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Molybdenum(0) Dinitrogen Complexes Supported by Pentadentate Tetrapodal Phosphine Ligands: Structure, Synthesis, and Reactivity toward Acids

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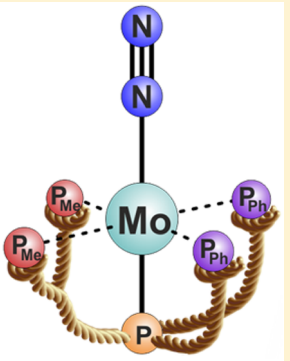
Supporting Information

ABSTRACT: The syntheses of two pentadentate tetrapodal phosphine (pentaPod^{P}) ligands, $P_2^{Ph}PP_2^{Ph}$ and $P_2^{Me}PP_2^{Ph}$, are reported, which derive from the fusion of a tripod and a trident ligand. Reaction of the ligand $P_2^{Ph}PP_2^{Ph}$ with $[MoCl_3(THF)_3]$ followed by an amalgam reduction under N_2 does not lead to well-defined products. The same reactions performed with the ligand $P_2^{Me}PP_2^{Ph}$ afford the mononuclear molybdenum dinitrogen complex $[MoN_2(P_2^{Me}PP_2^{Ph})]$. Because of the unprecedented topology of the pentaphosphine ligand, the Mo−P bond to the phosphine in the *trans* position to N_2 is significantly shortened, explaining the very strong activation of the dinitrogen ligand ($\tilde{\nu}_{NN}$ = 1929 cm^{-1}). The reactivity of this complex toward acids is investigated.



INTRODUCTION

Nitrogen is substantial for every living organism as it is a constituent of amino acids (and, thus, proteins), nucleic acids (DNA and RNA), and nucleotides involved in energy transfer.[1] Although nature provides an infinite supply of nitrogen in the form of dinitrogen in the earth's atmosphere, this molecule is not bioavailable because of its highly inert triple bond.[2] Only very few organisms are able to convert dinitrogen into a useful form, ammonia.[3,4] This process, called nitrogen fixation, is catalyzed by the enzyme nitrogenase. Although the structure of this enzyme has been fully elucidated, the detailed mechanism of biological dinitrogen reduction and protonation is still open to debate.[5−12] A fundamental problem in this respect relates to the question of whether the dinitrogen molecule during its conversion to NH_3 is exclusively protonated at its β-nitrogen atom ["asymmetric"[13,14] or "distal" (D)[8] pathway] or whether protonation occurs symmetrically on both nitrogen atoms of N_2 in a (more or less) alternating fashion ["symmetric"[13,14] or "alternating" (A)[8] pathway (Figure 1)]. Whereas the former pathway proceeds via a transition metal nitrido species (which are absent in an A pathway), the latter involves diazene (HN═NH) and hydrazine (H_2N-NH_2) intermediates, which are excluded from a D pathway. There is strong evidence that nitrogenase functions via an A pathway and not a D pathway.[9,15,16]

Dinitrogen can also be converted to ammonia under ambient conditions by transition metal complexes.[17,18] Using molybdenum (bis)dinitrogen complexes with phosphine coligands, Chatt and co-workers first successfully applied this approach.[19,20] On the basis of a tungsten bis(dinitrogen) complex, a cyclic conversion of N_2 to NH_3 could also be demonstrated.[20,21] In recent years, related systems have been established that allow a catalytic ammonia synthesis in a nitrogenase-like fashion with turnover numbers of up to 60 per mononuclear catalytic metal site.[22,23] The earliest of these systems was discovered by Schrock and co-workers in 2003 and is based on a molybdenum complex with a sterically shielding $HIPTN_3N$ ligand ($HIPTN_3N$ = $[\{3,5\text{-}(2,4,6\text{-}^{i}Pr_3C_6H_2)_2C_6H_3\text{-}NCH_2CH_2\}_3N]^{3-}$).[24,25] Using decamethylchromocene as a reductant and lutidinium BAr^F {BAr^F = tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate} as a proton source with this system, ammonia was generated from N_2 in four cycles with an overall yield of 65%.[25] A few years later, Nishibayashi et al. established a dinuclear molybdenum dinitrogen complex supported by a pincer ligand.[26−28] With a combination of decamethylcobaltocene and lutidinium triflate, this system generated 12 equiv of NH_3 per molybdenum. More recently, the original catalyst was modified by applying a tridentate triphosphine instead of a PNP pincer ligand, which led to a further increase in catalytic activity (63 equiv of NH_3/Mo) when collidinium triflate was applied as a proton source.[29] In 2013, Peters et al. demonstrated that a catalytic synthesis of ammonia from N_2 is also possible based on iron complexes.[30] Using KC_8 and $HBAr^F$ at low temperatures, up to 64 equiv of NH_3 are generated per Fe center.[23]

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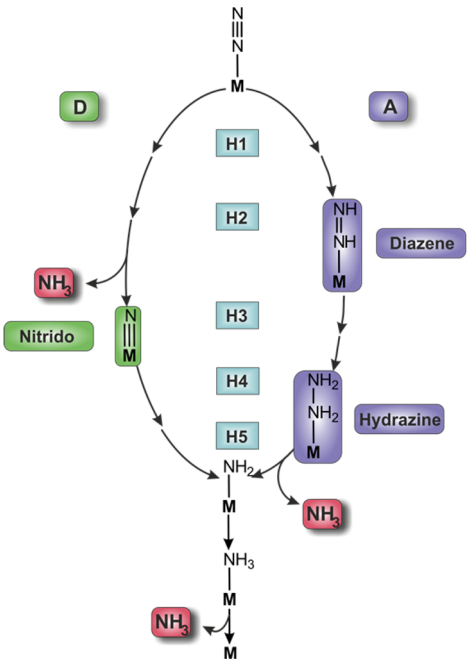

Figure 1. Distal (D) and alternating (A) pathways of nitrogenase (see the text).[8,12]

Importantly, these catalytic model systems of nitrogenase differ with respect to the mechanism of N_2 reduction (distal, D, or alternating, A). Further distinctions relate to the presence or absence of a dissociable anionic ligand in the *trans* position to N_2 or its protonated/reduced derivatives N_xH_y (x = 1 or 2, and y = 1−3). Moreover, the complex can function as a single-site (i.e., mononuclear) or dual-site (i.e., dinuclear) catalyst (cf. Table 1). The Schrock system clearly involves no dissociable coligand and follows a D pathway (Figure 2).[31] In the iron dinitrogen complexes developed by Peters, the *trans* donor is strapped to the equatorial donors, as well, thus precluding its dissociation. However, the corresponding reduction pathway is probably not strictly D but also involves protonation steps at the proximal nitrogen atom, indicating a mixed D/A pathway.[23] The Nishibayshi system, finally, does contain a dissociable ligand and appears to follow a strictly distal pathway, in analogy to classic Chatt-type complexes that contain dissociable anionic coligands and predominantly follow a D reduction pathway. However, this pathway has not yet fully been elucidated experimentally.[32]

Table 1. Molybdenum and Iron Systems Active in the Conversion of N_2 to NH_3 under Ambient Conditions (see the text)

system	mechanism	single site	catalytic	exchange of *trans* ligand
Schrock	distal (D)	yes	yes	no
Peters	distal and proximal	yes	yes	no
Nishibayashi	distal (D)	no	yes	yes
Classic Chatt	predominantly D (?)	yes	no	yes
Chatt P_5	distal and proximal (?)	yes	no	no

In spite of the apparent preference of the classic Chatt systems for a D pathway, a full quantum chemical analysis of the corresponding mechanistic cycle also reveals steps that involve a protonation of N_α.[34] Unfortunately, an experimental study of these steps is hampered by dissociation/association reactions of anionic coligands or solvent molecules that have been observed during the protonation of Mo−N_2 complexes,[35−38] the N−N cleavage of Mo−NNH_2 (or NNR_2) complexes,[39−42] and the reduction/protonation of Mo−imido complexes.[43,44] A detailed mechanistic analysis of these key reactions of nitrogen fixation in the absence of coligand or solvent exchange reactions would require an entirely new type of molybdenum dinitrogen complex in which the *trans* donor is strapped to the ligand frame in a fashion similar to that of the $HIPTN_3N$ ligand of Schrock, the P_3P^{Cy} ligand of Mézailles [P_3P^{Cy} = tris(dicyclohexylphosphinoethyl)phosphine],[45] and the P_3E ligands of Peters (E = B, C, or Si). In contrast to the corresponding Mo(III) triamidoamine and low-valent Fe phosphine complexes exhibiting trigonal symmetry, Mo(0) prefers an octahedral coordination. What we were seeking therefore was a pentadentate tetrapodal phosphine (pentaPod^P) ligand supporting Mo(0) centers in pseudo-4-fold symmetry and allowing the bonding and reduction of N_2 at a single site in the *trans* position to the focal P donor. The topology of these ligands can be regarded as resulting from the combination of a tripod and a trident ligand that are fused at one P donor of the tripod and the central donor atom of the trident ligand (Figure 3, bottom). The synthesis of such ligands has not been described to date.

In this paper, we first present a synthetic access to the envisioned pentaPod^P ligands. Then, we describe a strategy that allows, via precoordination to a Mo(III) precursor and subsequent amalgam reduction, the rational synthesis of mononuclear molybdenum(0) dinitrogen complexes supported by this novel type of ligand. The X-ray crystal structure of one of these complexes is shown; its spectroscopic properties are described, and its protonation to the corresponding NNH_2 complex is demonstrated. These results build on our previous experience in the synthesis of molybdenum dinitrogen complexes supported by multidentate phosphine ligands.[46−51] In these studies, a pentaphosphine environment has been created through a combination of a tripod or a trident ligand with a diphos ligand (or two monophosphines). It, however, transpired that the phosphine donor in the axial position to the N_2 ligand was also prone to dissociation, again leading to coordination of an external ligand such as the conjugated base of the acid employed for protonation or a solvent molecule. These reactions should be absent in a complex supported by a pentaPod^P ligand. In such a complex, the pivotal phosphine in the *trans* position to N_2 is strapped to the molybdenum center by four linkages to the equatorial phosphine donors (Figure 3), thus precluding its dissociation.

Herein, the syntheses of two of such pentaPod^P ligands are described. The first, "symmetrically" substituted ligand, [2-({bis[3-(diphenylphosphino)propyl]phosphino}methyl)-2-methylpropane-1,3-diyl]bis(diphenylphosphine) ($P_2^{Ph}PP_2^{Ph}$), exhibits four diphenylphosphine end groups. The second, "asymmetrically" substituted version, [2-({bis[3-(diphenylphosphino)propyl]phosphino}methyl)-2-methylpropane-1,3-diyl]bis(dimethylphosphine) ($P_2^{Me}PP_2^{Ph}$), exhibits PMe_2 end groups in the tripod and PPh_2 end groups in the trident part. Coordination of these ligands to $[MoCl_3(THF)_3]$ is described. Sodium amalgam reduction of the resulting Mo(III) precursors yields Mo(0) dinitrogen complexes that are characterized by single-crystal X-ray crystallography and/or spectroscopy. The steric and electronic properties of these

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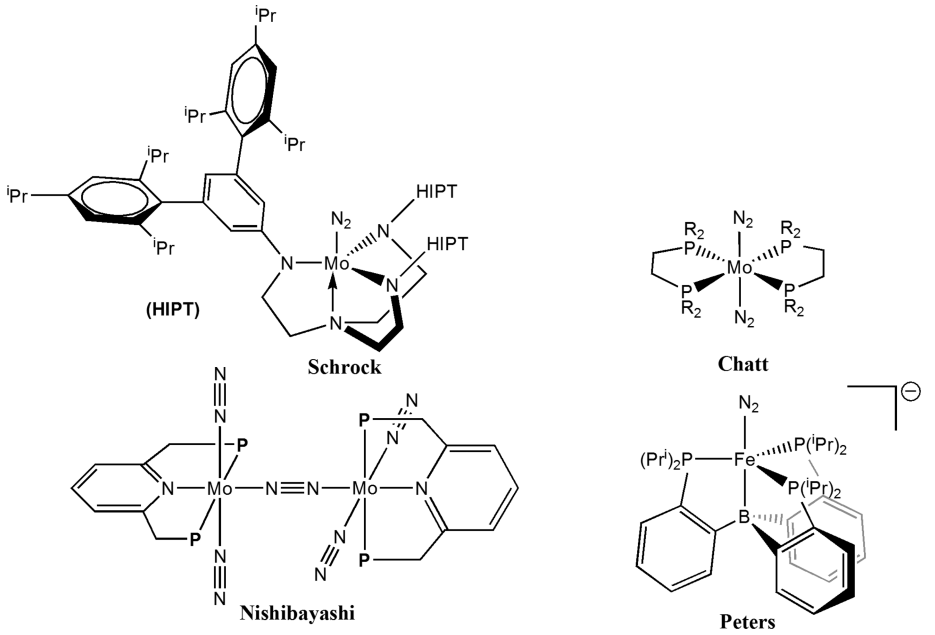


Figure 2. Model systems for synthetic nitrogen fixation.[23,25,26,33]

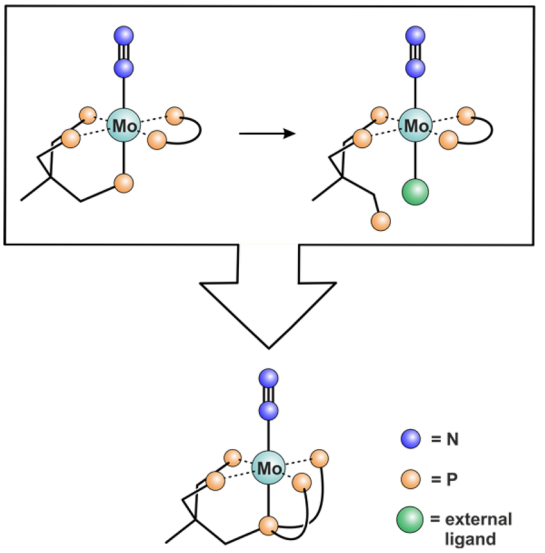


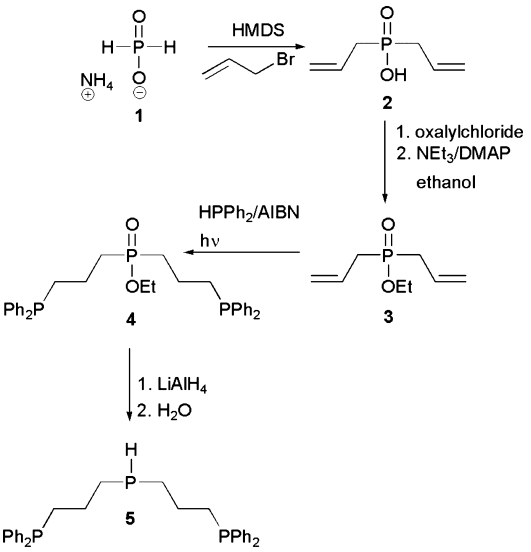
Figure 3. Schematic illustration of the pentaPod^{P} concept. To avoid decoordination of the P donor *trans* to the N_2 ligand, it is strapped to the molybdenum center. Color code: blue for nitrogen, turquoise for molybdenum, orange for the phosphine donor, and green for the external ligand (conjugate base of an acid used for protonation or solvent).

complexes are compared with those of similar Mo(0)−N_2 complexes with a triphos/diphos coordination sphere. Finally, the reactivity of a mononuclear Mo(N_2)pentaPod^{P} complex toward acids is investigated, providing evidence of the protonation to the NNH_2 complex under retention of the ligand environment.

RESULTS AND DISCUSSION

Ligand Synthesis. For both pentaPod^{P} ligands, the secondary phosphine bis[3-(diphenylphosphino)propyl]-phosphine (prPPHP, **5**) is needed. The preparation of **5** starts with ethyldiallylphosphinate (**3**), which was synthesized according to the route established by Bujard et al.[52] Reaction with AIBN and diphenylphosphine afforded ethyl-bis[3-(diphenylphosphino)propyl]phosphinate (**4**), which could be reduced with $LiAlH_4$[53] to produce **5** (Scheme 1).

Scheme 1. Synthetic Route for the Secondary Phosphine prPPHP (5)[52,53]



Synthesis of the asymmetrically substituted pentaPod^{P} ligand, $P_2^{Me}PP_2^{Ph}$, starts from 3,3′-dichloropivalic acid (**6**), which can be reduced with $LiAlH_4$ to yield 3-chloro-2-(chloromethyl)-2-methylpropan-1-ol (ClClOH, **7**). After reaction with trifluoromethanesulfonic anhydride,[54] 3-chloro-2-(chloromethyl)-2-methylpropyl-trifluoromethanesulfonate (ClClOTf, **8**) could be obtained. Adding lithiated prPPHP (**5**-Li) in THF to ClClOTf in THF afforded (3,3′-{[3-chloro-2-(chloromethyl)-2-methylpropyl]phosphinediyl}bis(propane-3,1-diyl))bis-(diphenylphosphine) (ClClprPPHP, **9**) (Scheme 2). In the last step, $LiPMe_2$ was reacted with **9** in THF, giving the asymmetrically substituted pentaPod^{P} ligand $P_2^{Me}PP_2^{Ph}$ (**10**).

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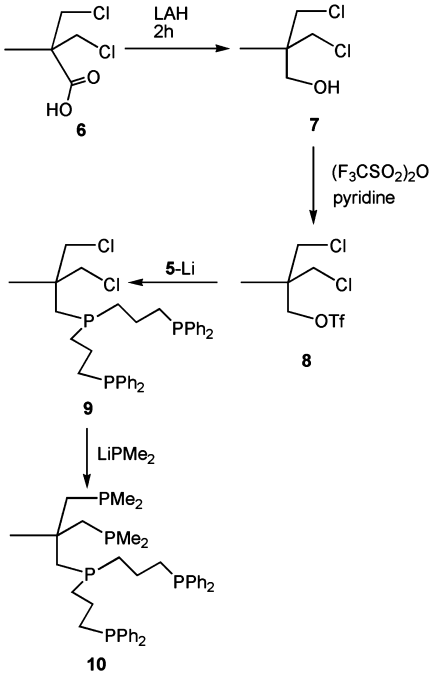
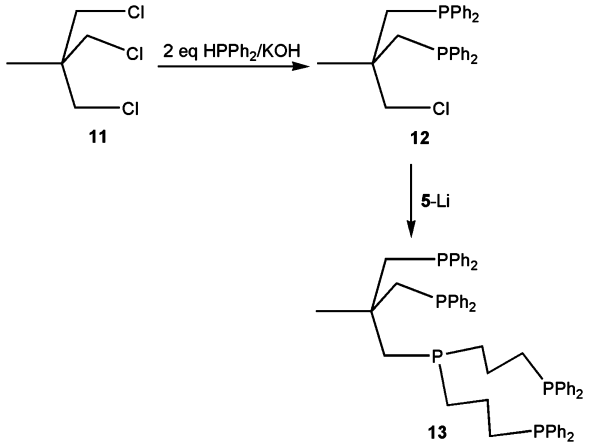
Scheme 2. Synthesis of the PentaPod^{P} Ligand $P_2^{Me}PP_2^{Ph}$ (10)



For the synthesis of the symmetrically substituted pentaPod^{P} ligand **13**, 1,3-dichloro-2-(chloromethyl)propane (**11**) was reacted with 2 equiv of $KPPh_2$, affording **12**.[55] Upon addition of **5**-Li, the pentaPod^{P} ligand $P_2^{Ph}PP_2^{Ph}$ (**13**) was obtained (Scheme 3).

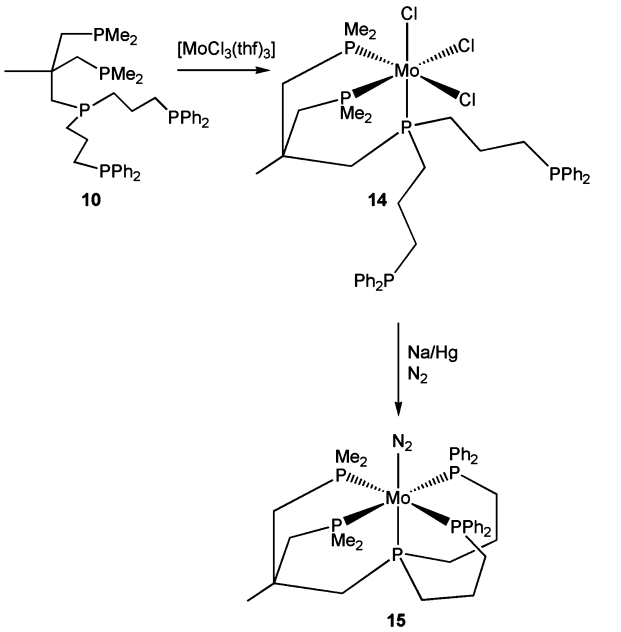
Scheme 3. Synthesis of the PentaPod^{P} Ligand $P_2^{Ph}PP_2^{Ph}$ (13)



Coordination to Mo(III) Precursors. Reaction of the asymmetrically substituted pentaPod^{P} ligand $P_2^{Me}PP_2^{Ph}$ (**10**) with Mo(III) precursors was achieved by stirring a mixture of **10** and $[MoCl_3(THF)_3]$ in THF and dichloromethane.[56,57] Coordination to the Mo(III) center can in principle occur with the tripod or the trident part of **10**. While the former necessarily leads to a *fac* geometry, the latter is known to result in *mer* complexes.[49,58]

Because of the stronger σ donor strength and the smaller steric demand of the dimethylphosphine as compared to that of the diphenylphosphine groups, the tripod part should coordinate selectively to $[MoCl_3(THF)_3]$, yielding *fac*(*trpd*)-$[MoCl_3(P_2^{Me}PP_2^{Ph})]$ (trpd = tripod) (**14**) (Scheme 4, top). This hypothesis is supported by EPR spectroscopy. In fact, the

Scheme 4. Coordination of 10 to $[MoCl_3(THF)_3]$ Yields 14[a]



[a]Sodium amalgam reduction under N_2 affords the molybdenum dinitrogen complex **15**.

EPR spectrum of **14** qualitatively corresponds to that of the Mo(III) complex $[MoCl_3(SiP_3)]$ that is facially coordinated by the SiP_3 tripod ligand [SiP_3 = tris(dimethylphosphinomethyl)-methylsilane] (cf. Figure S5).

Reaction of the symmetrically substituted ligand **13** with $[MoCl_3(THF)_3]$ under the same conditions that were used for **10** led to a product that has an elemental composition closely corresponding to the formula $[MoCl_3(P_2^{Ph}PP_2^{Ph})]$ and an EPR spectrum similar to that of the complex *mer*-$[MoCl_3(dpepp)]$ (cf. Figure S6). Amalgam reduction of this Mo(III) precursor in the presence of N_2 gave a product that showed several IR absorption bands (cf. Figure S8) in a spectral region where the N−N stretch of the mononuclear complex **15** derived from amalgam reduction of $[MoCl_3(P_2^{Me}PP_2^{Ph})]$ (**14**) is observed (see below). We thus conclude that several N_2-containing species have formed and that the symmetrically substituted ligand $P_2^{Ph}PP_2^{Ph}$ is unsuitable for the targeted synthesis of a mononuclear Mo(0)−dinitrogen complex supported in a κ^5 fashion by a pentaPod^{P} ligand.

Synthesis of $[MoN_2(P_2^{Me}PP_2^{Ph})]$. Sodium amalgam reduction of the Mo(III) precursor $[MoCl_3(P_2^{Me}PP_2^{Ph})]$ (**14**) coordinated by the asymmetrically substituted ligand $P_2^{Me}PP_2^{Ph}$ cleanly leads to the mononuclear molybdenum dinitrogen complex $[MoN_2(P_2^{Me}PP_2^{Ph})]$ (**15**) (Scheme 4, bottom). Importantly, both IR (ATR) and Raman spectra show a N−N stretching vibration of 1929 cm^{-1} (Figure 4), which corresponds to the lowest value of the N−N stretch ever found for a molybdenum monodinitrogen complex with a pentaphosphine ligation (cf. ref 48 for a compilation of N−N stretching frequencies). The reduction was also performed with $^{15}N_2$ gas, affording $[Mo^{15}N_2(P_2^{Me}PP_2^{Ph})]$ ([^{15}N]-**15**), which exhibits the N−N stretch at 1868 cm^{-1} (cf. Figure 4, red). The isotopic shift of Δ_{exp} = 61 cm^{-1} closely conforms to the value

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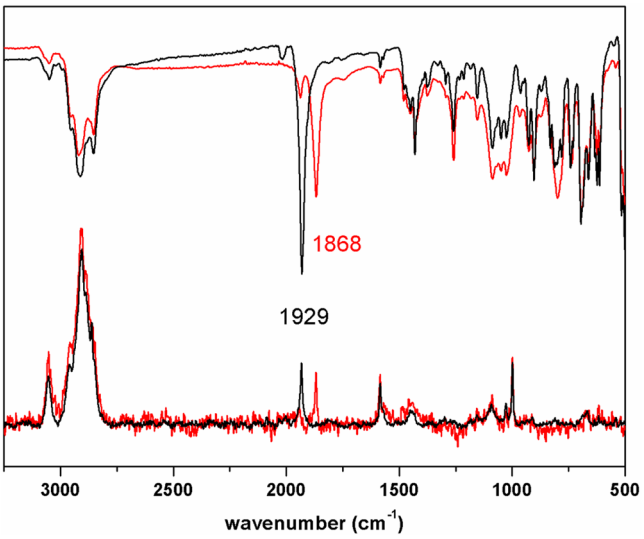

Figure 4. IR (ATR) (top) and Raman (bottom) spectra of $[MoN_2(P_2^{Me}PP_2^{Ph})]$ (**15**, black) and $[Mo^{15}N_2(P_2^{Me}PP_2^{Ph})]$ (red).

predicted for an isolated N−N stretch in the harmonic oscillator approximation (Δ_{theo} = 65 cm^{-1}).

As expected, the $^{31}P\{^1H\}$ NMR spectrum of **15** exhibits an AA′XX′M pattern. All coupling constants could be derived from an analysis of the AA′ and XX′ half-spectra according to the method described in ref 59 and were double-checked by comparison of the resulting simulation and the measured spectrum (Figure 5).

The metal-mediated *trans* coupling constant is ∼83 Hz, while the *cis* coupling constants vary from approximately −19 to 29 Hz. In the $^{31}P\{^1H\}$ NMR spectrum of $[^{15}N]$-**15**, all multiplets exhibit an additional splitting due to the $^{15}N_2$ ligand, which is most significant for the axial phosphine group (cf. Figure S9). The ^{15}N NMR spectrum of $[^{15}N]$-**15** exhibits two resonances at −28.75 and −18.64 ppm, corresponding to N_α and N_β of the coordinated N_2 ligand, respectively (cf. Figure S10). As there are only very few examples for ^{15}N-substituted molybdenum dinitrogen complexes with a P_5 coordination, an assessment of this result regarding the possible influence of the *trans*-phosphine donor on the ^{15}N chemical shift is not yet possible.

Crystal Structure of 15. Compound **15** crystallizes in space group $P2_1/n$ with all atoms located in general positions. In agreement with the information from NMR spectroscopy, the pentaPod^P ligand $P_2^{Me}PP_2^{Ph}$ coordinates to the Mo center in a pentadentate tetrapodal fashion with the N_2 ligand being bound to position 6. The Mo−N_α distance is 2.033(5) Å, and the N_α−N_β distance amounts to 1.099(5) Å, which is in fact slightly longer compared to that of elemental N_2 (1.0975 Å).[60] The Mo−P_{eq} distances in the equatorial plane are all very similar, ranging from 2.4433 to 2.4536 Å, whereas the Mo−P_{ax} bond *trans* to the N_2 ligand is distinctively shorter [2.3868 Å (Table S1)].

For comparison, crystal structure data from other molybdenum dinitrogen complexes supported by a combination of triphos and diphos ligands[46,49−51] are listed in Table 2. These systems exhibit Mo−P_{eq} distances in the range of 2.44−2.46 Å and Mo−P_{ax} distances in the range of 2.42−2.47 Å; in contrast to **15**, no significant shortening of the axial Mo−P bond is observed. In the complex $[MoN_2(SiP_3)(dppm)]$ (**16**), the

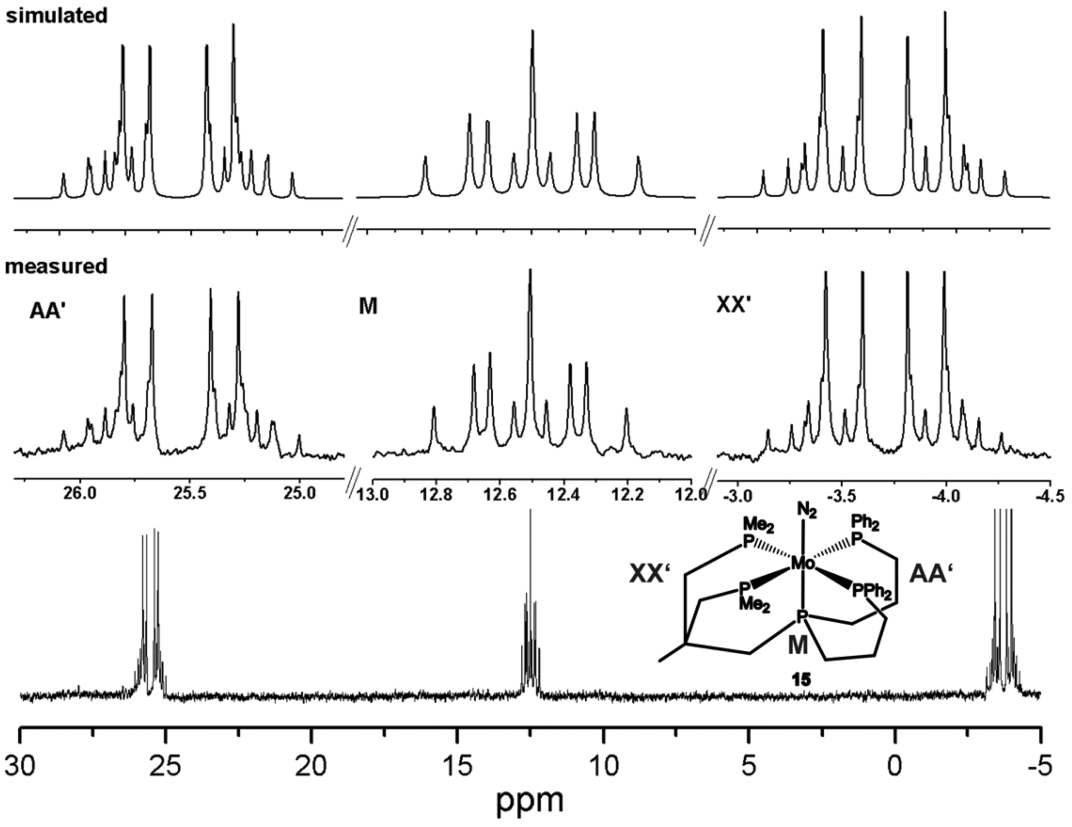

Figure 5. $^{31}P\{^1H\}$ NMR spectrum of **15** in benzene-d_6. The resulting AA′XX′M spectrum (bottom) and enlargements of the measured signals (middle) as well as the simulated spectrum (top) are shown.

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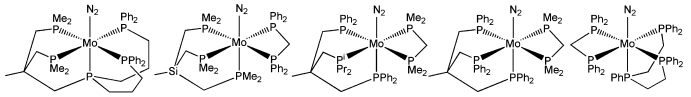
Table 2. Comparison of Selected Geometrical Parameters Retrieved from Single-Crystal Structures of Molybdenum Dinitrogen Complexes with a P_3/Diphos Coordination Sphere and the PentaPod^P Ligand (P_2 = dmpm; P_2' = dppm)



$[MoN_2(P_2^{Me}PP_2^{Ph})]$ $[MoN_2(SiP_3)P_2']$ $[MoN_2(trpd\text{-}1)P_2]$ $[MoN_2(tdppme)P_2]$ $[MoN_2(dpepp)P_2']$

	15	**16**[46]	**17**[50]	**18**[49]	**19**[51]	
$\tilde{\nu}_{NN}$	1929	1952	1965	1980	1979	[cm^{-1}]
N-N	1.099(5)	0.938(4)	1.055(3)	1.069(8)	1.119(8)	[Å]
Mo-N	2.033(5)	2.099(3)	2.047(2)	2.066(6)	2.025(6)	[Å]
Mo-$P_{ax.}$	2.3868(12)	2.4741(7)	2.4439(5)	2.4454(16)	2.4214(18)	[Å]
Mo-$P_{eq.}$ av.	2.4481	2.4392	2.4490	2.4621	2.4599	[Å]
Mo-N-N	174.1(4)	176.8(3)	178.7(8)	176.7(6)	179.2(6)	[°]
P_{ax}-Mo-N	170.93(11)	171.15(6)	174.35(5)	177.37(17)	167.04(15)	[°]
$P_{eq.}$-Mo-$P_{ax.}$ tripod av	85.01	87.21	85.438	85.871	-	[°]
$P_{eq.}$-Mo-$P_{eq.}$ tripod	82.05(5)	90.35(2)	85.158(2)	82.30(5)	-	[°]
$P_{eq.}$-Mo-$P_{ax.}$ trident av	90.92	-	-	-	80.15	[°]
$P_{eq.}$-Mo-$P_{eq.}$ trident	95.19(4)	-	-	-	97.86(6)	[°]
$P_{eq.}$Mo-$P_{eq.}$ diphos	-	68.83(2)	67.444(2)	66.86(6)	68.25(6)	[°]

Mo−P_{ax} bond (2.4741 Å) is even longer than the average value of the Mo−P_{eq} distance {2.4392 Å; SiP_3 = tris-[(dimethylphosphino)methyl]methylsilane}. This complex is closely related to **15** as it is supported by a tripod ligand with three dimethylphosphine end groups and a diphos ligand with two diphenylphosphine donors. With respect to this complex that exhibits Mo−P_{eq} distances comparable to those of **15**, the Mo−P_{ax} bond length is reduced by 0.0873 Å in the $[Mo(N_2)(pentaPod^P)]$ system.

The axial phosphine in **15** thus is strongly bound to the molybdenum center by its central trialkylphosphine donor. Remarkably, this does not cause an elongation of the Mo−N bond in the *trans* position as the Mo−N distance of **15** (2.033 Å) stays in the lower range of Mo−N distances observed for the Mo−N_2 complexes with triphos/diphos ligation [2.025−2.099 Å (cf. Table 2)]. The shortening of the Mo−P_{ax} bond enforced by the topology of the pentaPod^P ligand thus is responsible for the observed increase in the level of activation of **15** with respect to **16** ($\tilde{\nu}_{NN}$ = 1952 cm^{-1}), which has a phosphine donor set similar to that of **15** (see above) but lacks the strapping of the phosphine donor in the axial position to the N_2 ligand.

The Mo−N−N bond angle of 174.15° and the P_{ax}−Mo−N angle (170.93°) show that the N_2 ligand of **15** is tilted from the diphenylphosphine toward the smaller dimethylphosphine groups. This effect is stronger than in related systems having a diphosphine coligand terminated by diphenylphosphine groups in the equatorial plane (cf. Table 2). In these systems, two phenyl rings above and two below the equatorial plane point at the N_2 ligand; i.e., only two phenyl rings point in the direction of the N_2 ligand. By contrast, three of the four phenyl rings are directed toward the dinitrogen ligand in **15** (cf. Figure 6), which is due to the fact that these groups are connected to the axial position of the complex via alkyl bridges. The corresponding rotation of the PPh_2 groups around the equatorial Mo−P axes leads to a better shielding of the N_2 ligand but in the presence of other, sterically less demanding groups also gives rise to the observed tilt.

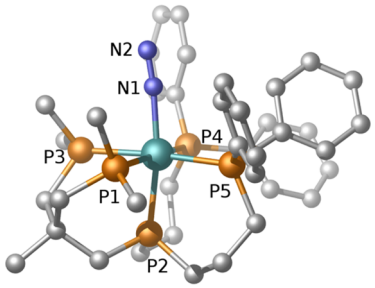


Figure 6. Single-crystal structure of $[MoN_2(P_2^{Me}PP_2^{Ph})]$ (**15**). The hydrogen atoms have been omitted for the sake of clarity. An ORTEP plot of **15** can be found in Figure S9. Selected bond lengths (angstroms) and angles (degrees): Mo(1)−N(1), 2.033(5); N(1)−N(2), 1.099(5); Mo(1)−P(2), 2.3868(12); Mo(1)−P(5), 2.4440(13); Mo(1)−P(1), 2.4518(13); Mo(1)−P(4), 2.4433(14); N(1)−Mo(1)−P(2), 170.93(11); N(2)−N(1)−Mo(1), 174.1(4).

A similar tilt of the N_2 ligand is observed in the complex $[MoN_2(dpepp)(dppm)]$ (**19**) {dpepp = bis-[(diphenylphosphino)ethyl]phenylphosphine},[61−64] where, in contrast to the C_3 bridges present in **15**, the diphenylphosphine end groups of the trident ligand are connected via C_2 bridges to the axial P donor. In this case, the P_{eq}−Mo−P_{ax} angles are reduced to an average value of 80.15°, whereas in **15**, both of these angles are close to 90°. This demonstrates that the C_3 bridges better match the octahedral geometry of **15** than the C_2 bridges in the dpepp complex. Moreover, the equatorial P−Mo−P angles of **15** are closer to 90° than in the systems supported by a triphos/diphos ligand combination. The distortion of octahedral geometry induced by the tripod part of **15**, on the other hand, is comparable to that observed for other tripod-supported systems.

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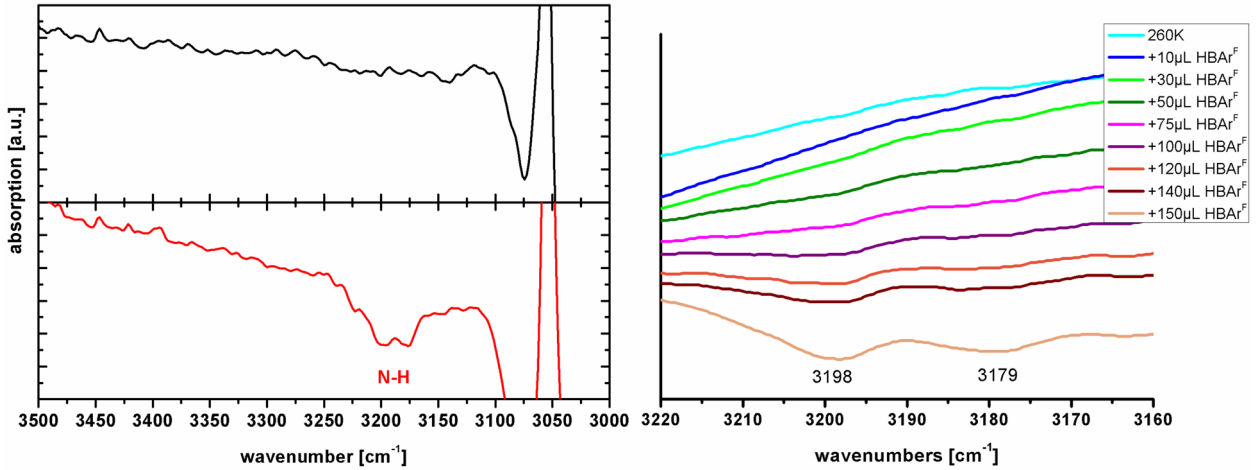

Figure 7. NH region (left) of solution-phase IR spectra of **15** in dichloromethane (top, black) and **15**-NNH_2 generated with $HBAr^F$ (bottom, red) at 300 K. In situ IR spectroscopic monitoring (right) of the addition of a CH_2Cl_2 $HBAr^F$ solution (75 μL = 1 equiv) to **15** at 250 K.

Reactivity of 15 toward Acids. To investigate the first critical steps of the Chatt cycle, namely the two protonations yielding the NNH_2 complex, the reactivity of [^{15}N]-**15** toward different acids has been examined. For these studies, two acids known from protonation reactions[50] or catalytic experiments[23] (see above) have been employed, i.e., trifluoromethanesulfonic acid (HOTf) and $HBAr^F$. ^{15}N substitution thereby allows monitoring of the protonation reactions by ^{15}N NMR spectroscopy. When [^{15}N]-**15** is exposed to $HBAr^F$ in dichloromethane at −20 °C, the corresponding NNH_2 complex is formed. The signals in the ^{31}P{^{1}H} NMR spectrum undergo a high-field shift compared to the signals in that of [^{15}N]-**15**, which is most significant for the *trans*-phosphine [Δ = 45.9 ppm (cf. Figure S11)]. Importantly, this signal still shows the additional splitting derived from coupling with the ^{15}N nuclei of the N_2 ligand. In addition, ^{15}N INEPT as well as ^{15}N−^{1}H HSQC experiments have been performed with $HBAr^F$ in CD_2Cl_2 (cf. Figures S12 and S13). The measured ^{15}N NMR shift of −234 ppm indicates the presence of a NNH_2 complex exhibiting a doubly protonated N_β atom.[65,66] The NNH_2 complex is thermally unstable at 270 K as it starts decaying during the NMR measurements, leading to the formation of paramagnetic species as evidenced by very broad signals and the paramagnetically shifted protons in the ^{1}H NMR spectrum (cf. Figure S15).

Further information regarding the protonation of coordinated dinitrogen can be obtained from vibrational spectroscopy. As attempts to isolate the NNH_2 complex as a solid were unsuccessful, a liquid IR experiment was performed in dichloromethane at room temperature. After addition of $HBAr^F$ to **15**, the N−N stretch disappears and N−H stretching vibrations appear in the expected spectral region, i.e., at ∼3200 cm^{-1} (Figure 7, left).[49] To obtain further information about this reaction, the protonation was additionally conducted at a low temperature (250 K) (Figure 7, right) and monitored in situ by IR spectroscopy. After addition of 2 equiv of $HBAr^F$ (=150 μL), two N−H stretches can clearly be assigned at 3198 and 3179 cm^{-1}. Interestingly, the spectrum after protonation also shows a band at 2008 cm^{-1}, which is a typical value for the N−N stretch in a hydrido-N_2 complex (cf. Figure S14), but further work will be required to verify that this band in fact corresponds to a hydrido-N_2 species similar to the chromium hydrido complex recently reported by Mock et al.[67]

Surprisingly, if HOTf is added to [^{15}N]-**15** in THF-d_8, no ^{15}N coupling can be found, either in the ^{31}P{^{1}H} spectrum or in the ^{15}N NMR spectrum. Mock et al. made the same observation with the chromium dinitrogen complex mentioned above.[67] To determine whether this effect is due to the employed acid (HOTf) or ligand exchange with THF, the protonation was performed with HOTf in the weakly coordinating solvent CD_2Cl_2. Under these conditions, the ^{15}N coupling with the *trans*-phosphine donor was again observable (cf. Figure S11), suggesting that in THF solution ligand exchange has in fact occurred. Nevertheless, the resulting NNH_2 complex with OTf^- as a counterion is also thermally unstable as paramagnetic species are formed during the NMR measurement.

SUMMARY AND CONCLUSION

In the preceding sections, novel pentadentate tetrapodal phosphine ligands and the first molybdenum dinitrogen complex supported by such a ligand, [$MoN_2(P_2^{Me}PP_2^{Ph})$], have been presented. These pentaPod^P ligands derive from a combination of a tripod and a linear trident ligand and were synthesized in two versions, a "symmetrically" substituted one terminated by four diphenylphosphine groups ($P_2^{Ph}PP_2^{Ph}$) and an "asymmetrically" substituted one terminated by two diphenylphosphine and two dimethylphospine groups ($P_2^{Me}PP_2^{Ph}$). Because coordination of $P_2^{Ph}PP_2^{Ph}$ to the Mo(III) precursor [$MoCl_3(THF)_3$] followed by amalgam reduction under N_2 did not lead to well-defined products, we conclude that the differential nucleophilicities of the donor groups present in the $P_2^{Me}PP_2^{Ph}$ ligand are crucial with respect to a targeted synthesis of a Mo dinitrogen complex supported by a pentaPod^P ligand. As the tripod part provides the more nucleophilic and less sterically demanding dimethylphosphine groups compared to the diphenylphosphine moieties in the trident part, we anticipated that the mononuclear complex *fac*(*trpd*)-[$MoCl_3(P_2^{Me}PP_2^{Ph})$] (trpd = tripod) (**14**) is selectively obtained at the Mo(III) stage (Scheme 4 top). This assumption is supported by EPR spectroscopy.

Amalgam reduction of **14** under N_2 leads to coordination of the formerly unbound diphenylphosphine groups to the metal center. This generates the κ^5-pentaphosphine Mo(0) mono-dinitrogen complex [$MoN_2(P_2^{Me}PP_2^{Ph})$] (**15**), which exhibits the lowest N−N stretch ever found for a molybdenum

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dinitrogen complex with phosphine coligands ($\tilde{\nu}_{NN}$ = 1929 cm^{-1}). First, this can be ascribed to the combination of an alkylphosphine donor in the *trans* position with two dimethylphosphine donors in the equatorial plane. However, there is an additional activation of the N_2 ligand in **15** with respect to the complex $[MoN_2(SiP_3)(dppm)]$ ($\tilde{\nu}_{NN}$ = 1952 cm^{-1}), which is also supported by three alkylphosphines in the tripod part and two arylphosphines in the diphos part.[46] Importantly, this activation enhancement can be traced back to the unprecedented ligand architecture of **15**, which enforces a shortening of the Mo−P bond in the *trans* position of the N_2 ligand by strapping this P atom to the four equatorial phosphine donors. In contrast, the Mo−P bond to the *trans*-phosphine donor is elongated in the complex $[Mo(N_2)(SiP_3)(dppm)]$ supported by the tripodal SiP_3 ligand, which also exhibits three alkylphosphine donors. In this complex, the *trans*-phosphine is connected to the ligand framework by only one linkage.

Protonation experiments employing $HBAr^F$ and HOTf as acids indicate that **15** can be transformed to the corresponding $[Mo(NNH_2)(P_2^{Me}PP_2^{Ph})]^{2+}$ complex with retention of pentaphosphine ligation, demonstrating that this system is able to mediate the first reactions of the Chatt cycle. The next steps in our investigation of this system will involve the generation of further intermediates based on the new Mo(pentaPod^P) platform and the investigation of this system regarding the formation of ammonia from N_2.

EXPERIMENTAL SECTION

General Information. All syntheses were conducted under a N_2 atmosphere, and the solvents were dried and freshly distilled under argon prior to use. All other reagents that were used were commercially available. $[MoCl_3(THF)_3]$,[68] $LiPMe_2{\cdot}0.5Et_2O$,[69] $Me(PPh_2)_2Cl$,[55] and ethyldiallylphosphinate[52] were prepared as described in the literature. Elemental analyses were performed using a Euro Vector CHNSO-element analyzer (Euro EA 3000). Samples were burned in sealed tin containers in a stream of oxygen. NMR spectra were recorded with a Bruker AVANCE III HD Pulse Fourier Transform spectrometer operating at frequencies of 400.13 MHz (^{1}H), 161.98 MHz (^{31}P), 100.62 MHz (^{13}C), 376.50 MHz (^{19}F), and 40.56 MHz (^{15}N). Referencing was performed either using the solvent residue signal (5.32 ppm for CD_2Cl_2, 7.16 ppm for C_6D_6, and 1.72 and 3.58 ppm for THF-d_8) or TMS (δ^1H = 0 ppm), 85% H_3PO_4 (δ^{31}P = 0 ppm), and CH_3NO_2 (δ^{15}N = 0 ppm) serving as substitutive standards. FT Raman spectra were recorded with a Bruker IFS 666/CS NIR FT-Raman spectrometer. Infrared spectra were recorded on a Bruker ALPHA FT-IR Spectrum with Platinum ATR setup. Solution-phase IR spectroscopy was performed with a Bruker Vertex 70 spectrometer at a resolution of 2 cm^{-1}. In situ IR spectroscopy was performed with a Nicolet iS10 instrument from Thermo Scientific using a modified Gateway-ATR-IR reaction system from specac. Room-temperature continuous wave X-band EPR spectra were recorded with an EMXplus spectrometer with a PremiumX microwave bridge and an HQ X-band cavity controlled by a computer running the Bruker Xenon Software. Samples were transferred and measured in a 0.3 mm quartz flat cell under an inert atmosphere.

Ethyl Bis[3-(diphenylphosphino)propyl]phosphinate (4). Ethyldiallylphosphinate (**3**, 10.0 g, 53.8 mmol) and diphenylphosphine (25.0 mL) were mixed with one tip of a spatula AIBN and irradiated with a construction site spotlight for 7 days. A tip of a spatula AIBN was added every day. Excess diphenylphosphine was removed in vacuo at 170 °C, and the residue was purified by column chromatography (3:1 ethyl acetate/cyclohexanes with 2% methanol; R_f = 0.5) giving a slightly yellowish viscous oil. Yield: 11.1 g (20.3 mmol, 38%). Anal. Calcd for $C_{32}H_{37}P_3O_2$: C, 70.3; H, 6.8. Found: C, 69.7; H, 6.9. The product still contains ethyl acetate in a 9:1 ratio (product:EE) that could not be removed because of the extreme viscosity of **4**. Therefore, the analysis has been recalculated for nine molecules of product and one molecule of EE. Anal. Calcd for $C_{292}H_{341}O_{20}P_{27}$: C, 70.0; H, 6.9. Found: C, 69.7; H, 6.9. IR (ATR): $\tilde{\nu}$ 3050 (m, CH arom.), 2979, 2933, 2898 (m, CH aliph.), 1584 (m, C−C), 1480, 1453, 1433 (P−C) cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 300 K, TMS): δ 7.40−7.27 (m, 20H, H arom.), 3.90 (quintet, 2H, ^3J = 7.06 Hz, P-O-CH_2-CH_3), 2.10 [m, 4H, P-(CH_2-CH_2-CH_2)$_2$], 1.80−1.59 [m, 8H, P-(CH_2-CH_2-CH_2-PPh_2)$_2$], 1.16 (t, 3H, ^3J = 7.04 Hz, P-O-CH_2-CH_3). ^{31}P{^{1}H} NMR (161.98 MHz, $CDCl_3$, 300 K, H_3PO_4): δ 49.79 (t, $^4J_{PP}$ = 2.0 Hz, 1P, EtO-*P*=O), −16.90 (d, $^4J_{PP}$ = 2.0 Hz, 2P, PPh_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 300 K): δ 138.09 (m, C_q), 132.72 (m, $C_{arom.}$), 128.52 (m, $C_{arom.}$), 60.12 (d, J = 6.88 Hz, OEt), 29.32 [m, P-(CH_2-CH_2-*C*H_2-PPh_2)$_2$], 18.78 [m, P-(CH_2-*C*H_2-CH_2-PPh_2)$_2$], 16.62 (m, CH_3).

prPPHP (5). Ethyl bis[3-(diphenylphosphino)propyl]phosphinate (**4**, 6.30 g, 11.5 mmol) was dissolved in 40 mL of diethyl ether and the mixture slowly added to a suspension of 5.22 g (138 mmol) of lithiumaluminumhydride in 80 mL of diethyl ether under ice cooling. The reaction mixture was stirred for 48 h followed by very slow addition of 10 mL of degassed water, 20 mL of a 15% degassed sodium hydroxide solution, and again 10 mL of degassed water under ice cooling. The white precipitate was filtered off and washed with 2 × 50 mL of diethyl ether. The filtrate was concentrated in vacuo yielding a colorless oil. Yield: 3.99 g (8.12 mmol, 72%). Anal. Calcd for $C_{30}H_{33}P_3$: C, 74.1; H, 6.8. Found: C, 74.0; H, 7.1. IR (ATR): $\tilde{\nu}$ 3050 (m, CH arom.), 2925 (m, CH aliph.), 2267 (m, PH), 1480, 1432 (s, P-aryl, P-alkyl) cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 300 K, TMS): δ 7.58−7.17 (m, 20H, R-PPh_2), 3.56−2.59 (td, 1H, P-*H*), 2.08 [t, 4H, PH-(CH_2-CH_2-CH_2-PPh_2)$_2$], 1.81−1.39 [m, 8H, 2 PH-(CH_2-*C*H_2-*C*H_2-PPh_2)$_2$]. ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6, H_3PO_4, 300 K): δ −16.93 (s, 2P, PPh_2), −72.96 (s, 1P, *P*H). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 300 K): δ 138.68 (d, J_{C-P} = 12.97 Hz, P-*C*-CH-CH-CH), 132.72 (d, J_{C-P} = 18.45 Hz, P-C-CH-CH-CH), 128.56 (s, P-C-CH-CH-*C*H), 128.44 (d, J_{C-P} = 6.64 Hz, P-C-CH-*C*H-CH), 29.38 [dd, J_{C-P} = 8.27 Hz, J_{C-P} = 12.15 Hz, PH-(CH_2-CH_2-CH_2-PPh_2)$_2$], 24.69 [dd, J_{C-P} = 9.92 Hz, J_{C-P} = 17.33 Hz, PH-(CH_2-CH_2-CH_2-PPh_2)$_2$], 21.76 [dd, J_{C-P} = 10.27 Hz, J_{C-P} = 12.98 Hz, PH-(CH_2-CH_2-CH_2-PPh_2)$_2$].

ClClOH (7). A solution of 10.1 g (59.4 mmol) of 3,3′-dichloropivalic acid (**6**) in 60 mL of diethyl ether was added at 0 °C to a suspension of 4.06 g (107 mmol) of lithiumaluminumhydride in 60 mL of diethyl ether. The reaction mixture was stirred for 2 h at room temperature and then poured carefully into 500 mL of 0.5 M HCl. The layers were separated, and the organic layer was extracted with 3 × 50 mL of diethyl ether and washed with 3 × 50 mL of water. The combined organic layers were dried over magnesium sulfate, and the solvent was removed in vacuo. Purification was achieved by distillation (10^{-1} bar, 58 °C), yielding a colorless liquid. Yield: 7.78 g (49.5 mmol, 83%). Anal. Calcd for $C_5H_{10}Cl_2O$: C, 38.2; H, 6.4. Found: C, 37.9; H, 6.3. IR (ATR): $\tilde{\nu}$ 3371 (OH), 2958, 2933, 2875 (CH) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K, TMS): δ 3.49 (m, 4H, CH_2Cl), 3.48 (d, 2H, ^3J = 5.4 Hz, CH_2OH), 1.83 (t, 1H, ^3J = 5.5 Hz, CH_2O*H*), 0.99 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 300 K): δ 65.28 (s, CH_2OH), 48.65 (s, CH_2Cl), 42.10 (s, quart. C), 18.15 (s, CH_3).

ClClOTf (8). To a solution of 5.00 g (31.8 mmol) of 3-chloro-2-(chloromethyl)-2-methylpropan-1-ol (**7**) in 300 mL of dichloromethane was added 15 mL (186 mmol) of pyridine. The reaction mixture was cooled to −15 °C, and a solution of 10.0 g (35.4 mmol) of trifluoromethanesulfonic anhydride in 30 mL of dichloromethane was added dropwise. After being stirred for 4 h at −15 °C, the reaction mixture was poured into 600 mL of an ice-cooled saturated sodium bicarbonate solution. The aqueous layer was extracted three times with 100 mL of dichloromethane. The combined organic layers were dried over magnesium sulfate, and the solvent was removed in vacuo. The product was purified by distillation (10^{-2} mbar, 58 °C). Yield: 4.20 g (14.5 mmol, 46%). Anal. Calcd for $C_6H_9Cl_2F_3O_3S$: C, 24.9; H, 3.1. Found: C, 25.0; H, 3.0. IR: $\tilde{\nu}$ 2978, 2963 (m, CH-valence aliph.), 1466 (CH), 1413, 1245, 1203, 1142 (s, S=O) cm^{-1}. ^{1}H NMR (400 MHz, CD_2Cl_2, 300 K, TMS): δ 4.43 (d, ^4J = 0.4 Hz, 2H, CH_2OTf), 3.50 (m,

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4H, CH_2Cl), 1.14 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 300 K): δ 136.37 (s, CF_3), 77.63 (s, CH_2OTf), 47.06 (s, CH_2Cl), 41.62 (s, quart. C), 18.06 (s, CH_3).^{19}F NMR (376.50 Hz, CD_2Cl_2, $CFCl_3$, 300 K): δ −74.74 (s, 3F).

ClClprPPHP (9). To a solution of 2.00 g (4.11 mmol) of prPPHP (**5**) in 20 mL of THF was added 1.64 mL (4.11 mmol) of *n*-butyllithium (2.5 M in hexanes) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and slowly added at −78 °C to a solution of 1.19 g (4.11 mmol) of **8** in 20 mL of THF. The cold bath was removed and the reaction mixture stirred for 90 min. Twenty milliliters of degassed water and 20 mL of diethyl ether were added, and the mixture was stirred for an additional 30 min. The aqueous layer was removed with a syringe, and the solvent was removed in vacuo. The residue was resolved in toluene and filtered over silica gel to give the product as a colorless viscous oil. Yield: 2.23 g (3.56 mmol, 87%). Anal. Calcd for $C_{35}H_{41}Cl_2P_3$: C, 67.2; H, 6.6. Found: C, 67.2; H, 6.9. IR (ATR): $\tilde{\nu}$ 3051 (m, CH arom.), 2930, 2891 (m, CH aliph.), 1586 (w, CC), 1481, 1433 (m, PC) cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, 300 K, TMS): δ 7.34−7.20 (m, 20H, H arom.), 3.41 (m, 4H, CH_2-Cl), 2.02 (m, 4H, CH_2-$P_{centr.}$), 1.50−1.35 (m, 8H, 2 × PPh_2-CH_2-CH_2), 1.32 (d, $^1J_{PH}$ = 4.24 Hz, 2H, CH_2-P tripod), 0.93 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, H_3PO_4, 300 K): δ −16.79 (s, 2P, PPh_2), −42.46 (s, 1P, $P_{centr.}$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 300 K): δ 139.03 (dd, C_q arom.), 132.77 (dd, C_{ortho}), 128.56 (m, $C_{meta,para}$), 51.32 (d, $^3J_{CP}$ = 10.6 Hz), 40.23 (d, $^2J_{CP}$ = 13.9 Hz, C_q tripod), 34.37 (d, $^1J_{CP}$ = 19.0 Hz, CH_2-$P_{centr.}$ tripod), 29.67 (m, P-$CH_2CH_2CH_2PPh_2$), 22.41 (dd, $^2J_{CP}$ = 14.2, 17.2 Hz, P-$CH_2CH_2CH_2PPh_2$) 21.73 (d, $^3J_{CP}$ = 10.0 Hz, CH_3).

$P_2^{Me}PP_2^{Ph}$ (10). A portion of 520 mg (4.74 mmol) of $LiPMe_2 \cdot 0.5Et_2O$ was dissolved in 20 mL of THF at −78 °C, and 1.90 mL (4.74 mmol) of *n*-butyllithium (2.5 M in hexanes) was added. After the mixture had been stirred for 5 min, a solution of 1.20 g (1.92 mmol) of ClClprPPHP (**9**) in 15 mL of THF was added and the reaction mixture was stirred for 15 min at −78 °C. Afterward, cooling was stopped, and the mixture was stirred for an additional 90 min followed by the addition of 10 mL of degassed water and 10 mL of diethyl ether. After the mixture had been stirred for 1 h, the aqueous layer was removed with a syringe and the solvent removed in vacuo. The residue was resolved in *n*-pentane and filtered over Celite, yielding a colorless viscous oil. Yield: 1.40 g (1.83 mmol, 95%) Anal. Calcd for $C_{39}H_{53}P_5$: C, 69.2; H, 7.9. Found: C, 69.4; H, 8.3. IR (ATR): $\tilde{\nu}$ 3068, 3050, 3000 (m, CH arom.), 2950, 2925, 2892, 2811 (m, CH aliph.), 1584 (w, CC), 1480, 1432 (s, PC) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 300 K, TMS): δ 7.43−7.27 (m, 20H, H arom.), 2.10 (m, 4H, $CH_2P_{centr.}$), 1.49−1.37 [m, 14H, CH_2P(tripod), 2 × $CH_2CH_2PPh_2$], 0.89−0.86 [m, 15H, 2 × P(CH_3)$_2$, CH_3 backbone]. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, H_3PO_4, 300 K): δ −16.43 (m, 2P, PPh_2), −41.76 (m, 1P, $P_{centr.}$), −60.83 (m, 2P, PMe_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): δ 139.59 (m, ArC-1), 133.18 (ddd, J = 18.53, 7.10, 1.8 Hz, ArC-2,6), 128.98 (d, J = 4.61 Hz, ArC-4), 128.90 (d, J = 6.54 Hz, ArC-3,5), 48.05 {ddd, $^1J_{CP}$ = 14.9 Hz, $^3J_{CP}$ = 8.5 Hz, $^3J_{CP}$ = 8.4 Hz, C-[CH_2-P(CH_3)$_2$]$_2$}, 42.67 (dt, ^1J = 16.74 Hz, ^2J = 8.54 Hz, C-CH2-P), 38.11 (td, $^2J_{CP}$ = 13.4 Hz, $^2J_{CP}$ = 11.8 Hz, C_q tripod), 30.56 [dd, $^1J_{CP}$ = 12.68 Hz, $^3J_{CP}$ = 12.71 Hz, 2C, P-(CH_2-CH_2-CH_2-PPh_2)$_2$], 30.13 [dd, $^1J_{CP}$ = 12.14 Hz, $^3J_{CP}$ = 12.12 Hz, P-(CH_2-CH_2-CH_2-PPh_2)$_2$], 28.89 (td, $^3J_{CP}$ = 8.71 Hz, $^3J_{CP}$ = 8.69 Hz, CH3), 23.03 [dd, $^2J_{CP}$ = 17.0 Hz, $^2J_{CP}$ = 14.2 Hz, P-(CH_2-CH_2-CH_2-PPh_2)$_2$], 16.40 [m, 2 × P(CH_3)$_2$].

$P_2^{Ph}PP_2^{Ph}$ (13). To a solution of 290 mg (0.59 mmol) of prPPHP (**5**) in 15 mL of THF was added 0.38 mL (0.94 mL) of *n*-butyllithium (2.5 M in hexanes) under ice cooling. The resulting orange solution was stirred for 60 min at room temperature. The reaction mixture was slowly added at 0 °C to a solution of 375 mg (0.79 mmol) of methyl(2-methyldiphenylphosphino)-1-chloro-3-diphenylphosphino-propane (**12**) in 20 mL of THF and the mixture stirred overnight while being warmed to room temperature. After the addition of 10 mL of degassed water, the solution was stirred for 30 min and 10 mL of diethyl ether was added. The water was removed with a syringe and the organic phase dried in vacuo. The product was purified by column chromatography (3:1 toluene/cyclohexanes; R_f = 0.05), yielding a colorless highly viscous oil. Yield: 250 mg (0.27 mmol, 34%). Anal. Calcd for $C_{58}H_{59}P_5$: C, 76.6; H, 6.7. Found: C, 77.0; H, 7.1. IR (ATR): $\tilde{\nu}$ 3067, 3049 (m, CH arom.), 2922, 2801 (m, CH aliph.), 1570 (m, CC), 1479, 1451, 1432 (s, PC) cm^{-1}. ^1H NMR (400 MHz, CD_2Cl_2, 300 K, TMS): δ 7.47−7.21 (m, 40H, arom.), 2.41 (dd, 4H, $^1J_{HH}$ = 14.3 Hz, $^2J_{PH}$ = 3.1 Hz, CH_2PPh_2 trpd), 2.03 (m, 4H, CH_2P_{centr} trident), 1.62 (d, 2H, $^2J_{PH}$ = 4.5 Hz, CH_2P_{centr} trpd), 1.49−1.33 (m, 8H, 2 × CH_2-CH_2-PPh_2), 0.91 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, H_3PO_4, 300 K): δ −17.24 (s, 2P, PPh_2 trident), −25.91 (d, 2P, $^4J_{P-P}$ = 2.5 Hz, PPh_2 tripod), −43.00 (m, 1P, central P). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 300 K): δ 140.03−140.11 (m, C_q arom.), 139.29−139.06 (m, C_q arom.), 133.23−132.61 (m, C PPh_2 meta), 128.79−128.26 (m, PPh_2 ortho, para), 42.93−42.43 (m, CH_2PPh_2 tripod), 42.09−41.86 (m, $CH_2P_{centr.}$), 38.36 (m, C_q tripod), 29.98−29.37 (m, 2 × CH_2-CH_2-CH_2-PPh_2), 29.06 (m, CH_3), 22.50 (m, 2 × CH_2-CH_2-CH_2-PPh_2).

$MoCl_3(P_2^{Me}PP_2^{Ph})$ (14). A mixture of 1.30 g (1.92 mmol) of $P_2^{Me}PP_2^{Ph}$ (**10**) and 887 mg (1.92 mmol) of [$MoCl_3(THF)_3$] was dissolved in 20 mL of THF and 10 mL of dichloromethane and stirred overnight. The solution was concentrated in vacuo, and 20 mL of diethyl ether was added. The yellow precipitate was filtered off and washed with 5 mL of THF, diethyl ether, and *n*-hexane. Yield: 1.43 g (1.63 mmol, 85%). Anal. Calcd for $C_{39}H_{53}P_5MoCl_3$: C, 53.3; H, 6.1. Found: C, 53.0; H, 6.0. IR (ATR): $\tilde{\nu}$ 3052 (m, CH arom.), 2909 (m, CH aliph.), 1587 (w, CC), 1484, 1434 (s, PC) cm^{-1}.

$MoN_2(P_2^{Me}PP_2^{Ph})$ (15). A portion of 300 mg (0.34 mmol) of [$MoCl_3(P_2^{Me}PP_2^{Ph})$] (**14**) was dissolved in 20 mL of THF and the mixture added to sodium amalgam prepared from 2 mL of Hg and 200 mg of sodium. The reaction mixture was stirred overnight under a nitrogen atmosphere. Stirring was stopped, and the remaining mercury was collected in a neck of the flask. The red solution was carefully filtered over a frit to avoid any residue of the mercury, and the solvent of the filtrate was removed in vacuo. The residue was resolved in diethyl ether and filtered over neutral alumina. The bright yellow solution was concentrated to dryness in vacuo, yielding an orange solid. Single crystals could be grown from benzene-d_6 by slow evaporation. Yield: 118 mg (0.147 mmol, 43%). Anal. Calcd for $C_{39}H_{53}P_5MoN_2$: C, 58.5; H, 6.7; N, 3.5. Found: C, 58.6; H, 7.0; N, 1.3. The nitrogen value is too low because of the thermal instability of the product. IR (ATR): $\tilde{\nu}$ 3049 (m, CH arom.), 2955, 2912, 2852 (m, CH aliph.), 1929 (s, NN), 1584 (w, CC), 1480, 1451, 1430 (m, PC) cm^{-1}. Raman: $\tilde{\nu}_{NN}$ 1930 cm^{-1}. $^{31}P\{^1H\}$ NMR (161. 98 MHz, C_6D_6, H_3PO_4, 300 K): δ 25.52 (dddd, J = 83.4, 14.7, −19.8, 20.4 Hz, 2P, PPh_2), 12.40 (tt, J = 20.4, 28.7 Hz, 1P, $P_{centr.}$), −3.69 (dddd, J = 83.4, 27.4, −19.8, 28.7 Hz, 2P, PMe_2). A sample of [^{15}N]-**15** was prepared following an analogous synthetic procedure using $^{15}N_2$ instead of $^{14}N_2$. IR (ATR): $\tilde{\nu}$ 3050 (m, CH arom.), 2957, 2925, 2852 (m, CH aliph.), 1868 (s, NN), 1585 (w, CC), 1480, 1453, 1432 (m, PC) cm^{-1}. Raman: $\tilde{\nu}_{NN}$ 1868 cm^{-1}. $^{31}P\{^1H\}$ NMR (161.98 MHz, C_6D_6, H_3PO_4, 300 K): δ 25.79 (m, 2P, PPh_2), 12.74 (m, 1P, P_{ax}), −3.48 (m, 2P, PMe_2). $^{15}N\{^1H\}$ NMR (40.56 MHz, C_6D_6, CH_3NO_2, 300 K): δ −18.6 (d, 1N, $^1J_{NN}$ = 6.9 Hz, N_β), −28.8 (m, 1N, N_α).

[$Mo^{15}NNH_2(P_2^{Me}PP_2^{Ph})$]$X_2$ (X = BAr^F or OTf) ($^{15}NNH_2$-15). Protonation was performed as a NMR experiment. In a typical run, 10 mg of [^{15}N]-**15** was dissolved in 0.3 mL of the NMR solvent in a glass vial and cooled to −20 °C. In another vial, the acid was dissolved in 0.2 mL of the NMR solvent and also cooled to −20 °C. The acid solution was added quickly to the complex solution, resulting in a change in color. The reaction mixture was transferred to a NMR tube and measured immediately at 270 K. Data for [$Mo^{15}NNH_2(P_2^{Me}PP_2^{Ph})$]($BAr^F$)$_2$. IR ($CH_2Cl_2$, 300 K): $\tilde{\nu}_{NH}$ 3223, 3177 cm^{-1}. $\tilde{\nu}_{NN}$ is masked by other vibrations. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, H_3PO_4, 270 K): δ 8.95 (m, 2P, PPh_2), −15.24 (m, 2P, PMe_2), −33.09 (m, 1P, P_{axial}). ^{15}N INEPT (40.56 MHz, CD_2Cl_2, CH_3NO_2, 300 K): δ −233.67 (m, 1N, -$N_\beta H_2$).

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■ ASSOCIATED CONTENT

Supporting Information

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Synthetic attempts regarding the coordination of $P_2^{Ph}PP_2^{Ph}$, EPR spectra, spectroscopic details for $[Mo^{15}N(P_2^{Ph}PP_2^{Ph})]$ and the protonation experiments, and an ORTEP plot (PDF)

Selected crystal structure data of **15** (CIF)

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