# Preparation of dinitrogen complexes $Mo(N_2)_2P_4$ stabilised by phosphonite $PPh(OEt)_2$ and phosphinite $PPh_2(OEt)$ ligands

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## Abstract

Dinitrogen complexes $Mo(N_2)_2P_4$ **1**, **2** [P = $PPh(OEt)_2$ and $PPh_2OEt$] were prepared by allowing a $MoCl_3(THF)_3$ solution containing an excess of phosphine to react with magnesium under nitrogen. Substitution reactions with CO and *p*-tolylisocyanide were studied, and led to $Mo(CO)_2P_4$, $Mo(CO)_3P_3$, and $Mo(p$-tolylNC$)_2P_4$ derivatives. Treatment of dinitrogen compound $Mo(N_2)_2[PPh(OEt)_2]_4$ with an excess of HCl gave the hydrazido(2-) $[MoCl(NNH_2)\{PPh(OEt)_2\}_4]$Cl derivative. Reduction reactions with zinc amalgam of complexes **1** and **2** in the presence of lutidine·HCl gave ammonia in about 8–10% yield. © 2002 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The coordination chemistry of the dinitrogen molecule has been studied for many decades in several metal ligand systems, with the aim of obtaining insights into $N_2$ binding and activation through metal complexation [1–5]. Among central metals, molybdenum is one of the most frequently investigated [2–5], as classic dinitrogen derivatives [6] $Mo(N_2)_2P_4$, containing phosphines as ancillary ligands, show interesting properties in protonation and reduction reactions [3–5,7,8]. Extensive investigations have in fact shown the formation of ammonia and/or hydrazine by treatment of these $Mo(N_2)_2P_4$ complexes with Brønsted acid [7,8]. Organonitrogen compounds have also been obtained from coordinated $N_2$, often through the hydrazido(2-) [Mo]$NNH_2$ intermediate [3]. However, the most popular ligand system in molybdenum dinitrogen chemistry involves tertiary phosphines as ancillary ligands, and extensive studies have shown how the steric and electronic properties of these supporting groups are crucial in determining the stoichiometry, structure, and reactivity of the $N_2$ derivatives [3–5].

However, despite the large number of reports in this field, no examples of molybdenum dinitrogen complexes containing phosphites $[P(OR)_3]$ or phenyl-substituted ones $[PPh(OEt)_2, PPh_2OEt]$ have been reported, although these ligands have shown interesting properties in stabilising "diazo" species such as diazene RN=NH, diazenido $RN_2$, and hydrazine bonded to a metal fragment [9].

Studies on the chemistry of such "diazo" complexes with phosphite ligands continue to be one subject of our research interest [10], which has involved several metal centres such as cobalt [10a,10b] and iron triads [10e,11], manganese [12], and rhenium [10c,10d]. We have now extended these studies to molybdenum, and this paper reports the synthesis and reactivity of new dinitrogen complexes of this metal, stabilised by phosphonite and phosphinite ligands.

## 2. Experimental

### 2.1. General considerations and physical measurements

All synthetic work was carried out in an inert atmosphere using standard Schlenk techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored in an

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inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Phosphines PPh(OEt)$_2$ and PPh$_2$OEt were prepared following the method of Rabinowitz and Pellon [13]. Phosphites P(OR)$_3$ (R = Me, Et, Ph, i-Pr) (Aldrich) were purified by distillation under nitrogen. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra ($^1$H, $^{31}$P) were obtained on a Bruker AC200 spectrometer at temperatures varying between −90 and +30 °C, unless otherwise noted. $^1$H spectra are referred to internal Me$_4$Si; $^{31}$P{$^1$H} chemical shifts are reported with respect to 85% H$_3$PO$_4$, with downfield shifts considered positive. The SwaN-MR software package [14] was used to treat NMR data. The conductivity of $10^{-3}$ mol dm$^{-3}$ solutions of the complexes in CH$_3$NO$_2$ at 25 °C was measured with a Radiometer CDM 83 instrument.

## 2.2. Synthesis of complexes

The complex MoCl$_3$(THF)$_3$ was prepared following the method previously reported [15].

### 2.2.1. Mo(N$_2$)$_2$[PPh(OEt)$_2$]$_4$ (1)

To a solution of MoCl$_3$(THF)$_3$ (1 g, 2.39 mmol) in 16 cm$^3$ of THF, under a N$_2$ atmosphere (1 atm), were sequentially added an excess of magnesium turnings (1.3 g, 53.5 mmol) and an excess of PPh(OEt)$_2$ (2.38 cm$^3$, 12.0 mmol). The reaction mixture was vigorously stirred at room temperature (r.t.) for 20 h and then filtered to separate the unreacted magnesium and the brown solid formed. The solvent was removed by evaporation at reduced pressure, giving a red–brown oil which was triturated with EtOH (25–30 cm$^3$). A yellow solid slowly separated out which was filtered, washed with EtOH, and dried under vacuum. The compound was crystallised by dissolving in benzene and, after filtration and concentration, by precipitation with EtOH; yield ≥ 40% (Found: 51.10; H, 6.29; N, 5.71. C$_{40}$H$_{60}$MoN$_4$O$_8$P$_4$ requires C, 50.85; H, 6.40; N, 5.93%).

### 2.2.2. Mo(N$_2$)$_2$[PPh$_2$OEt]$_4$ (2)

This complex was prepared following the method used for the related compound 1. In this case, however, the dinitrogen complex is little soluble in THF and can be obtained as a yellow solid by concentration (10 cm$^3$) and cooling (0 °C) of the reaction mixture. This solid was separated by filtration, obtaining a mixture of dinitrogen compound, magnesium and other solid species, from which complex 2 was extracted with two 5-cm$^3$ portions of benzene and, after concentration to 2–3 cm$^3$, precipitated with THF; yield ≥ 30% (Found:

62.48; H, 5.59; N, 5.01. C$_{56}$H$_{60}$MoN$_4$O$_4$P$_4$ requires C, 62.69; H, 5.64; N, 5.22%).

### 2.2.3. Mo(CO)$_2$[PPh(OEt)$_2$]$_4$ (3)

A solution of Mo(N$_2$)$_2$[PPh(OEt)$_2$]$_4$ (0.20 g, 0.21 mmol) in 20 cm$^3$ of THF was allowed to stand under CO atmosphere (1 atm) for 150 min. The solvent was removed under reduced pressure giving a red–brown oil, which was triturated with EtOH (2 cm$^3$). A yellow solid slowly separated out from the resulting solution, which was filtered and dried under vacuum; yield ≥ 80% (Found: 53.65; H, 6.33. C$_{42}$H$_{60}$MoO$_{10}$P$_4$ requires C, 53.40; H, 6.40%).

### 2.2.4. Mo(CO)$_2$[PPh$_2$OEt]$_4$ (4) and Mo(CO)$_3$[PPh$_2$OEt]$_3$ (5)

These complexes were obtained like the related 3 by allowing a solution of the dinitrogen compound Mo(N$_2$)$_2$[PPh$_2$OEt]$_4$ (0.30 g, 0.28 mmol) in 20 cm$^3$ of THF to react with CO (1 atm). The yellow solid obtained after evaporation of the solvent contains a mixture of 4 and 5, which were separated by fractional crystallisation. A typical separation involves the slow cooling to −25 °C of a solution prepared by dissolving the solid obtained in C$_2$H$_5$OH and enough CH$_2$Cl$_2$ to obtain a saturated solution at 20 °C. The first solid precipitated was the dicarbonyl Mo(CO)$_2$[PPh$_2$OEt]$_4$, which was filtered and dried under vacuum; yield ≥ 20%. By concentration and further cooling of the solution, the tricarbonyl Mo(CO)$_3$[PPh$_2$OEt]$_3$ separated out as yellow microcrystals; yield ≥ 30% (Found: 65.05; H, 5.51. C$_{58}$H$_{60}$MoO$_6$P$_4$ 4 requires: C, 64.93; H, 5.64. Found: 62.22; H, 5.28. C$_{45}$H$_{45}$MoO$_6$P$_3$ 5 requires C, 62.08; H, 5.21%).

### 2.2.5. Mo(p-tolylNC)$_2$P$_4$ (6, 7) [P = PPh(OEt)$_2$ (6), PPh$_2$OEt (7)]

An excess of p-tolylisocyanide (74 μl, 0.63 mmol) was added to a solution of the appropriate dinitrogen complex Mo(N$_2$)$_2$P$_4$ (0.25 mmol) in 10 cm$^3$ of THF and the reaction mixture stirred for about 3 h. The solvent was removed under reduced pressure to give a red–brown oil, which was triturated with 2 cm$^3$ of ethanol. A yellow solid slowly separated out, which was filtered and crystallised from CH$_2$Cl$_2$ and EtOH; yield ≥ 70% (Found: 60.11; H, 6.59; N, 2.58. C$_{56}$H$_{74}$Mo-N$_2$O$_8$P$_4$ 6 requires: C, 59.89; H, 6.64; N, 2.49. Found: 68.92; H, 5.85; N, 2.32. C$_{72}$H$_{74}$MoN$_2$O$_4$P$_4$ 7 requires: C, 69.12; H, 5.96; N, 2.24%).

### 2.2.6. [MoCl(NNH$_2$){PPh(OEt)$_2$}$_4$]Cl (8)

To a solution of Mo(N$_2$)$_2$[PPh(OEt)$_2$]$_4$ (0.40 g, 0.42 mmol) in 12 cm$^3$ of THF, cooled to −196 °C, an excess of HCl (1.7 mmol, 8.5 cm$^3$ of a 0.2 M solution in Et$_2$O) was added, and the reaction mixture was allowed to reach r.t. After 2 h of stirring, the solvent was removed

under reduced pressure to give a brown oil, which was triturated with EtOH (2 cm$^3$). A dark green solid slowly separated out from the resulting solution which, after cooling to $-25$ °C to complete the precipitation, was filtered and dried under vacuum; yield $\geq 25\%$; $\Lambda_M = 82.4$ S cm$^2$ mol$^{-1}$ (Found: 48.46; H, 6.25; N, 2.71; Cl, 7.01. C$_{40}$H$_{62}$Cl$_2$MoN$_2$O$_8$P$_4$ requires C, 48.55; H, 6.31; N, 2.83; Cl, 7.16%).

### 2.2.7. Reduction reactions

Reduction of dinitrogen complexes was carried out in THF at r.t. under N$_2$ using an excess of Zn/Hg as reducing agent in the presence of lutidine hydrochloride (Lu·HCl). A typical experiment involved the addition of a 20-fold excess of Zn (2.0 mmol), as 2% zinc amalgam (6.5 g), to a solution of the appropriate dinitrogen complex (0.1 mmol) in 10 cm$^3$ of THF. A 30-fold excess of lutidine hydrochloride (3.0 mmol, 0.43 g) in 10 cm$^3$ of THF was then added to the reaction mixture, which was stirred for a reaction time from 24 to 72 h. An excess of hydrochloric acid (2.0 mmol, 2 cm$^3$ of 1 M solution in Et$_2$O) was added to the reaction mixture, which was stirred for 1 h, and then the solvent was removed under reduced pressure. The resulting solid was treated with five 5-cm$^3$ portions of H$_2$O and, after filtration, ammonia from the solution was quantified by the indophenol method [16], while hydrazine was determined by the $p$-dimethylaminobenzaldehyde test [17].

## 3. Results and discussion

### 3.1. Synthesis of dinitrogen complexes

Phosphite-containing dinitrogen complexes of molybdenum Mo(N$_2$)$_2$P$_4$ **1**, **2** were prepared by reducing MoCl$_3$(THF)$_3$ solutions with magnesium turnings in a N$_2$ atmosphere and in the presence of an excess of phosphite, as shown in Scheme 1.

Crucial for the successful preparation of the dinitrogen complexes was the rigorous 1:5 ratio between MoCl$_3$(THF)$_3$ and phosphite, and carrying out the reaction at room temperature for 20 h. Otherwise, a low yield in dinitrogen complex and a large number of decomposition products, which prevented purification of the solid, were found in the final reaction products.

The nature of the reducing agent was also crucial for success of the synthesis, and only the use of magnesium turnings allowed dinitrogen complexes to be obtained. Sodium amalgam or finely-divided sodium metal also reacted with MoCl$_3$(THF)$_3$ solutions containing PPh(OEt)$_2$ and PPh$_2$OEt phosphite ligands, giving a reddish-brown solution from which no dinitrogen complex could be isolated. We also attempted to carry out the reaction in a two-step sequence by reacting MoCl$_3$(THF)$_3$ first with phosphite, to prepare the MoCl$_3$P$_3$ species, and then with magnesium, to reduce this intermediate to Mo(0) dinitrogen derivative. However, this procedure failed, giving only traces of species **1** or **2**, and only by adding magnesium immediately after the phosphite to the MoCl$_3$(THF)$_3$ solution and stirring the reaction mixture for about 20 h could solid samples of dinitrogen complexes be obtained.

We also attempted to prepare dinitrogen derivatives with phosphites different from PPh(OEt)$_2$ and PPh$_2$OEt, of the type P(OR)$_3$ (R = Me, Et, Ph, $i$-Pr) or PPh(OR)$_2$ (R = $i$-Pr, $n$-Bu), but only traces of dinitrogen species were obtained. It therefore seems that only with phosphonite PPh(OEt)$_2$ and phosphinite PPh$_2$OEt as ancillary ligands can stable dinitrogen complexes of molybdenum be obtained. Furthermore, when reduction of MoCl$_3$(THF)$_3$ gives rise to dinitrogen species, exclusively bis(derivatives) Mo(N$_2$)$_2$P$_4$ were obtained, and the infrared data on raw samples excluded the presence of other dinitrogen derivatives such as mono-species MoCl(N$_2$)P$_4$, observed in previous cases [6c].

Bis(dinitrogen) complexes **1** and **2** were isolated in relatively good yields (30–40%) as yellow solids stable in air and soluble in most common organic solvents. However, although these solutions are quite stable under N$_2$, they decompose upon exposure to air, giving rise to a change in colour and separation of a solid substance.

We also attempted to obtain crystals suitable for X-ray analysis from the solutions of complexes **1**, **2**, but only yellow powders were obtained. However, analytical and spectroscopic data (Table 1) strongly support the proposed formulation and suggest the mutually *trans* position of the two dinitrogen ligands, as shown in Fig. 1.

The infrared spectra, in fact, show only one strong $\nu_{N2}$ band at 2004 cm$^{-1}$ for **1** and at 1990 cm$^{-1}$ for **2**, fitting the proposed geometry. This was confirmed by the $^{31}$P{$^1$H}-NMR spectra which show, in the temperature range between $+30$ and $-80$ °C, only one sharp singlet, indicating the magnetic equivalence of the four phosphite ligands. It may also be noted that the $\nu_{N2}$ value of our compounds **1**, **2** is higher than the values found for related Mo(N$_2$)$_2$(P–P)$_2$ and Mo(N$_2$)$_2$P$_4$ compounds [3–5], containing phosphine instead of phosphite as supporting ligands, and this datum fits the better $\pi$-acceptor properties of phosphites as compared with tertiary phosphines. However, phosphites PPh(OEt)$_2$ and PPh$_2$OEt are able to stabilise dinitrogen complexes of molybdenum, the synthesis of which is now accessible relatively easily.

MoCl$_3$(THF)$_3$ + exc. P $\xrightarrow[\text{THF}]{\text{Mg, N}_2}$ Mo(N$_2$)$_2$P$_4$
**1, 2**
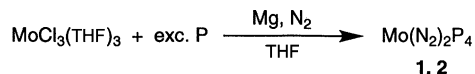
Scheme 1. P = PPh(OEt)$_2$ **1**, PPh$_2$OEt **2**.

Table 1
IR and NMR data for the molybdenum complexes

| Compound | IR [a] | | $^1$H-NMR[b] | | Spin system | $^{31}$P{$^1$H}-NMR [b,c] |
|---|---|---|---|---|---|---|
| | $\bar{v}$ (cm$^{-1}$) | Assignment | $\delta$ (*J* Hz) | Assignment | | $\delta$ (*J* Hz) |
| **1** Mo(N$_2$)$_2$[PPh(OEt)$_2$]$_4$ | 2085w<br>2004s | $v$(N≡N) | 7.60 (m) [d]<br>7.15 (m)<br>4.05 (m)<br>3.85 (m)<br>1.28 (t) | Ph<br><br>CH$_2$<br><br>CH$_3$ | A$_4$ [d] | 183.5 s |
| **2** Mo(N$_2$)$_2$[PPh$_2$OEt]$_4$ | 1990s | $v$(N≡N) | 7.60–6.90 (m) [d]<br>3.08 (m)<br>0.67 (t) | Ph<br>CH$_2$<br>CH$_3$ | A$_4$ [d] | 152.6 s |
| **3** Mo(CO)$_2$[PPh(OEt)$_2$]$_4$ | 1844s | $v$(CO) | 7.40–7.10 (m)<br>3.71 (m)<br>3.50 (m)<br>1.19 (t) | Ph<br>CH$_2$<br><br>CH$_3$ | A$_4$ | 186.4 s |
| **4** Mo(CO)$_2$[PPh$_2$OEt]$_4$ | 1832s | $v$(CO) | 7.60–7.00 (m)<br>3.68 (qnt)<br>1.19 (t) | Ph<br>CH$_2$<br>CH$_3$ | A$_4$ | 155.7 s |
| **5** Mo(CO)$_3$[PPh$_2$OEt]$_3$ | 1973m<br>1882s<br>1859s | $v$(CO) | 7.60–7.00 (m)<br>3.40–3.20 (m)<br>0.94 (t)<br>0.82 (t) | Ph<br>CH$_2$<br>CH$_3$ | A$_2$B | $\delta_A$ 149.0<br>$\delta_B$ 142.8<br>$J_{AB}$ = 30 |
| **6** Mo(*p*-tolylNC)$_2$[PPh(OEt)$_2$]$_4$ | 1925s | $v$(CN) | 7.50–6.40 (m)<br>4.10–3.40 (m)<br>2.30 (s)<br>1.13 (t) | Ph<br>CH$_2$<br>CH$_3$ *p*-tol<br>CH$_3$ phos | A$_4$ | 188.0 s |
| **7** Mo(tolylNC)$_2$[PPh$_2$OEt]$_4$ | 1940s | $v$(CN) | 7.87–6.60 (m)<br>4.01 (m)<br>2.25 (s)<br>1.18 (t) | Ph<br>CH$_2$<br>CH$_3$ *p*-tol<br>CH$_3$ phos | A$_4$ | 155.5 s |
| **8** [MoCl(NNH$_2$){PPh(OEt)$_2$}$_4$]Cl | 3385w<br>3255sh<br>1616 | $v$(NH)<br><br>$\delta$(NH$_2$) | 7.60–6.70 (m)<br>3.65 (m)<br>1.81 (qnt, br)<br>1.23 (t) | Ph<br>CH$_2$<br>NNH$_2$<br>CH$_3$ | A$_4$ | 150.1 s |

[a] In KBr pellets.
[b] In CD$_2$Cl$_2$ at 25 °C, unless otherwise noted.
[c] Positive shift downfield from 85% H$_3$PO$_4$.
[d] In C$_6$D$_6$.
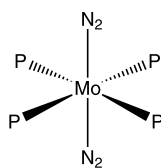


Fig. 1.
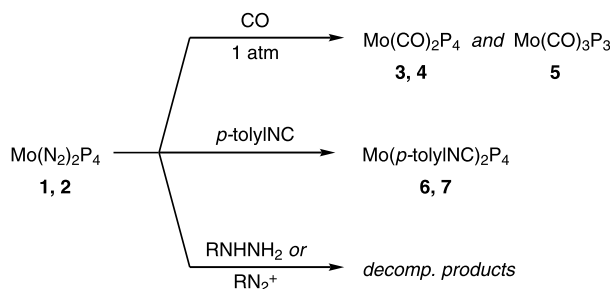


Scheme 2. P = PPh(OEt)$_2$ **3**, **6**, PPh$_2$OEt **4**, **5**, **7**.

### 3.2. Reactivity

The chemical reactivity of dinitrogen complexes **1** and **2** is summarised in Schemes 2 and 3. Carbon monoxide and *p*-tolylisocyanide can substitute the dinitrogen ligands in compounds **1** and **2** to give the related complexes **3–7**, which were isolated and characterised.

Treatment of Mo(N$_2$)$_2$[PPh(OEt)$_2$]$_4$ **1** with CO gave a pale yellow solution from which the bis(carbonyl)

Mo(CO)$_2$P$_4$ compound **3** was isolated. Instead, the reaction of the PPh$_2$OEt derivative Mo(N$_2$)$_2$(PPh$_2$OEt)$_4$ **2** with CO gave a mixture of bis (**4**) and tris(carbonyl) (**5**) compounds, which were separated by fractional crystallisation. The reactions were also monitored by infrared spectra, which showed the disappearance of the $v_{N2}$ bands of dinitrogen precursors **1**, **2**, and the

Scheme 3.
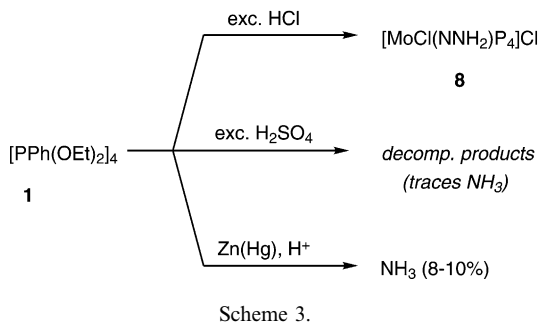
appearance of those due to the $\nu_{CO}$ of carbonyl species **3**–**5**. The spectra also reveal the absence of other absorptions attributable to $\nu_{N2}$ or $\nu_{CO}$, thus excluding the presence of any appreciable amounts of intermediates of the type $Mo(N_2)(CO)P_4$. In the case of $PPh_2OEt$, the spectra also indicate that CO replaces not only dinitrogen, but also one phosphite ligand, affording tricarbonyl species $Mo(CO)_3P_3$ (**5**). Both complexes **4** and **5**, however, were always present in the reaction mixture and were separated by fractional crystallisation.

*p*-Tolylisocyanide also replaces $N_2$ ligand in **1** and **2**, giving bis(isocyanide) complexes $Mo(p\text{-tolylNC})_2P_4$ **6**, **7**.

The lability of the $N_2$ group in molybdenum derivatives **1**, **2** prompted us to study the substitution reaction with ligands such as hydrazine and diazonium cations, in an attempt to prepare new "diazo" derivatives. The reaction proceeded with a colour change of the solution and evolution of $N_2$, but no stable compound was isolated.

Both carbonyl (**3**–**5**) and isocyanide (**6**, **7**) molybdenum derivatives are yellow or yellow–orange solids, stable in air, diamagnetic and soluble in most common organic solvents, in which they behave as non-electrolytes. Analytical and spectroscopic data (Table 1) support the proposed formulation for the complexes, and a geometry in solution of the type shown in Fig. 2 may also be established.
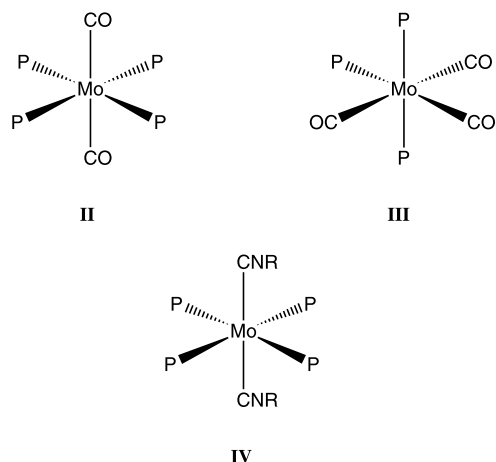
In the $\nu_{CO}$ region, the IR spectra of dicarbonyls $Mo(CO)_2P_4$ **3**, **4** showed only one strong band at 1844–1832 cm$^{-1}$, suggesting a *trans* arrangement of the two carbonyl ligands (**II**). This geometry was confirmed by the $^{31}P\{^1H\}$-NMR spectra which, in the temperature range between +30 and −80 °C, showed only one sharp singlet, fitting the magnetic equivalence of the four phosphite ligands.

The infrared spectrum of tricarbonyl compound $Mo(CO)_3P_3$ **5** shows one medium-intensity band at 1973 cm$^{-1}$ and two strong ones at 1882 and 1859 cm$^{-1}$, suggesting a *mer* arrangement of the three carbonyl ligands (**III**). In the temperature range between +30 and −80 °C, the $^{31}P$-NMR spectra display an $A_2B$ multiplet, thus confirming *mer* geometry **III** for the complex. The mutually *trans* position of the two isocyanide ligands occurs in $Mo(p\text{-tolylNC})_2P_4$ complexes **6**, **7**, whose IR spectra show only one $\nu_{CN}$ band at 1925 cm$^{-1}$ (**6**) and 1940 cm$^{-1}$ (**7**), whereas only one singlet is present in the $^{31}P\{^1H\}$-NMR spectra, suggesting the magnetic equivalence of the four phosphite ligands, as expected for geometry **IV**.

The protonation reactions of the dinitrogen complexes with Brønsted acids were also studied, and the results are shown in Scheme 3. Treatment with an excess of HCl in THF of $Mo(N_2)[PPh(OEt)_2]_4$ **1** gives a reddish-brown solution from which, after work-up, a dark-green solid was isolated and characterised as the hydrazido(2-) $[MoCl(NNH_2)P_4]Cl$ **8** derivative. The related $Mo(N_2)_2(PPh_2OEt)_4$ **2** also reacts with HCl in THF, giving a green solution, but no stable solid was separated.

Protonation reactions were also studied with other acids, such as $HBF_4 \cdot Et_2O$ and $H_2SO_4$, but no solids were isolated and no evidence of the formation of nitrogen-containing products was detected, although, in the case of $H_2SO_4$, traces of $NH_3$ were found in the reaction mixture.

Hydrazido(2-) $[MoCl(NNH_2)P_4]Cl$ **8** is a dark green, diamagnetic solid, soluble in polar organic solvents in which it behaves as 1:1 electrolyte [18]. It is stable as a solid, but its solution slowly decomposes at room temperature even in an inert atmosphere. Microanalysis and spectroscopic data support the proposed formulation, and *trans* geometry **V** (Fig. 3) in solution was also established.
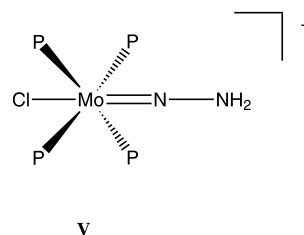


Fig. 2.



Fig. 3.

The presence of the hydrazido $NNH_2$ ligand in complex **8** was confirmed by the infrared spectra, which show two weak bands at 3385 and 3255 $cm^{-1}$, attributed to the $\nu_{NH}$ of the hydrazido ligand. The spectra also shows a medium-intensity band at 1616 $cm^{-1}$, attributed to the $\delta_{NH_2}$ of the $NNH_2$ group. Further support for the presence of hydrazido(2-) in the complex comes from $^1H$-NMR spectra, which show a broad quintet at 1.81 ppm, attributed to the $NNH_2$ protons. The $^{31}P\{^1H\}$-NMR spectrum consists of a sharp singlet at 150.1 ppm, indicating the magnetic equivalence of the four phosphite ligands, as in *trans* geometry **V**.

The protonation reactions of dinitrogen complexes of molybdenum have been reported to give various species, depending upon the nature of acid, solvent, and supporting ligands [3,8]. In some cases, hydrazido(2-) complexes were obtained, and these precedents [6f,8,19,20] support our formulation for species **8** obtained by protonation with HCl. The reaction probably proceeds first through protonation of one dinitrogen ligand, with concurrent substitution of the other by $Cl^-$ to give a "diazenido" $MoCl(NNH)P_4$ intermediate, which further reacts with $H^+$ to give the final $[MoCl(NNH_2)P_4]^+$ cation. Unfortunately, no intermediate was detected following the reaction in an NMR tube, since the spectrum only showed the formation of the final hydrazido(2-) derivative. Its separation, however, indicates that monodentate phosphites are able to stabilise the nitrogen-containing ligand obtained by protonation of the coordinated $N_2$ group. It can also be noted that the previously reported dinitrogen complexes of molybdenum [21] containing the monodentate phosphine $PPhMe_2$ give, by protonation with HCl, the neutral triphosphine species $MoCl_2(NNH_2)P_3$. Instead, cationic complexes with four phosphorus ligands like **8** were obtained with bidentate ligands or with tungsten as the central metal [3,21].

We have also begun to study reduction of dinitrogen complexes in the presence of a source of protons such as 2,6-lutidine hydrochloride (lut·HCl), in order to test the possibility of reducing dinitrogen to ammonia. Both complexes **1** and **2** are reduced by zinc amalgam in the presence of lut·HCl (in THF at room temperature), to give ammonia in about 8–10% yield. Traces of hydrazine are also present in the final reduction mixture. The reaction was carried out in both $N_2$ and argon atmosphere, but the yield did not change and is in any case rather low. However, although these are only preliminary results which need further investigation, reduction with zinc amalgam of our phosphite-containing dinitrogen complexes to give ammonia is an interesting result in the field of dinitrogen fixation processes.

## References

[1] M.D. Fryzuk, S.A. Johnson, Coord. Chem. Rev. 200 (2000) 379.

[2] M. Hidai, Coord. Chem. Rev. 185 (1999) 99.

[3] M. Hidai, Y. Mizobe, Chem. Rev. 95 (1995) 1115.

[4] J.R. Dilworth, R.L. Richards, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon, Oxford, 1982, p. 1073.

[5] J. Chatt, J.R. Dilworth, R.L. Richards, Chem. Rev. 78 (1978) 589.

[6] (a) M. Hidai, K. Tominari, Y. Uchida, J. Am. Chem. Soc. 94 (1972) 110;
(b) J. Chatt, A.J. Pearman, R.L. Richards, J. Chem. Soc. Dalton Trans. (1977) 2139;
(c) E. Carmona, J.M. Marin, M.L. Poveda, J.L. Atwood, R.D. Rogers, J. Am. Chem. Soc. 105 (1983) 3014;
(d) H. Dadkhah, J.R. Dilworth, K. Faiman, C.T. Kan, R.L. Richards, D.L. Hughes, J. Chem. Soc. Dalton Trans. (1986) 245;
(e) T.A. George, J.R.D. De Bord, B.B. Kaul, C.J. Pickett, D.J. Rose, Inorg. Chem. 31 (1992) 1295;
(f) M. Jimenez-Tenorio, M.C. Puerta, P. Valerga, D.L. Hughes, J. Chem. Soc. Dalton Trans. (1994) 2431.

[7] A.E. Shilov, Metal Complexes in Biomimetic Chemical Reactions, CRC, Boca Raton, FL, 1997.

[8] (a) J. Chatt, A.J. Pearman, R.L. Richards, J. Chem. Soc. Dalton Trans. (1977) 1852;
(b) G.J. Leigh, Acc. Chem. Res. 25 (1992) 177;
(c) T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida, M. Hidai, J. Am. Chem. Soc. 102 (1980) 7461.

[9] (a) D. Sutton, Chem. Rev. 93 (1993) 995;
(b) H. Kisch, P. Holzmeier, Adv. Organomet. Chem. 34 (1992) 67;
(c) B.F.G. Johnson, B.L. Haymore, J.R. Dilworth, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, 1987, p. 130.

[10] (a) G. Albertin, S. Antoniutti, E. Bordignon, A. Tasin, J. Organomet. Chem. 627 (2001) 99;
(b) G. Albertin, S. Antoniutti, E. Bordignon, F. Menegazzo, J. Chem. Soc. Dalton Trans. (2000) 1181;
(c) G. Albertin, S. Antoniutti, A. Bacchi, G.B. Ballico, E. Bordignon, G. Pelizzi, M. Ranieri, P. Ugo, Inorg. Chem. 39 (2000) 3265;
(d) G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, F. Miani, G. Pelizzi, Inorg. Chem. 39 (2000) 3283;
(e) G. Albertin, S. Antoniutti, A. Bacchi, D. Barbera, E. Bordignon, G. Pelizzi, P. Ugo, Inorg. Chem. 37 (1998) 5602.

[11] (a) G. Albertin, S. Antoniutti, E. Bordignon, S. Pattaro, J. Chem. Soc. Dalton Trans. (1997) 4445;
(b) G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, P.M. Dolcetti, G. Pelizzi, J. Chem. Soc. Dalton Trans. (1997) 4435.

[12] (a) G. Albertin, S. Antoniutti, E. Bordignon, G. Perinello, J. Organomet. Chem. 625 (2001) 217;
(b) G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, F. Busatto, G. Pelizzi, Inorg. Chem. 36 (1997) 1296.

[13] R. Rabinowitz, J. Pellon, J. Org. Chem. 26 (1961) 4623.

[14] G. Balacco, J. Chem. Inf. Comput. Sci. 34 (1994) 1235.

[15] J.R. Dilworth, R.L. Richards, Inorg. Synth. 28 (1990) 33.

[16] (a) M.W. Weatherburn, Anal. Chem. 39 (1967) 971;
(b) L. Solorzano, Limnol. Oceanogr. 14 (1969) 799.

[17] G.W. Watt, J.D. Chrisp, Anal. Chem. 24 (1952) 2006.

[18] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.

[19] M. Abu Bakar, D.L. Hughes, W. Hussain, G.J. Leigh, C.J. Macdonald, H. Mohd-Ali, J. Chem. Soc. Dalton Trans. (1988) 2545.

[20] J.E. Barclay, A. Hills, D.L. Hughes, G.J. Leigh, C.J. Macdonald, M. Abu Bakar, H. Mohd-Ali, J. Chem. Soc. Dalton Trans. (1990) 2503.

[21] (a) J. Chatt, A.J. Pearman, R.L. Richards, J. Chem. Soc. Dalton Trans. (1978) 1766;
(b) T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida, M. Hidai, J. Am. Chem. Soc. 102 (1980) 7461.