Remarkable catalytic activity of dinitrogen-bridged dimolybdenum complexes bearing NHC-based PCP-pincer ligands toward nitrogen fixation

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Intensive efforts for the transformation of dinitrogen using transition metal–dinitrogen complexes as catalysts under mild reaction conditions have been made. However, limited systems have succeeded in the catalytic formation of ammonia. Here we show that newly designed and prepared dinitrogen-bridged dimolybdenum complexes bearing N-heterocyclic carbene- and phosphine-based PCP-pincer ligands [{Mo(N₂)₂(PCP)}₂(μ-N₂)] (1) work as so far the most effective catalysts towards the formation of ammonia from dinitrogen under ambient reaction conditions, where up to 230 equiv. of ammonia are produced based on the catalyst. DFT calculations on 1 reveal that the PCP-pincer ligand serves as not only a strong σ-donor but also a π-acceptor. These electronic properties are responsible for a solid connection between the molybdenum centre and the pincer ligand, leading to the enhanced catalytic activity for nitrogen fixation.
Nitrogen is an essential element for all living things on earth. Since most of the nitrogen atoms on earth exist as inert dinitrogen gas, the fixing of molecular dinitrogen is necessary to be utilized. The industrial dinitrogen fixation system, called the Haber–Bosch process, plays an important role in producing ammonia from dinitrogen gas today. The operation of the process, however, requires high temperature and high pressure, resulting in large consumption of fossil fuels. On the other hand, nitrogenases transform dinitrogen gas into ammonia using a molybdenum–dinitrogen complex as a catalyst and in 2013 Peters and co-workers reported the iron-catalysed transformation using an iron–dinitrogen complex as a catalyst. We also found that several dinitrogen-bridged dimolybdenum complexes such as (Mo(N2)2(PNP)2)2(μ-N2) (2; PNP = 2,6-bis(di-tert-butylphosphinomethyl)pyridine) and molybdenum–nitride complexes bearing PNP-type pincer ligands or mer-tridentate triphosphine worked as more effective catalysts towards ammonia formation under ambient reaction conditions, where up to 63 equiv. of ammonia were produced based on the molybdenum atom of the catalyst.

During our continuous study, we have realized three promising clues to develop more effective catalysts. The first clue is the introduction of an electron-donating group to the pincer ligands to increase the backdonating ability of the molybdenum atom to the dinitrogen ligand. In fact, dinitrogen-bridged dimolybdenum complexes bearing the electron-donating group-substituted PNP-pincer ligands worked as more effective catalysts in our previous reaction system. The second clue is the inhibition of the dissociation of the pincer ligand from the molybdenum atom to increase the stability of the molybdenum complex. We generally increase the stability of the molybdenum complex. We generally...
observed the dissociation of the PNP-pincer ligand after the ammonia formation in the catalytic reaction. The third clue is the presence of the dinitrogen-bridged dimolybdenum core to promote the catalytic ammonia formation from the coordinated dinitrogen. Density functional theory (DFT) calculations demonstrated that the dinitrogen-bridged dimolybdenum structure plays a vital role in the protonation of a dinitrogen ligand, where one molybdenium moiety of the dinuclear molybdenum–dinitrogen complex works as a mobile ligand to the other molybdenum moiety as an active site.

Taking account of these clues, we have now planned to design an N-heterocyclic carbene– (NHC)-35,46 and phosphine-based PCP-type pincer ligand (a PCP-type pincer ligand composed of NHC and two phosphines) as a tridentate ligand in place of the so far employed PNP-type pincer ligand for preparing a new molybdenum–dinitrogen complex. It is known that NHC works as a stronger electron-donating ligand than pyridine and binds to a transition metal centre more strongly than pyridine. In this article, we demonstrate that dinitrogen-bridged dimolybdenum complexes bearing PCP-pincer ligands [(Mo(N2)2(PCP))2 (μ-N2)] (1) worked as effective catalysts towards ammonia formation under ambient reaction conditions, where up to 230 equiv. of ammonia were produced based on the catalyst (115 equiv. of ammonia based on the molybdenum atom of the catalyst). This is so far the most effective catalytic reduction of dinitrogen gas into ammonia under ambient reaction conditions using transition metal–dinitrogen complexes as catalysts.

**Results**

Preparation and characterization of 1. On the basis of our proposal, we designed two types of dinitrogen-bridged dimolybdenum complexes bearing PCP-type pincer ligands with two tert-butyl groups on each phosphorus atom (Fig. 1a). One is the complex bearing methylene linkers between the NHC skeleton and the phosphorus atom, where a similar PCP-pincer ligand bearing two phenyl groups on each phosphorus atom has quite recently been reported by Rieger and co-workers. The other is the complex bearing ethylene linkers, where similar PCP-pincer ligands bearing two phenyl groups on each phosphorus atom have already been reported by some research groups.47,48

According to our previous procedure,40–42, we newly prepared three dinitrogen-bridged dimolybdenum complexes bearing the PCP-type pincer ligands. Treatment of [MoCl3(PCP)] (3a, PCP = 1,3-bis((di-tert-butylphosphino)methyl)benzimidazol-2-ylidine (Bim-PCP[1]; 3b, PCP = 1,3-bis(2-(di-tert-butylphosphino)ethyl)imidazol-2-ylidine (Im-PCP[2]; 3c, PCP = 5,6-dimethyl-1,3-bis((di-tert-butylphosphino)methyl)benzimidazol-2-ylidine (Me-Bim-PCP[1])) with 6 equiv. of Na–Hg in tetrahydrofuran (THF) at room temperature for 17 h under an atmospheric pressure of molecular dinitrogen gave the corresponding dinitrogen-bridged dimolybdenum complexes [(Mo(N2)2(PCP))2 (μ-N2)] (1a; PCP = Bim-PCP[1], 1b; PCP = Im-PCP[2], 1c; PCP = Me-Bim-PCP[1]) in 37%, 53% and 46% yields, respectively. Detailed synthetic procedures for ligand precursors are included in Supplementary Methods and synthetic procedures for metal precursors 3a–3c are included in Methods section. These dinitrogen-bridged dimolybdenum complexes were characterized by 1H and 31P{1H} NMR. Detailed molecular structures of these complexes 1a–1c were determined by X-ray crystallography (Fig 1c for 1a and 1b; Supplementary Fig. 1 for 1c), which were similar to those of the dinitrogen-bridged dimolybdenum complexes bearing PNP-pincer ligands.40–42. However, the bond lengths, the bond angles and dihedral angles were significantly different between 1a and 1b according to the nature of the linkers in the PCP-pincer ligands (Supplementary Tables 3 and 4). The bond lengths defined by Mo(1)–C(1) of 1a and 1b were 2.064(2) Å and 2.153(4) Å, respectively, and the bond angles defined by P(1)–Mo(1)–P(2) of 1a and 1b were 153.95(3)° and 163.18(8)°, respectively. On the other hand, the dihedral angles defined by N(1)–C(1)–Mo(1)–N(5) of 1a and 1b were 82.35(5)° and 43.74(7)°, respectively. The shortened bond length of Mo(1)–C(1) of 1a suggests the stronger π-backdonation from the molybdenum centre to the NHC unit due to the almost-perpendicular orientation of the NHC unit. On the other hand, the longer CH2 linker of Im-PCP[2] forces the twisted coordination of the NHC and is likely to weaken the π-backdonation in 1b. Further information on this topic is discussed based on DFT calculations (vide infra).

Infrared spectra of 1a–1c in the solid state showed a strong absorption peak assignable to terminal dinitrogen ligands at 1978, 1911 and 1969 cm−1 respectively. The single peak of each complex corresponds to the dinitrogen-bridged dimolybdenum structure, as determined by X-ray crystallography. Compared with the infrared spectrum of 1b, those of 1a and 1c showed the peak at much higher frequency assignable to the strong π-backdonation from the molybdenum centre to the NHC. The infrared spectra of 1a and 1c in THF solution showed one strong absorption peak assignable to terminal dinitrogen ligands at 1979 and 1973 cm−1, respectively. Comparison of the infrared spectra of 1a and 1c in the solid state with that in the solution state indicates that the dinitrogen-bridged dinuclear structures of 1a and 1c are preserved even in solution. Furthermore, the 15N1{1H} NMR spectrum of 15N2-labelled 1a in CD2Cl2 under 15N2 showed two singlet and one doublet signal; δ 7.2 (s, Mo–N=N–Mo), −13.0 (d, 1J_{1\text{N–N}} = 5.4 Hz, Mo–N=N–Mo), −32.0 (br s, Mo–N=N(N)), which are consistent with the dinuclear structure (Fig. 2a)40,56,57. In contrast, the infrared spectrum of 1b in THF solution showed two peaks assignable to terminal dinitrogen ligands, suggesting that the structure of 1b in THF is no longer the same with that in the solid state. To obtain more information on real species of 1b in the THF solution, the 15N1{1H} NMR spectrum of 1b was measured in THF-d8 solution under an atmospheric pressure of 15N2 gas. The spectrum showed two doublet and two double triplet signals; δ 1.2 (d, 1J_{1\text{N–N}} = 6.0 Hz, Mo–N=N(Nequatorial)), −20.8 (d, 1J_{1\text{N–N}} = 6.1 Hz, Mo–N=N(Naxial)), −27.8 (dt, 1J_{1\text{N–N}} = 6.0 Hz and 2J_{N–P} = 1.6 Hz, Mo–N=N(Nequatorial)), −30.5 (dt, 1J_{1\text{N–N}} = 6.1 Hz and 2J_{N–P} = 2.3 Hz, Mo–N=N(Naxial); Fig. 2b), demonstrating the formation of the corresponding mononuclear dinitrogen complex [Mo(N2)3 (1m-PCP[2])] (1b‘) in THF. In fact, these spectroscopic features of 1b‘ in THF are in agreement with those of similar mononuclear dinitrogen complexes such as mer-[Mo(N2)3L3] structures55,58. The instability of 1b‘ in solution may be derived from the steric repulsion between the two molybdenum moieties bearing Im-PCP[2].

As shown in Fig. 1, we prepared two types of the PCP-pincer ligands, where Bim-PCP[1] has a benzimidazol-2-ylidine skeleton and Im-PCP[2] has an imidazol-2-ylidine skeleton. Unfortunately, we were unable to synthesize the corresponding two PCP-pincer ligands based on the same NHC skeleton bearing linkers of the different lengths between the NHC skeleton and each phosphorus atom (Bim-PCP[2] and Im-PCP[1] in Fig. 1a). However, we consider that the presence or absence of benzene ring has little influence on either the thermodynamic stability of the Mo=N=N=Mo structures or the electron-donating ability of the pincer ligands for the following reasons. To assess the influence of the benzene moiety in Bim-PCP[1] on the thermodynamic stability of the dinitrogen-bridged dimolybdenum structure, we calculated a model complex [(Mo(N2)3(1m-PCP[1]))(μ-N2)], where the benzimidazol-2-ylidine skeleton in Bim-PCP[1] is replaced by the imidazol-2-ylidine skeleton. The optimized distance of the Mo–N(bridging) bond and its bond...
dissociation energy (BDE) are 2.105 Å and 18.4 kcal mol\(^{-1}\), respectively, both of which are almost identical to those calculated for 1a (2.108 Å and 18.8 kcal mol\(^{-1}\)). The definition of BDE is described in the Methods section. On the other hand, Tuczek and co-workers\(^{52,53}\) have previously prepared two PCP ligands based on benzimidazol-2-ylidene and imidazol-2-ylidene, where these ligands have similar \(\sigma\)-donating ability. Gusev\(^{59,60}\) has previously estimated the donor ability of various NHC ligands based on the computational evaluation of \(v_{\text{CO}}\) (A1) of [Ni(CO)\(_2\)(NHC)]. The author showed that 1,3-dimethylbenzimidazol-2-ylidene and 1,3-dimethylimidazol-2-ylidene have almost the same values of \(v_{\text{CO}}\) (2.057 and 2.054 cm\(^{-1}\), respectively), suggesting that the electron-donating ability of the NHC ligands was scarcely influenced by the difference between benzimidazol-2-ylidene and imidazol-2-ylidene. We therefore expect that the introduction of a benzene ring to the NHC skeleton little influences either the thermodynamic stability of the Mo–N\(_{\equiv}\)N–Mo structure or the electron-donating ability of the pincer ligand.

We then performed DFT calculations to elucidate how the length of linkers connecting the NHC skeleton with the P\(^{\text{Bu}_2}\) groups in Bim-PCP[1] and Im-PCP[2] influences the thermodynamic stability of the dinorot-brided dimolybdenum structures in 1a and 1b. Figure 3 shows optimized structures of dimolybdenum complexes 1a and 1b. The N\(_{\equiv}\)N stretching frequencies of terminal dinorot ligands calculated for 1a (2.012 cm\(^{-1}\)) and 1b (1.969 cm\(^{-1}\)) reproduced the experimental trend. The Mo–N and N–N distances of a terminal dinorot ligand are calculated to be 2.032 and 1.137 Å for 1a and 2.016 and 1.142 Å for 1b, respectively, indicating that the terminal dinorot ligand in 1b is more activated than that in 1a. As a result, the BDE of a Mo–N\(_2\)(terminal) of 1a (11.9 kcal mol\(^{-1}\)) is considerably lower than that of 1b (16.7 kcal mol\(^{-1}\)). On the other hand, the Mo–N distance of the bridging dinorot ligand of 1a (2.108 Å) is shorter than that of 1b (2.133 Å). The BDE of the Mo–N\(_2\)(bridging) bond of 1a is 18.8 kcal mol\(^{-1}\), which is more than twice as high as that of 1b, 9.0 kcal mol\(^{-1}\). The very low BDE of the Mo–N\(_2\)(bridging) bond of 1b can be associated with the experimental observation that the dinuclear complex 1b is labile to be separated into two mononuclear complexes in solution.

Differences in thermodynamic stability of the Mo–N\(_{\equiv}\)N–Mo structure between 1a and 1b can be rationalized by optimized structures of the corresponding mononuclear dinorot complexes. Figure 4 presents space-filling models of [Mo(N\(_2\))\(_3\)(PCP)] (1a’; PCP = Bim-PCP[1], 1b’; PCP = Im-PCP[2]). Comparison of the Mo–N distance for the equatorial dinorot ligand of 1a’ (2.084 Å) with that of 1b’ (2.041 Å) suggests that 1b’ bearing Im-PCP[2] strongly binds dinorot at the equatorial position. Contrary to the BDEs of the Mo–N\(_2\)(bridging) bond calculated for dinuclear complexes 1a and 1b, the BDE of the Mo–N\(_2\)(equatorial) bond of 1b’ (21.5 kcal mol\(^{-1}\)) is almost the same with that of 1a’ (21.2 kcal mol\(^{-1}\)). The dramatic decrease in the Mo–N\(_2\)(equatorial) BDE of 1b’ in the formation of the dinorot complex can be ascribed to steric hindrance caused by the tert-butyl groups on each phosphorus atom in Im-PCP[2].

The optimized structure of 1a’ bearing Bim-PCP[1] with the methylene linkers has the P–Mo–P bond angle of 151.2°, while that of 1b’ bearing Im-PCP[2] with the ethylene linkers has the bond angle of 164.3°. The extension of the CH\(_2\) linkers in 1b’ forces the tert-butyl groups on each phosphorus atom in
First, we carried out the catalytic reaction in the presence of 1a as a catalyst using either cobaltocene (CoCp2; Cp = η5-C5H5), decamethylchromocene (CrCp*2; Cp* = η5-C5Me5), and decamethylcobaltocene (CoCp*2) as reductants, to produce 5.7, 17.6 and 11.8 equiv. of ammonia based on the catalyst, respectively (Table 1, runs 1–3). In the absence of a reductant, only 0.2 equiv. of ammonia were produced based on 1a (Table 1, run 4). We have previously obtained the result that 12.2 equiv. of ammonia were produced based on the catalyst from the reaction with CrCp*2 as a reductant in the presence of [{Mo(N2)2(PNP)}2(M–N2)] as a catalyst (Table 1, run 9) 40. This means that 1a promoted the catalytic nitrogen fixation more effectively than 2. Separately, we confirmed the direct conversion of molecular dinitrogen into ammonia by using 15N2 gas in place of normal 14N2 gas (see Supplementary Methods for detailed procedure).

In stark contrast to the catalytic activity of 1a, 1b did not work so effectively towards the formation of ammonia under the same reaction conditions. When CoCp2, CrCp*2 and CoCp*2 were used as reductants, only 1.4, 3.2 and 2.9 equiv. of ammonia were produced based on the catalyst, respectively (Table 1, runs 5–7). In the absence of a reductant, 1.5 equiv. of ammonia were produced based on 1b (Table 1, run 8).

Next, we investigated the influence of a proton source in the catalytic nitrogen fixation using 1a as a catalyst. Typical results are shown in Table 2, where larger amounts of both reductant and proton source were employed in order to sharpen the difference among the results (see Supplementary Methods for the detailed procedure). The catalytic reaction using larger amounts of reductant CrCp*2 (360 equiv. to 1a) and proton source [LutH]OTf (480 equiv. to 1a) afforded 79 equiv. of ammonia based on the catalyst (Table 2, run 1). When 2-picolinium trifluoromethanesulfonate ([PicH]OTf; Pic = 2-picoline) was used in place of [LutH]OTf, only a small amount of ammonia was produced based on the catalyst (Table 2, run 2). On the other hand, 2,4,6-collidinium trifluoromethanesulfonate ([ColH]OTf; Col = 2,4,6-collidine) worked rather effectively, where 61 equiv. of ammonia were produced (Table 2, run 3). When a non-coordinating anion BAR2+ (Ar = 3,5-(CF3)2C6H3) was used in place of OTf− in [LutH]OTf, only a small amount of ammonia was produced (Table 2, run 4). These results indicate that the use of [LutH]OTf as a proton source is an essential factor to achieve the high performance of 1a as a catalyst.

Catalytic nitrogen fixation using 1 as catalysts. The catalytic reduction of molecular dinitrogen into ammonia using 1 as catalysts was carried out according to the following procedure of the previous method40–42. To a mixture of 1 and 2,6-lutidinium trifluoromethanesulfonate (96 equiv. to 1; [LutH]OTf) as a proton source in toluene was added a solution of metallocene (72 equiv. to 1a) as a reductant in toluene via a syringe pump at room temperature over a period of 1 h, followed by stirring at room temperature for another 19 h under an atmospheric pressure of dinitrogen. After the reaction, the amounts of ammonia and molecular dihydrogen were determined by indophenol method61 and gas chromatography (GC), respectively. The yields of ammonia and molecular dihydrogen were calculated based on the metallocene. Typical results are shown in Table 1. In all cases, no formation of other products such as hydrazine was observed at all.

Im-PCP[2] to project towards the space surrounding the equatorial dinitrogen ligand (Fig. 4). As a result, the formation of a thermodynamically stable dimolybdenum complex bearing Im-PCP[2] is encumbered by steric repulsions between tert-butyl groups in two mononuclear molybdenum units facing each other.
Table 1 | Catalytic formation of ammonia from dinitrogen gas employing 1a or 1b as a catalyst.

| Run | Catalyst | Reductant | $E_{1/2}$ (V) | NH$_3$ (equiv.) | NH$_3$ (%) | H$_2$ (equiv.) | H$_2$ (%) |
|-----|----------|-----------|--------------|----------------|------------|--------------|-----------|
| 1   | 1a       | CoCp$_2$  | -1.15        | 5.7 ± 0.6      | 24         | 15.2 ± 1.5   | 42        |
| 2   | 1a       | CrCp$_2^*$ | -1.35        | 17.6 ± 0.7     | 73         | 3.9 ± 0.4    | 11        |
| 3   | 1a       | CoCp$_2^*$ | -1.78        | 11.8 ± 1.0     | 49         | 3.3 ± 0.8    | 9         |
| 4   | 1a       | none      | -            | 0.2            | 0.8        | 0.1          | 0.3       |
| 5   | 1b       | CoCp$_2$  | -1.15        | 1.4 ± 0.1      | 6          | 16.7 ± 1.9   | 47        |
| 6   | 1b       | CrCp$_2^*$ | -1.35        | 3.2 ± 0.3      | 13         | 15.1 ± 0.7   | 42        |
| 7   | 1b       | CoCp$_2^*$ | -1.78        | 2.9 ± 1.0      | 12         | 3.0 ± 1.0    | 8         |
| 8   | 1b       | none      | -            | 1.5            | 6          | 0.1          | 0.3       |
| 9t  | 2        | CrCp$_2$  | -1.35        | 12.2           | 51         | 4.2          | 12        |

A solution of a reductant in 4 ml of toluene was added to a mixture of the catalyst and [LutH]OTf in 1 ml of toluene at room temperature over a period of 1 h, followed by stirring at room temperature for another 19 h under 1 atm of dinitrogen gas.

*Equivs based on catalyst
$E_{1/2}$ values of reductant in MeCN versus Ag/Ag$^+$ (ref. 69).
1Yields based on reductant.
$t$Ref. 40.

Table 2 | Catalytic formation of ammonia from dinitrogen gas using 1a as a catalyst.

| Run | Proton source | pK$_a$ | NH$_3$ (equiv.) | NH$_3$ (%) | H$_2$ (equiv.) | H$_2$ (%) |
|-----|---------------|--------|----------------|------------|--------------|-----------|
| 1   | [LutH]OTf     | 6.77   | 79 ± 4         | 66         | 12 ± 2       | 6         |
| 2   | [PicH]OTf     | 5.97   | 19 ± 1         | 16         | 58 ± 11      | 28        |
| 3   | [ColH]OTf     | 7.48   | 61 ± 1         | 51         | 28 ± 8       | 12        |
| 4   | [LutH]BArF$_4$| 6.77   | 15 ± 5         | 13         | 42 ± 15      | 16        |

A solution of CrCp$_2$ in 4 ml of toluene was added to a mixture of 1a and a proton source in 1 ml of toluene at room temperature over a period of 1 h, followed by stirring at room temperature for another 19 h under 1 atm of dinitrogen gas.

*Equivs based on catalyst.
1pK$_a$ value of proton source in H$_2$O (ref. 70).
1Yield based on CrCp$_2^*$.

Figure 5 | Catalytic formation of ammonia using larger amounts of a reductant and a proton source in the presence of 1a or 1c as a catalyst. A solution of CrCp$_2$ in 5 ml of toluene was added to a mixture of the catalyst and [LutH]OTf in 1 ml of toluene at room temperature over a period of 1 h (for 1a) or 5 h (for 1c), followed by stirring at room temperature for another 19 h (for 1a) or 15 h (for 1c) under 1 atm of dinitrogen gas. The amounts of ammonia and hydrogen (equiv.) are based on the catalyst. Yields are based on CrCp$_2^*$. 

1A solution of a reductant in 4 ml of toluene was added to a mixture of the catalyst and [LutH]OTf in 1 ml of toluene at room temperature over a period of 1 h, followed by stirring at room temperature for another 19 h under 1 atm of dinitrogen gas.

*Equivs based on catalyst.
1$E_{1/2}$ values of reductant in MeCN versus Ag/Ag$^+$ (ref. 69).
1Yields based on reductant.
1Ref. 40.
On the basis of the results shown in Tables 1 and 2, we carried out the catalytic reaction using much larger amounts of CrCp$_2$ and [LutH]OTf as a reductant and a proton source to the catalyst, respectively (see Supplementary Methods for the detailed procedure). The reaction using 1,440 equiv. of CrCp$_2$ as a reductant and 1,920 equiv. of [LutH]OTf as a proton source in the presence of 1a as a catalyst under ambient reaction conditions gave $2.0 \times 10^2$ equiv. of ammonia based on the catalyst (Fig. 5). The catalytic activity of 1a towards the formation of ammonia is an order of magnitude greater than that of [[Mo(N$_2$)$_2$(PNP)]$_2$ ($\mu$-N$_2$)]$_2$ (up to 23 equiv. of ammonia based on 2). Ammonia was obtained in 42% yield together with molecular dihydrogen (14% yield). Furthermore, a higher catalytic activity has been achieved when 1c was used as a catalyst, where up to $2.3 \times 10^2$ equiv. of ammonia based on the catalyst were produced under similar reaction conditions (Fig. 5). We have not yet obtained the exact reason why 1c worked as the more effective catalyst than 1a, but we consider that the introduction of two methyl groups to the benzimidazol-2-ylidene skeleton in the PCP-pincer ligand may increase the back-donating ability of molybdenum centres to the coordinated dinitrogen ligand and activated the terminal dinitrogen ligands more strongly than 1a. The infrared spectrum of 1c in the solid state showed a strong absorption peak assignable to terminal dinitrogen ligands at 1,969 cm$^{-1}$, which is lower than that of 1a (vide supra). Previously, we reported that the introduction of electron-donating groups such as methyl and methoxy groups to the pyridine ring of the PNP-pincer ligand in 2 markedly enhanced the catalytic activity under the same reaction conditions.

The time profile of the catalytic reactions using 1a and 1c as catalysts was monitored (see Supplementary Methods for the detailed procedure). Typical results are shown in Fig. 6 together with the time profile using 2 as a catalyst. The turnover frequency (TOF) for ammonia formation, which was determined as mols of ammonia (based on the catalyst) produced in initial 1 h, was 42 h$^{-1}$ for 1a and 53 h$^{-1}$ for 1c. The TOFs for ammonia using 1a and 1c are ca. 2.5 and 3.1 times larger than that using 2 (17 h$^{-1}$), respectively. This result indicates that the dinitrogen-bridged dimolybdenum complexes bearing PCP[1]-type pincer ligands such as 1a and 1c have the effective performance not only on the catalytic activity but also on the rate for ammonia formation.

For comparison of the stability of the dinitrogen-bridged dimolybdenum complexes bearing PCP-pincer ligands with that of PNP-pincer ligands, we carried out the following catalytic reactions using 1a and 2 as catalysts. After the formation of 47 equiv. of ammonia based on the catalyst from molecular dinitrogen following the same procedure of the time profile experiment using 1a, the same amounts of [LutH]OTf and CrCp$_2$ were further added at room temperature, and the mixture was stirred for another 2 h to afford a total of 69 equiv. of ammonia based on the catalyst (Fig. 7; see Supplementary Methods for the detailed procedure). In this reaction system, 22 equiv. of ammonia were produced from a further reaction of molecular dinitrogen with excess amounts of a proton source and a reductant. This experimental result indicates that the active species derived from 1a remain even after the catalytic reaction. In fact, no free PCP-pincer ligand was observed from the reaction mixture after the catalytic reaction using 1a as a catalyst, suggesting that the active species derived from 1a were still active. In sharp contrast, no additional ammonia was produced from similar treatment using 2 as a catalyst (Fig. 7), where free PNP-pincer ligand was observed from the reaction mixture after the catalytic reaction using 2 as a catalyst. These results indicate that the stability of 1a is much improved compared with that of 2.

![Figure 6](image)

**Comparison of PCP and PNP ligands.** In this section, we compare the electronic properties and reactivity of 1a and 2. We have previously reported that the catalytic activity of 2 was improved by the introduction of electron-donating groups to the 4-position of the pyridine ring in PNP. In this report, DFT calculations demonstrated that the introduction of electron-donating groups to PNP enhances the back-donating ability of molybdenum centres and thereby leads to activation of dinitrogen ligands. As described in the Introduction, the NHC-based PCP ligand was expected to work as a strong electron donor to activate dinitrogen ligands coordinated to the molybdenum centre. For understanding the geometric and electronic structures of 1a and 2 upon the coordination of the pincer ligands, mononuclear molybdenum complexes 1a’ and 2’ were investigated in detail.

Figure 8a compares the electron-donating ability of Bim-PCP[1] and PNP in terms of differences in atomic charge ($\Delta q$) between the dinitrogen complexes (1a’ and 2’) and the free ligands (Bim-PCP[1] and PNP). The charges of the Mo atom and three N$_2$ ligands obtained with the natural population analysis (NPA) were set to zero for the free ligands, and hence the sum of the charges is identical to the $\Delta q$ value of the Mo(N$_2$)$_3$ moiety. The gross NPA charges of the Mo(N$_2$)$_3$ moiety in 1a’ and 2’ can be regarded as the amount of electron donated from the pincer ligands during complexation. To evaluate the electron-donating ability of Bim-PCP[1] and PNP, the $\Delta q$ values of the PBu$_3$ groups and the carbene or pyridine moiety containing the methylene linkers are separately given in Fig. 8a. The $\Delta q$ values of the PBu$_3$ groups are identical in both Bim-PCP[1] and PNP (+0.29), indicating that the electron-donating ability of Bim-PCP[1] and PNP is controlled by the carbene and pyridine moieties. Since the $\Delta q$ values of the carbene and pyridine moieties are +0.23 and +0.12, respectively, the pincer ligands donate 0.81e$^-$ (Bim-PCP[1]) and 0.70e$^-$ (PNP) to the Mo(N$_2$)$_3$ moiety during complexation. As we expected, the NHC-based pincer ligand exhibits a stronger electron-donating ability than the pyridine-based one from a viewpoint of atomic charge.

Optimized structures and BDEs between the molybdenum centre and dinitrogen ligands also reflect the strength of the
CoCp₂ for the same value as the time profile experiment. Each 'NH₃ second' is collected by the following procedure. A solution of a reductant (CrCp₂ for amount of ammonia (equiv.) is based on the catalyst.

Figure 7 | Reactions of further addition of proton source and reductant. 'NH₃ first' and 'NH₃ second' were collected in separated runs. Each 'NH₃ first' is the same value as the time profile experiment. A solution of a reductant (CrCp₂ for 1a or CoCp₂ for 2, 216 equiv) in toluene (4 ml) was added to a mixture of 1a or 2 (0.0033 mmol for 1a and 0.010 mmol for 2) and [LutH]OTf (288 equiv) at room temperature over a period of 1 h under 1 atm of dinitrogen gas, followed by stirring for 20 h. Then, [LutH]OTf (288 equiv) was added in one portion and another solution of the same reductant (216 equiv) in toluene (4 ml) was added over a period of 1h, followed by stirring at room temperature for another 1h under 1 atm of dinitrogen gas. The difference between the amount of ammonia obtained in this experiment and the 'NH₃ first' is the 'NH₃ second'. The amount of ammonia (equiv.) is based on the catalyst.

Figure 8a). The gross NPA charge on the dinitrogen ligands to the thermodynamic instability of the dinitrogen-bridged catalyst. NH₃ NH₃

**Figure 7**: Reactions of further addition of proton source and reductant. 'NH₃ first' and 'NH₃ second' were collected in separated runs. Each 'NH₃ first' is the same value as the time profile experiment. A solution of a reductant (CrCp₂ for amount of ammonia (equiv.) is based on the catalyst.

On the other hand, the strong trans influence of the carbene ligand weakens the Mo–N₂(equatorial) bond in 1a’. The Mo–N₂(equatorial) bond distance of 2.084 Å (b.o. = 0.50) in 1a’ is much longer than that of 2.018 Å (b.o. = 0.62) in 2’, and the BDEs of the Mo–N₂(equatorial) bond are 21.2 kcal mol⁻¹ for 1a’ and 30.1 kcal mol⁻¹ for 2’. Interestingly, the coordination of Bim-PCP[1] to molybdenum would influence all dinitrogen ligands at both trans- and cis-positions so as to weaken all the Mo–N₂ bonds. The Mo–N₂(axial) bond distances (b.o.) are calculated to be 2.034 Å (0.53) for 1a’ and 2.024 Å (0.54) for 2’. The BDE of the Mo–N₂(axial) bond of 1a’ (12.5 kcal mol⁻¹) is also lower than that of 2’ (14.0 kcal mol⁻¹). A similar trend was observed for the Mo–N₂(bridging) and Mo–N₂(terminal) bonds in dimolybdenum–dinitrogen complexes 1a and 2. The bond dissociation energies are 18.8 and 11.9 kcal mol⁻¹ for 1a, both of which are smaller than those obtained for 2 (24.9 and 14.4 kcal mol⁻¹).

The origin of the weaker Mo–N₂ bonds in 1a’ and 1a is understood by looking at frontier orbitals responsible for the bonding between the molybdenum centre and the carbene C atom of Bim-PCP[1]⁵²,⁵³,⁶⁴,⁶⁵. As depicted in Fig. 8b, the HOMO-6 (1a’) and HOMO-5 (2’) contribute to a σ-bond between the Mo atom and the carbene C atom (or the pyridine N atom). The large size of the lobe about the Mo and C atoms indicates that Bim-PCP[1] works as a strong σ-donor compared to PNP. The HOMO-1 in Fig. 8c mainly contributes to π-backdonation from an out-of-plane d orbital of Mo to a π⁺ orbital of dinitrogen ligands. The backdonation from metal to dinitrogen is essential for the activation of dinitrogen upon the formation of metal–dinitrogen complexes. Occupation of the HOMO-1 strengthens all of the Mo–N₂ bonds in 1a’ and 2’ because of their symmetrical structures. By comparing the HOMO-1 of 1a’ and 2’, one can find a bonding interaction between the Mo atom and the carbene C atom through π-backdonation from the d orbital of Mo to the vacant ρ orbital of C perpendicular to the carbene ring in 1a’. This backdonation decreases the amount of electron transferred to both the equatorial and axial dinitrogen ligands, leading to the lower BDEs of the Mo–N₂ bonds in 1a’ (1a) as presented in Fig. 8a, the ΔG value of the dinitrogen ligands in 1a’ (–0.26) is smaller than that in 2’ (–0.31) in spite of the electron-donating ability of Bim-PCP[1] superior to PNP. The backdonation from the Mo atom to the carbene C atom also contributes to the strong binding of Bim-PCP[1] to Mo.

On the other hand, the Mo–C bond distance (b.o.) in 1b’ bearing Im-PCP[2] (2.178 Å (0.79)) indicates that the Mo–C bond in 1b’ is weaker than that in 1a’, as summarized in Table 3. Owing to the longer CH₂ linkers, the coordination of the carbene moiety to the molybdenum centre in 1b’ is highly twisted compared to 1a’; the dihedral angles of N(1)–C–(C–N(1)–N(3) are 69.6° for 1a’ and 43.8° for 1b’ (Supplementary Fig. 21). The twisted coordination of the carbene moiety in 1b’ reduces the overlap between the out-of-plane d orbital of the Mo atom and the vacant ρ orbital of the carbene C atom. As a result, Im-PCP[2] works only as a very strong σ-donor (0.90 e⁻ donation to Mo; Fig. 8a). The gross NPA charge on the dinitrogen ligands (–0.36) as well as the large BDE of the Mo–N₂(axial) bond of 1b’ (14.3 kcal mol⁻¹) implies that the coordination of Im-PCP[2] to the molybdenum centre effectively activates the coordinated dinitrogen ligands. However, we theoretically confirmed that the mononuclear molybdenum–dinitrogen complexes such as 1b’ and [cis-Mo(N₂)₂(Im-PCP[2])] cannot be protonated by LutH⁺, similar to 1a’ and [Mo(N₂)₂(PNP)]⁴³. All attempts to optimize a product complex comprise the protonated 1a’ (1b’), and Lut resulted in formation of a reactant complex comprising 1a’ (1b’) and LutH⁺, even though the optimization started from a structure with the N₂…H⁺ distance of 5 Å. Thus, the lack of the catalytic activity of 1b for nitrogen fixation can be attributed to the thermodynamic instability of the dinitrogen-bridged dimolybdenum structure, as mentioned in the former section.
theoretically investigated possible reaction pathways catalysed by 1a. In the present article, we particularly focus on the first protonation process shown in Fig. 9, since the protonation of a terminal dinitrogen ligand in 2 by [LutH]OTf is energetically the most unfavourable process in the catalytic cycle. In the calculated reaction pathway, a terminal dinitrogen ligand in 1a is first protonated by LutH$^+$ (1a−A−PCP), and then the dinitrogen ligand trans to the generated NNH group is eliminated (A−PCP−B−PCP). The protonation of 1a yielding A−PCP is endothermic by 8.1 kcal mol$^{-1}$ with an activation energy of 8.3 kcal mol$^{-1}$. This energy profile indicates that proton detachment from A−PCP can easily occur like the PNP system. On the other hand, the following N$_2$ elimination yielding B−PCP is exothermic by 5.2 kcal mol$^{-1}$ with a low activation energy of 4.0 kcal mol$^{-1}$. The coordination of OTf$^-$ to B−PCP is highly exothermic by 20.7 kcal mol$^{-1}$, and thus the whole reaction pathway leading to C−PCP is energetically downhill. Comparison of the energy profiles of the PCP and PNP systems suggests that the reactivity of the dinitrogen complexes 1a and 2 with [LutH]OTf would not be a major factor for rationalizing the high catalytic activity of 1a.

**Discussion**

On the basis of our previous findings on the catalytic nitrogen fixation, we have newly designed and prepared novel dinitrogen-bridged dimolybdenum complexes bearing NHC and phosphine-based PCP-pincer ligands, Bim-PCP$[1]$ and Im-PCP$[2]$. The dimolybdenum–dinitrogen complexes bearing Bim-PCP$[1]$ as PCP-pincer ligands have been found to work as so far the most effective catalysts towards the ammonia formation from
molecular dinitrogen under ambient reaction conditions, where up to 230 equiv. of ammonia were produced based on the catalyst (115 equiv. of ammonia based on the molybdenum atom of the catalyst). The superior activity of dimolybdenum–dinitrogen complexes bearing Bim-PCP[1] included the high TOF for complexes bearing Bim-PCP[1] included the high TOF for ammonia formation and the catalyst stability. DFT calculations reveal that Bim-PCP[1] as a PCP-pincer ligand serves as not only a strong σ-donor but also a π-acceptor. These electronic properties are responsible for a solid connection between the molybdenum centre and the pincer ligand, leading to the enhanced catalytic activity for nitrogen fixation.

Methods

General information. Detailed experimental procedures, characterization of compounds and the computational details can be found in the Supplementary Figs 1–21, Supplementary Tables 1–10 and Supplementary Methods. Cartesian coordinates are available in Supplementary Data 1.

Synthesis of [{Mo(N2)2(PCP)}2(PCP)] (1a–1c). A typical procedure for the preparation of 1a is described below. To a mixed solid of 1,3-bis(di-tert-butylphosphino)methyl)-1H-benzo[d]imidazol-3-ium hexafluorophosphate (7a, 1.16 g, 2.00 mmol) and K2[N(SiMe3)2] (559 mg, 2.80 mmol) was added toluene (40 ml), and the resulting solution was stirred for 20 min at room temperature. [MoCl3(thf)2] (733 mg, 1.75 mmol) and toluene (15 ml) were added to the suspension and stirred at 80 °C for 19 h. The solvent was removed under vacuum, and the residue was washed with hexane (5 ml × 2), toluene (10 ml) and hexane (5 ml × 2). The solid was dried under vacuum. The solid was extracted with CH2Cl2 (10 ml × 1, 5 ml × 7), recrystallized from CH2Cl2–hexane and dried under vacuum to afford 3a. 0.5CH2Cl2 (712 mg, 1.05 mmol, 60%). Anal. Calcd. for C25H40Cl1MoN2P2: C, 42.94; H, 6.68; N, 4.12. Found: C, 45.41; H, 6.61; N, 4.44.

Figure 9 | A possible reaction pathway and energy profiles of the first protonation process on a terminal dinitrogen ligand in 1a (highlighted in yellow) and 2. Energy changes (activation energies in parentheses) are presented in kcal mol−1.

Table 3 | Selected bond distances in Å and Mo–N2 BDEs in kcal mol−1 of mononuclear molybdenum–dinitrogen complexes.

|             | 1a'           | 2'            | 1b'           |
|-------------|---------------|---------------|---------------|
| Mo–C(carbene)/N(pyridine) | 2.099 (0.91) | 2.240 (0.39) | 2.178 (0.79) |
| Mo–N(equatorial)      | 2.084 (0.50) | 2.018 (0.62) | 2.041 (0.55) |
| Mo–N(axial)           | 2.034 (0.53) | 2.024 (0.54) | 2.026 (0.53) |
| BDE(equatorial N2)    | 21.2          | 30.1          | 21.5          |
| BDE(axial N2)         | 12.5          | 14.0          | 14.3          |

BDE, bond dissociation energy.
The Mayer bond orders are presented in parenthesis.

Synthesis of [{Mo(N2)3(Bim-PCP[1])}2(PCP)] (1a–1c). A typical procedure for the preparation of 1a is described below. To a suspension of Na–Hg (0.5 wt% Na, 13.8 g, 3.00 mmol) in THF was added [MoCl3(Bim-PCP[1])] (0.5CH2Cl2: C, 42.94; H, 7.21; N, 4.26. Found: C, 43.04; H, 7.44; N, 4.19. Crystals suitable for X-ray analysis were prepared by recrystallizing from 1,2-dichloroethane–hexane to afford 1b 1/3CH2Cl2. The structure is included in Supplementary Fig. 2 and selected bond lengths and angles in 1b are included in Supplementary Table 6.

|             | 1a'           | 2'            | 2'           |
|-------------|---------------|---------------|---------------|
| Mo–C(carbene)/N(pyridine) | 2.099 (0.91) | 2.240 (0.39) | 2.178 (0.79) |
| Mo–N(equatorial)      | 2.084 (0.50) | 2.018 (0.62) | 2.041 (0.55) |
| Mo–N(axial)           | 2.034 (0.53) | 2.024 (0.54) | 2.026 (0.53) |
| BDE(equatorial N2)    | 21.2          | 30.1          | 21.5          |
| BDE(axial N2)         | 12.5          | 14.0          | 14.3          |

BDE, bond dissociation energy.
The Mayer bond orders are presented in parenthesis.
considered to be due to the labile property of the coordinated dinitrogen ligand in 1a under the analytical conditions.

1b Recrystallization from benzene–hexane afforded 1b 2/3CH₂Cl₂ as dark-brown crystals. 53% yield. Anal. Calcld. for C₃₂H₃₃Cl₁₉Mo₂N₈P₄: C, 41.55; H, 3.47; Cl, 18.02; Mo, 11.49; N, 15.19. Found: C, 41.45; H, 3.3; Cl, 18.0; Mo, 11.6; N, 15.05.

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Acknowledgements

The present project is supported by CREST, JST. We thank KAKENHI (Nos JP26288044, JP26150708, JP15K13687, JP15H05798 to Y.N., No. JP24109014 to K.Y. and No. JP26888008 to H.T.) from JSPS and MEXT. A.E. and S.K. are recipients of the JSPS Predoctoral Fellowships for Young Scientists. We also thank the Research Hub for Advanced Nano Characterization at The University of Tokyo for X-ray analysis.

Author contributions

K.Y. and Y.N. directed and conceived this project. A.L., K.A. and K.N. conducted the experimental work. H.T. and Y.M. conducted the computational work. All authors discussed the results and wrote the manuscript.

Additional information

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing interests: The authors declare no competing financial interests.

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How to cite this article: Eizawa, A. et al. Remarkable catalytic activity of dinitrogen-bridged dimolybdenum complexes bearing NHC-based PCP-pincer ligands toward nitrogen fixation. Nat. Commun. 8, 14874 doi: 10.1038/ncomms14874 (2017).

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