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ARTICLE

Bonding and Activation of N_2 in Molybdenum(0) Complexes Supported by Tripod Ligands with Phospholane End Groups

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Dedicated to Prof. Hansgeorg Schnöckel on the Occasion of his 80th Birthday

Tripod ligands with a neopentyl backbone and one (**trpd-1 pln**), two (**trpd-2 pln**) or three (**trpd-3 pln**) phospholane end groups are synthesized and used for the synthesis of MoX_3 (X=Cl, Br, I) complexes supported by these ligands. Na_xHg reduction of [$MoBr_3$(**trpd-3 pln**)], in the presence of N_2 and the bidentate coligand dppm leads to the molybdenum(0) mono(dinitrogen) complex [$Mo(N_2)$(**trpd-3 pln**)(dppm)] with a moderately activated N_2 ligand. An attempt to further increase the activation by using dmpm as coligand leads to a mixture containing desired [$Mo(N_2)$(**trpd-3 pln**)(dmpm)], but also the bis(dinitrogen) complex [$Mo(N_2)_2(\kappa_2$-**trpd-3 pln**)$_2$] and the homoleptic complex [Mo(**trpd-3 pln**)$_2$]. Protonation of [$Mo(N_2)$(**trpd-3 pln**)(dppm)] with $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$ generates the hydrazido(2-) complex $[Mo(NNH_2)$(**trpd-3 pln**)(dppm)$][Al\{OC(CF_3)_3\}_4]_2$.

Introduction

The activation and stoichiometric or catalytic conversion of highly inert dinitrogen into ammonia has been one of the most demanding tasks in bioinorganic and organometallic chemistry.[1] In nature, this reaction is catalyzed by the enzyme nitrogenase with the FeMo cofactor as active site.[2] As part of synthetic nitrogen fixation, transition metal compounds were developed to mimic this process; among these, molybdenum phosphine complexes have been particularly successful.[3–8] With $[M(N_2)_2(PR_3)_4]$ (M=W or Mo, PR_3=PMe_2Ph or $PMePh_2$), the first complexes showing stoichiometric conversion of dinitrogen into ammonia were presented by Chatt *et al.* in 1975.[8] After the first catalytic conversion discovered by Schrock *et al.* in 2003 using a triamidoamine molybdenum complex,[7] further active catalysts based on molybdenum centers[5,9–15] and phosphine ligands have been described,[4,5,10–19] but also other metals and ligands have been explored in this context until today.[3,4,7,16,18–20]

As part of these studies, our working group has investigated the effect of different oligodentate phosphine ligands in Chatt-type molybdenum complexes on the activation of coordinated N_2 during the last 15 years. There are several parameters affecting the ability of these complexes for synthetic nitrogen fixation such as the donor properties of the ligands, mostly determined by the electronic influence of their residues (e.g. $-PMe_2$ vs. $-PPh_2$), their denticity (mono-, bi-, tridentate…) and topology (i.e.; linear tridentate, tripodal, tetrapodal…), and steric influences imparted by the residues on the coordinating donor atoms.[21] For a better understanding of these effects and the underlying correlations, we employed several linear tridentate (e.g. **prPP(R)P**, R=H, Ph)[22] or tripodal (e.g. **tdppme**, **trpd-1**, **SiP$_3$**),[23–27] phosphine ligands in combination with bidentate coligands for N_2 activation (Figure 1). The properties of the corresponding dinitrogen complexes were analyzed by comparison of the, e.g., highly diagnostic N–N stretching frequency and by the protonability of the coordinated N_2

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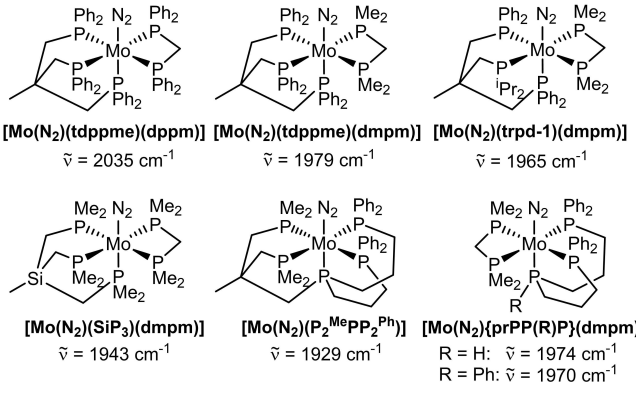


Figure 1. Selected molybdenum(0) mono(dinitrogen) complexes synthesized by our working group and corresponding N–N stretching frequencies.[22–25,28,29,33]

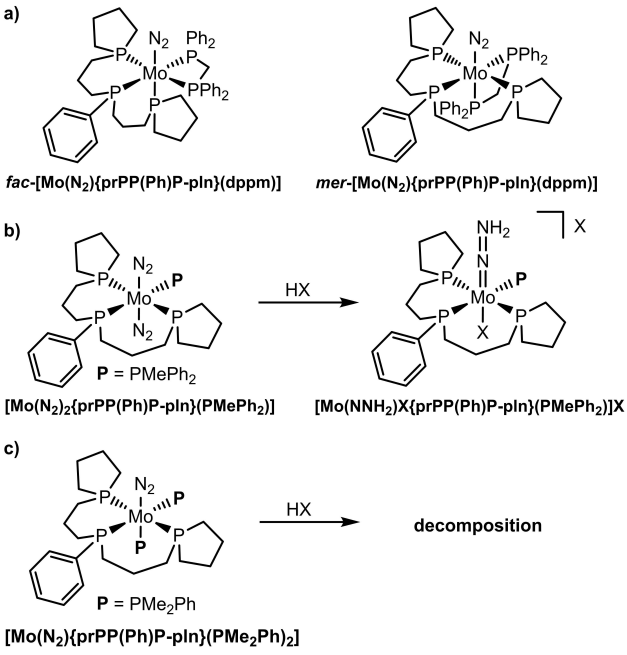
ligand. By combining tridentate and tripodal ligand design, we recently developed the pentadentate tetrapodal (**pentaPod**) ligand $\mathbf{P_2^{Me}PP_2^{Ph}}$, leading to the first catalytically active Chatt complex with a single coordination site, [$MoN_2(\mathbf{P_2^{Me}PP_2^{Ph}})$] (Figure 1).[28,29] The design of this complex was the result of an evolution during which clear trends had been identified. Molybdenum dinitrogen complexes supported by (linear) tridentate ligands, e.g., suffered from isomerization[30,31] or coordination of the conjugate base upon protonation,[31,32] which affects the stability of the systems and/or their catalytic activity.[28] This was the reason to include tripod ligands in our investigations. In order to increase the activation of the coordinated N_2, we raised the σ donor strength of the coligands by replacement of aryl by alkyl phosphines (**tdppme** vs. **trpd-1** vs. $\mathbf{SiP_3}$, Figure 1).[22–26,29] In doing so, we noticed that the steric demand of the substituents can be a limiting factor.[24,26]

Oligodentate ligand systems with diisopropylphosphino end groups, for instance, are sterically too demanding for certain applications,[24] and therefore, smaller substituents such as methyl groups were employed.[25,26,29] On the other hand, a certain degree of shielding can be beneficial to enhance the stability of the N_2 ligand and its protonated derivatives and exclude unwanted reactive pathways.[7,34] This led to the idea of using ligands with phospholane end groups in our Mo–N_2 chemistry.

In an earlier publication, we employed the tridentate ligand **prPP(Ph)P-pln** in combination with monodentate- and bidentate phosphine coligands for the synthesis of molybdenum(0) mono- and bis(dinitrogen) complexes.[31] However, as expected, the flexible structure of **prPP(Ph)P-pln** led in the presence of bidentate phosphine coligands to isomerization, and *fac*- and *mer* isomers were obtained (Scheme 1, a). Nevertheless, it was possible to protonate the bis(dinitrogen) complex [$Mo(N_2)_2$**{prPP(Ph)P-pln}**($PMePh_2$)] to the corresponding hydrazido (2-) complex $[Mo(NNH_2)(OTf)$**{prPP(Ph)P-pln}**$(PMePh_2)]^+$ (Scheme 1, b), demonstrating the ability of such systems to activate N_2. On the other hand, the mono(dinitrogen) complex [$Mo(N_2)$**{prPP(Ph)P-pln}**$(PMe_2Ph)_2$)] decomposed under acidic conditions (Scheme 1, c). This and the mechanistically unfavourable coordination of the conjugate base of the employed acid (HOTf) to the hydrazido(2-) complex indicate that further optimization of the ligand design is necessary to achieve a catalytic N_2-to-NH_3 conversion on the basis of such systems. Still, the complexes shown in Scheme 1 represent rare examples of molybdenum complexes coordinated by phospholane groups.[31,35]

To avoid isomerization and decoordination of the ligand in the pivotal position *trans* to N_2, we decided to combine the phospholane end groups with a tripodal topology based on a neopentyl backbone (Figure 2).

For the introduction of phospholane end groups into the linear tridentate ligand **prPP(Ph)P-pln**, we recently employed lithium phospholanide (**Li–Pln**) as suitable P nucleophile.[31] Herein, we describe the synthesis of three different tripod ligands with neopentyl backbone and one (**trpd-1 pln**), two (**trpd-2 pln**), or three (**trpd-3 pln**) phospholane end groups, using the same strategy. Due to the rigidity of the neopentyl



Scheme 1. Complexes supported by tridentate **prPP(Ph)P-pln** ligand, containing phospholane end groups and phosphine coligands (dppm, $PMePh_2$, PMe_2Ph), a) leading to isomerization (*fac* and *mer*), b) to coordination of the conjugate base (X) in *trans* position of N_2 during protonation or c) decomposition.[31]

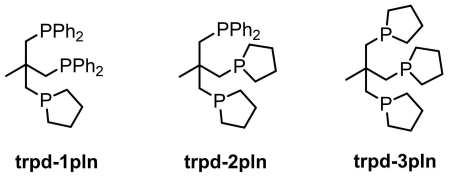


Figure 2. Tripodal P donor ligands with phospholane end groups employed in this study.

backbone only a *facial* coordination for this type of tripod ligands to a metal center is possible. Moreover, the tripodal geometry ensures that the pivotal *trans* position of coordinated N_2 is occupied by a part of the supporting tripod ligand.

The coordination behavior of the tripod ligands **trpd-Xpln** (X = 1–3) to molybdenum(III) precursors is investigated. Aiming at a molybdenum(0) dinitrogen complex with a highly activated dinitrogen ligand, the molybdenum(III) complex supported by **trpd-3 pln** is further subjected to a sodium amalgam reduction, and the protonation of the resulting molybdenum(0) dinitrogen complex is examined. Finally, the results are compared to similar systems supported by tripodal phosphine ligands.

Results and Discussion

Syntheses of tripod ligands with phospholane end groups (trpd-1 pln, trpd-2 pln, trpd-3 pln)

The tripod ligands **trpd-1 pln**, **trpd-2 pln** and **tripd-3 pln** were synthesized by chlorine substitution in the corresponding ligand precursors by **Li**–**Pln** in the presence of *n*-butyllithium in tetrahydrofuran (Scheme 2).

While the ligands **trpd-1 pln** and **trpd-2 pln** could be synthesized in pure form and in excellent yields (**trpd-1 pln**: 90 %, **trpd-2 pln**: 99 %, Figure S1–9) synthesis of the most demanding – and potentially most interesting – tripod ligand **trpd-3 pln** is accompanied by the formation of side products (compare NMR spectra, Figure S10–S13). Possible side reactions involve a lithium halogen exchange caused by **Li**–**Pln** or *n*-butyllithium, as known from the literature.[36] This assumption is supported by traces of 2,2-bis(phospholanomethyl)propane which could be observed in the ^{13}C NMR spectrum (Figure S12).

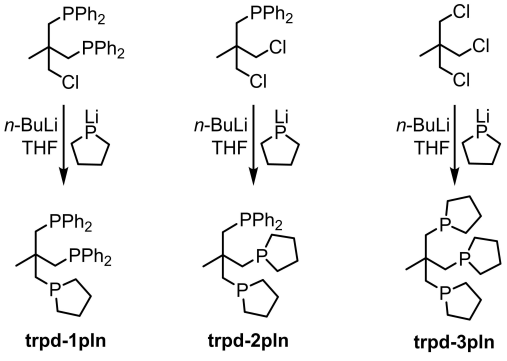
To minimize the amount of side products it is important to add the ligand precursor 1,3-dichloro-2-(chloromethyl)-2-methylpropane to a solution of **Li**–**Pln** and *n*-butyllithium in THF at 0 °C. Furthermore, the amount of *n*-butyllithium has a huge impact on the side product formation. The best results were obtained with 1/6 equivalent of *n*-butyllithium with regard to **Li**–**Pln**. As we have shown before,[31] it is important to break up the **Li**–**Pln** aggregates present in solution, which reduce the reactivity of **Li**–**Pln** by addition of *n*-butyllithium. After a reaction time of 4 d the reaction mixture was reduced *in vacuo*. The residue was redissolved in *n*-pentane, and the suspension was filtered over Celite®. A large amount of lithium species could be separated by this filtration, which was followed by an aqueous work up. Further purification was achieved by an additional filtration over neutral aluminium oxide. After these steps, **trpd-3 pln** was obtained in a sufficient quality for further reactions (see below).

Molybdenum(III) complexes

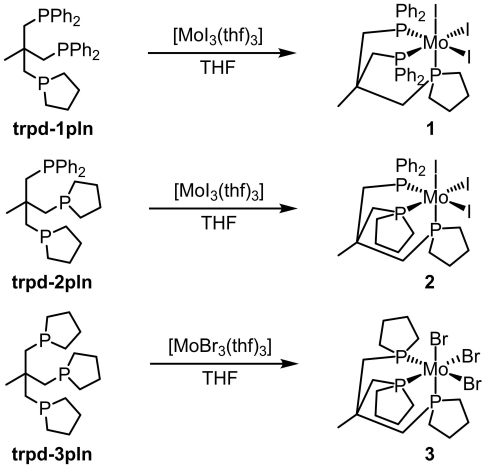
In order to obtain information about the coordination behaviour of the prepared tripod ligands **trpd-1 pln**, **trpd-2 pln** and **trpd-3 pln** and to investigate their suitability for N_2 activation, molybdenum(III) complexes were prepared first (Scheme 3). Reaction of **trpd-1 pln** and **trpd-2 pln** with the precursor $[MoI_3(thf)_3]$ in THF afforded the corresponding molybdenum(III) complexes $[MoI_3$(**trpd-1 pln**)] (**1**) and $[MoI_3$(**trpd-2 pln**)] (**2**) in reasonable yields (60 and 61 %, resp.) after stirring at room temperature for 62 h and 42 h, respectively. In contrast to that, it was not possible to obtain the analogous $[MoI_3$(**trpd-3 pln**)] complex by using $[MoI_3(thf)_3]$. Therefore, $[MoBr_3(thf)_3]$ was employed. Stirring with **trpd-3 pln** in THF for 18 h at room temperature afforded the molybdenum(III) complex $[MoBr_3$(**trpd-3 pln**)] (**3**) in satisfying purity and yield (71 %). Due to the presence of side products in the ligand (see above), it was necessary to apply an excess of **trpd-3 pln**. All three complexes were characterized by elemental analysis and IR spectroscopy (see Experimental Section).

Synthesis of dinitrogen complexes supported by the tridentate tripod ligand trpd-3 pln

To examine the effect of phospholane end groups on the ability of transition metal complexes to bind and activate dinitrogen, molybdenum(0) complexes of the type $[MoN_2$(tripod)(diphos)], tripod = **trpd-Xpln** (X = 1–3) and diphos = dppm (1,1-bis-(diphenylphosphino)methane) or dmpm (1,1-bis(dimethylphosphino)methane) were synthesized. Analogous complexes with other tripod ligands are known to mediate N_2 activation and functionalization.[23,24,37] In this context, $[MoBr_3$(**trpd-3 pln**)] (**3**) supported by the tripod ligand **trpd-3 pln** was chosen as the most promising candidate for an amalgam reduction to the corresponding molybdenum(0) mono(dinitrogen) complex as the presence of three phospho-



Scheme 2. Synthesis of the tripod ligands **trpd-1 pln**, **trpd-2 pln** and **trpd-3 pln**.



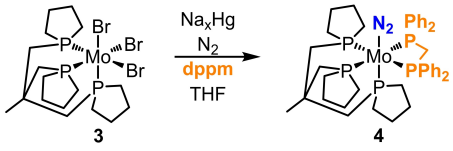
Scheme 3. Syntheses of the molybdenum(III) complexes $[MoI_3$(**trpd-1 pln**)] (**1**), $[MoI_3$(**trpd-2pln**)] (**2**) and $[MoI_3$(**trpd-3 pln**)] (**3**).

lane donors should lead to the most activated N_2 ligand. Moreover, using a symmetric tripodal PPP ligand the formation of only one complex isomer was expected which should simplify the characterization of the product.

Na_xHg reduction of [$MoBr_3$(trpd-3 pln)] (3) in the presence of dppm

For the synthesis of a molybdenum(0) dinitrogen complex supported by **trpd-3 pln** the corresponding molybdenum(III) precursor, [$MoBr_3$(**trpd-3 pln**)] (**3**), was stirred with sodium amalgam and one equivalent of dppm under nitrogen atmosphere in THF for 22 h (Scheme 4). The product was precipitated as a red solid by addition of methanol and characterized by NMR, IR and Raman spectroscopy.

In the ^{31}P NMR spectrum, the AA'XX'M pattern of the desired mono(dinitrogen) complex [Mo(N_2)(**trpd-3 pln**)(dppm)] (**4**) is observed (Figure 3). The AA' part (δ = 36.7–35.3 ppm) is assigned to the equatorially coordinated phospholane donors of **trpd-3 pln**, the signal at 32.1–31.4 ppm (M signal) belongs to the axially coordinated phospholane donor and the XX' subspectrum, located at 13.3–12.0 ppm, is attributed to the P atoms of the diphenylphosphino groups of the coligand dppm.



Scheme 4. Na_xHg reduction of [$MoBr_3$(**trpd-3 pln**)] (**3**) in presence of dppm.

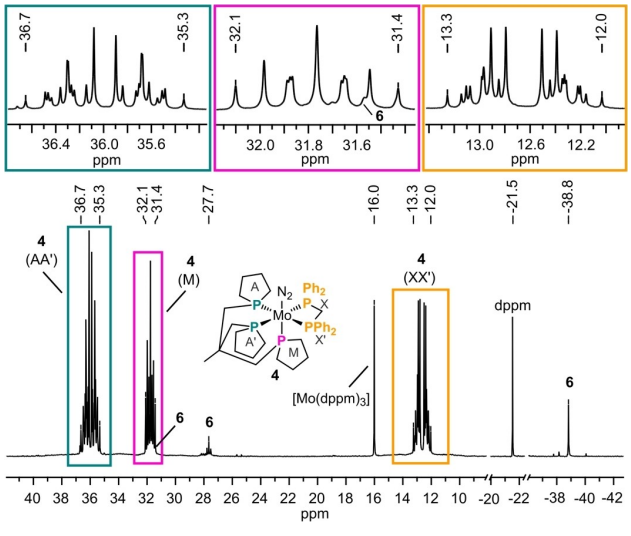


Figure 3. $^{31}P\{^1H\}$ NMR spectrum of the product of the sodium amalgam reduction of [$MoBr_3$(**trpd-3 pln**)] (**3**) in the presence of one equivalent dppm measured in [D_8]-THF. Furthermore, enlarged signals are shown (top).

The ^{31}P NMR spectrum, however, shows additional signals. The singlet at 16.0 ppm can be assigned to the homoleptic complex [Mo(dppm)$_3$],[31,38] and the singlet at −21.5 ppm is due to uncoordinated dppm.

Further signals in the ^{31}P-NMR spectrum of the product are located at 31.5 ppm, 27.7 ppm and −38.8 ppm (**6**), whereas the signal at 31.5 ppm is hidden by the M signal of compound **4**. To determine the identity of this side product, the filtrate remaining after precipitation of the product with methanol was investigated by NMR and IR spectroscopy. Analysis of the ^{31}P NMR and the ^{1}H,^{31}P HMBC and ^{31}P,^{31}P COSY NMR spectra (see SI, Figure S14–S18) along with the IR spectrum (see SI, Figure S19) indicate that the side product must be *cis*-[Mo(N_2)$_2$(κ^2-**trpd-3 pln**)$_2$] (**6**) The triplets at 31.5 ppm and 27.7 ppm belong to the coordinating phospholane groups and the singlet at −38.8 ppm to the uncoordinated ones (Figure 3). Overall the desired product **4** was obtained in a ratio of 26:1:1:1 (**4**:[Mo(dppm)$_3$]:**6**:dppm).

The complex [Mo(N_2)(**trpd-3 pln**)(dppm)] (**4**) was also analyzed by vibrational spectroscopy. In the IR spectrum an intense NN stretch appears at 1960 cm^{-1}, along with a weak NN-stretch at 2005 cm^{-1} (Figure 4, top). The corresponding Raman spectrum shows a NN stretching vibration at 1970 cm^{-1} (Figure 4, bottom). The band at 1960 cm^{-1} (IR) and the peak at 1970 cm^{-1} (Raman) are attributed to the N–N stretch of [Mo(N_2)(**trpd-3 pln**)(dppm)] (**4**). Comparison with analogous systems supported by tripod ligands in combination with dppm shows that the activation induced by the phospholane groups is comparable to that of –PMe_2, stronger than –PEt_2 and much stronger than –PPh_2 (Figure 5).[23,25,39] It should be noted, however, that in some cases the electron-donating properties of –PEt_2 are higher than of –PMe_2 groups.[40] A general comparison of the electron-donating properties of phosphines containing –PEt_2, –PMe_2 and –Pln endgroups thus appears problematic and will not be attempted here.

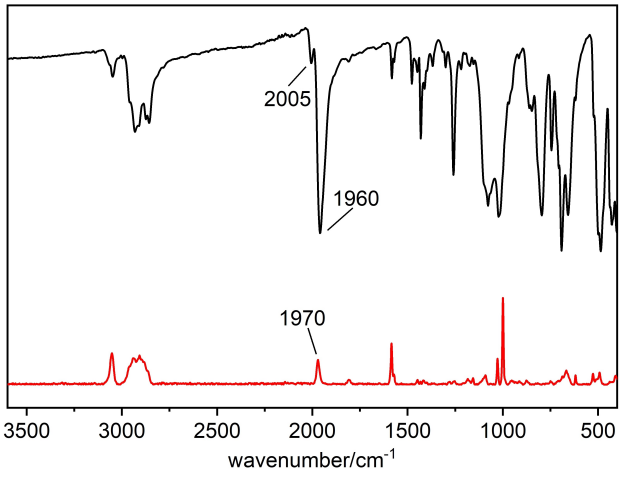


Figure 4. IR and Raman spectra of the product of the sodium amalgam reduction of [$MoBr_3$(**trpd-3 pln**)] (**3**) in the presence of one equivalent dppm which was precipitated by methanol.

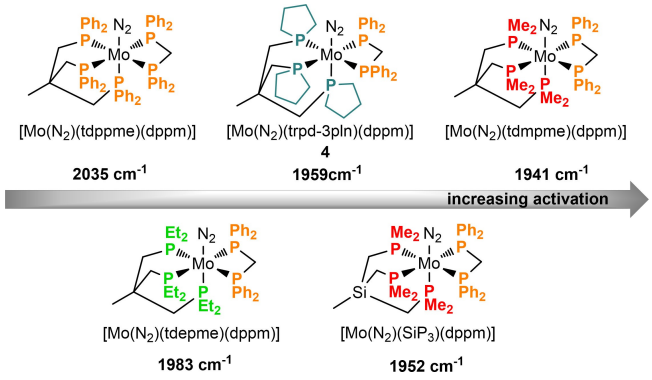


Figure 5. Comparison of [Mo(N_2)(tripod)(dppm)] systems (tripod = tdppme,[23] tdepme,[39] **trpd-3 pln** (**4**, this study), SiP_3,[25] tdmpme[39]) containing differently activated N_2 ligands.

To check whether the small IR-band at 2005 cm^{-1} is caused by a side product, e.g. a bis(dinitrogen) complex, the filtrate remaining from the precipitation with methanol (compare above) was also examined by IR spectroscopy. The corresponding IR spectrum (Figure S19, top) shows two NN stretching vibrations at 2004 cm^{-1} and 1942 cm^{-1} with nearly the same intensity. This is a typical NN-vibrational pattern for a *cis*-bis (dinitrogen) complex. Along with the corresponding NMR spectra (see above and Figure S14–S18) this feature therefore can be assigned to *cis*-[Mo(N_2)$_2$(κ^2-**trpd-3 pln**)$_2$] (**6**), which was also present in the precipitated product to a small extent (cf Figure 3 and Figure 4). By slow diffusion of *n*-pentane into a solution of **4** in THF crystals suitable for single crystal diffraction could be obtained. [Mo(N_2)(**trpd-3 pln**)(dppm)] (**4**) crystallizes in the monoclinic space group $P2_1/c$ with two crystallographically independent complexes exhibiting slightly different bond lengths (Figure 6). The phospholane rings have the envelope conformation. Interestingly, the crystal contains 5% of a bromido instead of the dinitrogen complex (see SI, Figure S26, Table S1 and S2). This [MoBr(**trpd-3 pln**)(dppm)] complex is most likely an intermediate of the reduction from [$MoBr_3$(**trpd-3 pln**)] (**3**) to [Mo(N_2)(**trpd-3 pln**)(dppm)] (**4**) (Figure 6).

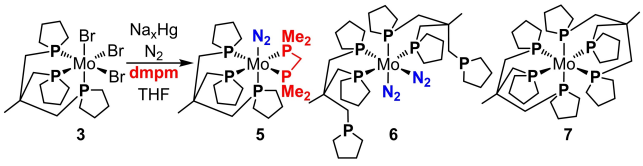
To further increase the activation of the N_2 ligand the sodium amalgam reduction was also performed in the presence of the coligand dmpm having two stronger electron-donating dimethylphosphino groups instead of diphenylphosphino groups in dppm.

Na_xHg reduction of [$MoBr_3$(trpd-3 pln)] (3) in the presence of dmpm

For the synthesis of a second molybdenum(0) dinitrogen complex supported by **trpd-3 pln** the corresponding precursor, [$MoBr_3$(**trpd-3 pln**)] (**3**), was stirred with sodium amalgam and one equivalent of dmpm under N_2 in THF for 18 h (Scheme 5), and a yellow-orange oil was obtained. This reduction did not result in a single product. Characterization with IR and NMR spectroscopy showed that besides the desired mono (dinitrogen) complex [Mo(N_2)(**trpd-3 pln**)(dmpm)] (**5**), a *cis*-bis (dinitrogen) complex, probably *cis*-[Mo(N_2)$_2$(κ^2-**trpd-3 pln**)$_2$] (**6**), and the homoleptic complex [Mo(**trpd-3 pln**)$_2$] (**7**) were formed.

The IR spectrum exhibits two NN stretching bands at 2005 cm^{-1} and 1944 cm^{-1} (Figure 7). The intensity of these bands is relatively weak compared to other similar molybdenum(0) dinitrogen complexes such as [Mo(N_2)(**SiP_3**)(dmpm)][25] or [Mo(N_2)(**trpd-3 pln**)(dppm)] (**4**), which indicates that the mixture contains only smaller amounts of molybdenum dinitrogen complexes.

The band at 1944 cm^{-1} can be assigned to the NN stretching vibration of [Mo(N_2)(**trpd-3 pln**)(dmpm)] (**5**) (see



Scheme 5. Na_xHg reduction of [$MoBr_3$(**trpd-3 pln**)] (**3**) in the presence of dmpm.

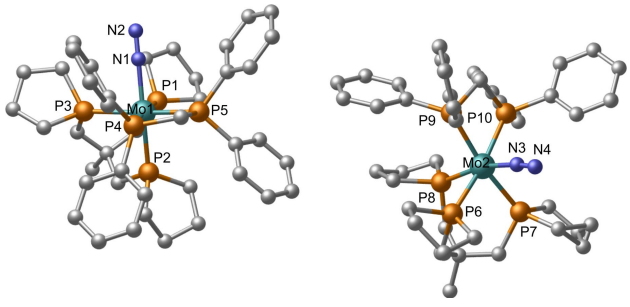


Figure 6. IR (ATR) spectrum of the product of the sodium amalgam reduction of [$MoBr_3$(**trpd-3 pln**)] (**3**) in the presence of one equivalent dmpm.

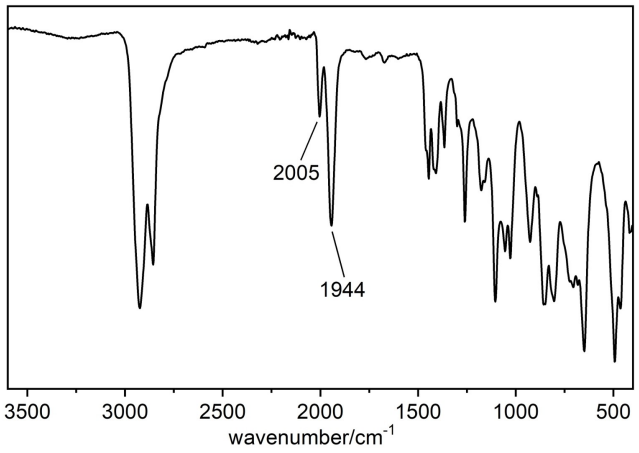


Figure 7. $^{31}P\{^1H\}$ NMR spectrum of the product of the sodium amalgam reduction of [$MoBr_3$(**trpd-3 pln**)] (**3**) in the presence of one equivalent dmpm measured in [D_8]-THF.

below) and the asymmetric NN stretch of the *cis*-bis(dinitrogen) complex *cis*-[Mo(N$_2$)$_2$(κ^2-**trpd-3 pln**)$_2$] (**6**), whereas the band at 2005 cm^{-1} belongs to the symmetric NN stretching vibration of *cis*-[Mo(N$_2$)$_2$(κ^2-**trpd-3 pln**)$_2$] (**6**). Notably, complex **6** has also been formed as side product of the sodium amalgam reduction in the presence of the other coligand dppm, which was described above (Figure 4). With a NN stretching vibration of 1944 cm^{-1}, the dinitrogen ligand in [Mo(N$_2$)(**trpd-3 pln**)(dmpm)] (**5**) is more activated than in [Mo(N$_2$)(**trpd-3 pln**)(dppm)] (**4**) exhibiting a ν(NN) with 1960 cm^{-1}. This is due to the stronger σ-donation of dmpm as compared to dppm.

The ^{31}P NMR spectrum of the reaction mixture shows the formation of several products. The AAXX'M pattern of the mono (dinitrogen) complex [Mo(N$_2$)(**trpd-3 pln**)(dmpm)] (**5**) is clearly visible (Figure 8). The AA' part (δ = 39.3 ppm–38.2 ppm) can be assigned to the equatorially coordinated phospholane donors of **trpd-3 pln** whereas the M-signal for the axial coordinated phospholane donor appears at 34.8 ppm. Moreover the P atoms of the dimethylphosphane groups of the coligand dmpm lead to the XX' subspectra at −20.8 to −21.8 ppm. At 31.3 and 27.4 ppm appear two triplets which can be assigned to the coordinated P atoms of *cis*-[Mo(N$_2$)$_2$(κ^2-**trpd-3 pln**)$_2$] (**6**). The corresponding uncoordinated phospholane groups cause the singlet at −39.1 ppm. The complex **6** could also be identified as side product of the sodium amalgam reduction of [MoBr$_3$(**trpd-3 pln**)] (**3**) in the presence of the coligand dppm (see above and Figure 3).

Finally, the singlet at 36.4 ppm is attributed to the six P atoms of the tripod ligand **trpd-3 pln** in the homoleptic complex [Mo(**trpd-3 pln**)$_2$] (**7**). This assignment is supported by the fact that in the ^{1}H, ^{31}P-HMBC NMR spectrum a coupling of these ^{31}P nuclei (δ = 36.4 ppm) to only aliphatic protons was visible (Figure S20). The product also contained a large amount of uncoordinated **trpd-3 pln** (δ = −36.6 ppm, Figure 8), which reveals that formation of molybdenum dinitrogen complexes

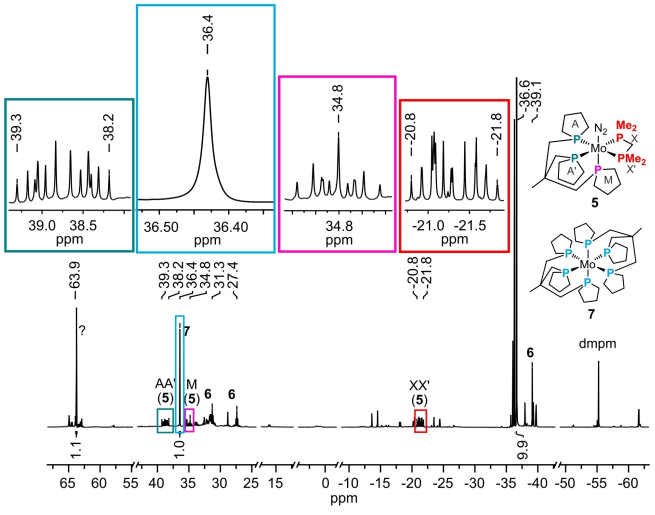


Figure 8. View of the two crystallographically independent complexes in the crystal structure of [Mo(**trpd-3 pln**)$_2$] (**7**). Hydrogen atoms are omitted for clarity.

using dmpm as coligand is not particularly favourable. The signal of the homoleptic complex [Mo(**trpd-3 pln**)$_2$] (**7**) also appeared in the ^{31}P NMR spectrum of the reaction solution of the sodium amalgam reduction of **3** in the presence of dppm (Figure S18, a and b). Furthermore, crystals suitable for single-crystal X-ray structure could be obtained by diffusion of *n*-pentane in a solution of the product obtained from the sodium amalgam reduction in [D$_8$]-THF (Figure 9). The complex [Mo(**trpd-3 pln**)$_2$] (**7**) crystallizes in the space group R-3 with Z = 24. The crystal structure exhibits two crystallographic independent complexes in which each Mo center is in a slightly distorted octahedral coordination **9** geometry, with only small differences in the bond lengths and angles (Figure S27, Table S3). Interestingly, in one of these complexes all P–Mo(2)–P angles of the *trans* phosphines are identical (P(41)–Mo(2)–P(51) = 174.01°) whereas the corresponding P–Mo(1)–P angles vary in a range between 171.80° and 175.04°.

Protonation of [Mo(N$_2$)(trpd-3 pln)(dppm)] (4)

With 1960 cm^{-1} the NN-stretching frequency of [Mo(N$_2$)(**trpd-3 pln**)(dppm)] (**4**) is low enough (i.e., below 2000 cm^{-1}) to allow protonation, which represents a first step towards dinitrogen fixation and functionalization with electrophiles.[41] [H(OEt$_2$)$_2$][Al{OC(CF$_3$)$_3$}$_4$] turned out to be a suitable acid for this application as it combines protonated ether as strong acid with the stabilizing effect of the weakly coordinating anion [Al{OC(CF$_3$)$_3$}$_4$]$^-$.[42] Furthermore, in case of pentaphosphine complexes, the aluminate led to better results and purer products than the commonly used [BAr$^F_4$]$^-$ anion.[43] Therefore, [Mo(N$_2$)(**trpd-3 pln**)(dppm)] (**4**) was treated with 3 equivalents of [H(OEt$_2$)$_2$][Al{OC(CF$_3$)$_3$}$_4$] (Scheme 6).

The ^{31}P NMR spectrum of the product solution (Figure 10, top) shows the expected AA'XX'M pattern of a pentaphosphine environment, and the high-field shift of all three signals indicate the formation of a hydrazido complex.[23,24,28,29] The XX' signal of the equatorial dppm phosphine donor atoms is at 5.2–4.4 ppm, which corresponds to a high-field shift of 7.9 ppm compared to **4**.

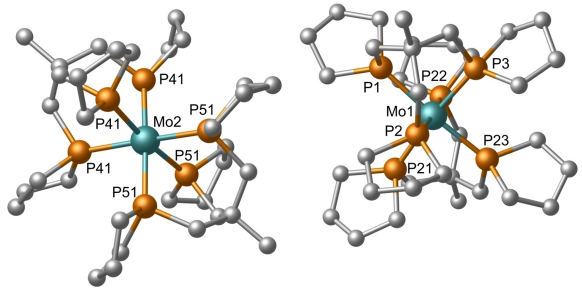
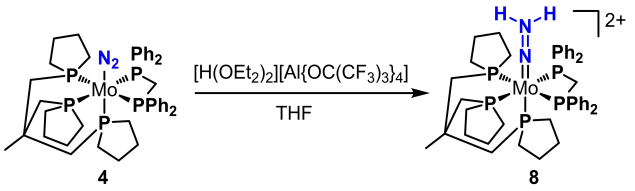


Figure 9. Comparison of the ^{31}P{^{1}H} NMR spectrum of [Mo(N$_2$)(**trpd-3 pln**)(dppm)] (**4**) (bottom) and the products of the protonation **4** with [H(OEt$_2$)$_2$][Al{OC(CF$_3$)$_3$}$_4$] (top), [Mo(NNH$_2$)(**trpd-3 pln**)(dppm)][Al{OC(CF$_3$)$_3$}$_4$]$_2$ (**8**) and side products [Mo(**trpd-3 pln**)(dppm)] (**9**) and protonated dppm (*). Both spectra were measured in [D$_8$]-THF.



Scheme 6. Protonation of [Mo(N_2)(**trpd-3 pln**)(dppm)] (**4**) with [H-(OEt_2)$_2$][Al{$OC(CF_3)_3$}$_4$] leading to hydrazido complex [Mo-(NNH_2)(**trpd-3 pln**)(dppm)][Al{$OC(CF_3)_3$}$_4$]$_2$ (**8**) (anion omitted for clarity).

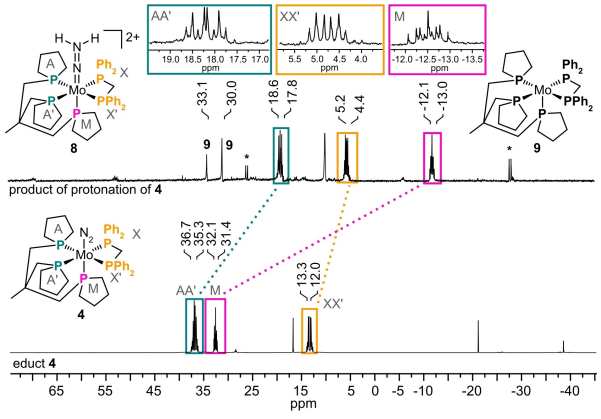


Figure 10. View of the two crystallographic independent complexes in the crystal structure of the mono(dinitrogen) complex [MoN_2(**trpd-3pln**)(dppm)] (4). Hydrogen atoms are omitted for clarity.

The AA' signal of the equatorial phospholane groups can be found at 18.6–17.8 ppm, which is a shift of around 18 ppm to higher field compared to **4**. The signal of the axial phospholane group (M) is most strongly affected by changes at the sixth coordination site due to its *trans* position; i.e., the signal between −12.1 and −13.0 ppm exhibits the largest shift ($\triangle\delta =$ 44.4 ppm). Similar values were also found in comparable systems [Mo(N_2)(**P^5**)]/[Mo(NNH_2)(**P^5**)]$^{2+}$ with **P^5**=$P^{Me}{}_2PP^{Ph}{}_2$ ($\triangle\delta =$ 45.5 ppm),[28,29] tdppme and dmpm ($\triangle\delta = 44.7$ ppm)[23] or trpd-1 and dmpm, $\triangle\delta = 46.8$ ppm.[24] Furthermore, in the ^{1}H NMR spectrum a singlet at 8.94.ppm is visible (Figure S22) which ist in line with the proposed doubly protonated hydrazido complex [Mo(NNH_2)(**trpd-3 pln**)(dppm)][Al{$OC(CF_3)_3$}$_4$]$_2$ (**8**).[44] Additionally, signals of small amounts of protonated dppm and [Mo(**trpd-3 pln**)(dppm)] (**9**) as product of the decoordination of N_2 are visible at 33.1 and 30.0 ppm in the ^{31}P NMR, ^{31}P, ^{31}P COSY and ^{1}H, ^{31}P HMBC NMR (Figure 10 and Figure S23–25). This observation is in analogy with the formation of [Mo(**trpd-1**)(dppm)] by reduction of [MoI_3(**trpd-1**)] we described earlier[24] and these pentacoordinated Mo(0) phosphine complexes seem to be common side products under harsh conditions.

Summary and Conclusion

Three novel tripod ligands **trpd-1 pln**, **trpd-2 pln** and **trpd-3 pln**, were prepared by using **Li**–**Pln** as synthon for phospholane end groups. This shows not only the versatility of **Li**–**Pln** for the synthesis of new oligodentate phosphine ligand systems but also highlights the fact that entire series of ligands with differing residues can be obtained, which opens up many possibilities for fine-tuning of their electronic and steric properties. The accessibility of metal complexes supported by the above ligands was demonstrated by synthesis of the molybdenum(III) complexes [MoI_3(**trpd-1 pln**)] (**1**), [MoI_3(**trpd-2 pln**)] (**2**) and [$MoBr_3$(**trpd-3 pln**)] (**3**) containing all three ligands. One of them, **3**, was selected for further reactions aiming at N_2 activation and functionalization. Reduction of **3** by sodium amalgam in the presence of dppm led to molybdenum(0) mono(dinitrogen) complex [Mo(N_2)(**trpd-3 pln**)(dppm)] (**4**) containing a N_2 ligand with an NN stretching frequency of 1960 cm^{-1}. This value indicates an activation high enough for protonation.

Replacement of the coligand by the stronger ligand dmpm, which should further increase activation of the N_2 ligand, led to a mixture of products containing the desired complex [Mo-(N_2)(**trpd-3 pln**)(dmpm)] (**5**), but also *cis*-[Mo(N_2)$_2$(κ^2-**trpd-3 pln**)$_2$] (**6**) and homoleptic [Mo(**trpd-3 pln**)$_2$] (**7**). Because of its purity, **4** was chosen for further functionalization, and protonation with [H(OEt_2)$_2$][Al{$OC(CF_3)_3$}$_4$] was found to lead to the hydrazido(2-) complex [Mo(NNH_2)(**trpd-3 pln**)(dppm)][Al{$OC(CF_3)_3$}$_4$]$_2$. ^{31}P NMR showed the expected changes of the chemical shifts ($\triangle\delta$) under protonation in [Mo(N_2)(**P^5**)]/[Mo(NNH_2)(**P^5**)]$^{2+}$ systems with **P^5** = pentaphosphine environment. In conclusion, this paper along with its predecessor, ref.[31], shows that multidentate phosphine ligands with terminal phospholane groups can be prepared along a user-friendly route and successfully employed for the synthesis of a wide range of molybdenum dinitrogen complexes suitable for nitrogen fixation. Further exploration and application of this methodology is under way.

Experimental Section

General Information. Commercially available starting materials were used as received. Water and oxygen-sensitive reagents were handled in an M. Braun Labmaster 130 Glovebox under N_2. All syntheses were performed under a N_2 atmosphere by using Schlenk techniques. The solvents were dried and freshly distilled under argon prior to use. Solvents were dried with CaH_2 (dichloromethane, *n*-hexane, *n*-pentane), $LiAlH_4$ (THF, diethyl ether) or magnesium methanolate (methanol). [$MoBr_3$(thf)$_3$][45] as well as [MoI_3(thf)$_3$][46] were prepared as described in the literature and Lithiumphospholanide (**Li**–**Pln**) as described in our previous study.[31] The ligand precursors 3-Chloro-2-(chloromethyl)-2-methylpropyl)diphenylphosphane and (2-(Chloromethyl)-2-methylpropane-1,3-diyl)bis(diphenylphosphane) are literature known.,[46,47] but the syntheses were modified as already decribed by H. Broda[48] (modified syntheses see SI).

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). Referencing was performed using the solvent residue signal (7.26 ppm for $CDCl_3$, 5.32 ppm for CD_2Cl_2, 3.58 ppm for THF-d_8). ^{31}P NMR spectra were referenced to H_3PO_4 85 % [$\delta(^{31}P) = 0$ ppm] as substitutive standard. Infrared spectra were recorded at room temperature on a Bruker Alpha FT-IR Spectrum with Platinum ATR setup or on a Bruker Vertex70 FT-IR spectrometer using a broadband spectral range extension VERTEX FM for full mid and far IR in the range of 6.000–80 cm^{-1}. Raman spectra were recorded at RT on a Bruker RAM II FT-Raman spectrometer using a liquid nitrogen cooled, highly sensitive Ge detector, 1064 nm radiation and 3 cm^{-1} resolution.

Single Crystal Structure Analysis of 4 and 7

Data collections were performed using an Imaging Plate Diffraction System (IPDS-2 from STOE using Mo–Kα radiation. The structures were solved with SHELXT[49] and refinement was performed against F^2 using SHELXL-2018.[50] For all compounds a numerical absorption correction was performed using X-Red and X-Shape of the software package X-Area.[51] All non-hydrogen atoms were refined with anisotropic displacement parameters. The C–H hydrogen atoms were positioned with idealized geometry (methyl H atoms in **7** allowed to rotate but not to tip) and were refined isotropically with U_{iso} (H) = 1.2 U_{eq} (C) (1.5 for methyl H atoms) using a riding model. The structure of compound **4** contains about 5 % of bromine that might originate from the reactant that occupy the same position as N_2. Therefore, the structure was refined using a split model with restraints. If this bromide ligand is not considered a much too short N–N distance is observed. The structure is additionally pseudo-merohedral twinned with β close to 90° indicating an orthorhombic crystal system. Therefore, a twin refinement was performed leading to a BASF parameter of 0.0331 (4). After structure refinement of compound **7** there is one peak on the difference map around the −3 axis, indicating for some disordered solvent of unknown identity. Therefore, the data were corrected for disordered solvent using Squeeze in Platon.[52] Selected crystal data and details of the structure refinements are given in Table S1–S3.

CCDC 2081802 (**4**), and CCDC 2081803 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of trpd-1 pln

The ligand precursor 1-chloro-2,2-bis(diphenylphosphinomethyl)-propane) (421 mg, 886 µmol) was dissolved in 5 mL. THF. To a solution of lithium phospholanide (100 mg, 1.06 mmol) in THF (10 mL) a solution of *n*-butyllithium in *n*-hexane (2.5 M, 0.20 mL, 0.50 mmol) was added at 0 °C. Within 10 min the lithium phospholanide/*n*-butyllithium solution was added to the precursor solution at 0 °C. The solution was stirred for 44 h at room temperature. The solvent was removed *in vacuo*. The residue was redissolved in *n*-pentane (10 mL), filtered over Celite® and washed with *n*-pentane (30 mL). After removing the solvent *in vacuo* the product was obtained as colorless oil (425 mg, 807 µmol, 91 %). The chemical shifts here are differing from these ones in the discussion part due to the use of different NMR solvents. The resolution of the signals in the experimental part is better so that coupling constants can be determined. Furthermore, the NMR spectra in the discussion belong to a batch with higher purity.

^{31}P{^{1}H} NMR: (161.98 MHz, CD_2Cl_2, 300 K): $\delta = -25.1$ (d, $^{4}J_{PP} = 3.1$ Hz, 2 P, PPh$_2$), −36.5 (t, $^{4}J_{PP} = 3.1$ Hz, 1 P, P_{pln} ppm.

^{1}H-NMR (400.13 MHz, CD_2Cl_2, 300 K): $\delta = 7.47–7.41$ (m, 8 H, CH_{phenyl}), 7.33–7.28 (m, 12 H, CH_{phenyl}), 2.55–2.45 (m, 4 H, C–CH_2–PPh$_2$), 1.69–1.54 (m, 6 H, CH_2 (pln)), 1.60 (d, $^{2}J_{HP} = 4.0$ Hz, 2 H, C_q–CH_2–P_{pln}), 1.36–1.30 (m, 2 H, CH_2 (pln)), 1.01 (s, 3 H, CH_3) ppm.

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2, 300 K): $\delta = 140.7$ (m, 4 C, C_i), 133.7 (d, $J_{CP} = 2.0$ Hz, 4 C, CH_{phenyl}), 133.5 (d, $J_{CP} = 2.0$ Hz, 4 C, CH_{phenyl}), 128.9–128.8 (m, 12 C, CH_{phenyl}), 46.1–45.7 (dt, $^{1}J_{CP} = 21.2$ Hz, $^{3}J_{CP} = 8.0$ Hz, 1 C, C_q–CH$_2$–P_{pln}), 43.2–42.9 (pseudo-„dt“ (ddd), $^{1}J_{CP} = 16.6$ Hz, $^{3}J_{CP} = 9.1$ Hz, 2 C, C_q–CH$_2$–PPh$_2$), 39.3–38.9 (dt, $^{2}J_{CP} = 12.7$ Hz, $^{2}J_{CP} = 13.7$ Hz, 1 C, C_q–CH$_3$), 29.7–29.4 (pseudo-„q“ (dt), $^{3}J_{CP} = 9.1$ Hz, 1 C, CH$_3$), 28.5 (d, $J_{CP} = 11.2$ Hz, 2 C, CH$_2$ (pln)), 28.4 (d, $J_{CP} = 3.5$ Hz, 2 C, CH$_2$ (pln)) ppm.

IR (ATR): $\tilde{\nu} = 3069$ (w), 3050 (w), 3027 (w), 3013 (w), 2999 (w), 2948 (m), 2925 (m), 2875 (sh), 2857 (m), 2819 (sh), 1951 (vw), 1884 (vw), 1806 (vw), 1585 (w), 1571 (w), 1480 (m), 1454 (br m), 1433 (s), 1400 (m), 1370 (m), 1328 (w), 1303 (w), 1259 (m), 1183 (w), 1155 (w), 1108 (m), 1091 (m), 1067 (m), 1024 (m), 998 (m), 970 (w), 949 (w), 912 (br w), 866 (sh), 846 (w), 816 (br m), 738 (s), 694 (s), 673 (sh), 653 (vw), 618 (vw), 597 (vw), 580 (vw), 560 (vw), 511 (s), 479 (m), 443 (vw), 426 (w) cm^{-1}.

Synthesis of trpd-2 pln

The ligand precursor 1,3-dichloro-2-(diphenylphosphinomethyl)-2-methylpropane (205 mg, 630 µmol) was dissolved in 5 mL. THF. To a solution of lithium phospholanide (142 mg, 1.51 mmol) in THF (10 mL) a solution of *n*-butyllithium in *n*-hexane (2.5 M, 0.60 mL, 1.50 mmol) was added at 0 °C. Within 30 min the lithium phospholanide/*n*-butyllithium solution was added to the precursor solution at 0 °C. The solution was stirred for 20 h at room temperature. The solvent was removed *in vacuo*. The residue was redissolved in *n*-pentane (10 mL), filtered over Celite® and washed with *n*-pentane (40 mL). Degassed water (10 mL) was added. The organic layer was separated with a syringe and the aqueous layer was extracted three times with diethyl ether (5 mL). The solvent of the organic layers was removed *in vacuo*. The residue was redissolved in dichloromethane (5 mL), filtered over basic aluminum oxide and washed with dichloromethane (30 mL) After removing the solvent *in vacuo* the product was obtained as colorless oil (270 mg, 630 µmol, 99 %).

^{31}P{^{1}H} NMR: (161.98 MHz, CD_2Cl_2, 300 K): $\delta = -24.3$ (t, $^{4}J_{PP} = 3.6$ Hz, 1 P, PPh$_2$), −36.6 (d, $^{4}J_{PP} = 3.6$ Hz, 2 P, P_{pln}) ppm.

^{1}H-NMR (400.13 MHz, CD_2Cl_2, 300 K): $\delta = 7.51–7.46$ (m, 4 H, CH_{phenyl}), 7.34–7.28 (m, 6 H, CH_{phenyl}), 2.50 (d, $^{2}J_{HP} = 3.7$ Hz, 2 H, C_q–CH_2–PPh$_2$), 1.78–1.68 (m, 5 H, CH_2 (pln)), 1.67–1.57 (m, 7 H, CH_2 (pln)), 1.63 (d, $^{2}J_{HP} = 1.4$ Hz, 2 H, C_q–CH_2–P_{pln}), 1.62 (d, $^{2}J_{HP} = 1.4$ Hz, 2 H, C_q–CH_2–P_{pln}), 1.45–1.37 (m, 4 H, CH_2 (pln)), 1.04 (s, 3 H, CH_3) ppm.

^{13}C{^{1}H}-NMR (101 MHz, CD_2Cl_2, 300 K): $\delta = 140.7$ (d, $^{1}J_{CP} = 13.0$ Hz, 2 C, C_i), 133.5 (d, $J_{CP} = 19.6$ Hz, 4 C, CH_{phenyl}), 128.7 (s, 2 C, C_p), 128.7 (d, $J_{CP} = 2.0$ Hz, 4 C, CH_{phenyl}), 45.8–45.4 (pseudo-„dt“ (ddd), $^{1}J_{CP} = 21.3$ Hz, $^{3}J_{CP} = 8.2$ Hz, 2 C, C_q–CH$_2$–P_{pln}), 42.5–42.2 (dt, $^{1}J_{CP} = 15.8$ Hz, $^{3}J_{CP} = 8.8$ Hz, 1 C, C_q–CH$_2$–PPh$_2$), 38.8–38.5 (dt, $^{2}J_{CP} = 12.4$ Hz, $^{2}J_{CP} = 13.9$ Hz, 1 C, C_q–CH$_3$), 29.3–29.0 (pseudo-„q“ (dt), $^{3}J_{CP} = 9.1$ Hz, 1 C, CH$_3$), 28.5–28.3 (m, 8 C, CH$_2$ (pln)) ppm.

IR (ATR): $\tilde{\nu} = 3069$ (w), 3051 (w), 3029 (vw), 3013 (vw), 3000 (vw), 2946 (sh), 2926 (s), 2873 (sh), 2857 (s), 2822 (sh), 2326 (br vw), 1946 (vw), 1882 (vw), 1808 (vw), 1753 (vw), 1584 (w), 1571 (vw), 1480 (m), 1460 (m), 1446 (m), 1432 (s), 1423 (sh), 1402 (br m), 1378 (sh), 1367 (br m), 1329 (vw), 1317 (vw), 1302 (w), 1260 (br m), 1207 (sh), 1185 (br w), 1157 (w), 1139 (vw), 1109 (m), 1093 (m), 1067 (m), 1053 (sh),

1027 (m), 999 (w), 970 (w), 951 (w), 939 (vw), 911 (br vw), 867 (sh), 846 (m), 804 (br m), 739 (vs), 695 (vs), 670 (sh), 652 (m), 619 (sh), 513 (m), 482 (m), 452 (vw), 422 (w) cm^{-1}.

Synthesis of trpd-3 pln

To a solution of lithium phospholanide (194 mg, 2.06 mmol) in THF (20 mL) a solution of *n*-butyllithium in *n*-hexane (2.5 M, 0.14 mL, 0.35 mmol) was added at 0 °C. to this solution. The ligand precursor 1,3-Dichloro-2-(chloromethyl)-2-methylpropane (117 mg, 667 µmol) was added to this solution at 0 °C. The solution was stirred for 4 d at room temperature. The solvent was removed *in vacuo*. The residue was redissolved in *n*-pentane (10 mL), filtered over Celite® and washed with *n*-pentane (30 mL). The solvent was removed *in vacuo*. After redissolving the oily residue in diethyl ether (5 mL) degassed water (5 mL) was added and it was stirred for 5 min. The solvent of the separated organic layer was removed *in vacuo*. The oily residue was redissolved in dichloromethane (5 mL), filtered over basic aluminum oxide and washed with dichloromethane (30 mL). After removing the solvent *in vacuo* the product was obtained as colorless oil (213 mg). The formation of **trpd-3 pln** was accompanied by side reactions and not all side products, which were probably caused by a lithium halogen exchange, could be separated and identified. So that the yield of **trpd-3 pln** could not be determined. Therefore, a small excess of the product was used for the synthesis of [$MoBr_3$(**trpd-3 pln**)] (**3**).

$^{31}P\{^1H\}$ NMR: (161.98 MHz, $CDCl_3$, 300 K): δ = −36.5 (s, 3 P, P_{pln}) ppm.

^{1}H-NMR (400.13 MHz, $CDCl_3$, 300 K): δ = 1.83–1.59 (2 m, 22 H, CH_2 (pln)), 1.64 (br d, 6 H, C_q–CH_2–P_{pln}), 1.54–1.46 (m, 7 H, CH_2 (pln)), 1.07 (s, 3 H, CH_3) ppm.

$^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$, 300 K): δ = 44.0–43.6 (dt, $^1J_{PC}$ = 20.9 Hz, $^3J_{CP}$ = 8.3 Hz, 3 C, C_q–CH_2–P_{pln}), 37.2–36.8 (q, $^2J_{CP}$ = 11.8 Hz, 1 C, C_q–CH_3), 27.7–27.4 (q, $^3J_{CP}$ = 8.9 Hz, 1 C, CH_3), 27.0–26.9 (m, 12 C, CH_2 (pln)) ppm.

IR (ATR): $\tilde{\nu}$ = 2949 (sh), 2928 (s), 2875 (sh), 2857 (s), 1666 (w), 1640 (w), 1616 (w), 1603 (w), 1460 (s), 1445 (s), 1422 (s), 1405 (s), 1365 (s), 1315 (w), 1300 (m), 1259 (br s), 1203 (m), 1189 (sh), 1166 (s), 1110 (s), 1075 (s), 1049 (s), 1027 (s), 1008 (sh), 974 (w), 952 (w), 917 (w), 875 (sh), 861 (sh), 847 (s), 808 (br s), 792 (br s), 773 (sh), 727 (br m), 720 (br m), 680 (sh), 665 (m), 649 (s), 545 (sh), 512 (br s), 474 (br s) cm^{-1}.

[MoI_3(trpd-1 pln)] (1)

The ligand **trpd-3 pln** (105 mg, 199 µmol) was dissolved in THF (10 mL). This solution was added to a suspension of [MoI_3(thf)$_3$] (135 mg, 195 µmol) and THF (5 mL). It was stirred for 62 h at room temperature. The suspension was reduced *in vacuo* to a quantity of 6 mL and diethyl ether (15 mL) was added. The precipitate was filtered, washed with diethyl ether (15 mL) and *n*-hexane (15 mL) and dried *in vacuo*. The product was obtained as red-brown solid (117 mg, 117 µmol, 60 %).

Anal. Calcd $C_{33}H_{37}I_3MoP_3$ (1003.25): C 39.5, H 3.7, I^- 38.0; found C 39.3, H 4.1, I^- 38.1.

MIR-FIR: $\tilde{\nu}$ = 3078 (vw), 3055 (vw), 3029 (vw), 2974 (sh), 2955 (w), 2932 (w), 2918 (w), 2857 (br w), 1586 (w), 1574 (w), 1483 (m), 1458 (vw), 1448 (w), 1433 (s), 1416 (w), 1413 (sh), 1402 (w), 1375 (w), 1364 (vw), 1336 (w), 1318 (w), 1305 (w), 1277 (w), 1267 (sh), 1256 (sh), 1234 (sh), 1223 (w), 1212 (vw), 1189 (w), 1158 (w), 1139 (w), 1115 (m), 1089 (br m), 1080 (vw), 1066 (m), 1048 (w), 1027 (w), 999 (w), 985 (vw), 953 (vw), 934 (vw), 914 (br w), 905 (br w), 876 (w), 854 (m), 835 (m), 815 (w), 777 (vw), 769 (vw), 752 (m), 743 (s), 723 (m), 699 (s), 691 (s), 674 (m), 627 (vw), 620 (w), 610 (w), 601 (vw), 596 (vw), 592 (vw), 586 (vw), 579 (vw), 574 (vw), 567 (vw), 546 (vw), 540 (vw), 537 (vw), 521 (sh), 515 (s), 502 (s), 489 (m), 477 (m), 461 (br w), 442 (vw), 411 (m), 406 (br m), 375 (vw), 364 (vw), 352 (vw), 336 (w), 328 (vw), 323 (vw), 314 (vw), 312 (vw), 305 (vw), 301 (vw), 290 (vw), 286 (vw), 282 (vw), 272 (br vw), 261 (vw), 253 (vw), 250 (sh), 245 (vw), 239 (vw), 234 (vw), 230 (vw), 225 (sh), 220 (m), 212 (sh), 208 (s), 203 (s), 192 (br s), 183 (sh), 178 (w), 173 (vw), 169 (m), 166 (m), 161 (m), 157 (m), 155 (sh), 147 (sh), 145 (m), 142 (m), 136 (m), 131 (m), 126 (w), 116 (br s), 110 (s), 106 (m), 102 (m), 97 (sh), 95 (s), 89 (s), 85 (m) cm^{-1}.

[MoI_3(trpd-2 pln)] (2)

The ligand **trpd-2 pln** (128 mg, 299 µmol) was dissolved in THF (5 mL). This solution was added to a suspension of [MoI_3(thf)$_3$] (200 mg, 289 µmol) and THF (15 mL). It was stirred for 42 h at room temperature. The suspension was reduced *in vacuo* to a quantity of 5 mL and diethyl ether (20 mL) was added. The precipitate was filtered, washed with diethyl ether (15 mL) and dried *in vacuo*. The product was obtained as red-brown solid (159 mg, 299 µmol, 61 %).

Anal. Calcd $C_{25}H_{35}I_3MoP_3$ (905.15): C 33.2, H 3.9, I^- 42.1; C 33.0, H 4.0, I^- 40.6.

MIR-FIR: $\tilde{\nu}$ = 3077 (sh), 3052 (w), 2970 (sh), 2936 (m), 2865 (m), 2658 (vw), 2115 (vw), 2080 (vw), 2051 (vw), 1981 (vw), 1939 (w), 1875 (w), 1825 (sh), 1809 (br w), 1636 (sh), 1616 (sh), 1587 (w), 1573 (w), 1480 (w), 1457 (w), 1435 (s), 1406 (m), 1378 (m), 1337 (w), 1317 (sh), 1303 (w), 1279 (vw), 1253 (w), 1182 (w), 1150 (w), 1139 (sh), 1113 (s), 1094 (sh), 1067 (s), 1028 (m), 999 (w), 974 (sh), 952 (br m), 912 (w), 877 (sh), 856 (s), 836 (sh), 824 (sh), 794 (sh), 740 (br s), 720 (vw), 694 (br s), 664 (sh), 617 (vw), 605 (vw), 574 (w), 553 (m), 513 (s), 498 (s), 428 (br m), 398 (sh), 313 (vw), 303 (vw), 273 (vw), 260 (vw), 248 (sh), 204 (s), 182 (sh), 160 (m), 156 (m), 145 (m), 136 (m), 127 (m), 111 (m), 98 (m), 93 (vw), 87 (m), 83 (sh) cm^{-1}.

[$MoBr_3$(trpd-3 pln)] (3)

The ligand **trpd-3 pln** (207 mg, 627 µmol) was dissolved in THF (15 mL). This solution was added to [$MoBr_3$(thf)$_3$] (300 mg, 543 µmol) and it was stirred for 18 h at room temperature. The suspension was reduced *in vacuo* to a quantity of 5 mL and diethyl ether (20 mL) was added. The precipitate was filtered, washed with diethyl ether (20 mL), *n*-hexane (10 mL) and again with diethyl ether (10 mL) and dried *in vacuo*. The product was obtained as yellow solid (258 mg, 387 µmol, 71 %).

Anal. Calcd $C_{17}H_{33}Br_3MoP_3$ (666.04): C 30.7, H 5.0, Br^- 36.0; found C 31.2, H 5.0, Br^- 35.6.

MIR-FIR: $\tilde{\nu}$ = 2978 (sh), 2936 (m), 2865 (m), 1473 (sh), 1464 (sh), 1457 (m), 1446 (m), 1437 (sh), 1419 (sh), 1406 (br m), 1399 (sh), 1388 (vw), 1380 (m), 1363 (sh), 1339(vw), 1320 (vw), 1304 (w), 1262 (br w), 1225 (vw), 1203 (sh), 1180 (w), 1111 (s), 1061 (s), 1029 (m), 950 (m), 914 (vw), 875 (sh), 857 (s), 821 (sh), 791 (vw), 764 (vw), 747 (vw), 717 (w), 675 (m), 543 (sh), 512 (m), 495 (s), 462 (sh), 280 (vw), 252 (sh), 245 (sh), 234 (vs), 228 (sh), 214 (vw), 209 (vw), 203 (w), 197 (vw), 193 (vw), 188 (vw), 182 (vw), 177 (w), 170 (w), 163 (sh), 158 (s), 152 (m), 146 (sh), 140 (w), 132 (w), 127 (vw), 122 (w), 110 (w), 105 (w), 99 (m), 95 (w), 91 (sh), 85 (br m), 80 (m) cm^{-1}.

[$Mo(N_2)$(trpd-3 pln)(dppm)] (4)

[$MoBr_3$(**trpd-3 pln**)] (**3**, 320 mg, 480 µmol) and the coligand dppm (185 mg, 481 µmol) was added to sodium amalgam (200 mg,

8.70 mmol Na, 2 mL of Hg) and THF (5 mL). After further THF (25 mL) was added the reaction mixture was stirred for 22 h at room temperature under nitrogen atmosphere. The supernatant solution was separated from sodium amalgam and the solvent was reduced *in vacuo*. The received red oil was redissolved in 5 mL THF and methanol (10 mL) was added. After reducing the solvent *in vacuo* to a quantity of 5 mL, additional methanol (10 mL) was added. The solvent was reduced *in vacuo* once more to a quantity of 5 mL. The precipitate was filtered, washed with methanol (15 mL) and dried *in vacuo* to obtain the product as a red solid (29 mg). The product contains side products which were discussed in the discussion part.

$^{31}P\{^{1}H\}$ NMR (161.98 MHz, [D_8]THF, 300 K): $\delta = 36.7–35.3$ (m, 2 P, $P_{AA'}$), 32.1–31.4 (m, 1 P, P_M), 13.3–12.0 (m, 2 P, $P_{XX'}$) ppm.

Side product [Mo(dppm)$_3$]: $\delta = 16.0$ ppm, side product **6**: $\delta =$ 31.5 ppm (t, 2 P), 27.7 ppm (br t, 2 P) and −38.8 ppm (s, 2 P).

MIR: $\tilde{\nu} = 3066$ (vw), 3050 (w), 3015 (vw), 2999 (vw), 2961 (m), 2933 (m), 2907(m), 2875 (m), 2857 (m), 2005 (w), 1960 (br s), 1583 (w), 1571 (vw), 1478 (w), 1450(w), 1430 (m), 1410 (w), 1398 (sh), 1368 (w), 1318 (vw), 1301 (w), 1259 (s), 1220 (w), 1177 (br w), 1156 (vw), 1104 (sh), 1079 (s), 1063 (sh), 1018 (br s), 967 (m), 952 (sh), 917 (vw), 860 (m), 848 (m), 821 (sh), 798 (br s), 744 (m), 717 (sh), 708 (sh), 694 (s), 659 (s), 617 (m), 522 (sh), 500 (s), 486 (s), 470 (sh), 438 (s), 427 (s) cm^{-1}.

FT-Raman: $\tilde{\nu} = 3052$ (m), 2961 (sh), 2939 (br m), 2915 (sh), 2907 (m), 2895 (sh), 2881 (m), 2862 (sh), 1970 (w), 1808 (vw), 1584 (m), 1571 (w), 1448 (vw), 1432 (vw), 1416 (vw), 1399 (vw), 1371 (vw), 1184 (vw), 1174 (sh), 1156 (vw), 1091 (vw), 1028 (w), 1000 (s), 877 (vw), 708 (vw), 689 (vw), 668 (vw), 619 (vw), 527 (vw), 509 (sh), 491 (vw), 408 (vw), 400 (sh) cm^{-1}.

Na_xHg reduction of [$MoBr_3$(trpd-3 pln)] (3) in the presence of dmpm

[$MoBr_3$(**trpd-3 pln**)] (**3**, 200 mg, 300 μmol) was added to sodium amalgam (200 mg, 8.70 mmol Na, 2 mL of Hg) and THF (5 mL). After the addition of further THF (15 mL), a solution of the coligand dmpm (44.8 mg, 327 μmol) in THF (5 mL) was added. The reaction mixture was stirred for 18 h at room temperature under nitrogen atmosphere. The supernatant solution was separated from sodium amalgam and the solvent was reduced *in vacuo* to a quantity of 8 mL and filtered subsequently over neutral aluminium oxide. The solvent was reduced to a quantity of 5 mL and methanol (10 mL) was added. After reducing the solvent again to a quantity of 5 mL further methanol (10 ml) was added. The product couldn't be precipitated by the addition of methanol so that the solvent was reduced *in vacuo*. No pure product could be obtained. The received products were discussed in the discussion part.

[Mo(NNH_2)(trpd-3 pln)(dppm)] (8), Protonation of [Mo(N_2)(trpd-3 pln)(dppm)] (4)

The complex [Mo(N_2)(**trpd-3 pln**)(dppm)] (**4**) (7.50 mg, 8.90 μmol) was dissolved in 0.3 mL [D_8]THF and 3.0 equivalents [$H(OEt_2)_2$][Al{$OC(CF_3)_3$}$_4$] dissolved in in 0.2 mL [D_8]THF were added at a temperature of −20 °C. The solution was transferred in a young tube and characterized via NMR spectroscopy immediately. Measurement of vibrational spectra was not possible. The usage of [D_8]THF led to gelation of the reaction mixture most likely due to acid-catalyzed polymerisation of THF. For the measurement of vibrational specta the gel-like and yellow product was dissolved in dichormethane first and the solvent was subsequently removed *in vacuo*. Unfortunately, the product seems to be unstable in DCM.

$^{31}P\{^{1}H\}$ NMR (161.98 MHz, [D_8]THF, 300 K): $\delta = 18.6–17.8$ (m, 2 P, $P_{AA'}$), 5.2–4.4 (m, 1 P, $P_{XX'}$), −12.1–(−13.0) (m, 2 P, P_M) ppm.

Side products: $\delta = 33.1$ (q, $^3J_{PP} = 6.3$ Hz, 2 P, **9**), 30.0 (t, $^3J_{PP} = 6.3$ Hz, 3P, **9**), 25.0 (*d*, $^3J_{PP} = 60.0$ Hz, 1 P, $[HPh_2PCH_2PPH_2]^+$), −28.4 (*d*, $^3J_{PP} =$ 60.0 Hz, 1 P, $[HPh_2PCH_2PPH_2]^+$).

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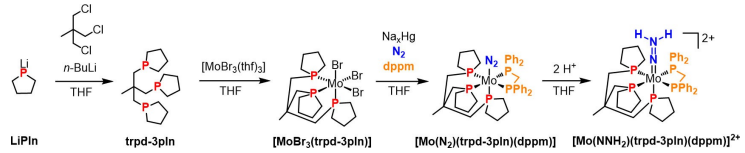

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