Nitrogen Fixation Hot Paper

Deutsche Ausgabe: DOI: 10.1002/ange.201606090
Internationale Ausgabe: DOI: 10.1002/anie.201606090

Direct Transformation of Molecular Dinitrogen into Ammonia Catalyzed by Cobalt Dinitrogen Complexes Bearing Anionic PNP Pincer Ligands

Shogo Kuriyama, Kazuya Arashiba, Hiromasa Tanaka, Yuki Matsuo, Kazunari Nakajima, Kazunari Yoshizawa, and Yoshiaki Nishibayashi**

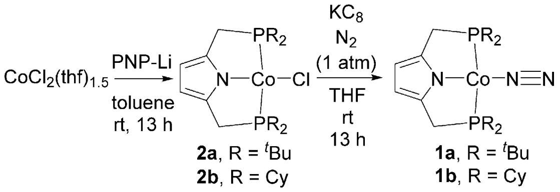
Abstract: *The direct formation of ammonia from molecular dinitrogen under mild reaction conditions was achieved by using new cobalt dinitrogen complexes bearing an anionic PNP-type pincer ligand. Up to 15.9 equivalents of ammonia were produced based on the amount of catalyst together with 1.0 equivalent of hydrazine (17.9 equiv of fixed nitrogen atoms).*

In nature, molecular dinitrogen is converted into ammonia at ambient temperature under atmospheric pressure by nitrogenases. The active site of the FeMo cofactor in nitrogenases has been found to contain molybdenum and iron atoms.[1] To elucidate the reaction mechanism of nitrogen fixation catalyzed by nitrogenases, the synthesis and reactivity of various transition-metal dinitrogen complexes have been extensively studied.[2,3] As a result, nitrogen fixation with molybdenum dinitrogen complexes as the catalysts under ambient reaction conditions was achieved by Schrock and Yandulov in 2003[4] and by our groups in 2010.[5] Recently, Peters and co-workers developed an iron-catalyzed reduction of molecular dinitrogen into ammonia using iron dinitrogen complexes as catalysts under mild reaction conditions.[6] However, the transformation of molecular dinitrogen into ammonia under mild reaction conditions using other transition-metal dinitrogen complexes as the catalysts has not yet been achieved.[2,3]

The first cobalt dinitrogen complex, $[Co(H)(N_2)(PPh_3)_3]$, was reported by Yamamoto and co-workers as the successful example of the synthesis of a transition-metal dinitrogen complex directly from dinitrogen gas.[7] Since the discovery of this complex, detailed studies on the stoichiometric reactivity of a variety of cobalt dinitrogen complexes have been carried out by several research groups.[2c,d,8,9] In 2015, our group and Lu and co-workers independently found that some cobalt complexes are effective catalysts for the reduction of dinitrogen gas into silylamine ($N(SiMe_3)_3$), which is regarded as an ammonia equivalent, under ambient reaction conditions.[10,11] In sharp contrast to the catalytic formation of $N(SiMe_3)_3$, the cobalt-catalyzed direct formation of ammonia from molecular dinitrogen has not been reported to date. In 2015, Peters and co-workers reported the "superstoichiometric" direct formation of ammonia by using a cobalt dinitrogen complex bearing a tris(phosphine)borane ligand, but the amount of formed ammonia (2.4 equiv) based on the amount of catalyst used was not sufficient for the reaction to be considered catalytic.[12]

Based on our findings while developing a method for catalytic nitrogen fixation under ambient reaction conditions, we designed new cobalt dinitrogen complexes bearing an anionic PNP-type pincer ligand, $[Co(N_2)(^{R}PNP)]$ (**1a**: R = *t*Bu, ^{tBu}PNP = 2,5-bis(di-*tert*-butylphosphinomethyl)pyrrolide; **1b**: R = Cy, ^{Cy}PNP = 2,5-bis(dicyclohexylphosphinomethyl)pyrrolide)[13] because the PNP ligand contains both hard and soft donors to stabilize cobalt centers with various oxidation states. We then investigated whether these complexes show catalytic activity towards the direct formation of ammonia from nitrogen gas under mild reaction conditions. As expected, these complexes were indeed found to work as catalysts for the direct reduction of dinitrogen gas into ammonia under mild reaction conditions. Up to 15.9 equiv of ammonia were produced based on the amount of catalyst together with 1.0 equiv of hydrazine (17.9 equiv of fixed N atoms). Herein, we detail the preparation and characterization of these novel cobalt dinitrogen complexes and their catalytic behavior.

Treatment of $CoCl_2(thf)_{1.5}$ with lithium 2,5-bis(dialkylphosphinomethyl)pyrrolide (^{R}PNP−Li) in toluene at room temperature for 13 h gave the paramagnetic cobalt chloride complexes $CoCl(^{tBu}PNP)$ (**2a**) and $CoCl(^{Cy}PNP)$ (**2b**) in 88% and 71% yield, respectively (Scheme 1). The molecular



Scheme 1. Synthesis of cobalt dinitrogen complexes with anionic PNP pincer ligands.

---

[*] Dr. S. Kuriyama, Dr. K. Arashiba, Dr. K. Nakajima,
Prof. Dr. Y. Nishibayashi
Department of Systems Innovation
School of Engineering, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
E-mail: ynishiba@sys.t.u-tokyo.ac.jp

Prof. Dr. H. Tanaka, Y. Matsuo, Prof. Dr. K. Yoshizawa
Institute for Materials Chemistry and Engineering
Kyushu University, Nishi-ku, Fukuoka 819-0395 (Japan)
and
Elements Strategy Initiative for Catalysts and Batteries (ESICB)
Kyoto University, Nishikyo-ku, Kyoto 615-8520 (Japan)
E-mail: kazunari@ms.ifoc.kyushu-u.ac.jp

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201606090.

structures of **2a** and **2b** were confirmed by X-ray analysis (for ORTEP drawings of **2a** and **2b**, see the Supporting Information, Figures S3 and S4).[14] The crystal structures of both **2a** and **2b** show a distorted square-planar geometry around the cobalt atom with geometry indexes τ_4 of 0.10 and 0.12, respectively ($\tau_4 = 0.00$ for a perfectly square-planar and $\tau_4 = 1.00$ for a tetrahedral geometry).[15] No distinct differences were observed for the metrical parameters in **2a** and **2b**. At 296 K, complexes **2a** and **2b** have solution magnetic moments of 2.3 ± 0.2 and 2.1 ± 0.1 μ_B, respectively. These measured magnetic moments are larger than the spin-only value for an $S = 1/2$ spin state (1.73 μ_B), but still within the range of values reported for square-planar cobalt(II) complexes with a low-spin state.[16]

Reactions of **2a** and **2b** with 1.1 equiv of KC_8 as a reductant in THF at room temperature for 13 h under an atmospheric pressure of dinitrogen afforded the corresponding diamagnetic cobalt(I) dinitrogen complexes **1a** and **1b** in 68% and 35% yield, respectively (Scheme 1). The molecular structure of **1a** was confirmed by X-ray analysis (Figure 1).

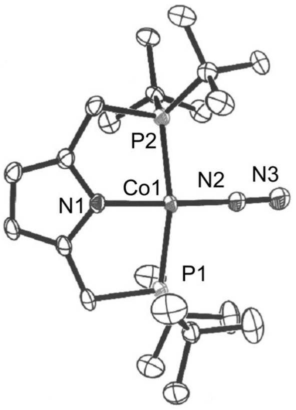


Figure 1. ORTEP drawing of **1a**. Hydrogen atoms are omitted for clarity.

The crystal structure of **1a** shows a distorted square-planar geometry around the cobalt atom ($\tau_4 = 0.11$) with a terminal dinitrogen ligand. The structure of **1a** is similar to those of reported cobalt(I) dinitrogen complexes with a distorted square-planar geometry.[17] The IR spectra of **1a** and **1b** in the solid state (KBr) show strong ν_{NN} bands at 2016 cm^{-1} and 2020 cm^{-1}, which were assigned to the terminal dinitrogen ligand. In solution (THF), complexes **1a** and **1b** show ν_{NN} bands at 2017 cm^{-1} and 2023 cm^{-1}, which are similar to those in the solid state. These ν_{NN} values are within the range of those reported for cobalt(I) dinitrogen complexes.[17]

We then investigated the catalytic reduction of molecular dinitrogen using **1a** as a catalyst under the reaction conditions developed by Peters and co-workers.[6,12] Representative results are shown in Table 1. The reaction of an atmospheric pressure of dinitrogen with KC_8 (40 equiv with respect to **1a**) as a reductant and $[H(OEt_2)_2]BAr^F_4$ (38 equiv with respect to **1a**; Ar^F = 3,5-bis(trifluoromethyl)phenyl) as a proton source in the presence of **1a** as a catalyst in Et_2O at −78 °C for 1 h gave 4.2 equiv of ammonia based on the amount of catalyst together with 2.1 equiv of molecular dihydrogen as a side product (Table 1, entry 1; see also Table S9, run 1). In this reaction, the formation of hydrazine was not detected. When the reaction was carried out at room temperature for 1 h, only a stoichiometric amount of ammonia was produced based on the amount of catalyst (entry 2). We separately confirmed that ammonia was not formed at all in the absence of **1a** or KC_8 under similar reaction conditions. These results indicate that the use of **1a** as a catalyst and KC_8 as a reductant at low reaction temperatures such as −78 °C is necessary to promote the catalytic formation of ammonia from molecular dinitrogen.[18] We also confirmed by using $^{15}N_2$ gas instead of $^{14}N_2$ gas that molecular dinitrogen was certainly converted into ammonia (see the Supporting Information for details).

Table 1: Cobalt-catalyzed reduction of dinitrogen into ammonia under various reaction conditions.[a]

$$\underset{(1\ \text{atm})}{N_2} + \underset{(40\ \text{equiv})}{\text{reductant}} + \underset{(38\ \text{equiv})}{[H(OEt_2)_2]BAr^F_4} \xrightarrow[\substack{\text{solvent} \\ -78\ ^\circ\text{C, 1 h}}]{\text{cat.}} NH_3 + NH_2NH_2$$

Entry	Cat.	Solvent	Reductant	NH_3 [equiv][b]	NH_2NH_2 [equiv][b]	Fixed N atoms [equiv][c]
1	**1a**	Et_2O	KC_8	4.2 ± 0.1	0	4.2
2[d]	**1a**	Et_2O	KC_8	1.3 ± 0.3	0	1.3
3	**1a**	MTBE	KC_8	4.0 ± 0.3	0.1 ± 0.1	4.2
4	**1a**	THF	KC_8	1.7 ± 0.1	0.2 ± 0.1	2.1
5	**1a**	Et_2O	$CoCp^*_2$	0.6	0	0.6
6	**1a**	Et_2O	K	0	0	0
7	**1b**	Et_2O	KC_8	3.1 ± 0.1	0.1 ± 0.1	3.3
8	**3a**	Et_2O	KC_8	2.2 ± 0.1	0	2.2
9	**4a**	Et_2O	KC_8	2.0 ± 0.2	0	2.0
10	**2a**	Et_2O	KC_8	1.2	0	1.2
11	**2b**	Et_2O	KC_8	0.8	0	0.8

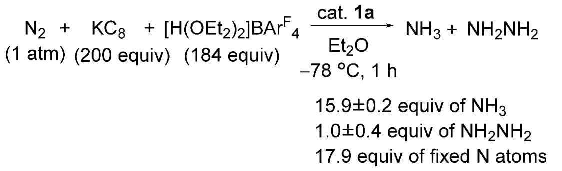
[a] A mixture of catalyst (0.010 mmol, 1.0 equiv), reductant (0.40 mmol, 40 equiv), and $[H(OEt_2)_2]BAr^F_4$ (0.38 mmol, 38 equiv) was stirred in the indicated solvent at −78 °C for 1 h under 1 atm of N_2 and then at room temperature for 20 min. [b] Based on the amount of catalyst. [c] Number of fixed nitrogen atoms (equiv) = $[NH_3\ (\text{equiv})] + 2[NH_2NH_2\ (\text{equiv})]$. [d] At room temperature for 1 h.

The amount of produced ammonia depends on the nature of the solvent. When MeO*t*Bu (MTBE) was used instead of Et_2O, a similar amount of ammonia (4.0 equiv) was produced based on the catalyst together with a small amount of hydrazine (0.1 equiv; entry 3). Compared to the reactions in Et_2O and MTBE, a lower amount of ammonia (1.7 equiv) was produced when the reaction was carried out in THF (entry 4). We surmise that the stronger coordination ability of THF may reduce the catalytic activity. The use of a strong reductant such as KC_8[19] was necessary to render the catalytic reaction effective. In fact, $CoCp^*_2$ (Cp^* = pentamethylcyclopentadienyl), which was used as an effective reductant for our molybdenum-catalyzed nitrogen fixation,[5] and elemental potassium were not suitable as reductants (entries 5 and 6).

Next, we investigated other cobalt complexes as catalysts under the same reaction conditions. The cobalt dinitrogen complex **1b** was also an effective catalyst, and 3.1 equiv of ammonia were produced based on the number of cobalt atoms together with a small amount (0.1 equiv) of hydrazine (entry 7). When cobalt hydride and cobalt methyl complexes

(**3a** and **4a**), which were prepared from reactions of **2a** with $KBHEt_3$ in THF and MeMgCl in Et_2O at room temperature for 1 h (see the Supporting Information for details), were employed, only a stoichiometric amount of ammonia was produced based on the complexes (2.2 and 2.0 equiv, respectively; entries 8 and 9). We separately confirmed that the reaction of **3a** with 1 equiv of $[H(OEt_2)_2]BAr^F_4$ in Et_2O at room temperature and subsequent addition of 1 equiv of KC_8 under N_2 (1 atm) gave **1a** together with molecular dihydrogen (see the Supporting Information for details). The starting cobalt chloride complexes **2a** and **2b** did not work as catalysts of this process as 1.2 and 0.8 equiv of ammonia were formed based on the complexes, respectively (entries 10 and 11).

When **1a** was employed as the catalyst, the use of larger amounts of both KC_8 and $[H(OEt_2)_2]BAr^F_4$ dramatically increased the amount of nitrogenous products. The use of 200 equiv of KC_8 and 184 equiv of $[H(OEt_2)_2]BAr^F_4$ gave the largest amounts of ammonia and hydrazine (15.9 and 1.0 equiv based on the catalyst, respectively; Scheme 2). These results indicate that the cobalt dinitrogen complexes bearing an anionic PNP-type pincer ligand are effective catalysts for the conversion of molecular dinitrogen into ammonia and hydrazine, and up to 17.9 equiv of N atoms were fixed based on the amount of catalyst.



$$\underset{(1\ \text{atm})}{N_2} + \underset{(200\ \text{equiv})}{KC_8} + \underset{(184\ \text{equiv})}{[H(OEt_2)_2]BAr^F_4} \xrightarrow[\substack{Et_2O\\ -78\,°C,\ 1\ h}]{\text{cat. }\mathbf{1a}} NH_3 + NH_2NH_2$$

15.9±0.2 equiv of NH_3
1.0±0.4 equiv of NH_2NH_2
17.9 equiv of fixed N atoms

Scheme 2. Catalytic reduction of dinitrogen with **1a** as the catalyst.

We carried out several experiments to gain insight into the reaction pathway. The reaction of **1a** with excess amounts of KC_8 (10 equiv relative to **1a**) and $[H(OEt_2)_2]BAr^F_4$ (9.5 equiv relative to **1a**) in Et_2O at −78 °C for 1 h under 1 atm of N_2 gave no cobalt-containing products except for **1a**. We could not detect the free PNP-H ligand. We believe that the formation of a small but certain amount of hydrazine in the present catalytic reaction provides an important key to elucidate the reaction pathway. Based on the experimental result that hydrazine is formed as a nitrogenous product, we suggest that a cobalt hydrazine complex may be formed as a key reactive intermediate in the catalytic reaction.[8b,20] We thus carried out a control experiment using hydrazine as the substrate. The reaction of hydrazine (4 equiv relative to **4a**) with excess amounts of KC_8 (40 equiv relative to **4a**) and $[H(OEt_2)_2]BAr^F_4$ (38 equiv relative to **4a**) in the presence of **4a** as the catalyst in Et_2O at −78 °C for 1 h under 1 atm of Ar gave 0.8 equiv of ammonia based on **4a** together with the recovery of hydrazine in 60 % (2.4 equiv to **4a**). The formation of molecular dinitrogen was not detected in this reaction system. This result indicates that hydrazine is partially converted into ammonia when hydrazine is formed in the catalytic reaction (see the Supporting Information). Further studies are necessary to elucidate the detailed reaction pathway.

Interestingly, other cobalt complexes did not truly catalyze ammonia formation. For example, when $[Co(H)(N_2)(PPh_3)_3]$[7] was used as the catalyst, only a stoichiometric amount of ammonia was obtained (0.6 equiv of ammonia based on the catalyst). Recently, Peters and co-workers evaluated the catalytic activity of some cobalt dinitrogen complexes towards ammonia formation using excess amounts of KC_8 and $[H(OEt_2)_2]BAr^F_4$ in Et_2O at −78 °C.[12] In all reactions, almost a stoichiometric amount of ammonia was produced based on the catalyst (up to 2.4 equiv of ammonia).[12,21] Although a cobalt dinitrogen complex bearing an anionic PBP-type pincer ligand (**5**) has a similar molecular structure to **1a** and a similar ν_{NN} value of 2013 cm^{-1},[17c] this complex did not work well as a catalyst, and only 0.4 equiv of ammonia were produced based on the amount of catalyst. This result indicates that the presence of PNP-type pincer ligands with the pyrrole skeleton is important to promote the cobalt-catalyzed nitrogen fixation.

We performed DFT calculations to compare the geometric and electronic structures of the cobalt dinitrogen complexes **1a** and **5**. Figure 2 a shows their optimized

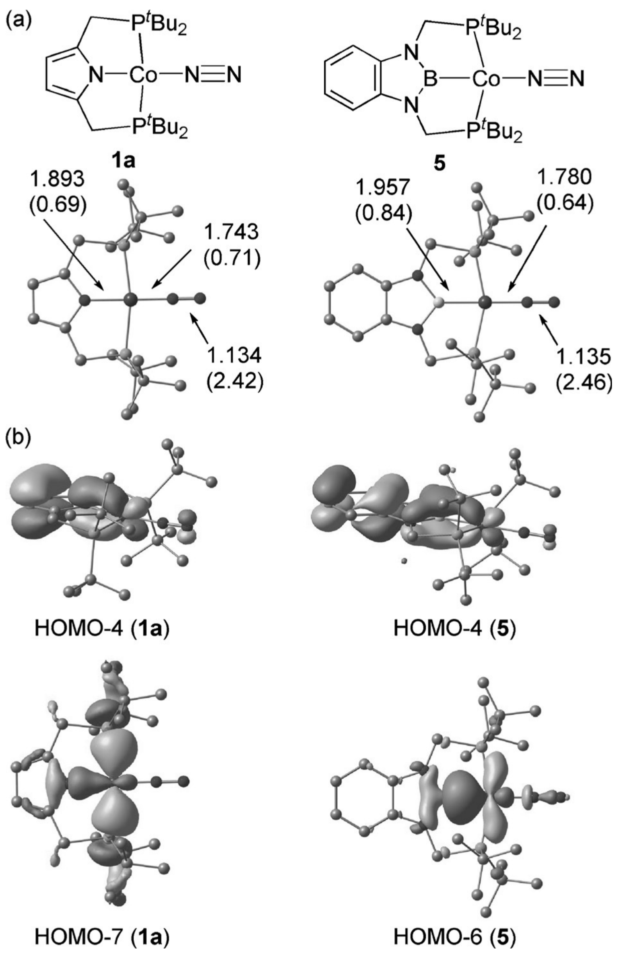


Figure 2. a) Optimized structures of **1a** and **5** in the closed-shell singlet state. Bond lengths are given in Å. The Mayer bond orders are given in parentheses. Hydrogen atoms are omitted for clarity. b) The molecular orbitals of **1a** and **5** corresponding to the σ bond between Co and the pincer ligands (HOMO-7 for **1a** and HOMO-6 for **5**) and the π bond (HOMO-4).

structures in the ground spin state (closed-shell singlet), together with the Mayer bond orders[22] of selected bonds. The optimized structures well reproduce the crystal structures. A striking finding is that the Co–N$_2$ distance of **1a** (1.743 Å) is much shorter than that of **5** (1.780 Å). The long Co–N$_2$ bond in **5** implies a significant *trans* influence of the PBP ligand, which is due to its strong electron-donating ability.[23] The degree of N$_2$ activation upon coordination is hardly affected by the pincer ligands: The N≡N bond distances (Mayer bond orders) are 1.134 Å (2.42) for **1a** and 1.135 Å (2.46) for **5**. Figure 2b shows the molecular orbitals corresponding to the σ and π bonds between the cobalt center and the pincer ligands of **1a** and **5**. Comparing HOMO-7 of **1a** and HOMO-6 of complex **5** suggests that the PBP ligand serves as a strong σ donor. As shown in Figure 2a, the Mayer bond order (b.o.) of the Co–N$_{py}$ bond (0.69) is smaller than that of the corresponding Co–B bond (0.84). On the other hand, the strong *trans* influence of the PBP ligand in **5** weakens the binding of dinitrogen in the *trans* position. The Co–N$_2$ bond in **1a** (b.o. = 0.71) is stronger than that in **5** (b.o. = 0.64). For dissociation of dinitrogen from the cobalt center in the singlet state, the free energy changes at 195 K (ΔG_{195}) in Et$_2$O were calculated to be 19.1 kcal mol^{-1} for **1a** and 16.5 kcal mol^{-1} for **5**. The moderate σ-donating ability of the PNP ligand[24] might be essential in the effective catalytic transformation of dinitrogen into ammonia by **1a**, although the exact role of the PNP ligand has not yet been clarified.[25]

In summary, we have designed new cobalt dinitrogen complexes with anionic PNP-type pincer ligands that are effective catalysts for the reduction of molecular dinitrogen into ammonia under mild reaction conditions. Whereas molybdenum- and iron-catalyzed variants have been reported previously,[26] this is the first clear-cut example of cobalt-catalyzed direct formation of ammonia from dinitrogen under mild reaction conditions. We believe that the present findings provide valuable insight for the development of nitrogen fixation systems using transition-metal dinitrogen complexes as catalysts.

Acknowledgements

The present project was supported by CREST, JST, and the Mitsubishi Foundation. We acknowledge Grants-in-Aid for Scientific Research (JP26288044, JP26105708, JP15K13687, and JP15H05798 to Y.N., JP24109014 to K.Y., and JP26888008 to H.T.) from the JSPS and MEXT. S.K. is the recipient of a JSPS Predoctoral Fellowship for Young Scientists.

Keywords: ammonia · catalysis · cobalt · dinitrogen · pincer ligands

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 14291–14295
Angew. Chem. **2016**, *128*, 14503–14507

---

[1] For a recent review, see; B. M. Hoffman, D. Lukoyanov, Z.-Y. Yang, D. R. Dean, L. C. Seefeldt, *Chem. Rev.* **2014**, *114*, 4041.

[2] For selected recent reviews, see; a) H.-P. Jia, E. A. Quadrelli, *Chem. Soc. Rev.* **2014**, *43*, 547; b) C. J.; Rittle, C. C. L. McCrory, J. C. Peters, *J. Am. Chem. Soc.* **2014**, *136*, 13853 M. van der Ham, M. T. M. Koper, D. G. H. Hetterscheid, *Chem. Soc. Rev.* **2014**, *43*, 5183; c) C. Köthe, C. Limberg, *Z. Anorg. Allg. Chem.* **2015**, *641*, 18; d) N. Khoenkhoen, B. de Bruin, J. N. H. Reek, W. I. Dzik, *Eur. J. Inorg. Chem.* **2015**, 567; e) Y. Nishibayashi, *Inorg. Chem.* **2015**, *54*, 9234; f) H. Tanaka, Y. Nishibayashi, K. Yoshizawa, *Acc. Chem. Res.* **2016**, *49*, 987; g) Y. Tanabe, Y. Nishibayashi, *Chem. Rec.* **2016**, *16*, 1549.

[3] For selected recent examples, see; a) I. Klopsch, M. Finger, C. Würtele, B. Milde, D. B. Werz, S. Schneider, *J. Am. Chem. Soc.* **2014**, *136*, 6881; b) A. J. Keane, B. L. Yonke, M. Hirotsu, P. Y. Zavalij, L. R. Sita, *J. Am. Chem. Soc.* **2014**, *136*, 9906; c) K. C. MacLeod, D. J. Vinyard, P. L. Holland, *J. Am. Chem. Soc.* **2014**, *136*, 10226; d) J.; Rittle, C. C. L. McCrory, J. C. Peters, *J. Am. Chem. Soc.* **2014**, *136*, 13853; e) K. Grubel, W. W. Brennessel, B. Q. Mercado, P. L. Holland, *J. Am. Chem. Soc.* **2014**, *136*, 16807; f) Y. Ishida, H. Kawaguchi, *J. Am. Chem. Soc.* **2014**, *136*, 16990; g) Z. M. Heiden, S. Chen, L. A. Labios, R. M. Bullock, E. D. Walter, E. L. Tyson, M. T. Mock, *Organometallics* **2014**, *33*, 1333; h) C. J. Weiss, J. D. Egbert, S. Chen, M. L. Helm, R. M. Bullock, M. T. Mock, *Organometallics* **2014**, *33*, 2189; i) Y. Lee, F. T. Sloane, G. Blondin, K. A. Abboud, R. García-Serres, L. J. Murray, *Angew. Chem. Int. Ed.* **2015**, *54*, 1499; *Angew. Chem.* **2015**, *127*, 1519; j) A. J. Keane, W. S. Farrell, B. L. Yonke, P. Y. Zavalij, L. R. Sita, *Angew. Chem. Int. Ed.* **2015**, *54*, 10220; *Angew. Chem.* **2015**, *127*, 10358; k) S. E. Creutz, J. C. Peters, *J. Am. Chem. Soc.* **2015**, *137*, 7310; l) A. McSkimming, W. H. Harman, *J. Am. Chem. Soc.* **2015**, *137*, 8940; m) L. D. Field, N. Hazari, H. L. Li, *Inorg. Chem.* **2015**, *54*, 4768; n) M. T. Mock, A. W. Pierpont, J. D. Egbert, M. O'Hagan, S. Chen, R. M. Bullock, W. G. Dougherty, W. S. Kassel, R. Rousseau, *Inorg. Chem.* **2015**, *54*, 4827; o) T. Suzuki, Y. Wasada-Tsutsumi, T. Ogawa, T. Inomata, T. Ozawa, Y. Sakai, M. D. Fryzuk, H. Masuda, *Inorg. Chem.* **2015**, *54*, 9271; p) Y. Ohki, K. Aoyagi, H. Seino, *Organometallics* **2015**, *34*, 3414; q) I. Čorić, B. Q. Mercado, E. Bill, D. J. Vinyard, P. L. Holland, *Nature* **2015**, *526*, 96; r) I. Klopsch, M. Kinauer, M. Finger, C. Würtele, S. Schneider, *Angew. Chem. Int. Ed.* **2016**, *55*, 4786; *Angew. Chem.* **2016**, *128*, 4864.

[4] a) D. V. Yandulov, R. R. Schrock, *Science* **2003**, *301*, 76; b) V. Ritleng, D. V. Yandulov, W. W. Weare, R. R. Schrock, A. S. Hock, W. M. Davis, *J. Am. Chem. Soc.* **2004**, *126*, 6150; c) R. R. Schrock, *Acc. Chem. Res.* **2005**, *38*, 955; d) W. W. Weare, X. Dai, M. J. Byrnes, J. M. Chin, R. R. Schrock, P. Müller, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 17099; e) R. R. Schrock, *Angew. Chem. Int. Ed.* **2008**, *47*, 5512; *Angew. Chem.* **2008**, *120*, 5594.

[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) S. Kuriyama, K. Arashiba, K. Nakajima, H. Tanaka, N. Kamaru, K. Yoshizawa, Y. Nishibayashi, *J. Am. Chem. Soc.* **2014**, *136*, 9719; d) S. Kuriyama, K. Arashiba, K. Nakajima, H. Tanaka, K. Yoshizawa, Y. Nishibayashi, *Chem. Sci.* **2015**, *6*, 3940.

[6] a) J. S. Anderson, J. Rittle, J. C. Peters, *Nature* **2013**, *501*, 84; b) S. E. Creutz, J. C. Peters, *J. Am. Chem. Soc.* **2014**, *136*, 1105; c) G. Ung, J. C. Peters, *Angew. Chem. Int. Ed.* **2015**, *54*, 532; *Angew. Chem.* **2015**, *127*, 542; d) J. S. Anderson, G. E. Cutsail III, J. Rittle, B. A. Connor, W. A. Gunderson, L. Zhang, B. M. Hoffman, J. C. Peters, *J. Am. Chem. Soc.* **2015**, *137*, 7803.

[7] A. Yamamoto, S. Kitazume, L. S. Pu, S. Ikeda, *Chem. Commun.* **1967**, 79.

[8] For selected recent examples, see; a) L. J. Clouston, V. Bernales, R. K. Carlson, L. Gagliardi, C. C. Lu, *Inorg. Chem.* **2015**, *54*, 9263; b) B. Wu, K. M. Gramigna, M. W. Bezpalko, B. M. Foxman, C. M. Thomas, *Inorg. Chem.* **2015**, *54*, 10909.

[9] A. Yamamoto, Y. Miura, T. Ito, H.-L. Chen, K. Iri, F. Ozawa, *Organometallics* **1983**, *2*, 1429.

[10] R. Imayoshi, H. Tanaka, Y. Matsuo, M. Yuki, K. Nakajima, K. Yoshizawa, Y. Nishibayashi, *Chem. Eur. J.* **2015**, *21*, 8905.

[11] 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.

[12] T. J. Del Castillo, N. B. Thompson, D. L. M. Suess, G. Ung, J. C. Peters, *Inorg. Chem.* **2015**, *54*, 9256.

[13] a) G. T. Venkanna, S. Tammineni, H. D. Arman, Z. J. Tonzetich, *Organometallics* **2013**, *32*, 4656; b) G. T. Venkanna, H. D. Arman, Z. J. Tonzetich, *ACS Catal.* **2014**, *4*, 2941; c) M. Kreye, M. Freytag, P. G. Jones, P. G. Williard, W. H. Bernskoetter, M. D. Walter, *Chem. Commun.* **2015**, *51*, 2946; d) D. S. Levine, T. D. Tilley, R. A. Anderson, *Organometallics* **2015**, *34*, 4647.

[14] CCDC 1487275 (**1a**), 1487276 (**1b**), 1487271 (**2a**), 1487272 (**2b**), 1487273 (**3a**), and 1487274 (**4a**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

[15] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955.

[16] For selected examples, see: a) C. G. Barraclough, R. L. Martin, J. M. Stewart, *Aust. J. Chem.* **1969**, *22*, 891; b) G. W. Everett, R. H. Holm, *J. Am. Chem. Soc.* **1965**, *87*, 5266; c) S. J. Carter, B. M. Foxman, L. S. Stuhl, *J. Am. Chem. Soc.* **1984**, *106*, 4265; d) Z. Mo, Y. Li, H. K. Lee, L. Deng, *Organometallics* **2011**, *30*, 4687.

[17] a) C. C. H. Atienza, C. Milsmann, S. P. Semproni, Z. R. Turner, P. J. Chirik, *Inorg. Chem.* **2013**, *52*, 5403; b) S. S. Rozenel, R. Padilla, J. Arnold, *Inorg. Chem.* **2013**, *52*, 11544; c) T.-P. Lin, J. C. Peters, *J. Am. Chem. Soc.* **2013**, *135*, 15310; d) S. P. Semproni, C. Milsmann, P. J. Chirik, *J. Am. Chem. Soc.* **2014**, *136*, 9211.

[18] To clarify whether or not cobalt nanoparticles generated in situ act as heterogeneous catalysts in the present reaction, we carried out the catalytic reaction in the presence of cobalt powder. The reaction only gave a trace amount of ammonia based on the amount of cobalt.

[19] I. S. Weitz, M. Rabinovitz, *J. Chem. Soc. Perkin Trans. 1* **1993**, 117.

[20] S. Vogel, A. Barth, G. Huttner, T. Klein, L. Zsolnai, R. Kremer, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 303; *Angew. Chem.* **1991**, *103*, 325.

[21] Peters and co-workers confirmed that some simple cobalt complexes such as $CoI_2(PPh_3)_3$, $Co_2(CO)_8$, and cobaltocene did not work as catalysts at all under the same reaction conditions; see Ref. [12].

[22] a) I. Mayer, *Chem. Phys. Lett.* **1983**, *97*, 270; b) I. Mayer, *Int. J. Quantum Chem.* **1984**, *26*, 151; c) A. J. Bridgeman, G. Cavigliasso, L. R. Ireland, J. Rothery, *J. Chem. Soc. Dalton Trans.* **2001**, 2095.

[23] Y. Segawa, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2009**, *131*, 9201.

[24] Pyrrolide ligands are weaker σ donors than phenyl ligands; see: J. A. Flores, J. G. Andino, N. P. Tsvetkov, M. Pink, R. J. Wolfe, A. R. Head, D. L. Lichtenberger, J. Massa, K. G. Caulton, *Inorg. Chem.* **2011**, *50*, 8121.

[25] The result described in the Peters paper[12] indicates that the corresponding anionic cobalt dinitrogen complexes may play a major role in the transformation of molecular dinitrogen into ammonia. In fact, our preliminary calculations have shown that protonation of the dinitrogen ligand in neutral **1a** with $[H(OEt_2)_2]^+$ is endergonic. We also computationally observed that reduction of the neutral cobalt dinitrogen complex **1a** significantly increases the negative NPA charge on dinitrogen. Cyclovoltammetric analysis of **1a** also suggests the formation of an anionic cobalt dinitrogen complex under the catalytic reaction conditions (see the Supporting Information for details).

[26] a) During the preparation of the present manuscript, Peters and co-workers reported the formation of 59 equiv of ammonia based on the iron atom of their catalyst upon modifying the reaction conditions; see: T. J. Del Castillo, N. B. Thompson, J. C. Peters, *J. Am. Chem. Soc.* **2016**, *138*, 5341; b) S. Kuriyama, K. Arashiba, K. Nakajima, Y. Matsuo, H. Tanaka, K. Ishii, K. Yoshizawa, Y. Nishibayashi, *Nat. Commun.* **2016**, *7*, 12181.

Received: June 23, 2016
Revised: July 19, 2016