Commun.* **1992**, 364.
- [27] G. K. B. Clentsmith, V. M. E. Bates, P. B. Hitchcock, F. G. N. Cloke, *J. Am. Chem. Soc.* **1999**, *121*, 10444.
- [28] (a) Separately, we confirmed that hydrazine was partially converted into ammonia under the catalytic reaction conditions. (b) Separately, we confirmed that no formation of ammonia and hydrazine was observed when $[VCl_3(thf)_3]$ and VCl_3 as catalysts under the same reaction conditions. (c) When the catalytic reaction was carried out using **5a** in the presence of NaCl as a chloride source under the same reaction conditions, slightly lower amounts of ammonia and hydrazine were obtained. This experimental result suggests that the presence of chloride source did not affect the catalytic reaction.
- [29] As a preliminary DFT result, a direct cleavage of the bridging dinitrogen ligand of **4a** is not likely to occur under the present reaction conditions because it requires an activation energy of more than 30 kcal/mol.
- [30] Many dinitrogen-bridged divanadium complexes with an end-on bridging N₂ ligand have been prepared; however, only one example of a fully characterized mononuclear vanadium-dinitrogen complex **7** has appeared until now; Y. Ishida, H. Kawaguchi, *Top. Organomet. Chem.* **2017**, *60*, 45.
- [31] We already carried out catalytic reactions using vanadium complexes bearing methyl- and phenyl-substituted pyrrole-based PNP-type pincer ligands $[V(OXyl)(Bu-PNP^R)]$ (**5b**: R = Me, **5c**: R = Ph); however, only lower amounts of ammonia and hydrazine were produced based on the vanadium atom (see the Supporting Information for details).
- [32] (a) Y. Tanabe, K. Arashiba, K. Nakajima, Y. Nishibayashi, *Chem. Asian J.* **2017**, *12*, 2544. (b) R. Imayoshi, K. Nakajima, J. Takaya, N. Iwasawa, Y. Nishibayashi, *Eur. J. Inorg. Chem.* **2017**, 3769.

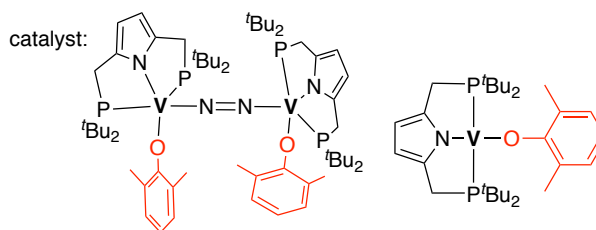
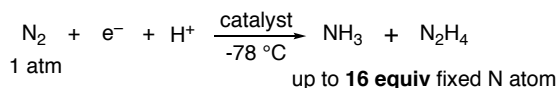
Entry for the Table of Contents

Nitrogen Fixation

Yoshiya Sekiguchi, Kazuya Arashiba,
Hiromasa Tanaka, Aya Eizawa,
Kazunari Nakajima, Kazunari
Yoshizawa,* and Yoshiaki Nishibayashi*

_____ Page – Page

Catalytic Reduction of Molecular
Dinitrogen into Ammonia and Hydrazine
Using Vanadium Complexes



Newly designed and prepared vanadium complexes bearing anionic pyrrole-based PNP-type pincer and aryloxy ligands are found to work as effective catalysts toward the direct conversion of molecular dinitrogen into ammonia and hydrazine under mild reaction conditions. This is the first successful example of vanadium-catalyzed dinitrogen reduction under mild reaction conditions.

Accepted Manuscript