

Stereoselective Synthesis of the First Chatt-Type Bis(dinitrogen)-Molybdenum(0) Complex with a Tetraphosphane Ligand

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The first Chatt-type Mo⁰ dinitrogen complex with a tetraphosphane ligand has been prepared and characterized by NMR as well as infrared and Raman spectroscopy. Importantly, the employed reaction route allows the stereospecific synthesis of this complex as *trans*-[Mo(N₂)₂(*meso*-prP₄)] (prP₄ = a tetraphos ligand with a central propylene bridge). The stereoselectivity in the reaction course is induced by the oxido-iodido-molybdenum(IV) precursor [Mo(O)I(prP₄)]⁺ which directs both phenyl groups of the bridging P atoms of prP₄ into a *meso* configuration. The paper establishes a general

strategy to synthesize mononuclear Mo⁰ dinitrogen and related molybdenum complexes with multidentate phosphane ligands which has not been possible to date. Moreover, the obtained molybdenum tetraphos N₂ complex should exhibit a higher thermodynamic stability in the reactions of the Chatt cycle of synthetic nitrogen fixation than the conventional bis(diphos) complexes, due to the linkage of the two diphosphane units by an alkyl bridge.

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Introduction

One of the great challenges of bioinorganic and organometallic chemistry is a biomimetic process of ammonia synthesis under ambient conditions.^[1] A major breakthrough in this respect has been the synthesis and characterization of the Mo^{III} triamidoamine complex [Mo(HIPTN₃N)] by Schrock et al.^[2] Employing decamethylchromocene as a reductant and a special lutidinium salt as acid, this complex allowed the catalytic synthesis of NH₃ from N₂ in 6 turnovers with an overall yield of 65%. In a pioneering study, Pickett and Talarmin had already achieved a cyclic conversion of N₂ to NH₃ on the basis of a phosphane-tungsten complex many years before, however, only in three cycles and with much smaller yield.^[3] Nevertheless, the underlying type of dinitrogen complexes provided the first rational and complete reactive Scheme for synthetic nitrogen fixation, the Chatt cycle,^[4] and the realization of a truly catalytic ammonia synthesis on the basis of phosphane-Mo/W complexes still represents a significant goal.

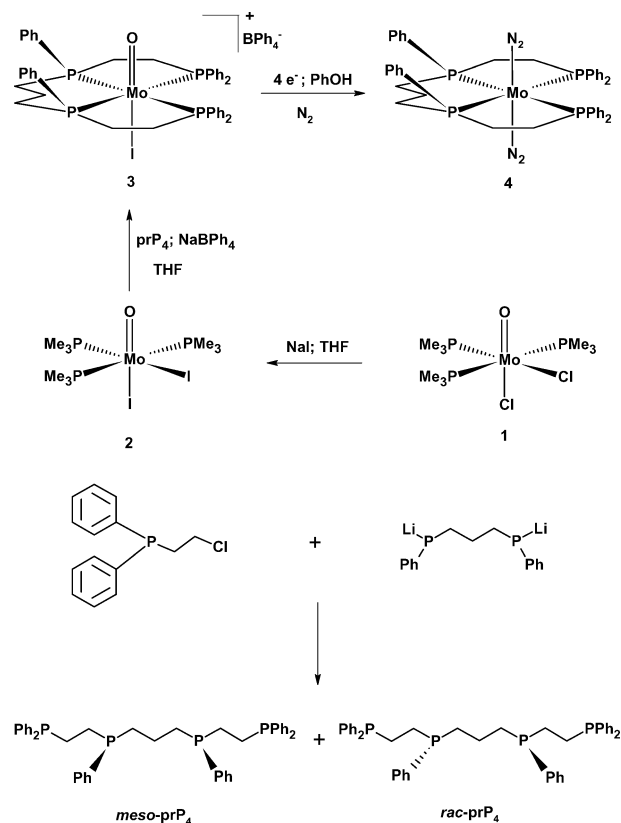
Our group has been involved in the spectroscopic characterization of the intermediates of the Chatt cycle and the investigation of their reactivities for a number of years.^[5]

Recently we have performed a complete quantum-chemical investigation of the Chatt cycle and found a close mechanistic relationship to the Schrock cycle which has been theoretically treated before.^[6,7] It is evident from this investigation and experimental studies,^[3–5] that the basic problem of the classic Chatt-type N₂-Mo/W complexes with diphosphane coligands is the presence of two coordination sites for external substrates which leads to the bonding of Lewis bases deriving from the added acid or the solvent in the course of the reactive cycle. These ligands either have to be de-coordinated from the metal center in order to rebind N₂ or even lead to complete deactivation of the catalyst. It is therefore desirable to employ a polydentate ligand which, in addition to a stable equatorial phosphane ligation, also occupies the *trans*-position of the dinitrogen ligand by a neutral donor atom (P or N). The coordination of more than tridentate phosphane ligands to mononuclear Mo⁰ centers, however, has not been achieved to date.^[8]

Herein the stereospecific synthesis of the first bis(dinitrogen)molybdenum(0) complex with a tetraphosphane ligand, [Mo(N₂)₂(prP₄)] (**4**; prP₄ = 1,1,4,8,11,11-hexaphenyl-1,4,8,11-tetraphosphaundecane), is presented. Compound **4** corresponds to the classic Chatt-type N₂ complex [Mo(N₂)₂(dppe)₂] {dppe = 1,2-bis(diphenylphosphanyl)ethane} but has a propylene bridge between the two 1,2-phosphanyl-ethane moieties (Scheme 1, top). The intermediates and the product of the synthesis are characterized by ³¹P NMR, vibrational and UV/Vis spectroscopy as well as X-ray structure analysis.

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Scheme 1.

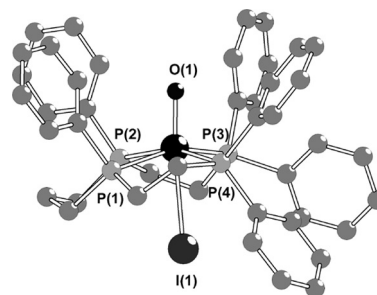
Results and Discussion

The synthesis of the tetraphos ligand is outlined in Scheme 1, bottom.^[9] In a first step (2-chloroethyl)diphenylphosphane is prepared by reaction of lithium diphenylphosphide with dichloroethane. This precursor is reacted with 1,3-dilithium diphenylphosphide obtained from 1,3-bis(diphenylphosphanyl)propane (dppp) by treatment with Li in THF to give a mixture of *meso*- and *rac*-prP₄. Note that the *meso* isomer has the two phenyl rings of the central phosphorus atoms oriented to the same side whereas in the *rac* isomer these two phenyl rings are located on the opposite sides of the ligand.^[10] Correspondingly the ³¹P NMR spectrum of the reaction product exhibits two (AX)₂ schemes with equal chemical shifts for the terminal but slightly different chemical shifts for the central phosphorus atoms (see Supporting Information). The *J*_{AX} coupling constants for both isomers are 28.5 Hz. No coupling between the central P atoms is observed, indicating that spin–spin interaction via the propylene bridge of the prP₄ ligand is negligible.

The crucial synthetic hurdle associated with the coordination of a tetraphos ligand to a low-valent, mononuclear molybdenum complex can be cleared by choosing the proper precursor. Our approach of synthesizing the Mo⁰–N₂ prP₄ complex **4** builds upon the ligand exchange chemistry of oxido-halide molybdenum(IV) complexes with PMe₃ coligands established by Carmona, Galindo et al.^[11] As demonstrated by these authors the neutral Mo^{IV} complex

mer-cis [Mo(O)Cl₂(PMe₃)₃] (**1**) is able to exchange two PMe₃ groups and one chloro ligand for two dmpe ligands, giving *trans*-[Mo(O)Cl(dmpe)₂]Cl [dmpe = 1,2-bis(dimethylphosphanyl)ethane]. The ³¹P NMR spectrum of **1** exhibits an AX₂ coupling Scheme with a *J*_{AX} coupling constant of –21.6 Hz, and its infrared and Raman spectra show the Mo=O stretch vibration at 952/951 cm^{–1}. In contrast to the reaction with dmpe, however, treatment of **1** with the sterically more demanding ligand dppe did not lead to a single product, but to a mixture of the starting complex and the di- and mono-substituted derivatives [Mo(O)Cl(dppe)₂]⁺ and [Mo(O)Cl₂(PMe₃)(dppe)], respectively. Due to the equivalence of all P-donors, the ³¹P-NMR spectrum of di-substituted complex shows one line. The spectrum of the monosubstituted complex corresponds to an AMX pattern with *J*_{AX} (*cis*) and *J*_{MX} (*trans*) coupling constants of –20.5 and +203.2 Hz, respectively. *J*_{AM} is vanishingly small as the A and M atoms are coupled via the metal and the ethylene bridge of dppe with coupling constants of equal magnitude, but opposite signs.^[12] Reaction of **1** with the tetradentate ligand prP₄, finally, did not lead to an isolable product at all.

In order to make the Mo^{IV} oxido precursor more reactive towards the coordination of prP₄, the chloro ligands of **1** were subsequently exchanged for iodides, leading to the complex *mer-cis* [Mo(O)I₂(PMe₃)₃] (**2**) which had been prepared and characterized by Poli et al. recently (Scheme 1, center).^[13] Like its chloro congener, **2** exhibits an AX₂ coupling Scheme in the ³¹P NMR spectrum, this time with a *J*_{AX} coupling constant of –22.7 Hz. In the infrared spectrum the Mo=O stretch is found at 948 cm^{–1}. In contrast to its chloro analog **1**, complex **2** reacts cleanly with the tetradentate prP₄ ligand in thf, affording crystalline [Mo(O)I(prP₄)]BPh₄ (**3**) after addition of NaBPh₄ to the reaction mixture. Importantly, ³¹P NMR spectroscopy shows the presence of only one isomer, indicating that the reaction product either contains the *meso* or the *rac* ligand but not a mixture of both. Moreover, single crystals could be grown, allowing to perform a X-ray structure determination of **3**.^[14] The structure of the complex cation shown in Figure 1 reveals that the reaction product contains the *meso* and not the *rac* ligand. These findings can be attributed to the steric influence of the iodo ligand which prevents formation of the *rac* complex in which one of the phenyl substituents on


 Figure 1. Crystal structure of the complex cation of [Mo(O)I(prP₄)] BPh₄ (**3**).

the central phosphorus atoms would point to this ligand (see below). The Mo–P distances are within the usual range (2.50 to 2.57 Å); the Mo=O and Mo–I bond lengths are 1.69 and 2.95 Å, respectively.^[15] The Mo⁰ central atom appears to tightly fit into the cavity provided by the tetraphospho ligand. A small steric strain can be inferred from the bending of the terminal P atoms out of the equatorial plane. This causes an increase of the P–Mo–P angle between the terminal P atoms to 108° whereas the angle between the central P atoms is about 90°. The angles between the central and the terminal P atoms are ca. 80°, as known from Mo⁰ complexes with dppe or depe ligands.^[16]

The ³¹P NMR spectrum of complex **3** is shown in Figure 2, top. As mentioned above, the spectrum corresponds to one isomer which, on the basis of the X-ray structure information, contains the *meso*-ligand. In contrast to the free prP₄ ligand which shows no coupling between the cen-

tral phosphorus atoms (see Supporting Information), the spectrum now exhibits an AA'XX' pattern (A = central, X = terminal P). The *trans* J_{AX} coupling constant is 110.4 Hz. The central and the terminal phosphorus atoms couple among each other with constants J_{AA} and J_{XX} of –18.4 and –28.2 Hz. We assume that the *cis*-interaction with the larger absolute value (28.2 Hz) corresponds to the interaction between the central P atoms where the bonding angle is almost exactly 90°; about the same coupling constant is observed between the central P atoms of the ligand dppp [1,2-bis(diphenylphosphanyl)propane] in the complex [Mo(CO)₄-(dppp)].^[17] For the terminal P atoms where the bonding angle is increased to 108° the absolute value of the coupling constant is decreased and thus corresponds to the smaller coupling constant, –18.4 Hz. The terminal and bridging P atoms, finally, are coupled via the metal and the ethylene bridge whence the resulting coupling constant is small (see

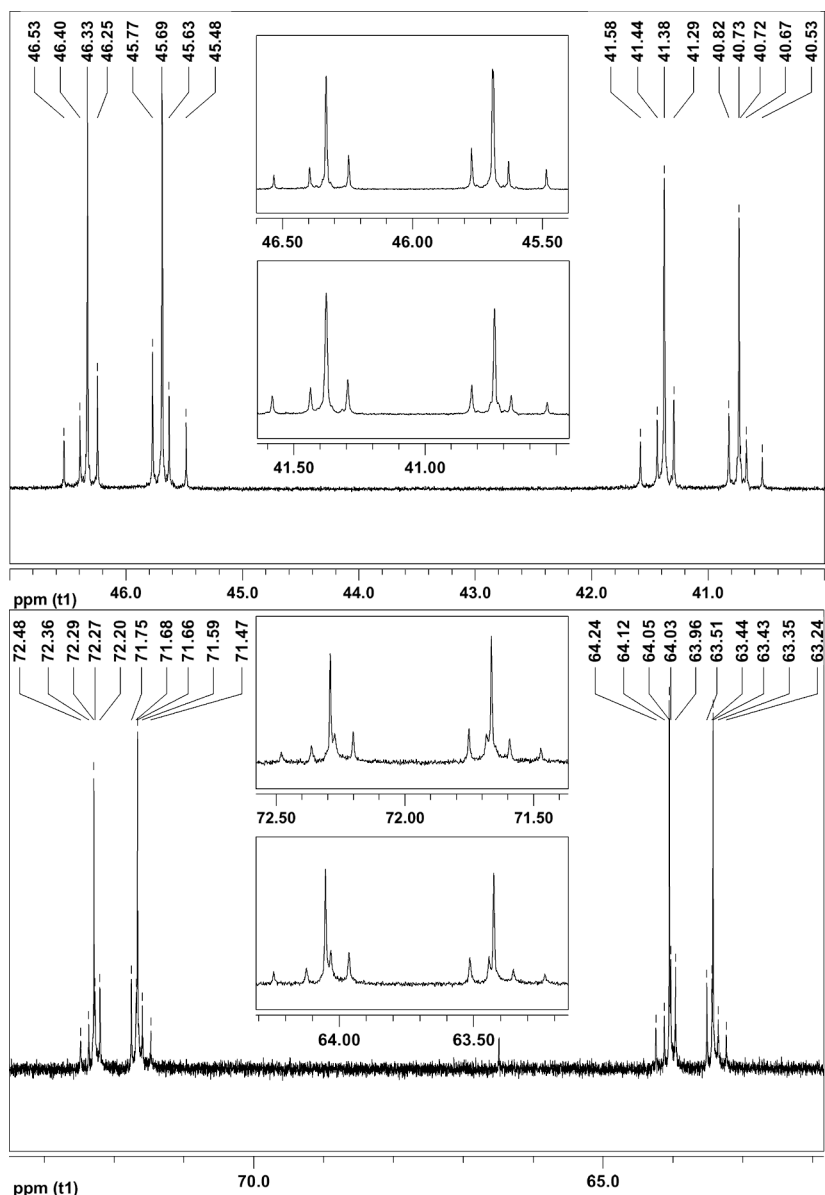


Figure 2. ³¹P{¹H}NMR spectra of *trans*-[Mo(O)I(*meso*-prP₄)]BPh₄ (**3**; top) and *trans*-[Mo(N₂)₂(*meso*-prP₄)] (**4**; bottom).

above; $|J_{AX}| = 4.9$ Hz). The infrared and Raman spectra of **3**, finally, show the MoO stretch at 954 and 958 cm^{-1} , respectively (see Supporting Information).

The hypothesis that the orientation of the phenyl substituents on the bridging phosphane groups of the prP_4 ligand is decisively influenced by the iodo ligand also supported by the reactivity of the complex $[\text{Mo}(\text{O})\text{I}_2(\text{PMe}_3)_3]$ (**2**) towards diphosphanes. In particular, **2** does not react with dppe, in contrast to the corresponding oxido-chlorido complex *mercis* $[\text{Mo}(\text{O})\text{Cl}_2(\text{PMe}_3)_3]$ (**1**) where reaction with dppe was hindered (as evident from the resulting mixture of non-, mono- and disubstituted products), but did occur. This indicates that coordination of a bis(phenylphosphanyl)ethane moiety with two phenyl groups pointing towards the halide ligand is even more disfavoured in the oxido-iodido complex **2** than in its chloro congener **1**. On the other hand, Bendix et al. found that a Mo^{IV} oxido-iodido complex with two dppe ligands, $[\text{Mo}(\text{O})\text{I}(\text{dppe})_2]^+$, can be prepared by reaction of the *trans*-dioxido complex $[\text{Mo}(\text{O})_2(\text{dppe})_2]$ with HI.^[18] The observed steric influence of the iodo ligand thus is a *kinetic* and not a thermodynamic effect, which also explains the observation that the prP_4 complex **3** tolerates the presence of four phenyl substituents at the *terminal* positions of the tetraphosphane ligand. On the basis of these observations, the coordination of the prP_4 ligand to the Mo oxido-iodido complex **3** may proceed in the following way: first, one of the (more nucleophilic) central phosphorus atoms binds – probably after exchange of the PMe_3 ligand in *trans*-position – to the equatorial iodo ligand. Then, in a second step, the other bridging phosphorus atom is coordinated in a stereoselective fashion with formation of the central *meso* unit of the ligand. Finally, the terminal phosphane groups are bound in the equatorial plane, which completes the metalation of prP_4 .

The conversion of the $[\text{Mo}(\text{O})\text{I}(\text{prP}_4)]^+$ precursor **3** to the corresponding dinitrogen complex was achieved by electrochemical reduction in the presence of dinitrogen and phenol, following the method of Pickett et al. (Scheme 1, top).^[19] The latter reagent was added as a weak acid to induce protonation of the oxido group and subsequent elimination as water. Four-electron reduction was effected by electrolysis in thf using a mercury pool electrode. The blue solution of the oxido-molybdenum complex thereby turned yellow, indicating the formation of the dinitrogen complex. The ^{31}P NMR spectrum of the yellow-orange reaction product, $[\text{Mo}(\text{N}_2)_2(\text{prP}_4)]$ (**4**), is shown in Figure 2, bottom. In analogy with complex **3**, it exhibits a single AA'XX' pattern, indicating the presence of only one isomer and a *trans*-geometry of the complex. On the basis of the structural information obtained on the precursor **3**, the dinitrogen complex **4** contains the *meso* ligand. The ^{31}P NMR spectrum of **4** can be fully analyzed, leading to the following parameters: J_{AX} (*trans*) = 105.2, $|J_{AX}|$ (*cis*) = 3.8, $J_{AA'}$ = –15.3 and $J_{XX'}$ = –29.8 Hz. Importantly, the derived parameters are very similar to those of the precursor **3**, corroborating the retention of the *trans-meso* configuration in the conversion to the dinitrogen complex. Again, the largest *cis*-coupling constant (XX') is derived from the metal-medi-

ated interaction between the terminal P atoms whereas the smaller one (AA') corresponds to a spin–spin interaction between the central P atoms. The smallest *cis*-coupling constant (AX) is the result of a metal-mediated and another interaction through the ethylene bridge (vide supra).

A second, independent spectroscopic proof of the identity of **4** as *trans*- $[\text{Mo}(\text{N}_2)_2(\text{meso-prP}_4)]$ is provided by vibrational spectroscopy. The comparison of the infrared and Raman spectrum (Figure 3) shows the existence of two N–N vibrations, a symmetric combination at 2044 cm^{-1} and an antisymmetric combination at 1964 cm^{-1} , indicating the coordination of *two* dinitrogen ligands. In the presence of a center of inversion the symmetric combination is Raman-allowed and the antisymmetric combination IR allowed. The intensities of ν_s and ν_{as} as shown in Figure 2 clearly reflect these relations, although the selection rules are slightly relaxed in comparison with the higher-symmetric complexes $[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$ ($\nu_s = 2030$, $\nu_{as} = 1970$ cm^{-1}) and $[\text{W}(\text{N}_2)_2(\text{dppe})_2]$ (2005 and 1950 cm^{-1} , resp.; cf. Supporting Information).^[5a,20] For bis(dinitrogen) complexes with a *cis*-configuration, in contrast, no vibrational exclusion principle applies and ν_s as well as ν_{as} are observed with comparable intensities both in the IR and in the Raman spectrum. Complex **4** therefore is unambiguously associated with a bis(dinitrogen) complex exhibiting a *trans*-configuration, as already inferred from ^{31}P -NMR spectroscopy. This is further corroborated by the UV/Vis absorption spectrum of **4** (Figure 4) showing the same absorption features as $\text{Mo}(\text{N}_2)_2(\text{dppe})_2$ and $\text{W}(\text{N}_2)_2(\text{dppe})_2$.^[5a,5b] In particular, the characteristic absorption band of the *trans* metal-bis(dinitrogen) unit is found at about 300 nm (for **4**: 318 nm). This band has been assigned to the transition from the metal d_{xz} and d_{yz} orbitals to the dinitrogen π^*_x and π^*_y orbitals. Likewise at lower energy, the typical absorption feature connected with phenylphosphane ligands (shoulders at 380 nm) is found. At 470 nm, finally, a weak absorption deriving from the lowest-energy spin-allowed ligand-field transition of the Mo^0 d^6 configuration ($^1A_{1g} \rightarrow ^1T_{1g}$) can be observed.

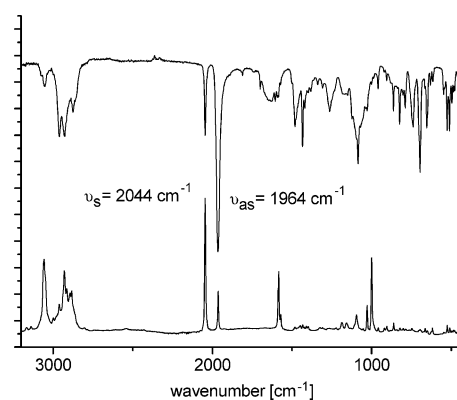


Figure 3. Infrared (top) and Raman spectrum (bottom) of *trans*- $[\text{Mo}(\text{N}_2)_2(\text{prP}_4)]$ (**4**), indicating the positions of the symmetric and antisymmetric N–N stretching vibrations [$\nu_s(\text{NN})$ and $\nu_{as}(\text{NN})$, respectively].

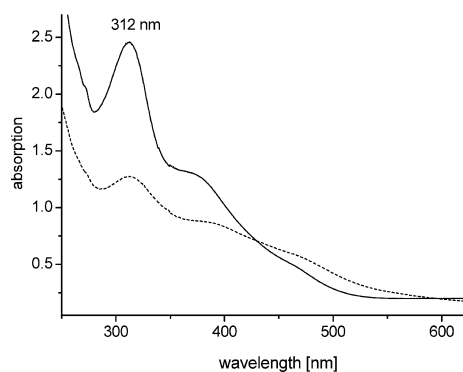


Figure 4. UV/Vis spectra *trans*-[Mo(N₂)₂(prP₄)] in KBr (dotted line) and in CH₂Cl₂ (solid line).

Conclusions

In summary, the first Chatt-type Mo⁰ dinitrogen complex with a tetraphosphane ligand has been prepared and characterized by NMR, infrared and Raman IR spectroscopy. Importantly, the employed reaction route allows the stereospecific synthesis of this complex as *trans*-[Mo(N₂)₂(*meso*-prP₄)] and nowhere requires the use of chromatographic separation techniques. The stereoselectivity in the reaction course is induced by the oxido-iodido-molybdenum(IV) precursor [Mo(O)I(prP₄)]⁺ which directs both phenyl groups of the bridging P atoms of prP₄ into a *meso* configuration. Moreover, the prP₄ ligand appears to have the right size to accommodate the Mo⁰ center. Although this result does not yet solve the basic problem of Chatt-type complexes, the possibility for the coordination of Lewis-basic ligands in *trans*-position to N₂, it has established a first pathway for the rational synthesis of mononuclear molybdenum dinitrogen complexes with tetraphosphane ligands which now can be applied to corresponding complexes with other polyphosphane or polydentate, mixed P/N ligands.^[21] Nevertheless, the obtained molybdenum prP₄/N₂ complex is of significant interest by itself as it should exhibit a higher thermodynamic stability in the reactions of the Chatt cycle than the conventional bis(diphos) complexes, due to the linkage of the two diphosphane units by an alkyl bridge. This is of particular relevance for the intermediates of higher oxidation states where the metal–phosphane bonds become labile,^[5c] and will be checked in further studies probing the reactivity of [Mo(N₂)₂(prP₄)] and its derivatives towards acids and reductants.

Experimental Section

General: All reactions were performed under an inert gas atmosphere using Schlenk techniques. The solvents were dried and freshly distilled under inert gas. Using the following drying agents during distillation: THF and diethylether, lithium aluminium hydride; benzene and dichloromethane, calcium hydride; ethanol, sodium; acetone, calcium sulfate. Sodium tetraphenylborate 99.5+ % (ACS) was used as obtained from Strem Chemicals. Tetrabutylammonium tetrafluoroborate puriss. was used as obtained from Fluka Riedel-de Haën. All other reagents were used without further purification. The ligand prP₄ was prepared by the reaction of (C₆H₅)₂P(CH₂)₂Cl^[22] with Lippert^[9] [MoOCl₂(PMe₃)₃] and [MoOI₂(PMe₃)₃] were prepared using the literature procedures.

IR spectra were obtained from KBr pellets using a Bruker IFS v66/ S FT-IR-Spectrometer. UV/Vis spectra were recorded on a Cary 5 UV/Vis/NIR-Spectrometer using quartz cuvettes with *d* = 1 cm.

NMR spectra were recorded on a Bruker Avance 400 pulse Fourier transform spectrometer operating at a ¹H frequency of 400.13 MHz (³¹P: 161.98 MHz) using a 5 mm inverse triple-resonance probe head. References as substitutive standards: H₃PO₄ 85 % pure, δ(³¹P) = 0 ppm.

Elemental analyses were performed using a Euro Vector CHNS-O-element analyzer (Euro EA 3000). Samples were burned in sealed tin containers by a stream of oxygen.

Cyclic voltammograms were recorded with a Metrohm Autolab PGstat 30 potentiostat controlled by the VA computrace or GPES software in a three-electrode cell with a mercury hanging drop working electrode and a silver rod as a pseudo-reference electrode. A solution of [MoOI(prP₄)]BPh₄ (0.5 mM), TBABF₄ (0.2 M) and 10 mmol phenol in THF was recorded at 25 °C. The scan rate was set to 100 mVs⁻¹. The potentials are referenced against ferrocenium/ferrocene.

The electrochemical syntheses were carried out in a three-electrode cell. The working-electrode was a mercury pool with a surface of about 7 cm². A coiled platinum wire counter electrode was separated from the working-electrode by a diaphragm made of clay. A silver rod was used as reference electrode. Potentiostatic control was effected by an EG&G PAR model 273A potentiostat controlled by the EG&G PAR M270 software.

[MoOI(prP₄)]BPh₄ (3): [MoOI₂(PMe₃)₃] (593 mg, 1 mmol), prP₄ (684 mg, 1 mmol) and NaBPh₄ (342 mg, 1 mmol) were refluxed for 6 h in 30 mL of THF. The solvent was removed in vacuo. The residue was extracted with 20 mL of acetone. The solution was filtered and cooled overnight at -42 °C. The violet solid was filtered and dried in vacuo yielded 844 mg (68 %). A cyclic voltammogram of the product is shown in Figure S6 (Supporting Information). A small amount of the solid was solved in 5 mL of CH₂Cl₂ and recrystallized by slow vapour diffusion of diethyl ether. The obtained deep blue crystals were suitable for X-ray diffraction studies. Elemental analysis calcd. for C₆₇H₆₄BIMoOP₄ (1242.77): C 64.75, H 5.19, I 10.21; found C 64.51, H 5.23, I 10.10%. ³¹P{¹H} NMR(161.975 MHz, CD₂Cl₂): δ = 46.01 (*J*_{ab} = -28.2 Hz, |*J*_{ac/bd}| = 4.9 Hz, *J*_{ad/bc} = 110.8 Hz, *J*_{cd} = -18.4 Hz, 2P; *P*_{a/b}), 41.06 (*J*_{ab} = -28.2 Hz, *J*_{ac/bd} = -4.9 Hz, *J*_{ad/bc} = 110.8 Hz, *J*_{cd} = -18.4 Hz, 2P; *P*_{c/d}) ppm.

[Mo(N₂)₂(prP₄)] (4): [MoOI(prP₄)]BPh₄ (700 mg, 0.56 mmol) and phenol (94 mg, 10 mmol) were dissolved in 15 mL of THF. The solution was transferred into a bulk electrolysis cell described above containing 35 mL of a 0.2 M TBABF₄ solution in THF. A constant stream of nitrogen was bubbled into the stirred solution all the time. The oxido complex was reduced at -2.1 V vs. the reference electrode (vide supra). The orange solution was transferred by syringe into a Schlenk flask. The solvent was removed in an atmosphere of nitrogen. The residue was extracted with benzene and filtered. The solution was concentrated and layered with ethanol. Cooling overnight gave 256 mg (39 %) of a yellow-orange solid, which corresponds to a mixture of the product and the supporting electrolyte, [NBu₄][BF₄]. In order to free the sample from the conducting salt, the mixture was repeatedly extracted with ethanol, as described in the literature.^[23] In further analogy with this procedure, the identity of the product of the electrosynthesis was shown spectroscopically. ³¹P{¹H} NMR(161.975 MHz, C₆D₆): δ = 71.98 (*J*_{ab} = -29.8 Hz, |*J*_{ac/bd}| = 3.8 Hz, *J*_{ad/bc} = 105.2 Hz, *J*_{cd} = -15.3 Hz, 2 P; *P*_{a/b}), 63.74 (*J*_{ab} = -29.8 Hz, *J*_{ac/bd} = 3.8 Hz, *J*_{ad/bc} = 105.2 Hz, *J*_{cd} = -15.3 Hz, 2P; *P*_{c/d}) ppm. IR/Raman ν_s(NN) = 2044, ν_{as}(NN) = 1964 cm⁻¹.

Supporting Information (see footnote on the first page of this article): ³¹P NMR spectrum of the prP₄ ligand, spectroscopic and cy-

clovoltammetric characterization of compound **3** and reference vibrational spectra of dinitrogen complexes.

Acknowledgments

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