Top Organomet Chem
DOI: 10.1007/3418_2016_10

Catalytic Nitrogen Fixation Using Molybdenum–Dinitrogen Complexes as Catalysts

Aya Eizawa and Yoshiaki Nishibayashi

Abstract This chapter describes recent advances of molybdenum-catalyzed catalytic nitrogen fixation such as catalytic formation of silylamine and ammonia from dinitrogen under ambient reaction conditions. Hidai, Nishibayashi, Masuda, Mézailles, and their coworkers have achieved the molybdenum-catalyzed silylation and Schrock, Nishibayashi, and their coworkers have achieved the molybdenum-catalyzed formation of ammonia from nitrogen gas under ambient reaction conditions.

Keywords Ammonia • Catalyst • Dinitrogen • Molybdenum • Reduction • Silylamine

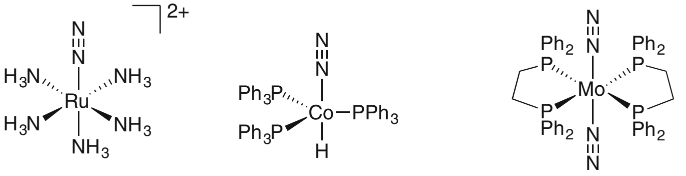
Contents

A. Eizawa and 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

1 Introduction: Brief History of Preparation of Transition Metal–Dinitrogen Complexes and Their Use for Stoichiometric Nitrogen Fixation

In 1965, the first transition metal–dinitrogen complex $[Ru(N_2)(NH_3)_5]^{2+}$ (**1**) was reported by Allen and Senoff (Fig. 1) [1]. The first transition metal–dinitrogen complex $[Co(N_2)H(PPh_3)_3]$ (**2**), whose dinitrogen ligand was directly derived from nitrogen gas, was reported by Yamamoto and coworkers in 1967 [2]. With regard to molybdenum–dinitrogen complex, the first example is *trans*-$[Mo(N_2)_2(dppe)_2]$ (**3**, dppe = 1,2-bis(diphenylphosphino)ethane) reported by Hidai and coworkers in 1969 [3].

The first conversion of coordinated dinitrogen ligand to ammonia was achieved by Chatt and coworkers in 1975 (Fig. 2) [4, 5]. The reaction of *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo, **4**; M = W, **5**) with strong acids such as sulfuric acid and hydrobromic acid afforded up to 0.88 equivalents of ammonia for **4** and up to 1.98 equivalents of ammonia for **5**. Stoichiometric reactions of **4** and **5** with strong acids afforded the corresponding hydrazido(2–) complexes, which were considered to be reactive intermediates in the



1 The first dinitrogen complex

2 The first dinitrogen complex derived from nitrogen gas

3 The first molybdenum–dinitrogen complex

Fig. 1 Historic transition metal–dinitrogen complexes

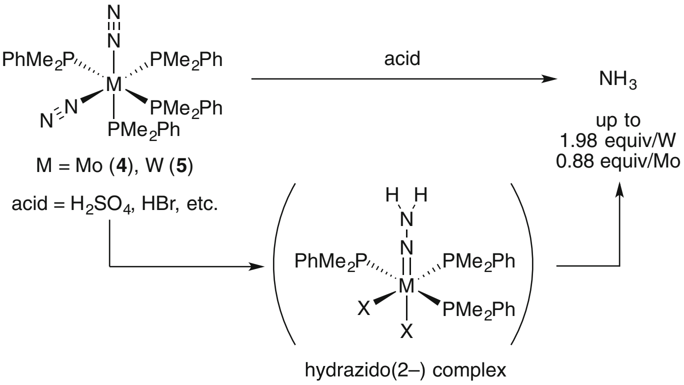


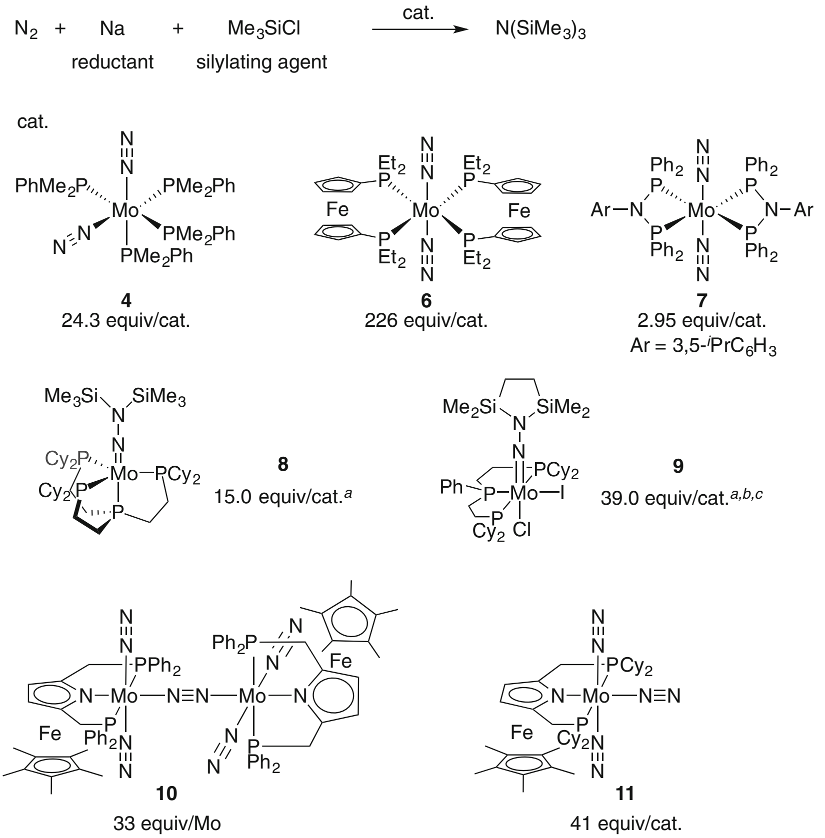
Fig. 2 Protonation of molybdenum– and tungsten–dinitrogen complexes with strong acids

formation of ammonia from dinitrogen complexes [6–8]. Since this discovery, synthesis and reactivity of a number of molybdenum–dinitrogen complexes have been reported [9–29]. In this chapter, we describe a recent advance on catalytic conversion of nitrogen gas using molybdenum–dinitrogen and related complexes as catalysts under ambient reaction conditions.

2 Catalytic Transformation of Dinitrogen to Silylamine with Molybdenum Complexes

Catalytic transformation of dinitrogen to silylamine was first accomplished by Shiina using chromium trichloride $CrCl_3$ as a catalyst in 1972 [30]. However, the possibility of lithium–nitride as nitrogen source was not completely excluded because Li was used as a reductant. With regard to molybdenum catalysis, the first example was achieved by Hidai, Mizobe, and coworkers in 1989 [31]. This report is the first example of catalytic transformation of the coordinated dinitrogen into silylamine. In the presence of a molybdenum–dinitrogen complex *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ (**4**) as a catalyst, the reaction of an atmospheric pressure of nitrogen gas with sodium and Me_3SiCl in THF at room temperature afforded 24.3 equivalents of tris(trimethylsilyl)amine ($N(SiMe_3)_3$) (Fig. 3). After this report, several molybdenum-catalyzed reactions of nitrogen gas into silylamine were reported by some research groups. In 2011, the use of a molybdenum–dinitrogen complex bearing ferrocenyldiphosphine ligands (**6**) as a catalyst was found to produce 226 equivalents of silylamine per catalyst by Nishibayashi, Yoshizawa, and coworkers [32]. Masuda and coworkers reported that a molybdenum–dinitrogen complex bearing diphosphine ligands (**7**) worked as a catalyst in transforming dinitrogen into silylamine [33]. Recently, molybdenum–bis(silyl)hydrazido(2–) complexes bearing a tetradentate tetraphosphine ligand (**8**) [34] and a tridentate triphosphine ligand (**9**) [35] have also been revealed to work as effective catalysts for the catalytic silylation by Mézailles and coworkers. Quite recently, Nishibayashi and coworkers found that the use of molybdenum–dinitrogen complexes bearing azaferrocene-based PNP pincer ligands **10** and **11** promoted the same catalytic reaction [36]. Typical results are shown in Fig. 3.

Novel plausible reaction pathways for the catalytic silylation using **6**, **8**, and **9** as catalysts have been examined (Fig. 4). As to the catalytic cycle for using **6**, a reaction pathway was studied with DFT calculations (Fig. 4a) [32]. Chlorotrimethylsilane is reduced to generate trimethylsilyl radical, which is a real silylating agent for this catalytic reaction. At first, one of the dinitrogen ligands of **I** is silylated to form $[Mo(NNSiMe_3)]$ (**II**) and then $[Mo(NN(SiMe_3)_2)]$ (**III**) species. Then further silylation proceeds at the nitrogen atom adjacent to the molybdenum atom to generate a silylhydrazido(1–) (**IV**) species. Successive one-electron reduction liberates $(Me_3Si)_2NN(SiMe_3)^-$ and the coordination of another dinitrogen molecule to the vacant site of the molybdenum atom of **V** regenerates the molybdenum–dinitrogen complex **I**. The generated $(Me_3Si)_2NN(SiMe_3)$ anion would be converted to two



[a] Potassium was used as a reductant in place of sodium.
[b] 1,2-Bis(chlorodimethylsilyl)ethane was used in place of Me_3SiCl.
[c] The amount of NH_4^+ obtained after hydrolysis.

Fig. 3 Molybdenum-catalyzed catalytic conversion of nitrogen gas to silylamine

molecules of $N(SiMe_3)_3$. On the other hand, Mézailles and coworkers carried out stoichiometric reactions of the molybdenum complexes **8** and **9** with reductants and/or silylating agents to obtain information on the catalytic cycle. Based on the stoichiometric reactions, a reaction pathway has been proposed (Fig. 4b) [34, 35]. First, a molybdenum–bis(silyl)hydrazido(2–) species **VI** is silylated to afford one molecule of silylamine and a molybdenum-imido complex **VII**. Further silylation of **VII** affords another silylamine and the coordination of another dinitrogen molecule generates a molybdenum–dinitrogen species **VIII**. Silylation to the dinitrogen ligand regenerates **VI**.

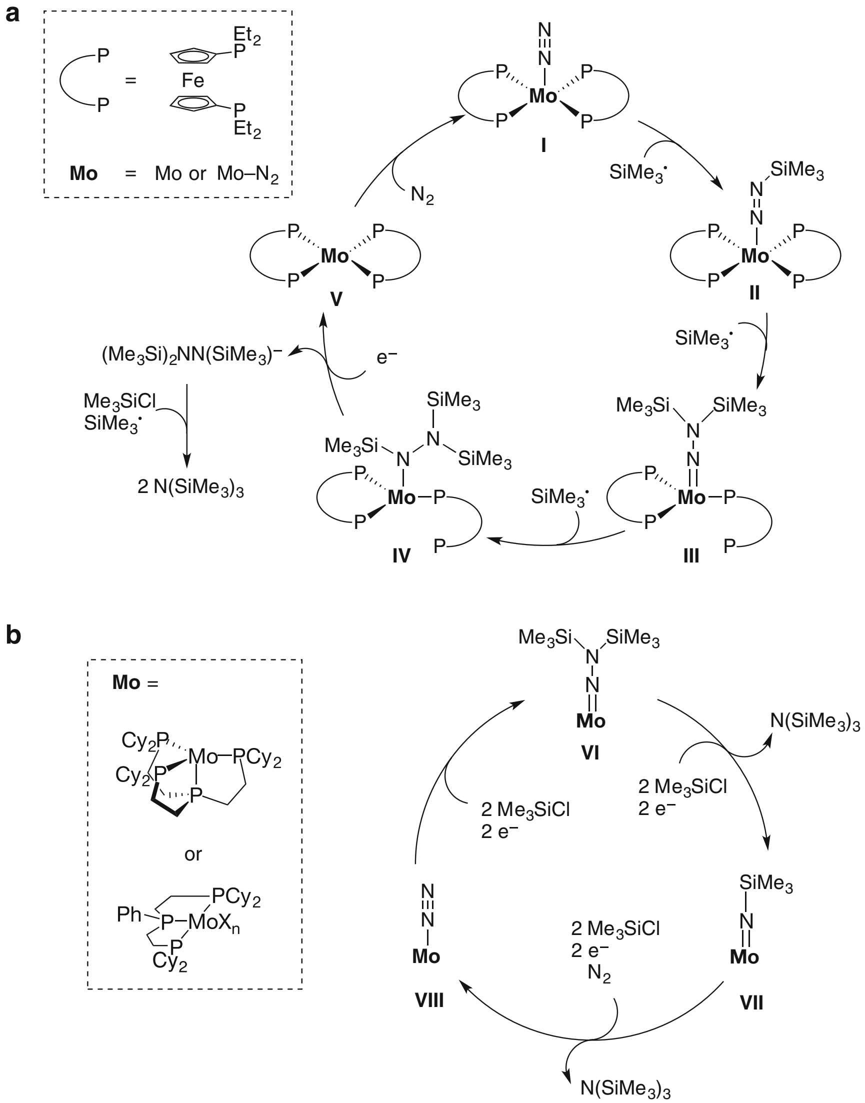


Fig. 4 Proposed catalytic cycle for the formation of silylamine. (**a**) Catalytic cycle for using **6**; (**b**) catalytic cycle for using **8** and **9**

3 Catalytic Transformation of Dinitrogen to Ammonia with Molybdenum Complexes

3.1 Molybdenum Complexes Bearing Tetradentate Ligands as Catalysts

The first successful example of the catalytic transformation of dinitrogen to ammonia under ambient reaction conditions was reported by Yandulov and Schrock in 2003 [37]. Employing a molybdenum–dinitrogen complex bearing a triamidoamine ligand $[\mathrm{HIPTN_3N}]\mathrm{MoN_2}$ (**12**, $\mathrm{HIPTN_3N} = (3{,}5\text{-}(2{,}4{,}6\text{-}i\text{-}\mathrm{Pr_3C_6H_2})_2\mathrm{C_6H_3NCH_2CH_2})_3\mathrm{N}$) as a catalyst, the reaction of an atmospheric pressure of nitrogen gas with decamethylchromocene ($\mathrm{CrCp^*_2}$, $\mathrm{Cp^*} = \eta^5\text{-}\mathrm{C_5Me_5}$; a reductant) and 2,6-lutidinium tetraarylborate ($[\mathrm{LutH}]\mathrm{BAr^F{}_4}$, Lut = 2,6-lutidine, $\mathrm{Ar^F} = 3{,}5\text{-}(\mathrm{CF_3})_2\mathrm{C_6H_3}$; a proton source) in heptane at room temperature afforded 7.56 equivalents of ammonia per catalyst (Fig. 5). A plausible reaction pathway is shown in Fig. 6, based on intensive stoichiometric reactions of **12** with a proton source and/or a reductant [16, 17, 38–41]. At first, the formation of a diazenido species **XI** from **12** proceeds via either one of the following two reaction pathways. One is the stepwise reduction and protonation of the coordinating dinitrogen ligand in **12**. The other pathway is the protonation of one of the amido nitrogens in the supporting ligand in **12** to give **X** and then successive protonation and reduction of **X** to afford **XI**. Next, stepwise protonation and reduction liberates one ammonia molecule and gives a nitrido species **XV**. Further protonation and reduction of **XV** affords an ammonia complex **XXI**. Finally, the ligand exchange liberates the second ammonia molecule and regenerates **12**. Electrochemical mechanistic study strongly suggested a proton-coupled electron transfer in the catalytic cycle

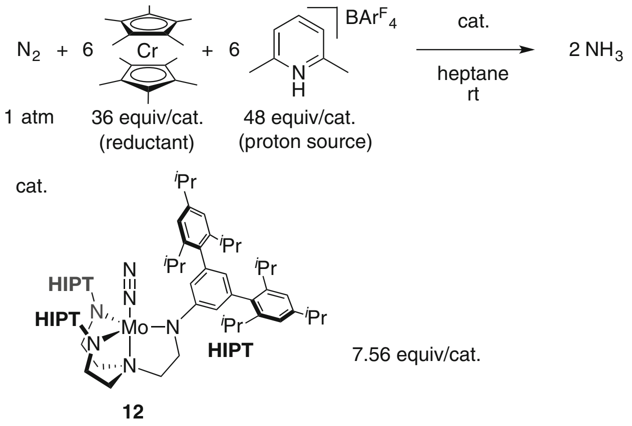


Fig. 5 The first catalytic transformation of nitrogen gas to ammonia using Schrock molybdenum–dinitrogen complex as a catalyst

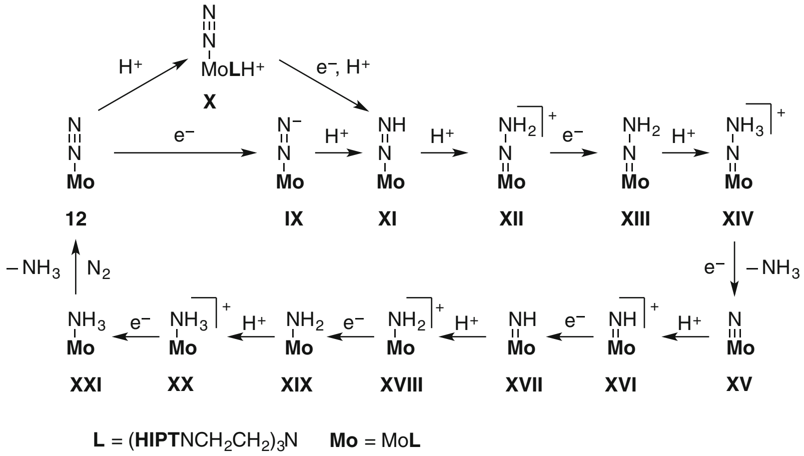
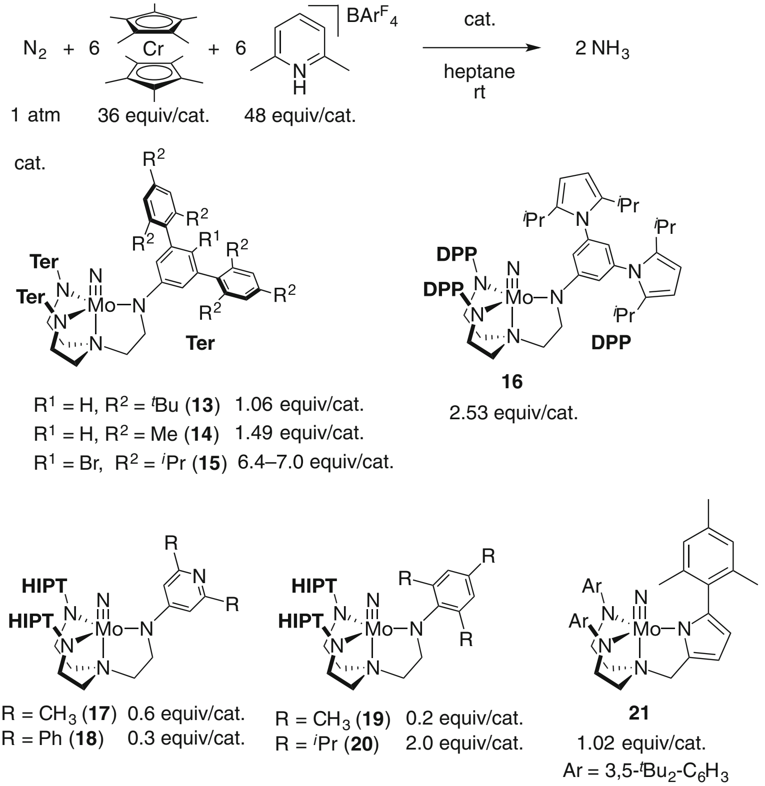


Fig. 6 A plausible reaction pathway of the catalytic transformation of dinitrogen to ammonia employing **12** as a catalyst

[42]. Some key intermediates **IX**, **XI**, **XII**, **XV**, **XVI**, **XX**, and **XXI** were isolated and characterized spectroscopically. Complexes **XI**, **XV**, and **XX** have almost the same catalytic activity as **12**.

Dozens of molybdenum complexes bearing slightly modified tetradentate ligands were synthesized and their catalytic activity was examined in detail (Fig. 7). Typical examples are as follows: molybdenum complexes with triamidoamine ligands containing hexa-*tert*-butylterphenyl groups (**13**), hexamethylterphenyl groups (**14**), *p*-bromohexaisopropylterphenyl groups (**15**) [43], DPP groups (**16**, DPP = 3,5-bis (2,5-diisopropylpyrrolyl)$_2$C$_6$H$_3$) [44], and with asymmetrical tetradentate ligands such as [(HIPTNCH$_2$CH$_2$)$_2$NCH$_2$CH$_2$N-aryl] ligands (**17–20**) [45] and diamidopyrrolyl ligand (**21**) [46]. Unfortunately, most of them, except for **15**, failed to catalytically convert dinitrogen to ammonia under the same reaction conditions.

Some other transition metal complexes bearing a HIPTN$_3$N ligand such as vanadium (**22**) [47], chromium (**23**) [48], and tungsten (**24**) [49] complexes were synthesized and their catalytic activity was examined in detail (Fig. 8). However, no catalytic reaction occurred at all when these complexes were used as catalysts.



36 equiv/cat.

48 equiv/cat.

R^1 = H, R^2 = ^{t}Bu (**13**) 1.06 equiv/cat.
R^1 = H, R^2 = Me (**14**) 1.49 equiv/cat.
R^1 = Br, R^2 = ^{i}Pr (**15**) 6.4–7.0 equiv/cat.

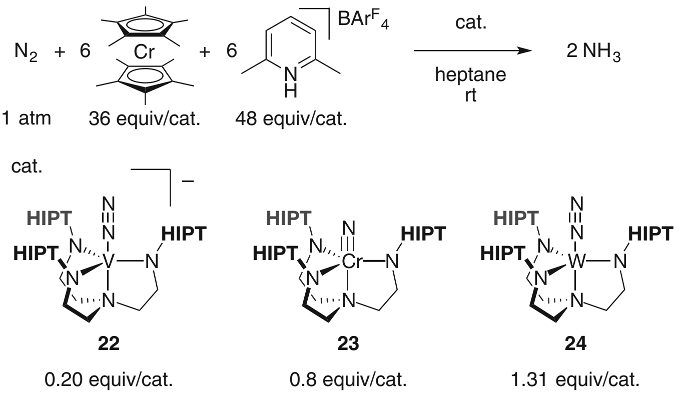
16
2.53 equiv/cat.

R = CH_3 (**17**) 0.6 equiv/cat.
R = Ph (**18**) 0.3 equiv/cat.

R = CH_3 (**19**) 0.2 equiv/cat.
R = ^{i}Pr (**20**) 2.0 equiv/cat.

21
1.02 equiv/cat.
Ar = 3,5-^{t}Bu_2-C_6H_3

Fig. 7 Catalytic activity of molybdenum complexes bearing slightly modified tetradentate ligands



36 equiv/cat.

48 equiv/cat.

22
0.20 equiv/cat.

23
0.8 equiv/cat.

24
1.31 equiv/cat.

Fig. 8 Catalytic activity of vanadium–, chromium–, and tungsten–HIPTN_3N complexes

3.2 Molybdenum Complexes Bearing Pincer Ligands as Catalysts

The second example of the catalytic transformation of dinitrogen into ammonia under ambient reaction conditions was reported by Nishibayashi and coworkers in 2011 [50]. The catalyst for this reaction system is a dinitrogen-bridged dimolybdenum–dinitrogen complex bearing PNP-type pincer ligands (**25**, PNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine; Fig. 9). The molecular structure of the molybdenum catalyst was determined to maintain its dinuclear structure also in a solution by measuring ^{15}N NMR of the $^{15}N_2$-labeled complex. In the presence of **25** as a catalyst, the reaction of an atmospheric pressure of nitrogen gas with lutidinium trifluoromethanesulfonate ([LutH]OTf; OTf = OSO_2CF_3; a proton source) and cobaltocene ($CoCp_2$; Cp = η^5-C_5H_5; a reductant) at room temperature afforded up to 23.2 equivalents of ammonia together with 43.5 equivalents of dihydrogen (Fig. 9). Since then, the preparation of a series of molybdenum complexes and the investigation of their catalytic activity have been reported by Nishibayashi and coworkers [51–55].

Detailed experimental studies on a plausible reaction pathway have been conducted by Nishibayashi, Yoshizawa, and coworkers [51]. Some molybdenum–nitrido complexes bearing the same PNP ligand were synthesized and their catalytic activity was investigated in detail (Fig. 10). The use of molybdenum–nitrido complexes **26** and **27** as catalysts produced a similar amount of ammonia with that using **25**. The result of DFT calculations indicated that a nitrido complex such as **27** is one of key reactive intermediates in the catalytic transformation of ammonia catalyzed by **25**.

A plausible reaction pathway is shown in Fig. 11. At first, one of the terminal dinitrogen ligands in **25** is protonated to give **XXII**. Successive protonation and reduction liberate one ammonia molecule and nitrido complex **XXIII**. Further stepwise protonation and reduction of **XXIII** afford an ammonia complex **XXIV** and ligand exchange liberates another ammonia molecule to regenerate **25**. A theoretical study also revealed that the dinuclear structure of the dinitrogen-bridged dimolybdenum complex is essential to the first protonation of one of the terminal

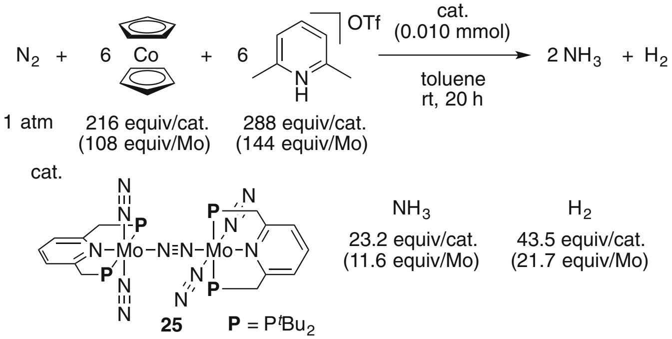


Fig. 9 Catalytic conversion of nitrogen gas to ammonia under ambient conditions employing **25** as a catalyst

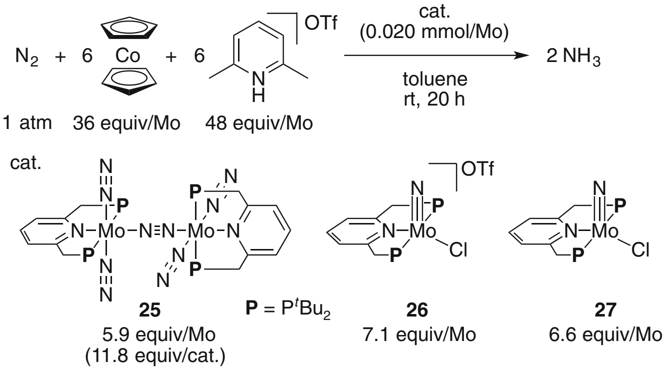


Fig. 10 Catalytic conversion of nitrogen gas to ammonia using molybdenum–dinitrogen complex and molybdenum–nitrido complexes as catalysts

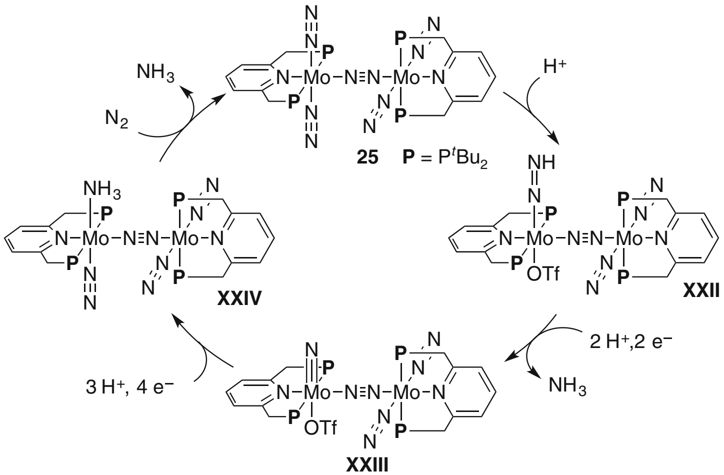


Fig. 11 Proposed catalytic cycle of converting dinitrogen to ammonia using **25** as a catalyst

dinitrogen ligands in **25** for the catalytic cycle (Fig. 12). Yoshizawa and Tanaka describe more detailed results in this book (Sect. 3.1 in ref. [56]).

Substituent effects on the phosphorus atoms of the PNP ligand were examined by Nishibayashi, Yoshizawa, and coworkers [50–52]. From the PNP ligand bearing either isopropyl (^{i}Pr) groups or 1-adamantyl (Ad) groups in place of *tert*-butyl (^{t}Bu) groups on both phosphorus atoms, the corresponding dimolybdenum–dinitrogen complexes cannot be prepared by the same procedure as that for **25**. On the other hand, dinitrogen-bridged dimolybdenum complexes bearing asymmetrical PNP ligands, where one phosphorus atom in the PNP ligand has two *tert*-butyl (^{t}Bu) groups and the other has two other substituents such as 1-adamantyl (Ad), phenyl (Ph), isopropyl, and cyclohexyl (Cy) groups, can be prepared (**28**, **29**, **30**, and **31**,

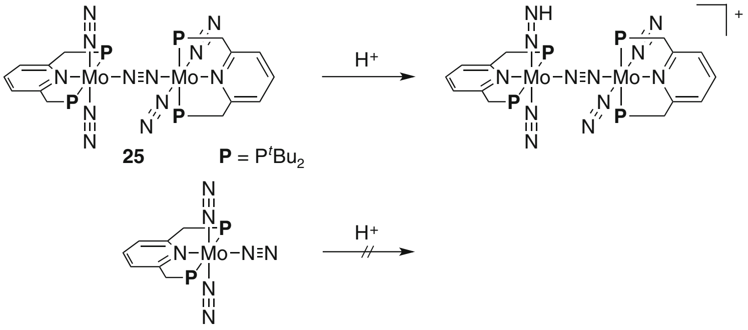
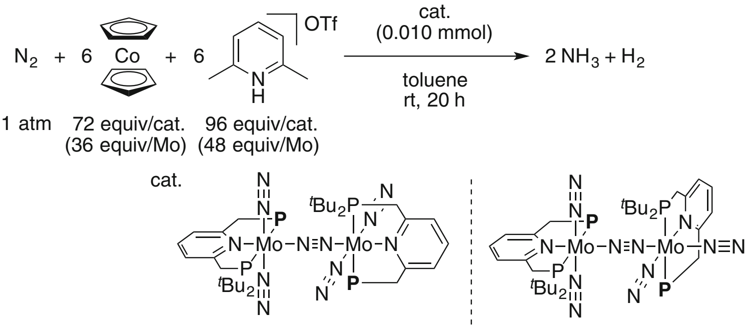


Fig. 12 The first protonation step of molybdenum–dinitrogen complex **25**



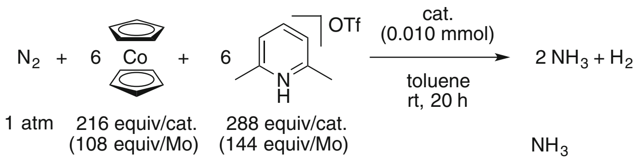
P	P^{t}Bu$_2$ (**25**)	PAd$_2$ (**28**)	PPh$_2$ (**29**)	P^{i}Pr$_2$ (**30**)	PCy$_2$ (**31**)
NH$_3$ (equiv/cat.)	12	14	2	3	1
H$_2$ (equiv/cat.)	10	8	22	21	22

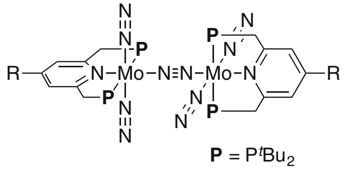
Fig. 13 Catalytic activity of molybdenum–dinitrogen complexes bearing asymmetrical PNP ligands

respectively; Fig. 13). Molecular structures of **28** and **29** were almost the same as **25**, where two *trans*-[Mo(N_2)$_2$(PNP)] units are bridged by one dinitrogen ligand in an end-on fashion. On the other hand, from the PNP ligands bearing isopropyl or cyclohexyl groups on one phosphorus atom, the complexes bearing a *trans*-[Mo (N_2)$_2$(PNP)] unit and a *cis*-[Mo(N_2)$_2$(PNP)] unit bridged by one dinitrogen ligand in an end-on fashion were obtained. The catalytic activity of **28–31** was also investigated in detail. In the presence of **28**, the reaction of an atmospheric pressure of nitrogen gas with 72 equivalents of $CoCp_2$ and 96 equivalents of [LutH]OTf in toluene at room temperature produced 14 equivalents of ammonia, which are comparable to the result using **25**. Meanwhile, the use of **29–31** as catalysts produced only a stoichiometric amount of ammonia under the same conditions (Fig. 13). These results show that the presence of bulky substituents on the phosphorus atoms in PNP ligands is necessary for catalytic conversion of nitrogen gas into ammonia.

Substituent effects at the 4-position in the pyridine ring of the PNP ligands were also explored (Fig. 14) [53]. The introduction of electron-withdrawing groups such as phenyl group (**32**) and trimethylsilyl group (**33**) at the 4-position in the pyridine ring weakened the activation of terminal dinitrogen ligands of the complexes. On the other hand, that of electron-donating groups such as *tert*-butyl group (**34**), methyl group (**35**), and methoxy group (**36**) strengthened the activation of the terminal dinitrogen ligands. In the presence of **32**–**36** as catalysts, reactions of an atmospheric pressure of nitrogen gas with 216 equivalents of $CoCp_2$ and 288 equivalents of [LutH]OTf in toluene at room temperature produced 21, 23, 28, 31, and 34 equivalents of ammonia and 46, 44, 45, 36, and 36 equivalents of dihydrogen, respectively. The activation of terminal dinitrogen ligands of the complexes succeeded in improving the catalytic activity to convert dinitrogen into ammonia. This is due to the acceleration of the first protonation step of the terminal dinitrogen ligand. The activation of terminal dinitrogen ligands of the complexes also succeeded in suppressing the formation of dihydrogen, which competes with ammonia formation. In addition, turnover frequency (TOF, defined as equivalents of ammonia produced in the initial 1 h) of catalytic reactions using **25**, **35**, and **36** as catalysts was monitored. For **25** and **35**, the TOFs were 17 and 28 h^{-1}, respectively. On the other hand, the TOF was 7 h^{-1} when **36** was used as a catalyst. These results indicated that the use of **36** as a catalyst reduces the reaction rate because of the difficulty of reducing steps.

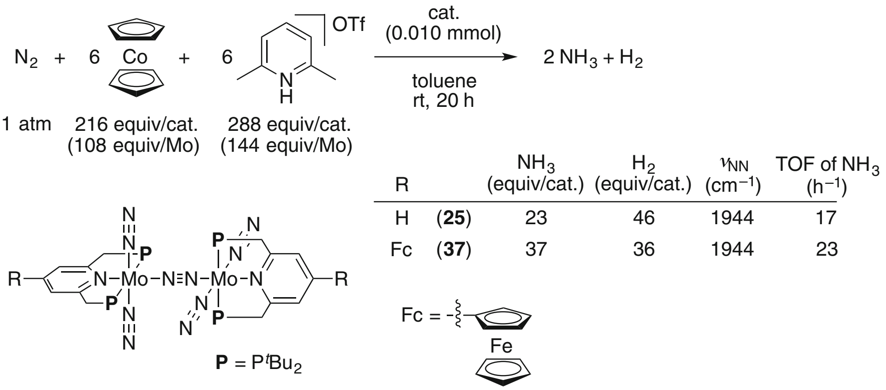
Redox active substituents such as ferrocene were also introduced at the 4-position of the PNP ligand (**37**, Fig. 15) [54]. The introduction of a ferrocene moiety to the PNP ligand did not affect the activation of terminal dinitrogen ligands, but an electronic interaction appeared between the molybdenum atom and the iron atom of ferrocene on the cyclic voltammetry of the molybdenum complexes bearing a ferrocene-substituted PNP ligand. In the presence of **37** as a catalyst, the reaction of an atmospheric pressure of nitrogen gas with 216 equivalents of $CoCp_2$ and





R		NH_3 (equiv/cat.)	H_2 (equiv/cat.)	ν_{NN} (cm^{-1})	TOF of NH_3 (h^{-1})
H	(**25**)	23	46	1944	17
Ph	(**32**)	21	46	1950	
Me_3Si	(**33**)	23	44	1947	
*t*Bu	(**34**)	28	45	1939	
Me	(**35**)	31	36	1939	28
MeO	(**36**)	34	36	1932	7

Fig. 14 Catalytic conversion of nitrogen gas to ammonia using molybdenum–dinitrogen complexes bearing 4-substituted PNP ligands

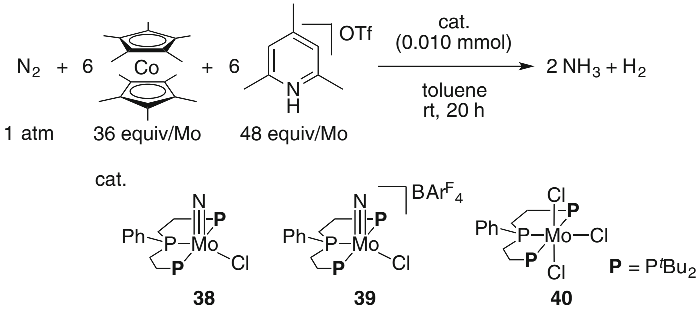


R		NH_3 (equiv/cat.)	H_2 (equiv/cat.)	ν_{NN} (cm^{-1})	TOF of NH_3 (h^{-1})
H	(**25**)	23	46	1944	17
Fc	(**37**)	37	36	1944	23

Fig. 15 Catalytic conversion of nitrogen gas to ammonia using a molybdenum–dinitrogen complex bearing 4-Fc-PNP ligands **37** as a catalyst

288 equivalents of [LutH]OTf in toluene at room temperature produced 37 equivalents of ammonia and 36 equivalents of dihydrogen, respectively. Mechanistic study indicates that an intramolecular electron transfer from the iron atom of ferrocene to the molybdenum center may accelerate the reduction step in the catalytic cycle.

The employment of PPP-type (PPP = bis(di-*tert*-butylphosphinoethyl)phenylphosphine) pincer ligand to the molybdenum complexes was investigated in detail [55]. The phosphines in the PPP ligand had advantages of lower Brønsted basicity and higher stability for the protonation in the catalytic reaction. Furthermore, the π-accepting property of the PPP ligand can stabilize a variety of molybdenum complexes bearing a broad range of oxidation states of the molybdenum center in the catalytic cycle. The corresponding dinitrogen-bridged dimolybdenum complex bearing the PPP ligands could not be prepared probably due to the low bond energy of the terminal dinitrogen ligand; however, molybdenum–nitrido complexes **38** and **39** were prepared according to the previous procedure (Fig. 16). In the presence of **38** and **39** as catalysts, reactions of an atmospheric pressure of nitrogen gas with 36 equivalents of decamethylcobaltocene ($CoCp^*_2$; a reductant) and 48 equivalents of 2,4,6-trimethylpyridinium trifluoromethanesulfonate ([ColH]OTf, Col = 2,4,6-trimethylpyridine; a proton source) per molybdenum atom in toluene at room temperature produced 9.6 and 11.0 equivalents of ammonia and 1.1 and 0.3 equivalents of dihydrogen per molybdenum atom, respectively. The presence of PPP ligand greatly suppressed the formation of dihydrogen. It is noteworthy that a molybdenum–trichloride complex bearing the PPP ligand **40** also worked as an effective catalyst, where 6.4 equivalents of ammonia were produced under the same reaction conditions. Finally, the use of a larger amount of a reductant and a proton source using **39** as a catalyst resulted in the formation of up to 63 equivalents of ammonia per molybdenum atom (Fig. 17). The molybdenum–nitrido complex **39** showed much higher performance for the catalytic conversion of dinitrogen into ammonia than other molybdenum complexes.



	38	39	40
NH_3 (equiv/Mo)	11.0	9.6	6.4
H_2 (equiv/Mo)	0.3	1.1	1.7

Fig. 16 Catalytic conversion of nitrogen gas to ammonia using molybdenum–nitrido complexes and a molybdenum–trichloride complex bearing PPP ligand

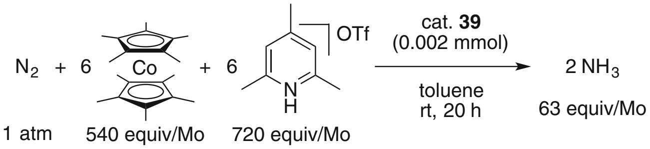


Fig. 17 Catalytic conversion of dinitrogen to ammonia using **39** as a catalyst with larger amounts of reductant and proton source

4 Perspective

As described in this chapter, a number of molybdenum–dinitrogen complexes have been prepared and their catalytic activity has been examined for the last decade. Subtle tuning of supporting ligands greatly improved the catalytic activity. Surely the catalytic activity is improved year by year, but multiple breakthroughs for improving catalytic activity are yet necessary for the industrial application [56].

References

1. Allen AD, Senoff CV (1965) Nitrogenopentammineruthenium(II) complexes. Chem Commun:621–622. doi:10.1039/c19650000621
2. Yamamoto A, Kitazume S, Pu LS, Ikeda S (1967) Study of the fixation of nitrogen. Isolation of tris(triphenylphosphine) cobalt complex coordinated with molecular nitrogen. Chem Commun:79–80. doi:10.1039/c19670000079
3. Hidai M, Tominari K, Uchida Y, Misono A (1969) A *trans*-dinitrogen complex of molybdenum. Chem Commun:1392–1392. doi:10.1039/c29690001392
4. Chatt J, Pearman AJ, Richards RL (1975) The reduction of mono-coordinated molecular nitrogen to ammonia in a protic environment. Nature 253:39–40. doi:10.1038/253039b0

5. Chatt J, Pearman AJ, Richards RL (1977) Conversion of dinitrogen in its molybdenum and tungsten complexes into ammonia and possible relevance to the nitrogenase reaction. J Chem Soc Dalton Trans:1852–1860. doi:10.1039/dt9770001852
6. Chatt J, Pearman AJ, Richards RL (1975) Diazenido (iminonitrosyl) (N_2H), hydrazido(2–) (N_2H_2), and hydrazido(1–) (N_2H_3) ligands as intermediates in the reduction of ligating dinitrogen to ammonia. J Organomet Chem 101:C45–C47. doi:10.1016/s0022-328x(00)92481-1
7. Chatt J, Pearman AJ, Richards RL (1978) Hydrazido(2–)-complexes of molybdenum and tungsten formed from dinitrogen complexes by protonation and ligand exchange. J Chem Soc Dalton Trans:1766–1776. doi:10.1039/dt9780001766
8. Anderson SN, Fakley ME, Richards RL, Chatt J (1981) Hydrazido(2–)-complexes as intermediates in the conversion of ligating dinitrogen into ammonia and hydrazine. J Chem Soc Dalton Trans:1973–1980. doi:10.1039/dt9810001973
9. Chatt J (1975) The reactions of dinitrogen in its mononuclear complexes. J Organomet Chem 100:17–28. doi:10.1016/s0022-328x(00)88931-7
10. Chatt J, Richards RL (1982) The reactions of dinitrogen in its metal complexes. J Organomet Chem 239:65–77. doi:10.1016/s0022-328x(00)94103-2
11. Hidai M, Mizobe Y (1995) Recent advances in the chemistry of dinitrogen complexes. Chem Rev 95:1115–1133. doi:10.1021/cr00036a008
12. Hidai M, Ishii Y (1996) Toward direct synthesis of organonitrogen compounds from dinitrogen: the chemistry of diazoalkane complexes derived from dinitrogen complexes. Bull Chem Soc Jpn 69:819–831. doi:10.1246/bcsj.69.819
13. Fryzuk MD, Johnson SA (2000) The continuing story of dinitrogen activation. Coord Chem Rev 200–202:379–409. doi:10.1016/s0010-8545(00)00264-2
14. Shaver MP, Fryzuk MD (2003) Activation of molecular nitrogen: coordination, cleavage and functionalization of N_2 mediated by metal complexes. Adv Synth Catal 345:1061–1076. doi:10.1002/adsc.200303081
15. MacKay BA, Fryzuk MD (2004) Dinitrogen coordination chemistry: on the biomimetic borderlands. Chem Rev 104:385–401. doi:10.1021/cr020610c
16. Schrock RR (2005) Catalytic reduction of dinitrogen to ammonia at a single molybdenum center. Acc Chem Res 38:955–962. doi:10.1021/ar0501121
17. Schrock RR (2008) Catalytic reduction of dinitrogen to ammonia by molybdenum: theory versus experiment. Angew Chem Int Ed 47:5512–5522. doi:10.1002/anie.200705246
18. Hinrichsen S, Broda H, Gradert C, Söncksen L, Tuczek F (2012) Recent developments in synthetic nitrogen fixation. Annu Rep Prog Chem Sect A Inorg Chem 108:17–47. doi:10.1039/c2ic90033e
19. Nishibayashi Y (2012) Molybdenum-catalyzed reduction of molecular dinitrogen under mild reaction conditions. Dalton Trans 41:7447–7453. doi:10.1039/c2dt30105a
20. Broda H, Hinrichsen S, Tuczek F (2013) Molybdenum(0) dinitrogen complexes with polydentate phosphine ligands for synthetic nitrogen fixation: geometric and electronic structure contributions to reactivity. Coord Chem Rev 257:587–598. doi:10.1016/j.ccr.2012.05.010
21. Tanabe Y, Nishibayashi Y (2013) Developing more sustainable processes for ammonia synthesis. Coord Chem Rev 257:2551–2564. doi:10.1016/j.ccr.2013.02.010
22. Sivasankar C, Baskaran S, Tamizmani M, Ramakrishna K (2014) Lessons learned and lessons to be learned for developing homogeneous transition metal complexes catalyzed reduction of N_2 to ammonia. J Organomet Chem 752:44–58. doi:10.1016/j.jorganchem.2013.11.024
23. Khoenkhoen N, de Bruin B, Reek JNH, Dzik WI (2015) Reactivity of dinitrogen bound to mid- and late-transition-metal centers. Eur J Inorg Chem:567–598. doi:10.1002/ejic.201403041
24. Nishibayashi Y (2015) Molybdenum-catalyzed reduction of molecular dinitrogen into ammonia under ambient reaction conditions. C R Chim 18:776–784. doi:10.1016/j.crci.2015.01.014
25. Nishibayashi Y (2015) Recent progress in transition-metal-catalyzed reduction of molecular dinitrogen under ambient reaction conditions. Inorg Chem 54:9234–9247. doi:10.1021/acs.inorgchem.5b00881

26. Tanaka H, Nishibayashi Y, Yoshizawa K (2016) Interplay between theory and experiment for ammonia synthesis catalyzed by transition metal complexes. Acc Chem Res 49:987–995. doi:10.1021/acs.accounts.6b00033
27. Ohki Y, Seino H (2016) N-heterocyclic carbenes as supporting ligands in transition metal complexes of N_2. Dalton Trans 45:874–880. doi:10.1039/c5dt04298d
28. Tanabe Y, Nishibayashi Y (2016) Catalytic dinitrogen fixation to form ammonia at ambient reaction conditions using transition metal–dinitrogen complexes. Chem Rec 16:1549–1577. doi:10.1002/tcr.201600025
29. Flöser BM, Tuczek F (2016) Synthetic nitrogen fixation with mononuclear molybdenum complexes: electronic-structural and mechanistic insights from DFT. Coord Chem Rev. doi:10.1016/j.ccr.2016.11.003
30. Shiina K (1972) Reductive silylation of molecular nitrogen *via* fixation to tris(trialkylsilyl) amine. J Am Chem Soc 94:9266–9267. doi:10.1021/ja00781a068
31. Komori K, Oshita H, Mizobe Y, Hidai M (1989) Catalytic conversion of molecular nitrogen into silylamines using molybdenum and tungsten dinitrogen complexes. J Am Chem Soc 111:1939–1940. doi:10.1021/ja00187a092
32. Tanaka H, Sasada A, Kouno T, Yuki M, Miyake Y, Nakanishi H, Nishibayashi Y, Yoshizawa K (2011) Molybdenum-catalyzed transformation of molecular dinitrogen into silylamine: experimental and DFT study on the remarkable role of ferrocenyldiphosphine ligands. J Am Chem Soc 133:3498–3506. doi:10.1021/ja109181n
33. Ogawa T, Kajita Y, Wasada-Tsutsui Y, Wasada H, Masuda H (2013) Preparation, characterization, and reactivity of dinitrogen molybdenum complexes with bis(diphenylphosphino) amine derivative ligands that form a unique 4-membered P–N–P chelate ring. Inorg Chem 52:182–195. doi:10.1021/ic301577a
34. Liao Q, Saffon-Merceron N, Mézailles N (2014) Catalytic dinitrogen reduction at the molybdenum center promoted by a bulky tetradentate phosphine ligand. Angew Chem Int Ed 53:14206–14210. doi:10.1002/anie.201408664
35. Liao Q, Saffon-Merceron N, Mézailles N (2015) N_2 reduction into silylamine at tridentate phosphine/Mo center: catalysis and mechanistic study. ACS Catal 5:6902–6906. doi:10.1021/acscatal.5b01626
36. Kuriyama S, Arashiba K, Nakajima K, Tanaka H, Yoshizawa K, Nishibayashi Y (2016) Azaferrocene-based PNP-type pincer ligand: synthesis of molybdenum, chromium, and iron complexes and reactivity toward nitrogen fixation. Eur J Inorg Chem:4856–4861. doi:10.1002/ejic.201601051
37. Yandulov DV, Schrock RR (2003) Catalytic reduction of dinitrogen to ammonia at a single molybdenum center. Science 301:76–78. doi:10.1126/science.1085326
38. Yandulov DV, Schrock RR (2002) Reduction of dinitrogen to ammonia at a well-protected reaction site in a molybdenum triamidoamine complex. J Am Chem Soc 124:6252–6253. doi:10.1021/ja020186x
39. Yandulov DV, Schrock RR, Rheingold AL, Ceccarelli C, Davis WM (2003) Synthesis and reactions of molybdenum triamidoamine complexes containing hexaisopropylterphenyl substituents. Inorg Chem 42:796–813. doi:10.1021/ic020505l
40. Yandulov DV, Schrock RR (2005) Studies relevant to catalytic reduction of dinitrogen to ammonia by molybdenum triamidoamine complexes. Inorg Chem 44:1103–1117. doi:10.1021/ic040095w
41. Weare WW, Dai X, Byrnes MJ, Chin JM, Schrock RR, Müller P (2006) Catalytic reduction of dinitrogen to ammonia at a single molybdenum center. Proc Natl Acad Sci U S A 103:17099–17106. doi:10.1073/pnas.0602778103
42. Munisamy T, Schrock RR (2012) An electrochemical investigation of intermediates and processes involved in the catalytic reduction of dinitrogen by [HIPTN$_3$N]Mo (HIPTN$_3$N = (3,5-(2,4,6-i-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$NCH$_2$CH$_2$)$_3$N). Dalton Trans 41:130–137. doi:10.1039/c1dt11287b

43. Ritleng V, Yandulov DV, Weare WW, Schrock RR, Hock AS, Davis WM (2004) Molybdenum triamidoamine complexes that contain hexa-*tert*-butylterphenyl, hexamethylterphenyl, or *p*-bromohexaisopropylterphenyl substituents. An examination of some catalyst variations for the catalytic reduction of dinitrogen. J Am Chem Soc 126:6150–6163. doi:10.1021/ja0306415
44. Reithofer MR, Schrock RR, Müller P (2010) Synthesis of $[(DPPNCH_2CH_2)_3N]^{3-}$ molybdenum complexes (DPP = 3,5-(2,5-diisopropylpyrrolyl)$_2C_6H_3$) and studies relevant to catalytic reduction of dinitrogen. J Am Chem Soc 132:8349–8358. doi:10.1021/ja1008213
45. Weare WW, Schrock RR, Hock AS, Müller P (2006) Synthesis of molybdenum complexes that contain "hybrid" triamidoamine ligands, [(hexaisopropylterphenyl-$NCH_2CH_2)_2NCH_2CH_2N$-aryl$]^{3-}$, and studies relevant to catalytic reduction of dinitrogen. Inorg Chem 45:9185–9196. doi:10.1021/ic0613457
46. Chin JM, Schrock RR, Müller P (2010) Synthesis of diamidopyrrolyl molybdenum complexes relevant to reduction of dinitrogen to ammonia. Inorg Chem 49:7904–7916. doi:10.1021/ic100856n
47. Smythe NC, Schrock RR, Müller P, Weare WW (2006) Synthesis of $[(HIPTNCH_2CH_2)_3N]V$ compounds (HIPT = 3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$) and an evaluation of vanadium for the reduction of dinitrogen to ammonia. Inorg Chem 45:9197–9205. doi:10.1021/ic061554r
48. Smythe NC, Schrock RR, Müller P, Weare WW (2006) Synthesis of $[(HIPTCH_2CH_2)_3N]Cr$ compounds (HIPT = 3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$) and an evaluation of chromium for the reduction of dinitrogen to ammonia. Inorg Chem 45:7111–7118. doi:10.1021/ic060549k
49. Yandulov DV, Schrock RR (2005) Synthesis of tungsten complexes that contain hexaisopropylterphenyl-substituted triamidoamine ligands, and reactions relevant to the reduction of dinitrogen to ammonia. Can J Chem 83:341–357. doi:10.1139/v05-013
50. Arashiba K, Miyake Y, Nishibayashi Y (2011) A molybdenum complex bearing PNP-type pincer ligands leads to the catalytic reduction of dinitrogen into ammonia. Nat Chem 3:120–125. doi:10.1038/nchem.906
51. Tanaka H, Arashiba K, Kuriyama S, Sasada A, Nakajima K, Yoshizawa K, Nishibayashi Y (2014) Unique behaviour of dinitrogen-bridged dimolybdenum complexes bearing pincer ligand towards catalytic formation of ammonia. Nat Commun 5:3737. doi:10.1038/ncomms4737
52. Kinoshita E, Arashiba K, Kuriyama S, Miyake Y, Shimazaki R, Nakanishi H, Nishibayashi Y (2012) Synthesis and catalytic activity of molybdenum–dinitrogen complexes bearing unsymmetric PNP-type pincer ligands. Organometallics 31:8437–8443. doi:10.1021/om301046t
53. Kuriyama S, Arashiba K, Nakajima K, Tanaka H, Kamaru N, Yoshizawa K, Nishibayashi Y (2014) Catalytic formation of ammonia from molecular dinitrogen by use of dinitrogen-bridged dimolybdenum–dinitrogen complexes bearing PNP-pincer ligands: remarkable effect of substituent at PNP-pincer ligand. J Am Chem Soc 136:9719–9731. doi:10.1021/ja5044243
54. Kuriyama S, Arashiba K, Nakajima K, Tanaka H, Yoshizawa K, Nishibayashi Y (2015) Nitrogen fixation catalyzed by ferrocene-substituted dinitrogen-bridged dimolybdenum–dinitrogen complexes: unique behavior of ferrocene moiety as redox active site. Chem Sci 6:3940–3951. doi:10.1039/c5sc00545k
55. Arashiba K, Kinoshita E, Kuriyama S, Eizawa A, Nakajima K, Tanaka H, Yoshizawa K, Nishibayashi Y (2015) Catalytic reduction of dinitrogen to ammonia by use of molybdenum–nitride complexes bearing a tridentate triphosphine as catalysts. J Am Chem Soc 137:5666–5669. doi:10.1021/jacs.5b02579
56. Tanaka H, Yoshizawa K (2017) Computational approach to nitrogen fixation on molybdenum–dinitrogen complexes. Top Organomet Chem 60:171–196. doi:10.1007/3418_2016_7