



ChemComm

**Catalytic reduction of dinitrogen into
tris(trimethylsilyl)amine using rhodium complexes with
pyrrole-based PNP-type pincer ligand**

Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-09-2019-006896.R2
Article Type:	Communication

SCHOLARONE™
Manuscripts

COMMUNICATION

Catalytic reduction of dinitrogen into tris(trimethylsilyl)amine using rhodium complexes with pyrrole-based PNP-type pincer ligand

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Ryosuke Kawakami,^a Shogo Kuriyama,^a Hiromasa Tanaka,^b Kazuya Arashiba,^a Asuka Konomi,^c Kazunari Nakajima,^d Kazunari Yoshizawa,^{*c} and Yoshiaki Nishibayashi^{*a}

Rhodium complexes bearing an anionic pyrrole-based PNP-type pincer ligand are synthesised and found to work as effective catalysts for the transformation of molecular dinitrogen into tris(trimethylsilyl)amine under mild reaction conditions. This is the first successful example of rhodium-catalysed dinitrogen reduction under mild reaction conditions.

Various transition metal-dinitrogen complexes have been intensively studied for the last decades to achieve efficient catalytic nitrogen fixation under mild reaction conditions. In 2003, Yandulov and Schrock reported the first example of the catalytic ammonia formation from dinitrogen using a molybdenum dinitrogen complex.¹ Since the pioneering report, titanium-,² vanadium-,³ molybdenum-,⁴ iron-,⁵ ruthenium-,⁶ osmium-,⁶ and cobalt⁷-catalysed reduction of dinitrogen into ammonia and hydrazine has been reported by us and other groups.⁸ In addition, catalytic transformation of dinitrogen into tris(trialkylsilyl)amines, which are easily converted into ammonia by acid hydrolysis, has been developed since the first report by Shiina in 1972⁹ as an alternative nitrogen fixation.¹⁰ Up to now, titanium-,¹¹ vanadium-,¹² chromium-,¹³ molybdenum-,¹⁴ tungsten-,^{14b} iron-,¹⁵ and cobalt-complexes¹⁶ worked as catalysts for the formation of tris(trimethylsilyl)amine (N(SiMe₃)₃) under mild reaction conditions.

In sharp contrast to the intensive study of the catalytic activity of early-to-mid transition metal-dinitrogen complexes toward nitrogen fixation, the catalytic reactivity of group 9-11 transition metal-dinitrogen complexes toward nitrogen fixation has been less explored except for cobalt-dinitrogen complexes,¹⁷ because the activation of dinitrogen by these

metals is often too weak to be functionalised into ammonia and its equivalent such as N(SiMe₃)₃. Although more than 30 examples of rhodium-dinitrogen complexes have been synthesised until now,^{17c} no successful example of the transformation of the coordinated dinitrogen on the rhodium atom of the rhodium-dinitrogen complexes has yet been reported not only in a catalytic fashion but also in a stoichiometric fashion, to the best of our knowledge.

Recently, we have found that vanadium-,³ iron-,^{5g} and cobalt⁷-dinitrogen complexes bearing an anionic pyrrole-based pincer ligand (PNP = 2,5-bis(di-*tert*-butylphosphinomethyl)pyrrolide) worked as effective catalysts for the formation of ammonia and hydrazine in the reaction of atmospheric pressure of dinitrogen gas with reductant and proton source at -78 °C. Based on these research backgrounds, we have newly designed rhodium-dinitrogen complexes bearing the same PNP ligand to investigate their catalytic activity toward formation of ammonia and N(SiMe₃)₃.[‡] As a result, we have found that the synthesized rhodium complex worked as an effective catalyst for the formation of N(SiMe₃)₃ as the first example of the rhodium-catalysed transformation of dinitrogen under mild reaction conditions. Herein, we report preliminary results.

The reaction of [RhCl₃(MeCN)₃] with 1 equiv. of lithium 2,5-bis(di-*tert*-butylphosphinomethyl)pyrrolide (PNP-Li) and KC₈ in THF at -30 °C for 1 min and then at room temperature for 4 h gave a rhodium(II)-chloride complex bearing the PNP ligand [RhCl(PNP)] (**1**) in 32% yield (Scheme 1). Isolation of mononuclear rhodium(II) complexes is relatively limited and rare because Rh(II) species are prone to disproportionation or dimerization.^{18,19} The molecular structure of **1** was confirmed by X-ray analysis. An ORTEP drawing is shown in Fig. 1(a). Complex **1** has a distorted square planar geometry around the rhodium centre. Rhodium(II) complex **1** is paramagnetic with a solution magnetic moment of 2.0 μ_B at 298 K. The measured magnetic moment is close to the spin-only value for an *S* = 1/2 spin state. The cyclic voltammogram (CV) of **1** in THF with NBu₄PF₆ as supporting electrolyte under an atmospheric pressure of dinitrogen or argon shows a reversible reduction wave at *E*_{1/2} = -1.36 V vs ferrocene^{0/+} (Fig. S1). The chemical reduction of **1** with 1.1 equiv. of KC₈ under an atmospheric

^a Department of Systems Innovation, and School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: ynishiba@sys.t.u-tokyo.ac.jp

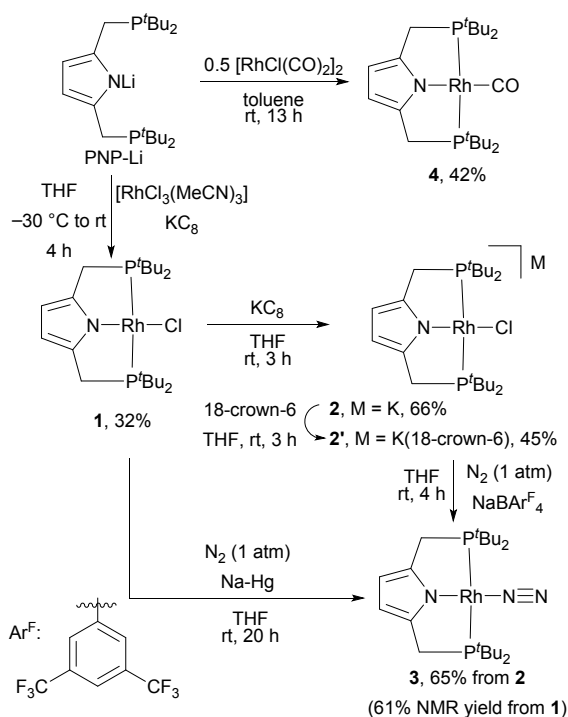
^b School of Liberal Arts and Science, Daido University, Minami-ku, Nagoya 457-8530, Japan.

^c Institute for Materials Chemistry and Engineering, Kyushu University, Nishi-ku, Fukuoka 819-0395, Japan. E-mail: kazunari@ms.ifoc.kyushu-u.ac.jp

^d Frontier Research Center for Energy and Resources, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

[‡] Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available. CCDC. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis of rhodium complexes bearing the pyrrole-based anionic PNP-type pincer ligand

pressure of dinitrogen did not afford the corresponding rhodium(I)-dinitrogen complex but an anionic rhodium(I)-chloride complex ($[K[RhCl(PNP)]]$) (**2**) in 66% yield. The formation of **2** was confirmed by treating **2** with 18-crown-6 in THF to afford $[K(18\text{-crown-6})][RhCl(PNP)]$ (**2'**), which was characterized as THF-adduct $\mathbf{2}'\cdot(\text{thf})_2$ by X-ray analysis (Fig. 1(b)). Rh(I) complex $\mathbf{2}'\cdot(\text{thf})_2$ has longer Rh-Cl and Rh-N bonds (2.4143(6) and 2.004(2) Å) than **1** (2.3218(8) and 1.952(2) Å), respectively, while the mean Rh-P distance of $\mathbf{2}'\cdot(\text{thf})_2$ (2.271 Å) is shorter than that of **1** (2.322 Å).

We investigated the cation exchange of **2** with Na^+ to eliminate the Cl anion as NaCl. The reaction of **2** with 1 equiv. of NaBARF_4 ($\text{Ar}^F = 3,5\text{-bis(trifluoromethyl)phenyl}$) in THF at room temperature for 20 h under an atmospheric pressure of dinitrogen afforded the corresponding rhodium(I)-dinitrogen complex **3** in 66% yield. Separately, **3** was obtained in 61% NMR yield by reduction of **1** with 1 equiv. of Na-Hg in THF at room temperature for 20 h under an atmospheric pressure of dinitrogen. The molecular structure of **3** shows that the rhodium atom of **3** adopts a distorted square planar structure with an end-on dinitrogen ligand (Fig. 1(c)). The IR spectra of **3** in solid (KBr) and solution (THF or C_6D_6) states exhibit strong ν_{NN} bands at 2110 and 2112 cm^{-1} , respectively, which are assigned as the terminal dinitrogen ligand. The ν_{NN} values of **3** is comparable to those of reported Rh(I)-dinitrogen complexes.^{17c} A larger ν_{NN} value of **3** than the cobalt-analogue complex $[\text{Co}(\text{N}_2)(\text{PNP})]^7$ (2017 cm^{-1} in THF) indicates weaker activation of the dinitrogen ligand in **3**. The CV spectrum of **3** in THF shows no reduction wave within the solvent window.

We have performed DFT calculations to get more information on **3**. Optimized structure of **3** and its selected

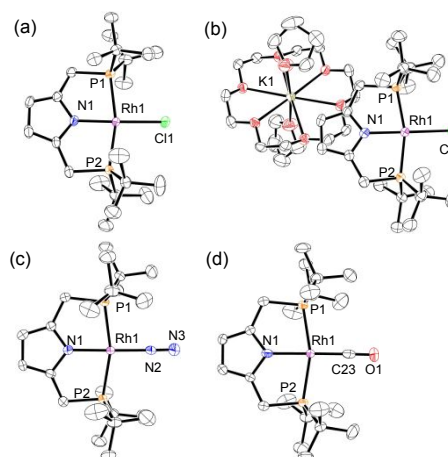


Fig. 1. ORTEP drawings of **1** (a), $\mathbf{2}'\cdot(\text{thf})_2$ (b), **3** (c), and **4** (d). Thermal ellipsoids are shown at the 50% level. Hydrogen atoms are omitted for clarity.

geometric parameters are presented in Fig. S6. The calculated ν_{NN} value of the singlet state of **3** in gas phase, 2128 cm^{-1} , is very close to the experimental values. The bond dissociation free energy of the Rh-N₂ bond (23.3 kcal/mol) of **3** is comparable with that of the Co-N₂ bond of the cobalt-analogue complex $[\text{Co}(\text{N}_2)(\text{PNP})]^7$ (21.3 kcal/mol). On the other hand, the electron affinity of **3** is calculated to be 21.0 kcal/mol, which is much smaller than those calculated for $[\text{Fe}(\text{N}_2)(\text{PNP})]^{5g}$ (28.6 kcal/mol) and $[\text{Co}(\text{N}_2)(\text{PNP})]^7$ (29.4 kcal/mol). The smaller electron affinity value of **3** could be consistent with the experimental fact that no reduction wave was observed in the CV measurement.

The reaction of $[\text{RhCl}(\text{CO})_2]_2$ with 1 equiv. of PNP-Li in toluene at room temperature for 13 h afforded a carbonyl complex $[\text{Rh}(\text{CO})(\text{PNP})]$ (**4**) in 42% yield. The single-crystal X-ray analysis of **4** (Fig. 1(d)) reveals that the metrical parameters of **4** are comparable to those of **3**. The IR spectrum (KBr) of **4** shows a strong absorption of CO at 1941 cm^{-1} .

We investigated the stoichiometric reaction of **3** toward the formation of ammonia. Protonation of **3** with sulfuric acid in THF neither afforded ammonia nor hydrazine. Next, catalytic formation of ammonia from the reaction of dinitrogen with reductants and proton sources was carried out by using **3** as a catalyst under the reported conditions (Table S1).^{4,5a} However, no formation of ammonia and hydrazine was observed under these reaction conditions, where only the formation of dihydrogen was observed in all cases (Table S1). This result is in sharp contrast to our previous result that iron- and cobalt-dinitrogen complexes $[\text{M}(\text{N}_2)(\text{PNP})]$ (M = Fe and Co) worked as effective catalysts toward the formation of ammonia and hydrazine.^{5g,7} In the iron-catalysed reaction,^{5g} we proposed a reaction pathway where an anionic Fe(0)-dinitrogen complex, which is prepared from one-electron reduction of $[\text{Fe}(\text{N}_2)(\text{PNP})]$, plays a key reactive intermediate to form a nitrogen-hydrogen bond at the terminal nitrogen atom of the coordinated dinitrogen ligand. We consider that protonation may not occur on the dinitrogen ligand but the rhodium atom in **3** to generate dihydrogen.²⁰

Next, we investigated the catalytic formation of $\text{N}(\text{SiMe}_3)_3$ from dinitrogen. Typical results are shown in Table 1. We

carried out the reaction of atmospheric pressure of dinitrogen with KC_8 (600 equiv. to **3**) as a reductant and Me_3SiCl (600 equiv. to **3**) as a silylating reagent in THF at room temperature for 20 h to afford $\text{N}(\text{SiMe}_3)_3$, which was quantified as ammonia after acid hydrolysis of the reaction mixture. This reaction gave 6.8 equiv. of ammonia based on **3** (Table 1, entry 1). Separately, we confirmed the formation of 6.2 equiv. of $\text{N}(\text{SiMe}_3)_3$ (3% yield based on the Me_3SiCl) by GC, together with $\text{Me}_3\text{SiSiMe}_3$ (7% yield), $\text{C}_4\text{H}_9\text{OSiMe}_3$ (3% yield), and $\text{Me}_3\text{SiC}_4\text{H}_8\text{OSiMe}_3$ (34% yield). After the catalytic run, we reloaded fresh KC_8 (600 equiv) and Me_3SiCl (600 equiv) and stirred the reaction mixture at room temperature for another 20 h under 1 atm of N_2 . However, the obtained amount of ammonia did not increase. This result indicates that the rhodium catalyst is no longer active after a catalytic run. Use of Na as a reductant instead of KC_8 afforded no $\text{N}(\text{SiMe}_3)_3$ (Table S2). We also examined other solvents such as Et_2O , DME, and toluene, but THF was the best solvent in the present reaction system (Table S3).

When rhodium complexes **1**, **2**, and **4** as well as a rhodium-ethylene complex $[\text{Rh}(\text{CH}_2\text{CH}_2)(\text{PNP})]$, which was independently reported by Yamashita and co-workers,²¹ were used as catalysts in place of **3**, lower amounts of ammonia were obtained based on the rhodium atom (Table 1, entries 2-5). Then, we employed commercially available simple rhodium complexes as catalysts (Table 1, entries 6-9), but these rhodium complexes worked less effectively than **3**.

Masuda and co-workers^{16d} previously reported that the catalytic activity of their cobalt complex toward the formation

of $\text{N}(\text{SiMe}_3)_3$ from dinitrogen dramatically increased at low temperature such as -40°C because the dinitrogen ligand binding to the metal becomes favourable at low temperature. Based on this previous result, we carried out the catalytic reaction at lower temperature using **3** as a catalyst. As the reaction temperature was decreased, the produced amount of ammonia increased gradually to 23.2 equiv. based on the rhodium atom at -40°C (Table 1, entries 10-13).§ In this case, the formation of 23.9 equiv. of $\text{N}(\text{SiMe}_3)_3$ was observed based on the rhodium atom of the catalyst (12% yield based on the Me_3SiCl), together with $\text{Me}_3\text{SiSiMe}_3$ (36% yield), $\text{C}_4\text{H}_9\text{OSiMe}_3$ (<1% yield), and $\text{Me}_3\text{SiC}_4\text{H}_8\text{OSiMe}_3$ (8% yield). However, the catalytic activity of **3** substantially dropped when the reaction was carried out at further low temperature such as -50 or -60°C (Table 1, entries 14-15).

We have not yet clarified the reaction mechanism of the catalytic silylation of dinitrogen using **3** as a catalyst. As proposed in the previous study,¹⁰ we consider that the present reaction proceeds homogeneously via Me_3Si radical, which is generated *in situ* from Me_3SiCl and KC_8 , as an active silylating reagent. In fact, no inhibition of the formation of $\text{N}(\text{SiMe}_3)_3$ in the presence of Hg was observed in the present reaction system, indicating that homogeneous rhodium complexes may work as reactive species for the silylation of dinitrogen.²²

Reactions of **3** with three Me_3Si radicals to yield $[\text{Rh}(\text{PNP})(\text{N}(\text{SiMe}_3)_x)]$ ($x = 1-3$) have been evaluated by DFT calculations. We found that the $\text{Rh}(\text{PNP})$ framework can accept up to three SiMe_3 radicals due to the bulkiness of the SiMe_3 group. Optimized structures of the silylated complexes $[\text{Rh}(\text{PNP})(\text{N}(\text{SiMe}_3)_x)]$ ($x = 1-3$) are presented in Fig. S7. $\text{Rh}(\text{I})$, $\text{Rh}(\text{II})$ and $\text{Rh}(\text{III})$ states are involved as intermediates. The free energy changes (ΔG_{298}) for the three successive addition of the SiMe_3 radical to **3** are calculated to be $+1.9$ kcal/mol ($x = 1$), -17.9 kcal/mol ($x = 2$), and -0.2 kcal/mol ($x = 3$). Although the steps in which the $\text{Rh}(\text{II})$ species are formed are less favourable, the calculated ΔG_{298} values indicate that the silylation reactions of **3** with three Me_3Si radicals to $[\text{Rh}(\text{PNP})(\text{N}(\text{SiMe}_3)_3)]$ can totally proceed from a thermodynamic point of view.

In summary, we have found that newly designed and prepared the rhodium dinitrogen complex bearing the anionic pyrrole-based PNP-type pincer ligand worked as an effective catalyst for the silylation of dinitrogen under mild reaction conditions, where up to 23 equiv. of $\text{N}(\text{SiMe}_3)_3$ were produced based on the rhodium atom of the catalyst. This result demonstrates the first successful example of the rhodium-catalysed-nitrogen fixation under mild reaction conditions. One of the possible roles of the PNP pincer ligand is to stabilize various oxidation states during the catalytic reaction. We hope that the finding described in the present paper provides the valuable suggestion to develop late transition metal-catalysed nitrogen fixation under mild reaction conditions. Further studies are ongoing in our laboratory to develop novel transition-metal catalysts for the nitrogen fixation.

The present project is supported by CREST, JST (Grant JPMJCR1541). We acknowledge Grants-in-Aid for Scientific Research (Grants JP17H01201, JP15H05798, JP18K19093, JP18K05148, and JP19K23645) from JSPS and MEXT.

Table 1 Catalytic reduction of dinitrogen into tris(trimethylsilyl)amine using rhodium complexes^a

Entry	Catalyst	T	NH_3 (equiv.) ^b
1	3	rt	6.8 ± 0.7^c (6.2^d)
2	1	rt	3.9
3	2	rt	5.4
4	4	rt	2.2
5	$[\text{Rh}(\text{CH}_2\text{CH}_2)(\text{PNP})]$	rt	5.3
6	$[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$	rt	3.5
7	$[\text{RhCl}(\text{PPh}_3)_3]$	rt	2.2
8	$[\text{Rh}_2(\text{OAc})_2]$	rt	2.8
9	$[\text{Rh}_4(\text{CO})_{12}]$	rt	0.1
10	3	0°C	6.2
11	3	-20°C	7.4
12	3	-30°C	17.3
13	3	-40°C	23.2 ± 0.3^c (23.9^d)
14	3	-50°C	12.3
15	3	-60°C	7.3

^a A mixture of rhodium complex (0.0025 mmol/Rh), KC_8 (1.5 mmol), and Me_3SiCl (1.5 mmol) in THF (3.0 mL) was stirred at room temperature for 20 h under 1 atm of N_2 . ^b Equiv. of ammonia based on the Rh atom of the catalyst after acid hydrolysis of the reaction mixture. ^c Averages of triplicate runs are shown. ^d GC yield of $\text{N}(\text{SiMe}_3)_3$.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Yamashita and co-workers independently reported the rhodium-ethylene and -dihydrogen complexes bearing the same PNP ligand. See a reference 21.

§ When $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ was used as a catalyst for the dinitrogen silylation at $-40\text{ }^\circ\text{C}$, 11.0 equiv. of ammonia based on the rhodium atom were produced after hydrolysis. This result indicates that the catalytic activity of $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ was higher than that at room temperature (see Table 1, entry 6).

- D. V. Yandulov and R. R. Schrock, *Science*, 2003, **301**, 76-78.
- L. R. Doyle, A. J. Wooles, L. C. Jenkins, F. Tuna, E. J. L. McInnes and S. T. Little, *Angew. Chem. Int. Ed.*, 2018, **57**, 6314-6318.
- Y. Sekiguchi, K. Arashiba, H. Tanaka, A. Eizawa, K. Nakajima, K. Yoshizawa and Y. Nishibayashi, *Angew. Chem. Int. Ed.*, 2018, **57**, 9064-9068.
- (a) K. Arashiba, Y. Miyake and Y. Nishibayashi, *Nat. Chem.*, 2011, **3**, 120-125. (b) K. Arashiba, E. Kinoshita, S. Kuriyama, A. Eizawa, K. Nakajima, H. Tanaka, K. Yoshizawa and Y. Nishibayashi, *J. Am. Chem. Soc.*, 2015, **137**, 5666-5669. (c) A. Eizawa, K. Arashiba, H. Tanaka, S. Kuriyama, Y. Matsuo, K. Nakajima, K. Yoshizawa and Y. Nishibayashi, *Nat. Commun.*, 2017, **8**, 14874. (d) K. Arashiba, A. Eizawa, H. Tanaka, K. Nakajima, K. Yoshizawa and Y. Nishibayashi, *Bull. Chem. Soc. Jpn.*, 2017, **90**, 1111-1118. (e) Y. Ashida, K. Arashiba, K. Nakajima and Y. Nishibayashi, *Nature*, 2019, **568**, 536-540. (f) Y. Ashida, K. Arashiba, H. Tanaka, A. Egi, K. Nakajima, K. Yoshizawa and Y. Nishibayashi, *Inorg. Chem.*, 2019, **58**, 8927-8932. (g) Y. Ashida, S. Kondo, K. Arashiba, T. Kikuchi, K. Nakajima, S. Kakimoto and Y. Nishibayashi, *Synthesis*, doi: 10.1055/s-0039-1690151.
- (a) J. S. Anderson, J. Rittle and J. C. Peters, *Nature*, 2013, **501**, 84-87. (b) S. E. Creutz and J. C. Peters, *J. Am. Chem. Soc.*, 2014, **136**, 1105-1115. (c) G. Ung and J. C. Peters, *Angew. Chem. Int. Ed.*, 2015, **54**, 532-535. (d) T. J. Del Castillo, N. B. Thompson and J. C. Peters, *J. Am. Chem. Soc.*, 2016, **138**, 5341-5350. (e) M. J. Chalkley, T. J. Del Castillo, B. D. Matson, J. P. Roddy and J. C. Peters, *ACS Cent. Sci.*, 2017, **3**, 217-223. (f) T. M. Buscagan, P. H. Oyala and J. C. Peters, *Angew. Chem. Int. Ed.*, 2017, **56**, 6921-6926. (g) S. Kuriyama, K. Arashiba, K. Nakajima, Y. Matsuo, H. Tanaka, K. Ishii, K. Yoshizawa and Y. Nishibayashi, *Nat. Commun.*, 2016, **7**, 12181. (h) P. J. Hill, L. R. Doyle, A. D. Crawford, W. K. Myers and A. E. Ashley, *J. Am. Chem. Soc.*, 2016, **138**, 13521-13524.
- J. Fajardo Jr. and J. C. Peters, *J. Am. Chem. Soc.*, 2017, **139**, 16105-16108.
- S. Kuriyama, K. Arashiba, H. Tanaka, Y. Matsuo, K. Nakajima, K. Yoshizawa and Y. Nishibayashi, *Angew. Chem. Int. Ed.*, 2016, **55**, 14291-14293.
- For a recent review on transition metal-catalysed formation of ammonia from dinitrogen, see Y. Nishibayashi, *Dalton Trans.*, 2018, **47**, 11290-11297.
- K. Shiina, *J. Am. Chem. Soc.*, 1972, **94**, 9266-9267.
- For a recent review on catalytic silylation of dinitrogen, see: Y. Tanabe and Y. Nishibayashi, *Coord. Chem. Rev.*, 2019, **389**, 73-93.
- P. Ghana, F. D. van Krüchten, T. P. Spaniol, J. van Leusen, P. Kögerler and J. Okuda, *Chem. Commun.*, 2019, **55**, 3231-3234.
- R. Imayoshi, K. Nakajima and Y. Nishibayashi, *Chem. Lett.*, 2017, **46**, 466-468.
- (a) A. J. Kendall, S. I. Johnson, R. M. Bullock and M. T. Mock, *J. Am. Chem. Soc.*, 2018, **140**, 2528-2536. (b) J. Yin, J. Li, G.-X. Wang, Z.-B. Yin, W.-X. Zhang and Z. Xi, *J. Am. Chem. Soc.*, 2019, **141**, 4241-4247.
- (a) K. Komori, H. Oshita, Y. Mizobe and M. Hidai, *J. Am. Chem. Soc.*, 1989, **111**, 1939-1940. (b) H. Tanaka, A. Sasada, T. Kouno, M. Yuki, Y. Miyake, H. Nakanishi, Y. Nishibayashi and K. Yoshizawa, *J. Am. Chem. Soc.*, 2011, **133**, 3498-3506. (c) Q. Liao, N. Saffon-Merceron and N. Mézailles, *Angew. Chem. Int. Ed.*, 2014, **53**, 14206-14210.
- (a) M. Yuki, H. Tanaka, K. Sasaki, Y. Miyake, K. Yoshizawa and Y. Nishibayashi, *Nat. Commun.*, 2012, **3**, 1254. (b) D. E. Prokopchuk, E. S. Wiedner, E. D. Walter, C. V. Popescu, N. A. Piro, W. S. Kassel, R. M. Bullock and M. T. Mock, *J. Am. Chem. Soc.*, 2017, **139**, 9291-9301. (c) R. B. Ferreira, B. J. Cook, B. J. Knight, V. J. Catalano, R. Garcia-Serres and L. J. Murray, *ACS Catal.*, 2018, **8**, 7208-7212. (d) R. Araake, K. Sakadani, M. Tada, Y. Sakai and Y. Ohki, *J. Am. Chem. Soc.*, 2017, **139**, 5596-5606. (e) Y. Ohki, Y. Araki, M. Tada and Y. Sakai, *Chem. – Eur. J.*, 2017, **23**, 13240-13248. (f) A. D. Piascik, R. Li, H. J. Wilkinson, J. C. Green and A. E. Ashley, *J. Am. Chem. Soc.*, 2018, **140**, 10691-10694.
- (a) R. B. Siedschlag, V. Bernales, K. D. Vogiatzis, N. Planas, L. J. Clouston, E. Bill, L. Gagliardi and C. C. Lu, *J. Am. Chem. Soc.*, 2015, **137**, 4638-4641. (b) R. Imayoshi, H. Tanaka, Y. Matsuo, M. Yuki, K. Nakajima, K. Yoshizawa and Y. Nishibayashi, *Chem. – Eur. J.*, 2015, **21**, 8905-8909. (c) Y. Gao, G. Li and L. Deng, *J. Am. Chem. Soc.*, 2018, **140**, 2239-2250. (d) T. Suzuki, K. Fujimoto, Y. Takemoto, Y. Wasada-Tsutsui, T. Ozawa, T. Inomata, M. D. Fryzuk and H. Masuda, *ACS Catal.*, 2018, **8**, 3011-3015.
- For reviews on group 9-11 transition metal-dinitrogen complexes, see: (a) N. Khoenkhon, B. de Bruin, J. N. H. Reek, and W. I. Dzik, *Eur. J. Inorg. Chem.*, 2015, **2015**, 567-598. (b) S. Kuriyama and Y. Nishibayashi, in *Nitrogen Fixation*, ed. Y. Nishibayashi, 2017, vol. 60, pp. 215-234. (c) C. C. Lu and S. D. Prinslow, in *Transition Metal – Dinitrogen Complexes: Preparation and Reactivity*, ed. Y. Nishibayashi, Wiley-VCH, Weinheim, Germany, 2019, ch. 7, pp. 337-402. (d) R. B. Ferreira and L. J. Murray in *Transition Metal – Dinitrogen Complexes: Preparation and Reactivity*, ed. Y. Nishibayashi, Wiley-VCH, Weinheim, Germany, 2019, ch. 8, pp. 403-440.
- For a review on mononuclear Rh(II) complexes, see: (a) D. G. DeWit, *Coord. Chem. Rev.* 1996, **147**, 209-246. (b) B. de Bruin and D. G. H. Hetterscheid, *Eur. J. Inorg. Chem.* 2007, **2007**, 211-230.
- For recent selected examples, see: (a) M. Gerisch, J. R. Krumper, R. G. Bergman and T. D. Tilley, *Organometallics*, 2003, **22**, 47-58. (b) M. Feller, E. Ben-Ari, T. Gupta, L. J. W. Shimon, G. Leitius, Y. Diskin-Posner, L. Weiner and D. Milstein, *Inorg. Chem.*, 2007, **46**, 10479-10490. (c) A. J. Rosenthal, M. Vogt, B. de Bruin and H. Grützmacher, *Eur. J. Inorg. Chem.*, 2013, **2013**, 5831-5835. (d) D. A. Smith, D. E. Herbert, J. R. Walensky and O. V. Ozerov, *Organometallics*, 2013, **32**, 2050-2058. (e) M. G. Schreiber, Y. Wu, A. C. Stückli, L. Krause, E. Carl, D. Stalke, B. de Bruin and S. Schneider, *J. Am. Chem. Soc.* 2013, **135**, 17719-17722.
- G. P. Connor, N. Lease, A. Casuras, A. S. Goldman, P. L. Holland and J. M. Mayer, *Dalton Trans.*, 2017, **46**, 14325-14330.
- S. Nakayama, S. Morisako and M. Yamashita, *Organometallics*, 2018, **37**, 1304-1313.
- R. H. Crabtree, *Chem. Rev.* 2012, **112**, 1536-1554.