Nitrogen Fixation

A Chatt-Type Catalyst with One Coordination Site for Dinitrogen Reduction to Ammonia

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Abstract: With [Mo(N\(_2\)](P\(_2\)MePP\(_2\)F\(_2\))] the first Chatt-type complex with one coordination site catalytically converting N\(_2\) to ammonia is presented. Employing SmI\(_2\) as reductant and H\(_2\)O as proton source 26 equivalents of ammonia are generated. Analogous Mo\(^V\)-N\(_2\) complexes supported by a combination of bi- and tridentate phosphine ligands are catalytically inactive under the same conditions. These findings are interpreted by analyzing structural and spectrosscopic features of the employed systems, leading to the conclusion that the catalytic activity of the title complex is due to the strong activation of N\(_2\) and the unique topology of the pentadentate tetrapodal (pentaPod) ligand P\(_2\)MePP\(_2\)F\(_2\). The analogous hydrazido(2-) complex [Mo(NNH\(_2\)](P\(_2\)MePP\(_2\)F\(_2\))(BA\(_2\))\(_2\)], generated by protonation with HBA\(_2\) in ether and characterized by NMR and vibrational spectroscopy. Importantly, it is shown to be catalytically active as well. Along with the fact that the structure of the title complex precludes dimerization this demonstrates that the corresponding catalytic cycle follows a mononuclear pathway. The implications of a PCET mechanism on this reactive scheme are considered.

The activation of molecular nitrogen has been of great interest over the last decades. This in particular refers to biological nitrogen fixation, which is mediated by the enzyme nitrogenase. Although the structure of this enzyme has been fully determined,[1] the mechanism of the dinitrogen reduction and protonation is still the subject of current research.[2] To mimic this process and elucidate its mechanism, various small-molecule based model systems have been studied in detail.[3] The earliest of these systems were established by Chatt and Hidal on the basis of molybdenum (bis)dinitrogen complexes with phosphine coligands.[4] In 1985 Pickett et al. demonstrated an electrochemical synthesis of NH\(_3\) mediated by a tungsten complex.[5] The first truly catalytic reduction of N\(_2\) to ammonia was achieved by Schrock et al. in 2003 using a triamidoamine molybdenum complex (Scheme 1) as catalyst, Cp\(^+\)Cr as reductant and LutH(BA\(_2\)) as proton source. This system generated 7.6 equivalents of NH\(_3\),[6] which clearly was a milestone in synthetic nitrogen fixation. A N\(_2\)-bridged dinuclear Mo system supported by pincer ligands, presented by Nishibayashi et al. in 2011, led to 23.2 equivalents of ammonia (through modification up to several hundred[7,8]) equivalents of ammonia. While this group first employed LutH(TOF) as acid and Cp\(^+\)Cr as reductant, an even more powerful protocol was established in 2019, involving SmI\(_2\)/H\(_2\)O as reductant and proton source. This way, 4,350 equivalents of ammonia could be generated.[9] In 2013, the first non-molybdenum catalytic system for N\(_2\) reduction was presented by Peters et al., employing a BP\(_2\) supported iron complex, KC\(_8\) as reductant and HBA\(_2\) as acid.[10]

On the basis of the classic Chatt-type bis(dinitrogen) Mo/W complexes containing diphenphosphate ligands (e.g., dppe or depe) the first mechanism for the transition-metal mediated conversion of N\(_2\) to NH\(_3\) was formulated, the so-called Chatt cycle (Scheme 2).[12]

This reactive scheme starts with the protonation of the parent N\(_2\) complex, leading to the hydrazido(2-) complex. In the subsequent steps, one additional proton and two electrons are required to cleave the N–N bond and generate the first equivalent of ammonia.[13,14] This mechanism is very similar (but not identical) to the Schrock cycle, which is based on the

\[\text{Chatt} \quad \text{Schrock} \]

\[\text{Nishibayashi} \]

Scheme 1. Molybdenum-based model systems for synthetic nitrogen fixation.[12]
In this context it should be noted that both the Chatt- and the Schrock cycle involve N–N splitting at the level of NNH$_2$- and NNH$_2$-complexes, whereas the dinuclear systems of Nishibayashi et al. (Scheme 1) mediate N–N cleavage of the parent N$_2$-complexes, leading to two nitrido intermediates, which subsequently are converted to NH$_2$.[7,9] Recently, this scenario has also been evidenced in a classic Chatt system by Masuda and co-workers, where the dinuclear Mo$^+$ complex ([Mo(depe)$_2$]$_2$($\mu$-N$_2$)$_2$)$^{2+}$ was found to split into two [Mo(N)(depe)$_2$]$_2$ cations by cleavage of the N–N bond (Scheme 3). Similar reactivities have been obtained with other dinuclear, dinitrogen-bridged transition metal complexes.[9,18]

An important disadvantage of the original Chatt systems has been the fact that protonation of the dinitrogen complex involves exchange of one of the two N$_2$ ligands by the conjugate base of the applied acid, causing a 50% loss of bound substrate. Moreover, this anionic trans-coligand had to be exchanged again at the end of the cycle leading to the bis(dinitrogen) complex, and Mo$^+$ complexes formed as intermediates during that stage were found to be prone to disproportionation.[18,19] These mechanistic drawbacks have traditionally been invoked to rationalize that classic Chatt-type systems, although in principle forming all relevant intermediates, are catalytically inactive towards the conversion of N$_2$ to NH$_3$. On the other hand, Nishibayashi et al. recently showed that Chatt complexes with mono- and bidentate ligands indeed catalyse the generation of ammonia from N$_2$, if SmI$_2$/H$_2$O (or SmI$_2$/alcohol) is used as reductant and proton source.[20] Using cis$_{\text{mer}}$-[Mo(N-NH$_3$)$_2$(OTf)$_2$]$_2$[PMePh$_3$]$_2$ as example for a NNH$_2$ intermediate also led to catalytic amounts of NH$_3$. From this observation it was inferred that the SmI$_2$-mediated reduction pathway of Chatt-type complexes probably follows the Chatt cycle.

In view of the above-mentioned problems of the classic Chatt complexes, we had in the past developed a series of molybdenum dinitrogen complexes in which the trans position is occupied by a donor atom of a multidentate ligand. These systems were intended to provide only one site for the coordination and reduction of N$_2$, and avoid all other ligand exchange reactions occurring at the single Mo center. Initially, we had employed a combination of a tripodal (1)$^{[21]}$ or a linear tridentate ligand (2)$^{[22]}$ with a bidentate co-ligand (Scheme 4) for this purpose. Compounds 2 and 1, however, suffered from isomerisation and, respectively, instability of the tridentate phosphine ligand coordination upon protonation of the N$_2$-complex, which was ascribed to the fact that the trans-donor is not fixed strongly enough to the center Mo atom. Later we succeeded combining the two described approaches into a unique pentadentate tetrapodal (pentaPod) phosphine ligand. Based on this concept, the molybdenum mono(dinitrogen) complex [Mo(N$_2$)$_2$(P$_4$(26PP$_{3}$)$_2$)] (3) was synthesized and characterized both experimentally and theoretically.$^{[21]}$

We now discovered that reaction of 3 in THF with N$_2$ gas at 1 atm, 180 equiv of SmI$_2$, and 180 equiv of H$_2$O gives 25.73 ± 0.37 equiv of ammonia based on the molybdenum atom (43% yield based on SmI$_2$; Table 1). Replacing $^{15}$N$_2$ by $^{15}$N$_2$ in these experiments correspondingly leads to $^{15}$NH$_3$, which was detected by $^1$H-NMR as $^{15}$NH$_3$Cl (cf. SI, Figure S1). To check if the pentadentate coordination of 3 is responsible for the catalytic activity, complexes 1 and 2 with tridentate or tripod ligands were investigated under the same conditions. However, both only led to substoichiometric amounts (less than 2 equiv) of ammonia, which indicates decomposition of the complexes. In order to understand the different catalytic activities of 1, 2 and 3, the electronic and geometric structures of these systems are analyzed in the following.

The key property of a molecular catalyst for synthetic nitrogen fixation is the activation of the N$_2$ ligand, enabling its protonation and further reduction to ammonia. The most sensitive probe of this capability is the N–N stretching frequency. In this respect, complex 3 exhibits the highest activation (Table 1). As a matter of fact, its N–N stretching frequency is the lowest of all known Mo-pentaphosphine complexes. In comparison, $v_{\text{NH}}$ of 1 and 2 are by 45 and 50 cm$^{-1}$ higher, re-
spectively. The activation of N₂ is a function of the electron density on the Mo³ center, which in turn sensitively depends on the type of phosphine donors. Note that all three complexes have an equatorial Pₐq coordination of two PMe₃ and two PPh₃ groups, whereas the nature of the phosphine in trans-position is different. In a first approximation, the activation of N₃ in complexes 1–3 thus is a function of the axial phosphine donor Pₐq and in view of the fact that electron donation increases within the sequence PPh₃ < PR₃H < PR₃ (R = alkyl), the observed sequence of ν₉θ can qualitatively be understood.

Besides these electronic factors, it is also of interest to analyze the Mo–N and Mo–Pₐq distances in 1–3. Importantly, 3 has the shortest Mo–Pₐq bond of all complexes, also being shorter than all Mo–Pₐq bonds (Table 1). The Mo–Pₐq distance of 2 is slightly longer, whereas that of 1 is much longer, getting similar to the Mo–Pₐq values (∼2.4 Å). The short Mo–Pₐq distances of 3 and 2 indicate strong Mo–Pₐq bonds, which serves to transfer electron density to the Mo³ center. Remarkably, the Mo–N bonds are short in these complexes as well. This should lead to strong Pₐq-Mo-Pₐq interactions which may be probed by ³¹P- and ¹⁵N-NMR spectroscopy.

The ³¹P NMR spectrum of 3 shows an AA’MXX’ pattern, in agreement with its pentaphosphine environment (Figure 1a). In order to obtain information regarding the coupling between the phosphine ligands and the N atoms of the coordinated N₃, the isotopically labeled complex was synthesized. Additional couplings between the P donors and the Nₐ and Nₐ atoms of the dinitrogen ligand are visible in the ³¹P-NMR spectrum of ¹⁴N-3 (Figure 1b and c). The M signal, which belongs to Pₐq (Figure 1d), exhibits much stronger couplings (J(¹⁴Pₐq, ¹⁴Nₐ) = 13.5 Hz, J(¹⁴Pₐq, ¹⁴Nₐ) = 1.4 Hz) than the phosphine groups Pₐq in cis-position (J(¹⁴Pₐq, ¹⁴Nₐ) = 3.1 Hz, J(¹⁴Pₐq, ¹⁴Nₐ) < 1.0 Hz; J(¹⁴Pₐq, ¹⁴Nₐ) = 3.0 Hz, J(¹⁴Pₐq, ¹⁴Nₐ) = 1.0 Hz; cf. SI, Figures S5, S3).

In the M part of the spectrum, an asymmetric positioning of the ¹⁴N (dd-) signal with regard to the ¹⁴N signal deriving from residual 3 is noticed (Figure 1d), which corresponds to a two-bond (tertiary) ¹⁴N-induced isotope effect on the chemical shift of the trans ³¹P nucleus (J(³¹P, ¹⁴N)(N)). We attribute this phenomenon to the anharmonicity of the Mo–N(ND) potential, leading to a slight reduction of the Mo–Nₐ equilibrium bond distance if the mass of the N₂ ligand is increased. This in turn increases the Mo–Pₐq bond length by virtue of the trans effect, causing an increased shielding of Pₐq. With an upfield shift of around 1 Hz (6.2 ppb) the two-bond isotope shift across the metal center is in a range where usually one-bond ¹⁴N—¹⁵N shifts (e.g., phosphoric acid amide: 9.6 ppb[26]) are observed. This indeed reflects a strong influence of the N₉ coordination on the bonding of the P atom in trans position.

In order to elucidate a possible dependence of this effect on the electronic structure of the Mo–N₉ complex, the ³¹P-NMR spectra of complex 2, which also exhibits a short Mo–Pₐq bond (cf. Table 1), were re-examined (cf. SI, Figures S4–S6). This analysis provided similar results (J(³¹P, ¹⁴N) = 1.1 Hz (6.9 ppb)). Moreover, the J(³¹Pₐq, ¹⁴N) coupling constants were determined to 14.1 (Nₐ) and 1.2 Hz (Nₐ), respectively, quite close to the values of 3 (Table 1). In case of complex 1 having the longest Mo–Pₐq bond of all three complexes, an analogous analysis was not possible due to its ³¹P-NMR spectrum being of higher order (cf. SI, Figure S7). As the bonding situation drastically changes along the Chatt cycle, it also appeared of interest to explore a possible correlation between J(³¹P(¹⁴N)) and the electronic structure of the respective intermediates.

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**Table 1.** Experimental and calculated spectroscopic and structural parameters of the employed molybdenum pentaphosphine complexes and ammonia formation in the presence of them.

| Catalyst | NH₃ production¹ | NN stretch (cm⁻¹) | d(Mo-Pₐq) (pm) | d(Mo-N) (pm) | d(N-N) (pm) | d(Mo-Pₐq) av (pm) | J(¹⁴Pₐq, ¹⁴Nₐ)(N) (Hz) | J(¹⁴Pₐq, ¹⁴Nₐ)(N) (Hz) |
|----------|-----------------|-------------------|----------------|---------------|---------------|------------------|---------------------|---------------------|
| [Mo(N₉)(tbdpm)](dnmpl) (1) | 0.82 ± 0.04 | 1979 | 244.54(16) | 206.6(6) | 106.9(8) | 246.21 | – | – |
| [Mo(N₉)(porPPh₃)](dnmpl) (2) | 1.77 ± 0.03 | 1974 | 240.15(6) | 202.1(2) | 111.6(3) | 242.96 | 14.1 | 1.2 |
| [Mo(N₉)(P₃P₃P₃)] (3) | 25.73 ± 0.37 | 1929 | 238.68(12) | 203.3(5) | 109.9(5) | 244.81 | 13.5 | 1.4 |
| [Mo(N₉(NH₃)₃)(P₃P₃P₃)] (4) | 26.14 ± 0.32 | 1490(š) | 261.17(š) | 177.4(š) | 131.7(š) | 252.51(š) | 23.2 | 7.6 |

(a) equivalents per Mo atom; N₉ gas at 1 atm, 180 equiv of SmI₂ and 180 equiv of H₂O; (b) PBOE-D(3)(B)/def2-SVP.

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**Figure 1.** a) Experimental (in C₆H₆) ³¹P-NMR spectra of 3 and b) a mixture of 3 and ⁴⁰N-3 (18 %). c) Simulated spectrum of ¹⁴N-3. d) Overlay of experimental M signals of ¹⁴N-3 and the mixture, showing the two-bond (tertiary) ¹⁴N-induced isotope effect (+ ³¹P = 1.0 Hz, 6.2 ppb).
Protonation of 3 with [H(OEt)₂][BARF]₀[27] in Et₂O (‘HBARF’ medium) affords the NH₂₃ complex [Mo(NH₂₃)(P₂₅₃PP,₉)]BARF₂ (4). This is, for example, evident from the vibrational spectra of solid 4 (¹⁴N-4) showing N–H (¹⁴N–H) stretches at 3312 (3307) cm⁻¹ (νₚ(NH)) and 3200 (3198) cm⁻¹ (ν₁(NH)) as well as the disappearance of ν₁(NH) at 1929 cm⁻¹ (cf. SI, Figure S8 and Table S1; preliminary spectroscopic data of 4 were already given in ref. [23]). In analogy to 3, the ³¹P-NMR spectrum of 4 exhibits an AAMIₓ pattern, with chemical shifts and coupling constants modified with respect to the former (Figure 2a; cf. SI, Figure S9–S13). This indicates that the pentaPod environment of 3 is retained upon protonation, a prerequisite for the catalytic activity of our system. Protonation was also performed with 3 containing a mixture of ¹⁵N₂ and ¹⁴N₂ (18% ¹⁵N; see above). Again, the resulting ³¹P-NMR spectrum (Figure 2b) shows a superposition of the spectra mainly deriving from the ¹⁵N₁⁵N₂ complex (Figure 2c) with small additional signals from the ¹⁴N¹⁴N₂ isotopomer. In contrast to the parent N₂ complex 3, however, no ¹⁵N-isotope effect on the ³¹P-NMR shift is visible in the M-part of ⁴¹⁴N-4 (Figure 2d).

In order to interpret this result, we note that DFT predicts a hydrazido(2-) configuration for 4 (cf. SI, Figure S14), with a triple bond between Mo and N₁⁵. [28] This is in contrast to classic Chatt-type NNH₂ complexes such as [MoF(NH₂₂)(diphos)] where an isodiazene description was found to be more appropriate. [28] The lack of ² J(¹⁵P⁻¹⁵N) on δ(PₓPᵧ) suggests that the anharmonicity in the Mo=N potential of 4 is much lower than in the Mo=N₁₅ bond of the parent dinitrogen complex 3. The triply bonded NNH₂ ligand should exert a strong trans effect. This is supported by DFT calculations which indicate a significant elongation of the Mo=Pₓ distance in 4 with respect to 3, making it even longer than the Mo=Pₓₓ bonds (Table 1). Correspondingly, the protonation-induced high-field shift is much larger for the M signal than for the A and X signals (cf. SI, Figure S13 and Table S2).

The flexibility of the metal-E bond in trans-position to the nitrogenic ligand has been considered by Peters et al. as an important criterion for the catalytic activity of their iron-dinitrogen complexes supported by EP₁ ligands (E=B, Si, C). [30] In spite of the short Mo=Pₓ bond observed for the Mo-dinitrogen complex 3 it appears that the pentaPod ligand framework is sufficiently flexible to allow elongation of the axial Mo=P bond in the NNH₂-complex 4. [28]

Formation of the hydrazido(2-) complex 4 is also evident from its ¹H-¹⁵N-HMBC spectrum which clearly shows the -NNH₂ moiety; i.e., a doublet in the ¹H dimension with a ¹ J(¹⁵Nₓ⁻¹⁵Nᵧ) of 94.6 Hz and a corresponding triplet in the ¹⁵N spectrum (Figure 3; cf. SI for complete spectrum, Figure S15). In the ¹⁵N spectrum the couplings of Nₓ to Nᵧ (11.2 Hz) and the trans standing Pₓ (7.6 Hz) are also observable (cf. SI, Figure S16, Tables S3 and S4).

In analogy to 3, compound 4 was applied as a catalyst for the reduction of N₂ at 1 atm with 180 equiv of SmI₃ and 180 equiv of H₂O in THF. As the stability of 4 in this solvent had been found to be limited, [28] we generated 4 in situ in diethyl ether and subsequently added this to a solution of SmI₃/ H₂O in THF. These experiments afforded 26.14 ± 0.32 equiv of NH₃ (Table 1), identical to the yield obtained with the N₂ complex 3 within the error limit. This proves the role of the hydrazido(2-) complex 4 as an intermediate in the catalytic conversion of N₂ to NH₃ mediated by 3 and suggests that the corresponding mechanism follows the Chatt cycle; e.g., avoids a direct N≡N cleavage (Scheme 2). Furthermore, the fact that dimerization of 3 is sterically hindered renders the existence of a dinuclear pathway (Scheme 3) improbable. A simulation of a corresponding Mo¹ or Mo² dimer leads to dissociation of one Mo–P bond (SI, Figure S17).

The usual formulation of the Chatt cycle starts with two protonations of the Mo–N₂ complex, leading to the NNH₂ complex (cf. Scheme 2); notably, 4 has been generated from 3 this way. On the other hand, the SmI₃/Water complex is known to react with protonatable/reducible substrates by proton-coupled electron transfer (PCET). [21] In this context, it has become customary to assess the N₂-reducing capacity of a catalytic nitro-
genase model system by quoting the N–H bond dissociation free energy (BDFE) of the respective NNH (diazenido) complex (cf. Scheme 2). In order to exergonically transfer one electron and one proton to the N₃ complex, the BDFE of the former has to exceed that of the employed PCET reagent or the effective BDFE of the employed acid/reductant combination, respectively.[32]

To determine the N–H BDFE of the NNH-intermediate for a given N₂-reduction catalyst, DFT calculations may be employed.[26] Transfer of one electron and one proton to the Mo⁶⁺ dinitrogen complex leads to the neutral Mo₁-diazenido(–) intermediate. An estimate of the corresponding energetics was obtained by DFT, simulating the reaction of [Mo(N₃)(pentaPod)] with TEMPO-H, a H-atom transfer reagent having a well-defined O–H BDFE of 65.2 kcal mol⁻¹ in benzene,[31] to give the [Mo(NH)(pentaPod)] complex. Subtraction of the reaction TEMPO-H—TEMPO⁺ + H⁻ leads to a N–H BDFE of 19.2 kcal mol⁻¹ for the Mo³⁺-diazenido(–) complex (ΔGₚcₚ[(solv, benzene), cf. SI, Table S6], which is somewhat lower than the O–H BDFE of SmI₂/water (26 kcal mol⁻¹).[31] PCET from this reagent to the Mo¹⁺(N₃) complex thus is slightly endergonic (ΔG¹ₚc = + 6.8 kcal mol⁻¹), but thermodynamically feasible.

In view of the fact that the diazenido(–) intermediates of the classic Chatt cycle correspond to Mo⁰ (and not Mo¹⁺) species,[26] we also theoretically investigated the formation of [Mo²⁺(NNH)(pentaPod)]⁻ by PCET from the corresponding cationic Mo(N₃)-complex. An analogous procedure as described above gives a N–H BDFE of 52.5 kcal mol⁻¹ for the Mo³⁺-diazenido(–) intermediate (ΔGₚcₚ[(solv, benzene), cf. SI, Table S6]). This value well exceeds the BDFE of Sml₂/water (see above), rendering PCET to the cationic [Mo²⁺(N₃)(pentaPod)]⁻ complex highly exergonic (ΔG¹ₚc = −26.5 kcal mol⁻¹). On the other hand, neutral [Mo²⁺(N₃)(pentaPod)] (3) was successfully employed as catalyst in our Sml₂/water-mediated N₂-to-NH₃ conversion experiments (see above). In the framework of a PCET mechanism it thus remains to be elucidated whether (and, if yes, how) our system switches from a pathway starting from a Mo¹⁺(N₃) complex to an energetically more favourable reaction path that involves a mononuclear, cationic Mo¹⁺(N₃) intermediate. In summary, three structurally related Mo-N₃ complexes with pentaphosphine environment have been investigated as catalysts for the conversion of N₂ to NH₃, using Sml₂/H₂O as protonating agent and reductant. Only the title complex [Mo(N₃)(P₅H₅PP₂P₅)²⁺] (3) was found to be catalytically active. This is attributed to the fact that it exhibits the highest activation of N₂ and the pentaPod coordination. The strong chelate effect of this ligand creates an inert and stable, yet flexible ligand environment allowing protonation and reduction of the Mo⁴⁺N₃ complex under retention of the pentaphosphine ligand. Protonation of the dinitrogen complex 3 leads to the hydrazido(2-) complex 4 which was isolated and spectroscopically characterized. Importantly, 4 was also found to be catalytically active. Along with the fact that the Mo(N₃)₃-pentaPod complex precludes dimerization this demonstrates the existence of a mononuclear pathway along the Chatt cycle for the N₂-to-NH₃ conversion catalyzed by this system. The implications of a PCET mechanism on this pathway are considered.

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Conflict of interest
The authors declare no conflict of interest.

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