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FULL PAPER

Molybdenum Complexes Supported by PN^3P Pincer Ligands: Synthesis, Characterization and Application to Synthetic Nitrogen Fixation

Nadja Stucke,[a] Jan Krahmer,[a] Christian Näther[a] and Felix Tuczek*[a]

Dedicated to Prof. Dr. Wolfgang Bensch on the occasion of his 65th anniversary

Abstract: Three PN^3P pincer ligands with a central pyridine ring, amine groups in the ligand backbone and different substituents at the terminal phosphine donors are synthesized and coordinated to molybdenum(III) precursors. Conversion of the resulting Mo(III) compounds to dinitrogen complexes is investigated and compared to the literature-known complex *trans*-[$Mo(N_2)_2(PMe_2Ph)(PNP^{tBu})$] supported by a classic PNP pincer ligand. The difference between PN^3P ligands terminated by di-*tert*-butyl and diphenyl substituents regarding the synthesis and the properties of corresponding Mo(0) dinitrogen complexes is elucidated. Application of the synthesized Mo(0)- and Mo(III)-PN^3P complexes in the conversion of dinitrogen to ammonia reveals a strong influence of the terminal substituents and the atoms in the backbone of the pincer ligand on the catalytic activity.

Introduction

One of the most challenging topics of bioinorganic and organometallic chemistry is the activation and (catalytic) derivatization of small molecules like dinitrogen, dioxygen or carbon monoxide. Transition metal complexes with an appropriate ligand environment are able to bind and activate such molecules which is a necessary requirement for their catalytic transformation.[1–6] In this context, an important and fascinating reaction is the reduction and protonation of dinitrogen to ammonia. In nature this reaction is catalyzed by the enzyme nitrogenase containing an iron molybdenum cofactor as active site.[7,8] Inspired by this biological process, different working groups have synthesized a number of transition metal complexes serving as catalysts for nitrogen fixation [1–3,9–20] Besides the investigation of the catalytic N_2-to-NH_3 conversion extensive efforts have also been directed towards elucidating the electronic structure of the initial N_2 adducts and the reactive intermediates along the reduction pathway.[21–33]

In the last decades it turned out that transition metal complexes with phosphine containing ligands are well suited for the activation and derivatization of dinitrogen.[2,3,10,34] In particular, synthetic and theoretical investigations concerning the use of phosphine-terminated pincer ligands in the transition metal mediated activation and reduction of dinitrogen have been performed by different groups.[2,10,11,16,17,35–40] In this context, molybdenum complexes supported by PNP pincer ligands comprise an interesting and well investigated class of molecules, not only in general coordination chemistry, but especially in the area of dinitrogen fixation.[2,10,41,42] In 2011 the working group of Nishibayashi *et al.* synthesized the dinitrogen-bridged dimolybdenum complex [{$Mo(N_2)_2(PNP^{tBu})$}$_2$(μ-N_2)] supported by the PNP^{tBu} pincer ligand which was able to generate 23.2 equivalents of ammonia (11.6 equiv./Mo) using $CoCp_2$ (216 equiv.) and [LutH]OTf (288 equiv.).[2] Substitution of the central pyridine ring by a NHC moiety, leading to the PCP^{tBu} ligand, increased the yield of ammonia to 230 equiv. per dinuclear catalyst.[11] Recently, this working group published new results concerning the catalytic transformation of dinitrogen into ammonia using the Mo(III) complexes [$MoX_3(PNP^{tBu})$] (X = Cl, Br, I).[12] The mechanism of this catalytic transformation starting from the [$MoI_3(PNP^{tBu})$] complex is assumed to proceed *via* a dinitrogen-bridged dimolybdenum(I) complex, which is cleaved into the respective nitrido complexes. In this way up to 415 equiv. ammonia per molybdenum atom were generated.[12]

On the background of the possibility of conducting nitrogen fixation in an electrocatalytic fashion,[43,44] we were interested in molybdenum complexes supported by pincer ligands which can be attached to metallic surfaces. PN^3P ligands, firstly prepared by Schirmer *et al.*,[45] turned out to be suitable for this purpose. Kirchner *et al.* have studied the coordination of PN^3P pincer ligands to different metal centers, including molybdenum.[41,42,46,47] Employing a suitably functionalized PN^3P ligand, we were recently able to synthesize a molybdenum(0) tricarbonyl complex, deposit this complex on Au(111) and elucidate the influence of the metallic substrate on the activation of the small-molecule ligand CO.[48] With the goal of extending these studies to the activation of N_2 we herein investigate PN^3P pincer ligands with different phosphine groups coordinated to molybdenum(III) centers and the subsequent reduction of these compounds to Mo(0) dinitrogen complexes. Moreover, both Mo(0) and Mo(III) complexes are evaluated regarding their capability to act as catalysts for the N_2-to-NH_3 conversion in homogeneous solution.

Results and Discussion

Synthesis of [MoX_3(R-$PN^3P^{R'}$)] (R=H, Me; R´= Ph, ^{t}Bu)

The ligands H-PN^3P^{Ph} (**1a**) and Me-PN^3P^{Ph} (**1b**) were prepared according to Schirmer *et al.* and Kirchner *et al.*[45,46] Reaction of

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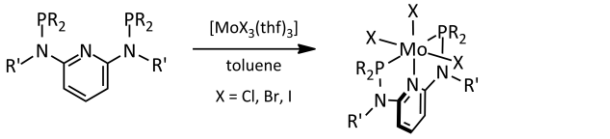

1a (R=Ph, R'=H)
1b (R=Ph, R'=Me)
1c (R=^{t}Bu, R'=H)

2a (R=Ph, R'=H, X=Cl)
2b (R=Ph, R'=H, X=Br)
3a (R=Ph, R'=Me, X=Cl)
3b (R=Ph, R'=Me, X=Br)

4a (R=^{t}Bu, R'=H, X=Cl)
4b (R=^{t}Bu, R'=H, X=Br)
4c (R=^{t}Bu, R'=H, X=I)

Scheme 1: Synthesis of [MoX_3(R'-PN^3P^R)] (X = Cl, Br, I, R=Ph, ^{t}Bu, R'=H, Me) (**2a**, **2b**, **3a**, **3b**, **4a**, **4b**, **4c**).

1a and **1b** with [MoX_3(thf)$_3$] (X = Cl, Br) in toluene afforded the corresponding Mo(III) complexes [MoX_3(R-PN^3P^{Ph})] (R = H, Me) (**2a**, **2b**, **3a**, **3b**) in good to excellent yields (79 - 95 %; Scheme 1). The complexes were characterized by elemental analysis, IR and paramagnetic ^{31}P NMR spectroscopy. Coordination of the pincer ligands **1a** and **1b** to the molybdenum center is reflected by a low-field shift of the corresponding signal in the ^{31}P NMR spectrum of about 65 ppm with respect to the uncoordinated ligands. Reaction of **1a** and **1b** with the triiodido precursor [MoI_3(thf)$_3$] did not lead to the respective Mo(III) complexes in a clean way.

Crystals of [$MoBr_3$(Me-PN^3P^{Ph})] (**3b**) suitable for single crystal X-ray structure determination were obtained by slow evaporation of the solvent (dichloromethane). The crystal structure of **3b** is shown in Figure 1; selected bond lengths and angles are listed in Table 1.

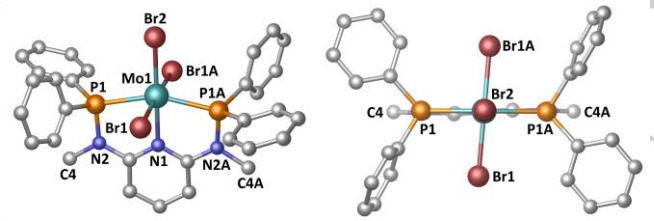

Figure 1: Crystal structure of [$MoBr_3$(Me-PN^3P^{Ph})] (**3b**). Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] of [$MoBr_3$(Me-PN^3P^{Ph})] (**3b**).

Mo(1)-Br(1)	2.5434(6)	N(1)-Mo(1)-Br(1A)	87.246(19)
Mo(1)-Br(1A)	2.5434(6)	P(1A)-Mo(1)-Br(1)	93.94(4)
Mo(1)-Br(2)	2.5471(10)	P(1)-Mo(1)-Br(1)	84.94(4)
Mo(1)-N(1)	2.185(6)	P(1A)-Mo(1)-Br(1A)	84.93(4)
Mo(1)-P(1)	2.5170(15)	P(1)-Mo(1)-Br(1A)	93.94(4)
N(2)-P(1)	1.687(5)	Br(1)-Mo(1)-Br(1A)	174.49(4)
N(2)-C(4)	1.478(7)	N(1)-Mo(1)-Br(2)	180.00(3)
C(1)-N(2)	1.390(7)	P(1A)-Mo(1)-Br(2)	101.73(3)
N(1)-C(1)	1.358(6)	Br(1)-Mo(1)-Br(2))	92.755(19)
		N(1)-C(1)-N(2)	119.1(5)
P(1A)-Mo(1)-P(1)	156.53(7)	C(1)-N(2)-C(4)	117.5(5)
N(1)-Mo(1)-P(1)	78.27(3)	C(1)-N(2)-P(1)	123.0(4)
N(1)-Mo(1)-Br(1)	87.245(19)	C(4)-N(2)-P(1)	119.3(4)

The structure of **3b** shows a molybdenum(III) center which is coordinated in a distorted octahedral fashion by Me-PN^3P^{Ph} (**1b**) and three bromido ligands. The Mo-Br bond lengths amount to 2.543 Å (Mo-Br1(A)) and 2.547 Å (Mo-Br2). The Mo-P1(A) bond length is shorter than in the complex [$MoCl_3$(PNP^{tBu})] by Nishibayashi *et al*. with a PNP^{tBu} pincer ligand (2.517 Å vs. 2.61 Å).[2] In contrast to the latter complex in which the pyridine ring is rotated around the Mo-N(pyridine) bond out of the P-Mo-Cl(*trans*) plane by ≈ 20°, the pyridine ring in **3b** is almost parallel to the P-Mo-Br(*trans*) plane. The bonds to the two out-of-plane (*cis*) bromido ligands in **3b** are not exactly perpendicular to this plane because two P-Mo-Br(*cis*) angles of 84.9° and 93.9°, respectively, are found (cf Figure 1, right). The P1-Mo-P1A angle of 156.5° is distinctly smaller than 180° and comparable to those in molybdenum(0) complexes with PN^3P^{Ph} pincer ligands as well as in the complex [$MoCl_3$(PNP^{tBu})].[2,48]

Apart from ligands **1a** and **1b** with diphenylphosphine groups, the ligand H-PN^3P^{tBu} (**1c**) with di-*tert*-butylphosphine residues was prepared according to the literature.[41] Crystals of **1c** suitable for single crystal X-ray structure determination could be obtained by slow evaporation of the solvent (*n*-hexane). The structure of **1c** is shown in Figure 2, selected bond lengths and angles are listed in Table 2.

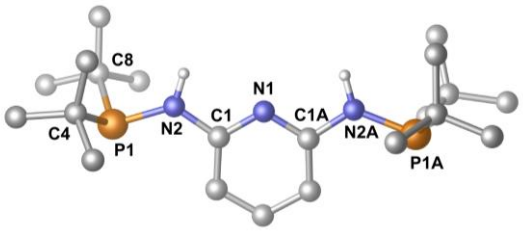

Figure 2: Crystal structure of H-PN^3P^{tBu} (**1c**). For clarity only the N-H hydrogen atoms are shown.

Table 2. Selected bond lengths [Å] and angles [°] of H-PN^3P^{tBu} (**1c**).

N(1)-C(1)	1.342(3)	C(1)-N(1)-C(1A)	117.4(3)
N(1)-C(1A)	1.342(3)	N(1)-C(1)-N(2)	114.3(2)
C(1)-N(2)	1.395(3)	C(1)-N(2)-P(1)	125.67(16)
N(2)-P(1)	1.699(2)	N(2)-P(1)-C(4)	100.75(12)
P(1)-C(4)	1.871(3)	N(2)-P(1)-C(8)	100.67(12)
P(1)-C(8)	1.874(3)	C(4)-P(1)-C(8)	111.56(12)

The free H-PN^3P^{tBu} ligand (**1c**) exhibits C_{2v} symmetry. The angle between the C1(A) carbon, the N2(A) nitrogen and phosphorous atom P1 amounts to 125.7°. This is about equal to the corresponding angle in **3b** (123.0°), indicating that this ligand is well suited to coordinate to Mo(III) centers.

In contrast to ligands **1a** and **1b** the H-PN^3P^{tBu} ligand (**1c**) could be coordinated to all three precursors [MoX_3(thf)$_3$] (X = Cl, Br, I) by reaction in toluene at 120 °C for 6 h and at room temperature for 14 h, respectively. The products [MoX_3(H-PN^3P^{tBu})] **4a** (X = Cl), **4b** (X = Br) and **4c** (X = I) were characterized by elemental analysis, IR and paramagnetic NMR spectroscopy (see Experimental).

Synthesis of Mo(0)-N_2 complexes containing H-PN^3P^{Ph} (1a)

In order to determine the capability of molybdenum(0) complexes supported by the pincer ligand **1a** to activate dinitrogen corresponding Mo(0)-N_2 complexes were synthesized under different conditions. Generally, this can be performed by two routes: Either the Mo(III) precursor complexes **2**-**4** are reduced using, e. g., sodium amalgam under a nitrogen atmosphere, or a Mo(0) bis(dinitrogen) complex with four monophosphine coligands is subjected to a ligand exchange reaction.[2,49–51] If the amalgam reduction is employed, monophosphines like PMe_2Ph

have to be added as coligands in order to generate octahedrally coordinated mononuclear Mo(0) complexes. In this context, Nishibayashi *et al.* showed with the complex *trans*-[Mo(N$_2$)$_2$(PMe$_2$Ph)(PNP^{tBu})] that for this system a bis(dinitrogen) complex (with the two dinitrogen ligands being in *trans*-position to each other) is obtained even if an excess of coligand is employed during the sodium amalgam reduction.[2]

a. Reduction of 2a in the presence of two equivalents of monophosphine. Complex **2a** was first subjected to a Na$_x$Hg reduction in the presence of two equivalents of PMe$_2$Ph. Since the reduction of **2b** gave the same results only the product of the Na$_x$Hg reduction of **2a** will be discussed. The product exhibits an intense N$_2$ stretching vibration in the IR spectrum at 1962 cm^{-1} (Figure 3). Based on this frequency the coordinated N$_2$ ligand shows a moderate activation.[52] Compared to the complex *trans*-[Mo(N$_2$)$_2$(PMe$_2$Ph)(PNP^{tBu})] mentioned above, which exhibits an antisymmetric N$_2$ stretching vibration at 1915 cm^{-1},[2] the dinitrogen ligand in the new Mo(0)-N$_2$ complex **5** is distinctly lower activated. The weak band at higher wavenumbers (2032 cm^{-1}) may be due to the presence of small amounts of a *trans*-dinitrogen complex. In this case, the smaller signal corresponds to the symmetric combination of the stretching vibrations of two N$_2$ ligands.[53,54]

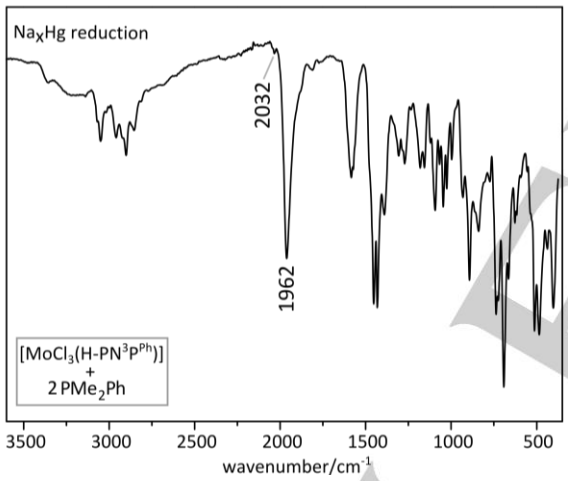

Figure 3: IR spectrum of the product of the Na$_x$Hg reduction of [MoCl$_3$(H-PN^{3}P^{Ph})] (**2a**) with two equiv. PMe$_2$Ph.

In order to obtain further information on the constitution of the Mo(0)-N$_2$ complexes **5** ^{31}P NMR spectroscopy was employed. The ^{31}P NMR spectrum of **5** is shown in Figure 4. Even though the IR spectrum exhibits only one dominant N$_2$ stretching vibration (Figure 3), the ^{31}P NMR spectrum reveals the presence of three mononuclear molybdenum(0) complexes supported by the H-PN^{3}P^{Ph} ligand (**1a**). The main product is the monodinitrogen complex *cis*-[Mo(N$_2$)(PMe$_2$Ph)$_2$(H-PN^{3}P^{Ph})] (**5a**) (Figure 4, blue). The second compound emerging from the reduction is the bis(dinitrogen) complex *trans*-[Mo(N$_2$)$_2$(PMe$_2$Ph)(H-PN^{3}P^{Ph})] (**5b**) (Figure 4, red). Furthermore, as a minor product, the monodinitrogen complex *trans*-[Mo(N$_2$)(PMe$_2$Ph)$_2$(H-PN^{3}P^{Ph})] (**5c**) is found (Figure 4, green). The product distribution is indicated in Figure 4 as well. All signals around 100 ppm can be assigned to the diphenylphosphine groups of the respective complex **5a**, **5b** and **5c**. The coordinated PMe$_2$Ph ligands give rise

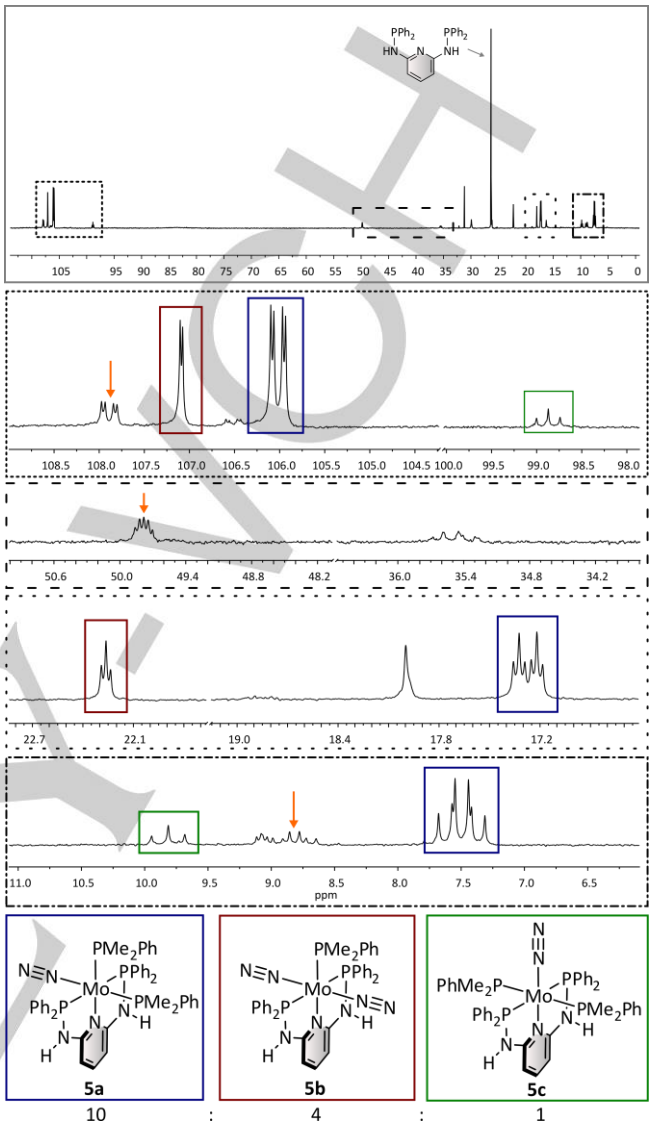

Figure 4: ^{31}P NMR spectrum of the product of the sodium amalgam reduction of [MoCl$_3$(H-PN^{3}P^{Ph})] (**2a**) with two equiv. PMe$_2$Ph measured in benzene-d$_6$.

to signals between 17-23 ppm (axial PMe$_2$Ph) as well as between 7-10 ppm (equatorial PMe$_2$Ph). A further set of signals can be seen in Figure 4, highlighted by orange arrows. The structure of the corresponding molybdenum complex possibly originates from a coordination of diphenylphosphine instead of PMe$_2$Ph (for a simulation see SI, Figure S3); the corresponding HPPh$_2$ ligand derives from a decomposition of H-PN^{3}P^{Ph} (**1a**) during the amalgam reduction (cf SI, Figure S4). Whereas **5a** and **5c** can be associated with the N-N stretch at 1962 cm^{-1}, the small band at 2032 cm^{-1} in the IR spectrum (Figure 3) arises from the symmetric N$_2$ stretching vibration of **5b** (see above). The sodium amalgam reduction of [MoCl$_3$(H-PN^{3}P^{Ph})] (**2a**) in the presence of two equivalents of PMe$_2$Ph was also performed under a ^{15}N atmosphere, and a distinct shift of the N$_2$ stretching vibration towards lower wavenumbers due to the ^{15}N-isotope effect was observed (cf SI, Figure S5).

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In order to check whether the formation of *trans*-[Mo(N$_2$)$_2$(PMe$_2$Ph)(H-PN^{3}P^{Ph})] (**5b**) can be suppressed the sodium amalgam reduction of **2a** was also performed with an excess (10 eq.) of the coligand PMe$_2$Ph. In fact, the IR spectrum of the resulting product exhibits a strong N$_2$ stretching vibration at 1964 cm^{-1} with no smaller band at higher wavenumbers corresponding to **5b** (cf SI, Figure S6). ^{31}P NMR spectroscopy indicates that this reaction mainly leads to *cis*-[Mo(N$_2$)(PMe$_2$Ph)$_2$(H-PN^{3}P^{Ph})] (**5a**), although other products are formed as well (cf SI, Figure S7).

b. Reduction of 2a in the presence of one equivalent of monophosphine. The targeted synthesis of *trans*-[Mo(N$_2$)$_2$(PMe$_2$Ph)(H-PN^{3}P^{Ph})] (**5b**) was attempted by performing the sodium amalgam reduction of [MoCl$_3$(H-PN^{3}P^{Ph})] (**2a**) with only one equivalent of PMe$_2$Ph, in analogy to the mononuclear complex *trans*-[Mo(N$_2$)$_2$(PMe$_2$Ph)(PNP^{tBu})] established by Nishibayashi *et al.*[2] In fact, the pattern of N$_2$ bands in the IR spectrum was found to differ from the one obtained after the Na$_x$Hg reduction with two equivalents of PMe$_2$Ph (Figure 5); i.e., the weak band at 2034 cm^{-1} and the intense band at 1962 cm^{-1} are comparable to the respective signals in the IR spectrum of the

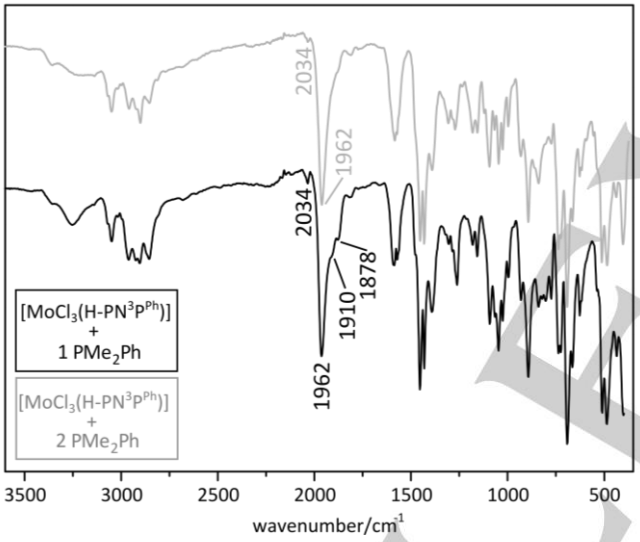

Figure 5: Comparison of the IR spectrum of the product of the sodium amalgam reduction of [MoCl$_3$(H-PN^{3}P^{Ph})] (**2a**) with one equiv. PMe$_2$Ph (black) and the IR spectrum of the product of the reduction of [MoCl$_3$(H-PN^{3}P^{Ph})] (**2a**) with two equiv. PMe$_2$P (grey). All spectra were normalized

sodium amalgam reduction of [MoCl$_3$(H-PN^{3}P^{Ph})] (**2a**) with two equivalents PMe$_2$Ph (Figure 5, grey), but further bands are observed at 1878 cm^{-1} and 1910 cm^{-1}.

The reaction product was further characterized using ^{31}P NMR spectroscopy (Figure 6 and SI, Figure S8). As expected, the main component is *trans*-[Mo(N$_2$)$_2$(PMe$_2$Ph)(H-PN^{3}P^{Ph})] (**5b**), giving rise to a doublet at 106.1 ppm (PPh$_2$) and a triplet at 22.3 ppm (PMe$_2$Ph) (Figure 6, red boxes). Moreover, the complexes *cis*-[Mo(N$_2$)(PMe$_2$Ph)$_2$(H-PN^{3}P^{Ph})] (**5a**) and *trans*-[Mo(N$_2$)(PMe$_2$Ph)$_2$(H-PN^{3}P^{Ph})] (**5c**) can be identified, albeit with different proportions compared to the reduction with two equivalents of PMe$_2$Ph (Figure 6, blue and green boxes). An additional set of signals is observable in the ^{31}P NMR spectrum (highlighted with orange arrows in Figure 6) which probably

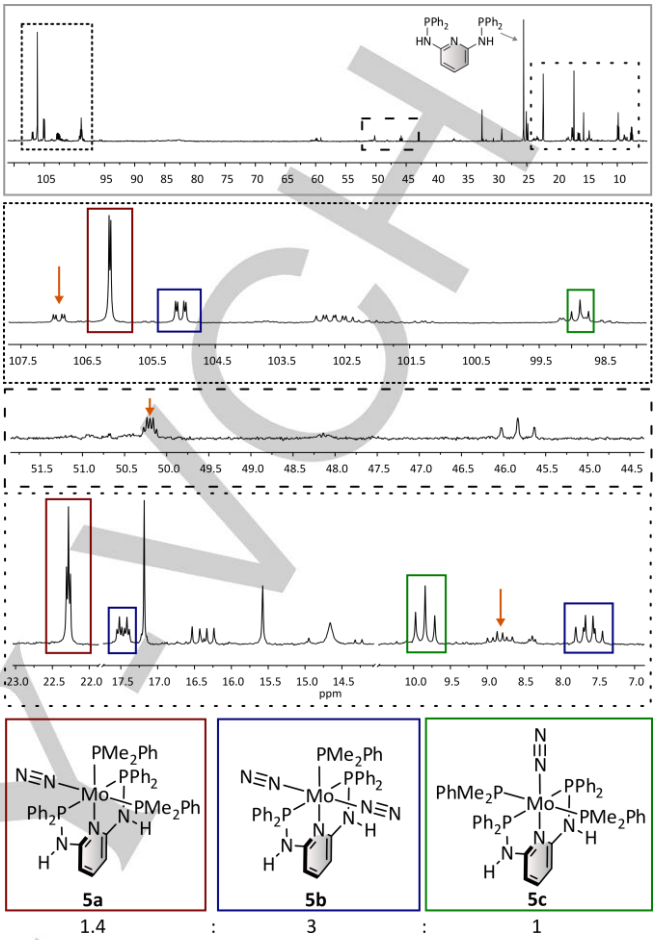

Figure 6: ^{31}P NMR spectrum of the product of the sodium amalgam reduction of [MoCl$_3$(H-PN^{3}P^{Ph})] (**2a**) with one equiv. PMe$_2$Ph in THF-d$_8$.

originates from a molybdenum complex coordinated by diphenylphosphine (see above).

In Figure S9 the ^{31}P NMR spectra of the Na$_x$Hg reduction of **2a** with one, two and ten equivalents PMe$_2$Ph are compared. As described, all of these reactions lead to formation of **5a**, **5b** and **5c** with varying proportions. However, only after Na$_x$Hg reduction of **2a** with one equivalent of PMe$_2$Ph another signal attributable to a molybdenum complex supported by ligand **1a** appears at 103.6 ppm. We speculate that this feature might correspond to a dinitrogen-bridged, dinuclear complex or a corresponding oligomer exhibiting one or both of the low-frequency N$_2$ stretching vibrations visible in Figure 5.

Synthesis of Mo(0)-N$_2$ complexes containing Me-PN^{3}P^{Ph} (1b)

The Mo(III) complex [MoCl$_3$(Me-PN^{3}P^{Ph})] (**3a**) supported by the methylated PN^{3}P^{Ph} ligand **1b** was first reduced using sodium amalgam under a nitrogen atmosphere in the presence of two equivalents of PMe$_2$Ph. The reduction of **3b** gave the same results. Therefore only the product of the Na$_x$Hg reduction of **3a** will be discussed in the following. The corresponding product, compound **6**, exhibits one intense N$_2$ stretching vibration in the IR spectrum at 1963 cm^{-1} (cf SI, Figure S10), indicating that methylation of the amines in the ligand backbone has no effect on the activation of the coordinated N$_2$ ligand. The ^{31}P NMR

spectrum of **6** shows that *cis*-[Mo(N_2)(PMe_2Ph)$_2$(Me-PN^3P^{Ph})] (**6a**) is the main product; furthermore, *trans*-[Mo(N_2)$_2$(PMe_2Ph)(Me-PN^3P^{Ph})] (**6b**) can be identified (cf SI, Figure S11). No set of signals associated with the formation of a possible *trans*-[Mo(N_2)(PMe_2Ph)$_2$(Me-PN^3P^{Ph})] complex (**6c**) is present. Further signals indicate at least three more complexes with a similar structure to that of complex **6a**. Possibly these involve coordination of diphenylphosphine to the molybdenum center (see above).

To summarize, the targeted synthesis of molybdenum(0) dinitrogen complexes supported by the ligands H-PN^3P^{Ph} (**1a**) and Me-PN^3P^{Ph} (**1b**) ligands is difficult. In contrast to the complex *trans*-[Mo(N_2)$_2$(PMe_2Ph)(PNP^{tBu})] by Nishibayashi *et al.*[2] no structurally defined complex can be isolated starting from [$MoCl_3$(H-PN^3P^{Ph})] (**2a**) or [$MoCl_3$(Me-PN^3P^{Ph})] (**3a**). Although the relative fraction of *cis*-[Mo(N_2)(PMe_2Ph)$_2$(H-PN^3P^{Ph})] (**5a**) or *trans*-[Mo(N_2)$_2$(PMe_2Ph)(H-PN^3P^{Ph})] (**5b**) can be increased by variation of the equivalents of the coligand, neither of these complexes can be synthesized selectively. We therefore conclude that the larger steric demand of the di-*tert*-butylphosphine groups in PNP^{tBu} compared to the less bulky diphenylphosphine residues of H-PN^3P^{Ph} (**1a**) and Me-PN^3P^{Ph} (**1b**) is responsible for the exclusive formation of the complex *trans*-[Mo(N_2)$_2$(PMe_2Ph)(PNP^{tBu})].[2]

Synthesis of Mo(0)-N_2 complexes containing H-PN^3P^{tBu} (1c)

In analogy to the dinitrogen-bridged dimolybdenum complex [{Mo(N_2)$_2$(PNP^{tBu})}$_2$(μ-N_2)] established by Nishibayashi *et al.*[2] the synthesis of a dinitrogen-bridged complex based on the H-PN^3P^{tBu} pincer ligand (**1c**) was first pursued by sodium amalgam reduction of [MoX_3(H-PN^3P^{tBu})] (X = Cl, Br, I) (**4a**, **4b**, **4c**) in THF in the absence of coligand. IR spectra of the raw product, however, did not show a N-N stretching vibration. Moreover, no signals above 100 ppm were found in the ^{31}P NMR spectrum, which would confirm the existence of molybdenum(0) complexes supported by ligand **1c** (the main signal at 59.1 ppm in the ^{31}P NMR spectrum of the raw product can be assigned to the free H-PN^3P^{tBu} ligand; cf SI, Figure S12). Consequently, the desired dinitrogen-bridged dimolybdenum complex with ligand **1c** is not formed.

Sodium amalgam reduction of [$MoBr_3$(H-PN^3P^{tBu})] (**4b**) was thus performed in the presence of two equivalents of PMe_2Ph, similar to analogous MoX_3 complexes with ligands **1a** and **1b** (see above). However, this neither led to the formation of Mo(0) dinitrogen complexes supported by ligand **1c**. The reason for this observation is unclear. In order to still obtain such Mo(0)-N_2 complexes the ligand exchange reaction starting from [Mo(N_2)$_2$(PPh_2Me)$_4$] was employed (see above).[49–51] Time-dependent IR spectra of this reaction are shown in Figure 7. The broad band of the complex [Mo(N_2)$_2$(PPh_2Me)$_4$] disappears after a few minutes and a sharp band emerges at 1923 cm^{-1}. Furthermore, a small broad band at 1982 cm^{-1} is observed. These bands can be assigned to the antisymmetric and symmetric stretching vibrations of the two dinitrogen ligands in the complex *trans*-[Mo(N_2)$_2$(PPh_2Me)(H-PN^3P^{tBu})] (**7**). After a short period of time the intensity of the N_2 stretching vibrations, however, decreases again (Figure 7), reflecting a thermal instability of **7**. For this reason characterization of this complex by ^{31}P NMR spectroscopy, in analogy to the congeners supported by ligands **1a** and **1b**, could not be performed.

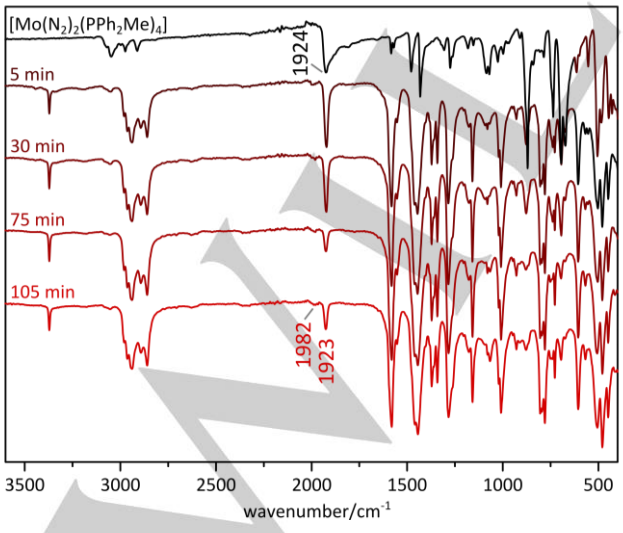

Figure 7: Reaction of *trans*-[Mo(N_2)$_2$(PPh_2Me)] with H-PN^3P^{tBu} (**1c**) monitored by IR spectroscopy. All spectra were normalized.

Catalytic Reduction of Dinitrogen to Ammonia

Following recent studies of Nishibayashi *et al.*[12] the Mo(III) complexes **2a**, **3a**, **4a** and **4c** were used as precatalysts in the transformation of dinitrogen to ammonia in homogeneous solution (Figure 8). Catalytic runs were performed applying the following procedure: to the respective complex and the proton source (Table 3) toluene is added under a dinitrogen atmosphere. The electron source in toluene is added dropwise during 1 hour using a syringe pump; then the reaction mixture is stirred for 19 hours at room temperature. Afterwards the generated ammonium triflate is deprotonated by a methanolic NaOH solution and the resulting ammonia is transferred into a 2M solution of HCl in ether using a constant N_2 flow. Ammonia is quantified *via* the indophenol method.[55]

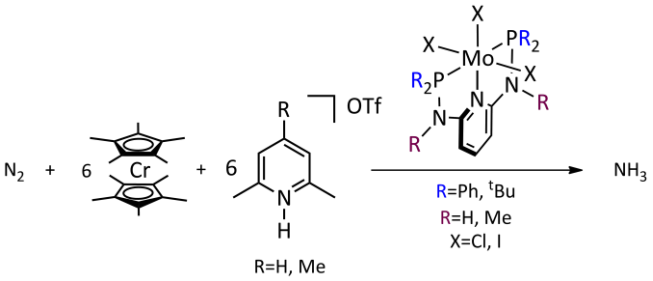

Figure 8: Conversion of Dinitrogen into ammonia using the complexes **2a**, **3a**, **4a** and **4c**.

The results of these experiments are collected in Table 3. Using [ColH]OTf and $CrCp^*_2$, complexes **2a** and **3a** supported by the pincer ligands H-PN^3P^{Ph} (**1a**) and Me-PN^3P^{Ph} (**1b**) are only able to generate substoichometric amounts of ammonia (run 1 and 2). Under the same reaction conditions, complex **4a** supported by the H-PN^3P^{tBu} ligand (**1c**) with more electron donating di-*tert*-butyl residues generates at least 1.47 equivalents of ammonia (run 3). Replacing the proton source [ColH]OTf by [LutH]OTf leads to the formation of overstoichiometric yields of ammonia (3.12

equivalents) with **4a** as catalyst (run 4). In order to check whether the amount of ammonia can be increased, 146 equivalents [LutH]OTf and 110 equivalents $CrCp^*_2$ were employed in run 5 (Table 1). The yield of ammonia (3.05 equivalents) was, however, comparable to that obtained using less proton and electron source (run 4). In run 6 $CoCp_2$ was used instead of the $CrCp^*_2$. No ammonia could be detected in this case, confirming the necessity of the stronger reducing agent $CrCp^*_2$. On the other hand, replacing **4a** by the triiodido analogue **4c** only generated 0.30 equivalents NH_3 when using [ColH]OTf and $CrCp^*_2$ (run 7) and 1.19 equivalents NH_3 when using [LutH]OTf and $CrCp^*_2$ (run 8).

In addition to the Mo(III) complexes **2a**, **3a**, **4a** and **4c** the product **5** of the sodium amalgam reduction of **2a** with two equivalents of PMe_2Ph (see above) was tested as a possible catalyst for the N_2-to-NH_3 conversion. Due to the presence of a mixture of molybdenum(0) complexes (**5a-c**) the yield of ammonia was referred to the quantity of Mo(III) precursor. As a minimum value the formation of 0.02 equivalents of ammonia was found. Nevertheless, this result illustrates only a substoichiometric formation of ammonia.

Table 3. Conditions used for the reduction of N_2 to NH_3 in the presence of Mo(III) and Mo(0) complexes with PN^3P pincer ligands.

Run	Complex	Proton source	Electron source	NH_3/equiv.[a]
1	**2a**	[ColH]OTf	$CrCp^*_2$	0.51
2	**3a**	[ColH]OTf	$CrCp^*_2$	0.44
3	**4a**	[ColH]OTf	$CrCp^*_2$	1.47
4	**4a**	[LutH]OTf	$CrCp^*_2$	3.12
5#	**4a**	[LutH]OTf	$CrCp^*_2$	3.05
6	**4a**	[ColH]OTf	$CoCp_2$	0
7	**4c**	[ColH]OTf	$CrCp^*_2$	0.30
8	**4c**	[LutH]OTf	$CrCp^*_2$	1.19
9	**5**	[ColH]OTf	$CrCp^*_2$	ca. 0.02

0.01 mmol of the respective complex, 48 equivalents proton source and 36 equivalents electron source were used in the catalytic runs. # 146 equivalents [LutH]OTf and 110 equivalents $CrCp^*_2$ were used. [a] Mol. Equiv. based on the catalyst.

In summary, the Mo(III) complexes with the R-PN^3P^{Ph} pincer ligands (R = H, Me) **2a** and **3a** as well as the mixture of molybdenum(0) complexes **5a-c** do not serve as catalysts for synthetic nitrogen fixation. Only with complex **4a** overstoichiometric amounts of ammonia (3.12 equivalents) are generated. We ascribe this to the higher electron donor strength of the di-*tert*-butyl residues in ligand **1c** compared to the diphenyl residues in ligand **1a** and **1b**.

The ability of molybdenum(0) complexes supported by PN^3P pincer ligands to activate small molecules has been already been investigated based on corresponding Mo(0) tricarbonyl compounds.[41,45,47,48] Going from R-PN^3P^{Ph} (**1a**, **1b**, R = H, Me) to H-PN^3P^{tBu} (**1c**; Table 4 and ref.s therein) a distinct shift of all CO stretching vibrations to lower wavenumbers, especially in the highest-frequency $A_1(1)$ vibration, was observed (Table 4). Due to the higher electron donating di-*tert*-butyl residues in ligand **1c** as compared to **1a** and **1b** complex $[Mo(CO)_3(H\text{-}PN^3P^{tBu})]$[47] exhibits the highest activation of CO ligands. A similar trend is observed for the Mo(0)-N_2 complexes **5**, **6** and **7** investigated herein where the N-N stretch shifts to lower frequencies if the donor strength of the pincer ligand is increased. In *trans*-$[Mo(N_2)_2(PMe_2Ph)(PNP^{tBu})]$ established by Nishibayashi *et al.*[2] the N_2 stretching vibration is located at even lower frequency than in **7** (1915 vs. 1923 cm^{-1}). This reflects the electron-withdrawing effect of the secondary amine group with respect to the parent PNP^{tBu} ligand having a CH_2 group at this position. Regarding the conversion of N_2 to NH_3 the increased electron donating property of **1c** compared to **1a** and **1b** leads to a higher activation of the coordinated dinitrogen ligand. This goes along with the observation that the N_2-to-NH_3 conversion is more efficiently mediated by the molybdenum complex supported by the H-PN^3P^{tBu} ligand (**1c**). Nevertheless, this system is inferior to the analogous molybdenum system supported by the classic PNP^{tBu} ligand, probably due to replacement of the CH_2 by more electron-withdrawing N-R (R = H, Me) groups.

Table 4. Comparison of the wavenumber of the totally symmetric CO stretching vibration ($A_1(1)$) of literature-known Mo(0)-CO complexes and the new dinitrogen complexes containing PN^3P pincer ligands.[2,47]

Complex	$A_1(1)(CO)$/ cm^{-1}	$\tilde{\nu}(N\equiv N)/cm^{-1}$
$[Mo(CO)_3(H\text{-}PN^3P^{Ph})]$	1964[47]	
$[Mo(N_2)_2(PMe_2Ph)(H\text{-}PN^3P^{Ph})]$ + $[Mo(N_2)(PMe_2Ph)_2(H\text{-}PN^3P^{Ph})]$ (5)		1962
$[Mo(CO)_3(Me\text{-}PN^3P^{Ph})]$	1956[47]	
$[Mo(N_2)_2(PMe_2Ph)(Me\text{-}PN^3P^{Ph})]$ + $[Mo(N_2)(PMe_2Ph)_2(Me\text{-}PN^3P^{Ph})]$ (6)		1963
$[Mo(CO)_3(H\text{-}PN^3P^{tBu})]$	1922[47]	
$[Mo(N_2)_2(PPh_2Me)(H\text{-}PN^3P^{tBu})]$ (7)		1923
$[Mo(N_2)_2(PMe_2Ph)(PNP^{tBu})]$		1915[2]

Conclusions

Application of the pincer ligands R-$PN^3P^{R'}$ (**1a**, **1b**, **1c**; R = H, Me, R' = Ph, ^{t}Bu) in molybdenum-based synthetic nitrogen fixation was explored. To this end ligands **1a-c** were coordinated to Mo(III) precursors, leading to the complexes ($[MoX_3(R\text{-}PN^3P^{R'})]$) (X = Cl, Br, I; **2a**-**b**, **3a**-**b**, **4a-c**). Amalgam reduction of **2a** and **3a** in the presence of PMe_2Ph generated mixtures of corresponding Mo(0) dinitrogen complexes (**5** and **6**, respectively) whereas for the H-PN^3P^{tBu} ligand (**1c**) a substitution reaction starting from $[Mo(N_2)_2(PPh_2Me)]$ gave a (thermally unstable) molybdenum(0) dinitrogen complex **7**. Mo(III) complexes **2a**, **3a** and **4a** as well as **5** containing a mixture of Mo(0)-N_2 complexes were tested regarding their capability to mediate the N_2-to-NH_3 conversion in

homogeneous solution. Only with the complex [$MoCl_3$(H-PN^3P^{tBu})] (**4a**) overstoichiometric amounts of ammonia were formed. These results demonstrate how sensitively the catalytic activity of pincer-supported transition metal complexes depends on the donor properties of the pincer ligand, fully in line with DFT calculations on these and related systems.[38,39,56,57]

Experimental Section

General Information. Commercially available starting materials and solvents were used as received. Water and oxygen-sensitive reagents were handled in an M. Braun Labmaster 130 Glovebox under N_2. Moisture- and air-sensitive reactions were carried out in dried solvents under N_2 atmosphere by using Schlenk techniques. Solvents were dried with CaH_2 (toluene, *n*-hexane) or $LiAlH_4$ (THF) under Ar and distilled prior to use. [$MoCl_3$(thf)$_3$],[58] [$MoBr_3$(thf)$_3$],[59] [MoI_3(thf)$_3$],[60] H-PN_3P^{Ph} (**1a**),[45] Me-PN^3P^{Ph} (**1b**),[46] H-PN^3P^{tBu} (**1c**)[41] were prepared as described in the literature. Elemental analyses were performed using a EuroVector CHNSO-element analyzer (Euro EA 3000) or a vario MICRO cube (Co. Elementar Analysensysteme). Samples were burned in sealed tin containers in a stream of oxygen. NMR spectra were recorded with a Bruker Avance 400 Pulse Fourier Transform spectrometer operating at frequencies of 400.13 MHz (^{1}H), 161.98 MHz (^{31}P) and 100.62 MHz (^{13}C). ^{31}P NMR spectra were referenced to H_3PO_4 85% [$\delta(^{31}P)$ = 0 ppm] as substitutive standard. Infrared spectra were recorded on a Bruker Alpha FT-IR Spectrum with Platinum ATR setup. Details on the structure determinations are given in the SI. CCDC- 1868380 (**3b**) and CCDC-1868379 (**1c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of [$MoCl_3$(H-PN^3P^{Ph})] (2a)
To 500 mg (1.05 mmol) H-PN^3P^{Ph} (**1a**) and 417 mg (1.00 mmol) [$MoCl_3$(thf)$_3$] were added 30 mL toluene. The reaction mixture was refluxed for 6 h and stirred for further 14 h at room temperature. The suspension was filtered and the precipitate was washed with 10 mL toluene, 10 mL ether and 10 mL *n*-hexane and dried in vacuum. The product was obtained as yellow solid (638 mg, 1.00 mmol, 95 %).
Anal. calcd for $C_{29}H_{25}Cl_3MoN_3P_2$: C, 51.2; H, 3.7; N, 6.2. Found: C, 50.9; H, 3.9; N, 6.1.
^{31}P NMR (162.0 MHz, CD_2Cl_2, 300 K): δ = 86.2 (s, 2P, *P*Ph_2) ppm.
IR (ATR): $\tilde{\nu}$ = 3257 (br, m), 3205 (br, m), 3049 (w), 1654 (sh), 1611 (m), 1573 (m), 1481 (w), 1455 (s), 1434 (s), 1410 (w), 1387 (m), 1334 (w), 1297 (w), 1281 (w), 1261 (w), 1205 (w), 1186 (w), 1173 (m), 1151 (br, m), 1127 (m), 1100 (m), 1070 (w), 1033 (m), 996 (m), 976 (w), 920 (w), 898 (m), 860 (m), 785 (m), 744 (sh), 731 (m), 707 (m), 687 (s), 629 (w), 552 (m), 514 (s), 479 (m), 453 (w), 430 (w), 405 (w), cm^{-1}.

Synthesis of [$MoBr_3$(H-PN^3P^{Ph})] (2b)
This complex has been prepared analogously to **2a** with 300 mg (692 µmol) H-PN^3P^{Ph} (**1a**), 330 mg (598 µmol) [$MoBr_3$(thf)$_3$] and 20 mL toluene. The product was obtained as yellow solid 455 mg, 560 µmol, 94 %).
Anal. calcd for $C_{29}H_{25}Br_3MoN_3P_2$: C, 42.8.; H, 3.1; N, 5.2. Found: C, 42.7; H, 3.4; N, 4.9.
^{31}P NMR (162.0 MHz, CD_2Cl_2, 300 K): δ = 85.0 (s, 2P, *P*Ph_2) ppm.
IR (ATR): $\tilde{\nu}$ = 3053 (w), 1607 (m), 1575 (m), 1481 (w), 1455 (s), 1434 (m), 1387 (w), 1335 (w), 1302 (w), 1261 (w), 1186 (sh), 1170 (w), 1125 (m), 1100 (m), 1067 (w), 1033 (sh), 1024 (m), 996 (m), 971 (m), 939 (w), 891 (w), 846 (w), 799 (br, m), 748 (sh), 730 (m), 687 (s),654 (w), 629 (w), 550 (m), 518 (s), 480 (m), 466 (w), 436 (w), 425 (w) cm^{-1}.

Synthesis of [$MoCl_3$(Me-PN^3P^{Ph})] (3a)
This complex has been prepared analogously to **2a** with 475 mg (940 µmol) Me-PN^3P^{Ph} (**1b**), 374 mg (893 µmol) [$MoCl_3$(thf)$_3$] and 15 mL toluene. The product was obtained as yellow brown solid (515 mg, 727 µmol, 81 %).
Anal. calcd for $C_{31}H_{29}Cl_3MoN_3P_2$: C, 52.6.; H, 4.1; N, 5.9. Found: C, 52.3; H, 4.3; N, 5.7.
^{31}P NMR (162.0 MHz, CD_2Cl_2, 300 K): δ = 116.2 (s, 2P, *P*Ph_2) ppm.
IR (ATR): $\tilde{\nu}$ = 3313 (br, w), 3055 (w), 2958 (w), 2917 (w), 1640 (m), 1593 (m), 1569 (m), 1480 (w), 1451 (m), 1434 (m), 1420 (m), 1339 (w), 1314 (w), 1274 (br, m), 1240 (w), 1189 (w), 1161 (m), 1125 (m), 1101 (sh), 1090 (m), 1074 (m), 1026 (w), 996 (w), 973 (m), 946 (m), 871 (m), 854 (sh), 779 (m), 745 (m), 728 (s), 688 (s), 652 (sh), 616 (w), 579 (w), 565 (m), 535 (w), 516 (s), 470 (s), 446 (w), 432 (w), 387 (w) cm^{-1}.

Synthesis of [$MoBr_3$(Me-PN^3P^{Ph})] (3b)
To 100 mg (198 µmol) Me-PN^3P^{Ph} (**1b**) and 104 mg (188 µmol) [$MoBr_3$(thf)$_3$] were added 10 mL toluene. The reaction mixture was refluxed for 6 h and stirred for 2 d at 80 °C. The suspension was filtered and the precipitate was washed with 10 mL toluene, 10 mL ether and 10 mL *n*-hexane and dried in vacuum. The product was obtained as yellow brown solid (124 mg, 148 µmol, 79 %).
Anal. calcd for $C_{31}H_{29}Br_3MoN_3P_2$: C, 44.3.; H, 3.5; N, 5.0. Found:C, 43.9; H, 3.6; N, 5.4.
^{31}P NMR (162.0 MHz, CD_2Cl_2, 300 K): δ = 116.2 (s, 2P, *P*Ph_2) ppm.
IR (ATR): $\tilde{\nu}$ = 3313 (br, w), 3055 (w), 2958 (w), 2917 (w), 1640 (m), 1593 (m), 1569 (m), 1480 (w), 1451 (m), 1434 (m), 1420 (m), 1339 (w), 1314 (w), 1274 (br, m), 1240 (w), 1189 (w), 1161 (m), 1125 (m), 1101 (sh), 1090 (m), 1074 (m), 1026 (w), 996 (w), 973 (m), 946 (m), 871 (m), 854 (sh), 779 (m), 745 (m), 728 (s), 688 (s), 652 (sh), 616 (w), 579 (w), 565 (m), 535 (w), 516 (s), 470 (s), 446 (w), 432 (w), 387 (w) cm^{-1}.

Synthesis of [$MoCl_3$(H-PN^3P^{tBu})] (4a)
To 122 mg (307 µmol) H-PN^3P^{tBu} (**1c**) and 115 mg (276 µmol) [$MoCl_3$(thf)$_3$] were added 10 mL toluene. The reaction mixture was refluxed for 5 h, stirred overnight at 80 °C and 20 h at room temperature. The suspension was filtered and the precipitate was washed with 10 mL toluene, 10 mL ether and 10 mL *n*-hexane and dried in vacuum. The product was obtained as brown solid (130 mg, 217 µmol, 79 %).
Anal. calcd for $C_{21}H_{41}Cl_3MoN_3P_2$: C, 42.1.; H, 6.9; N, 7.0. Found: C, 42.0; H, 7.0; N, 6.8.
^{31}P NMR (162.0 MHz, CD_2Cl_2, 300 K): δ = 134.1 (s, 2P, *P*Ph_2) ppm.
IR (ATR): $\tilde{\nu}$ = 3181 (br, w), 3086 (br, w), 2962 (m), 2897 (w), 2869 (m), 2767 (w), 2731 (w), 1616 (m), 1606 (m), 1567 (m), 1471 (sh), 1453 (s), 1393 (m), 1370 (m), 1311 (w), 1282 (w), 1230 (sh), 1205 (m), 1173 (m), 1102 (w), 1081 (w), 1043 (m), 1024 (m), 1000 (m), 986 (m), 935 (m), 901 (w), 886 (m), 843 (w), 806 (s), 730 (m), 694 (m), 669 (w), 660 (w), 636 (m), 619 (m), 588 (w), 578 (w), 541 (w), 508 (w), 483 (w), 469 (s), 433 (m), 404 (w), 398 (w), 388 (w), 378 (w) cm^{-1}.

Synthesis of [$MoBr_3$(H-PN^3P^{tBu})] (4b)
This complex has been prepared analogously to **4a** with 234 mg (589 µmol) H-PN^3P^{tBu} (**1c**), 308 mg (558 µmol) [$MoBr_3$(thf)$_3$] and 15 mL toluene. The product was obtained as brown solid (370 mg, 505 µmol, 91 %).
Anal. calcd for $C_{21}H_{41}Br_3MoN_3P_2$: C, 34.4.; H, 5.6; N, 5.7. Found: C, 34.2; H, 5.8; N, 5.6.
^{31}P NMR (162.0 MHz, CD_2Cl_2, 300 K): δ = 137.9 (s, 2P, *P*Ph_2) ppm.
IR (ATR): $\tilde{\nu}$ = 3063 (w), 2995 (m), 2962 (m), 2890 (m), 2867 (m), 2775 (w), 2723 (w), 1614 (m), 1605 (sh), 1587 (m), 1566 (m), 1470 (sh), 1453 (s), 1402 (m), 1393 (m), 1369 (m), 1305 (w), 1285 (w), 1274 (sh), 1207 (m), 1173 (m), 1100 (w), 1080 (w), 1046 (m), 1023 (m), 999 (m), 986 (m), 945 (m), 917 (w), 900 (m), 884 (m), 837 (m), 803 (s), 741 (sh), 727 (m), 693 (m), 679 (w), 659 (w), 636 (w), 618 (m), 586 (w), 578 (w), 550 (w), 483 (m), 467 (s), 432 (m), 405 (w), 391 (w), 381 (w) cm^{-1}.

Synthesis of [MoI_3(H-PN^3P^{tBu})] (4c)
This complex has been prepared analogously to **4a** with 150 mg (378 µmol) H-PN^3P^{tBu} (**1c**), 248 mg (358 µmol) [MoI_3(thf)$_3$] and 10 mL toluene. The product was obtained as brown solid (228 mg, 261 µmol, 73 %).

Anal. calcd for $C_{21}H_{41}I_3MoN_3P_2$: C, 28.9.; H, 4.7; N, 4.8. Found: C, 29.6; H, 4.3; N, 4.9.
^{31}P NMR (162.0 MHz, CD_2Cl_2, 300 K): δ = 139.7 (s, 2P, *P*Ph_2) ppm.
IR (ATR): $\tilde{\nu}$ = 3443 (br, w), 3114 (br, m), 3036 (w), 2961 (m), 2903 (w), 2867 (m), 1614 (sh), 1604 (m), 1586 (sh), 1563 (m), 1451 (s), 1390 (m), 1370 (m), 1302 (w), 1282 (w), 1197 (m), 1173 (m), 1100 (w), 1094 (w), 1044 (m), 1023 (m), 1000 (m), 988 (m), 939 (m), 901 (w), 874 (m), 822 (m), 796 (s), 730 (m), 694 (w), 670 (w), 636 (m), 616 (w), 579 (w), 551 (w), 535 (w), 482 (m), 466 (s), 450 (w), 432 (m), 385 (w) cm^{-1}.

Na_xHg reduction of [$MoCl_3$(H-PN^3P^{Ph})] (2a) with 2 equivalents PMe_2Ph
To sodium amalgam (210 mg, 9.13 mmol Na, 2 mL Hg) and 10 mL THF were added 200 mg (294 µmol) [$MoCl_3$(H-PN^3P^{Ph})] (**2a**), 81.2 mg (588 µmol) PMe_2Ph and further 10 mL THF. The reaction mixture was stirred at room temperature for 20 h. The supernatant solution was separated from Na_xHg, concentrated in vacuum and filtered over neutral Al_2O_3. The solvent was removed in vacuum and the product was dried for a short time in vacuum.
IR (ATR): $\tilde{\nu}$ = 2034 (w), 1962 (s) (N_2 stretching vibration) cm^{-1}.
^{31}P NMR (162.0 MHz, THF-d_8, 300 K): *cis*-[$Mo(N_2)(PMe_2Ph)_2$(H-PN^3P^{Ph})] (**5a**): δ = 106.0 (dd, $^2J_{PP}$=21.1 Hz, $^2J_{PP}$=5.5 Hz, 2P, *P*Ph_2), 17.4 (dt, $^2J_{PP}$=17.1 Hz, $^2J_{PP}$=5.5 Hz 1P, *P*Me_2Ph (axial)), 7.5 (td, $^2J_{PP}$=21.1 Hz, $^2J_{PP}$=17.1 Hz, *P*Me_2Ph (equatorial)) ppm. *trans*-[$Mo(N_2)_2(PMe_2Ph)$(H-PN^3P^{Ph})] (**5b**): δ = 107.1 (d, $^2J_{PP}$=4.4 Hz, 2P, *P*Ph_2), 22.3 (t, $^2J_{PP}$=4.4 Hz, *P*Me_2Ph) ppm. *trans*-[$Mo(N_2)(PMe_2Ph)_2$(H-PN^3P^{Ph})] (**5c**): δ = 98.9 (t, $^2J_{PP}$=21.1 Hz, 2P, *P*Ph_2), 9.8 (t, $^2J_{PP}$=21.1 Hz, *P*Me_2Ph) ppm.

Na_xHg reduction of [$MoCl_3$(H-PN^3P^{Ph})] (2a) with 1 equivalents PMe_2Ph
To sodium amalgam (41 mg, 1.78 mmol Na, 1 mL Hg) and 5 mL THF were added 200 mg (294 µmol) [$MoCl_3$(H-PN^3P^{Ph})] (**2a**), 45.0 mg (324 µmol) PMe_2Ph and further 10 mL THF. The reaction mixture was stirred at room temperature for 20 h. The supernatant solution was separated from Na_xHg, concentrated in vacuum and filtered over neutral Al_2O_3. The solvent was removed in vacuum and the product was dried for a short time in vacuum.
IR (ATR): $\tilde{\nu}$ = 2034 (w), 1962 (s) (N_2 stretching vibration), 1910 (sh), 1878 (sh) cm^{-1}.
^{31}P NMR (162.0 MHz, THF-d_8, 300 K): *trans*-[$Mo(N_2)_2(PMe_2Ph)$(H-PN^3P^{Ph})] (**5b**): δ = 106.1 (d, $^2J_{PP}$=4.3 Hz, 2P, *P*Ph_2), 22.3 (t, $^2J_{PP}$=4.3 Hz, *P*Me_2Ph) ppm. *cis*-[$Mo(N_2)(PMe_2Ph)_2$(H-PN^3P^{Ph})] (**5a**): δ = 105.1 (dd, $^2J_{PP}$=20.9 Hz, $^2J_{PP}$=5.3 Hz, 2P, *P*Ph_2), 17.5 (dt, $^2J_{PP}$=16.6 Hz, $^2J_{PP}$=5.3 Hz 1P, *P*Me_2Ph (axial)), 7.6 (td, $^2J_{PP}$=20.9 Hz, $^2J_{PP}$=16.6 Hz, *P*Me_2Ph (equatorial)) ppm. *trans*-[$Mo(N_2)(PMe_2Ph)_2$(H-PN^3P^{Ph})] (**5c**): δ = 98.9 (t, $^2J_{PP}$=21.2 Hz, 2P, *P*Ph_2), 9.9 (t, $^2J_{PP}$=21.2 Hz, *P*Me_2Ph) ppm.

Catalytic reduction of dinitrogen to ammonia under N_2
The catalytic runs were performed after the following procedure. To the respective complex (0.01 mmol) and the proton source (48 equiv.) 1 mL toluene is added under dinitrogen atmosphere. *Via* a syringe pump the electron source (36 equiv.) in 4 mL toluene is added dropwise during 1 hour. The reaction mixture is stirred for further 19 hours at room temperature. Afterwards the generated ammonium triflate is deprotonated by a methanolic NaOH solution and the resulting ammonia is transferred into 15 mL of a cold 2M solution of HCl in ether using a constant N_2 flow. Ammonia is quantified *via* the indophenol method.[55]

Keywords: Nitrogen Fixation • Pincer Ligands • N_2-to-NH_3 transformation • Molybdenum Complexes • Catalysis

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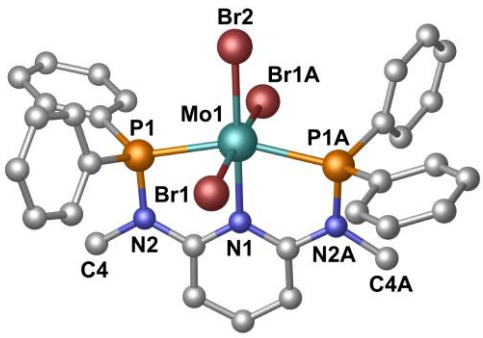

Nitrogen Fixation • Pincer Ligands

*N. Stucke, J. Krahmer, Prof. Dr. C. Näther, Prof. Dr. F. Tuczek**

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