# Protonation Reactions of Dinitrogen Complexes of Molybdenum and Tungsten with $PMe_3$ as Co-ligand. *X*-Ray Structure of the Hydrazidium Complex $[WCl(NNH_3)(PMe_3)_4]Cl_2$†

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The reactions of *cis*-$[M(N_2)_2(PMe_3)_4]$ or $[M(N_2)(PMe_3)_5]$ (M = Mo or W) with HX (X = Cl or I) give the hydrazido(2−) complexes $[MX(NNH_2)(PMe_3)_4]X$ as intermediate products. For M = Mo, the final product is ammonia, but for M = W, X = Cl, the final product is the hydrazidium complex $[WCl(NNH_3)(PMe_3)_4]Cl_2$ (**A**). These reactions have been monitored by $^{31}P$ and $^{15}N$ n.m.r. spectroscopy, and complex (**A**) has been structurally characterised by *X*-ray diffraction. It exists in the solid state as centrosymmetric dimer units consisting of two cations linked through Cl anions by strong hydrogen bonds. The W–N–N group is almost linear with W–N 1.785(15) and N–N 1.40(2) Å. Compound (**A**) can also be prepared from $[WCl(NNH_2)(PMe_3)_4]Cl$ and HCl, but it is converted by $Na[BPh_4]$ in methanol into the hydrazide complex $[WCl(NNH_2)(PMe_3)_4][BPh_4]$.

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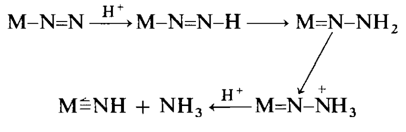
Essential for an understanding of the mechanism by which dinitrogen is reduced to ammonia by nitrogenase is the elucidation of the pathways of protonation of dinitrogen at metal sites in model systems.[1,2] Primary amongst compounds studied are mononuclear complexes of molybdenum and tungsten which give ammonia on treatment with an excess of mineral acid in solvents such as $CH_2Cl_2$, tetrahydrofuran (thf), or methanol.[1–4]

In general the co-ligands with dinitrogen are tertiary phosphines, but recently mixed (P,S)- or (P,O)-ligated complexes have been demonstrated to give ammonia.[5–7] In all these examples, a combination of spectroscopic studies and isolation of intermediates have indicated that, prior to cleavage of the N–N bond, the dinitrogen ligand passes through the diazenide (–N=H–H) and hydrazide (=N–$NH_2$) stages.[8,9]

In this paper we present the first example of a complex of the hydrazidium ligand $=N\text{–}\overset{+}{N}H_3$, which represents the penultimate step in the cleavage of ligating dinitrogen as shown in the Scheme. A preliminary account of this work has been published[10] and here we present full details of the characterisation of the hydrazidium complex $[WCl(NNH_3)(PMe_3)_4]Cl$, including its *X*-ray crystal structure; this shows interesting hydrogen-bonding effects which may be responsible for the stability of this ligand in the solid state. We also describe a $^{31}P$ and $^{15}N$ n.m.r. spectroscopic study of the reactions of the precursor dinitrogen complexes *cis*-$[M(^{15}N_2)_2(PMe_3)_4]$ and $[M(^{15}N_2)(PMe_3)_5]$ (M = Mo or W)[11] with HX (X = Cl or I) and isolation of hydrazido(2−) complexes from these reactions.



**Scheme.** M = Mo or W + co-ligands

## Results and Discussion

*Reactions of cis-*$[M(N_2)_2(PMe_3)_4]$ *and* $[M(N_2)(PMe_3)_5]$ (M = Mo *or* W) *with* HX (X = Cl *or* I) *to give Hydrazide Complexes.*—In general, the reactions of both *cis*-$[M(N_2)_2(PMe_3)_4]$[11] and $[M(N_2)(PMe_3)_5]$[11] with HX proceed as shown in equation (1); the reactions therefore resemble

$$cis\text{-}[M(N_2)_2(PMe_3)_4] + 2HX \longrightarrow [MX(NNH_2)(PMe_3)_4]X + N_2 \quad (1)$$

those of the analogues *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ and *trans*-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ and related complexes.[1–9] These reactions were carried out with anhydrous HCl under vacuum ($Et_2O$, hexane, or methanol solvent) or with $SiIMe_3$ added to a suspension of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ in methanol (to generate anhydrous HI). The hydrazido(2−) complexes precipitated out of the hexane or $Et_2O$ solvent (X = Cl or I) or remained after the removal of methanol, when it was the solvent. The yields of hydrazido(2−) compounds were highest for *cis*-$[M(N_2)_2(PMe_3)_4]$. For $[M(N_2)(PMe_3)_5]$ some dinitrogen gas was evolved, together with production of $[PHMe_3]X$ equivalent to the hydrazido(2−) complex formed.

Analytical and spectroscopic data for these complexes are shown in Table 1. They are direct analogues of *trans*-$[MX(NNH_2)(Ph_2PCH_2CH_2PPh_2)_2]X$[12] and *trans*-$[MX(NNH_2)(PMe_2Ph)_4]X$.[13] The latter complexes are intermediates in the formation of *mer*-$[MX_2(NNH_2)(PMe_2Ph)_3]$.[13] In contrast to the $PMe_2Ph$ system, the $PMe_3$ system appears to give exclusively tetrakis(phosphine) products and the stability of this unit appears to resemble that of the bis(diphosphine) unit in *trans*-$[MX(NNH_2)(Ph_2PCH_2CH_2PPh_2)_2]X$ and its analogues.[1,5,12]

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† Chloro(hydraziniumido)tetrakis(trimethylphosphine)tungsten dichloride.

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

**Table 1.** Analytical and spectroscopic data for hydrazide complexes

| $[MX(NNH_2)(PMe_3)_4]A$ | | | | Analysis[a]/% | | | I.r.[b]/cm$^{-1}$ | $^1$H N.m.r.[c] (δ) | | | $^{31}$P[d] N.m.r. | $\Lambda_M$[e]/$\Omega^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| M | X | A | Colour | C | H | N | ν(N–H) | $PMe_3$ | $NNH_2$ | Solvent | (δ/p.p.m.) | cm$^2$ mol$^{-1}$ |
| Mo | Cl | Cl | Yellow | 28.7<br>(27.8) | 7.6<br>(7.6) | 5.6<br>(5.0) | 3 400s (br)<br>3 100 (br) | 1.6 (br s) | 9.5 (br) | $C^2HCl_3$ | −146.8 | 46[f] |
| Mo | I | I | Red | 21.1<br>(21.5) | 5.6<br>(5.1) | 4.1<br>(3.8) | 3 420w<br>3 180s (br) | 1.7 (br s) | 8.3 (br) | $C^2HCl_3$ | −158.6 | 21 |
| W | Cl | Cl | Yellow-orange | 25.1<br>(24.5) | 6.6<br>(6.5) | | 3 350w<br>3 120s (br) | 1.8 (pst) | n.o. | $C^2H_3O^2H$ | −164.6<br>(280) | n.d. |
| W | Cl | $BPh_4$ | Orange | 48.9<br>(49.5) | 6.7<br>(6.7) | | 3 340w<br>3 250w<br>3 160w | 1.6 (pst) | 3.6 (qnt) | $C^2HCl_3$ | −166.5<br>(279) | n.d. |
| $[WCl(NNH_3)(PMe_3)_4]Cl_2$ | | | Red | 23.0<br>(23.1) | 6.2<br>(6.3) | 4.5<br>(4.3) | 3 420w<br>2 500 (vbr) | 1.7 (pst) | n.o. | $C^2H_3O^2H$ | −168.6<br>(281) | 59 |

[a] Calculated values in parentheses. [b] Hexachlorobutadiene or Nujol mulls. s = Strong, br = broad, w = weak, v = very, [c] s = Singlet, pst = pseudo-triplet, qnt = quintet, n.o. = not observed, n.d. = not determined. [d] Relative to $P(OMe)_3$, negative values to high field, unless otherwise stated. For tungsten complexes $^1J$(P–W) in parentheses. Singlets. [e] In *ca.* $10^{-2}$ mol dm$^{-3}$ $MeNO_2$ solution unless otherwise stated. [f] In *ca.* $10^{-2}$ mol dm$^{-3}$ dimethylformamide.

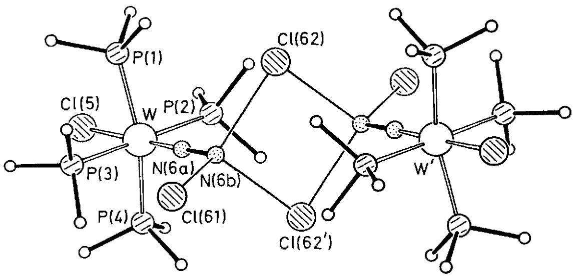

**Figure.** A hydrogen-bonded, dimeric unit of $[WCl(NNH_3)(PMe_3)_4]Cl_2$. The principal atoms are named; names with primes indicate atoms related by the centre of symmetry

The spectroscopic properties of the complexes $[MX(NNH_2)(PMe_3)_4]X$ are typical of this class of compound (Table 1): $NH_2$ i.r. absorptions in the 3 450—3 100 cm$^{-1}$ region; N$H_2$ resonance at δ 8—10 which disappears on addition of $D_2O$; single $^{31}$P resonance showing a *trans* structure; low conductivities because of strong hydrogen bonding between the $NH_2$ group and the X anions.

The complexes *trans*-$[MoX(NNH_2)(PMe_3)_4]X$ react further with an excess of HCl in methanol to give medium yields of ammonia and essentially no hydrazine (<0.2%). In separate experiments, protonation of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ and $[Mo(N_2)(PMe_3)_5]$ with HCl–MeOH gave varying yields of ammonia; the maximum yield was 0.4 $NH_3$ per Mo whether starting from the hydrazide or the dinitrogen complexes.

The course of the reaction of $[MoCl(NNH_2)(PMe_3)_4]Cl$ with HCl–MeOH was monitored by $^{31}$P n.m.r. spectroscopy which showed rapid degradation of the singlet at −146.8 p.p.m. [relative to $P(OMe)_3$] of the starting material, appearance of a resonance at −141 p.p.m., assigned to $[PHMe_3]^+$, which broadened and shifted to a final broad singlet at −126.0 p.p.m. These observations suggest initial loss of $PMe_3$ in the reaction followed by subsequent build-up of a paramagnetic species, as has been observed in related systems.[5,8] No final metal-containing product could be isolated. Nitrogen-15 n.m.r. studies of the reaction are discussed below.

*Preparation and Structural Characterisation of* $[WCl(NNH_3)(PMe_3)_4]Cl_2$ (**A**).—*Preparation.* The reaction of *trans*-$[WCl(NNH_2)(PMe_3)_4]Cl$ with HCl–MeOH was investigated as for its molybdenum analogues above. Red solutions were obtained without evolution of gas (Töpler measurement) from which could be isolated red crystals of composition $WCl_3(N_2H_3)(PMe_3)_4$ (**A**) by analysis (Table 1). The same compound could also be obtained by treatment of *cis*-$[W(N_2)_2(PMe_3)_4]$ or $[W(N_2)(PMe_3)_5]$ with HCl–MeOH. In these latter reactions no $NH_3$ or $N_2H_4$ was obtained and 1 mol of $N_2$ was evolved in the reaction of *cis*-$[W(N_2)_2(PMe_3)_4]$.

Originally compound (**A**) was considered to be $[WCl(NNH_2)(PMe_3)_4][HCl_2]$ by analogy with other $HCl_2$ salts obtained from analogous reactions,[1–9,12] especially since, on treatment with $Na[BPh_4]$ it gave *trans*-$[WCl(NNH_2)(PMe_3)_4][BPh_4]$ (Table 1).

Nevertheless, the poor solubility of (**A**) and its somewhat unusual i.r. features prompted us to determine its *X*-ray structure, which establishes it as the first example of a hydrazidium complex, as shown in the Figure.

*Structure.* The crystal comprises discrete centrosymmetric, dimeric units of two cations linked through $Cl^-$ anions by strong hydrogen bonds. Atomic co-ordinates are listed in Table 2, and molecular dimensions are in Table 3.

In the cation the W atom is co-ordinated by the four monophosphine ligands, which form a rather distorted square equatorial plane, and the other two ligands are *trans* in a virtually linear Cl–W–N–N system normal to that plane. The $N_\beta$ atom, N(6b), is approximately equidistant (Table 3) from three anions which are arranged in an almost equilateral triangle. The N–Cl distances are typical of strong, linear N–H ··· Cl hydrogen bonds, and this unique arrangement of three such contacts implies, even without the identification of the three H atoms, that this is a hydrazidium ($=N-\overset{+}{N}H_3$) ligand. Of the three $Cl^-$ ions bound to N(6b), two, Cl(62) and Cl(62′), are related by the centre of symmetry, and these bridge the two cations; the third, Cl(61), is not involved in further bonding.

The co-ordination dimensions are much as expected for an octahedral tungsten(IV) complex cation (see, for example, Table 6 of ref. 14 for comparison). The additional proton on N(6b) appears to have marginally increased the lengths of both the N–N and W–N bonds relative to those of hydrazido(2−) complexes.[14] This is not surprising, since protonation at the terminal nitrogen would be expected to reverse, to some extent, the drift of electrons towards the metal in hydrazido(2−) ligands, which leads to shortening of their N–N and W–N bonds.[14]

The *trans*-W–Cl bond is slightly longer than in $[WCl(NNH_2)(Ph_2PCH_2CH_2PPh_2)_2][BPh_4]$,[15] but this appears to be a steric effect; the $PMe_3$ groups of P(1) and P(4) are displaced

**Table 2.** Final atomic co-ordinates (fractional $\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for $[WCl(NNH_3)(PMe_3)_4]Cl_2$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| W | 2 470.1(5) | 292.2(5) | 2 347.6(5) |
| P(1) | 2 397(3) | 2 114(3) | 2 231(4) |
| C(11) | 2 972(12) | 2 704(12) | 1 317(12) |
| C(12) | 1 226(12) | 2 659(15) | 1 878(17) |
| C(13) | 2 864(14) | 2 745(13) | 3 393(13) |
| P(2) | 4 071(3) | 357(4) | 1 823(3) |
| C(21) | 4 080(14) | 608(14) | 463(13) |
| C(22) | 4 832(14) | −714(14) | 2 067(18) |
| C(23) | 4 929(13) | 1 265(14) | 2 482(17) |
| P(3) | 922(3) | 256(4) | 2 968(4) |
| C(31) | 803(12) | 1 143(13) | 3 932(14) |
| C(32) | −167(12) | 377(18) | 2 054(17) |
| C(33) | 731(15) | −833(15) | 3 679(16) |
| P(4) | 2 254(4) | −1 462(4) | 1 770(4) |
| C(41) | 1 050(13) | −1 868(17) | 1 264(16) |
| C(42) | 2 707(16) | −2 338(13) | 2 794(15) |
| C(43) | 2 813(18) | −1 854(15) | 690(16) |
| Cl(5) | 1 646(3) | 522(4) | 561(3) |
| N(6a) | 3 076(7) | 124(8) | 3 639(12) |
| N(6b) | 3 546(9) | 5(9) | 4 653(10) |
| Cl(61) | 2 269(3) | −337(3) | 6 162(4) |
| Cl(62) | 5 036(3) | 1 651(3) | 5 246(4) |

**Table 3.** Bond lengths (Å) and angles (°) with e.s.d.s in parentheses

| | | | |
|---|---|---|---|
| (*a*) In the co-ordination sphere of tungsten | | | |
| W–P(1) | 2.499(4) | W–P(3) | 2.521(5) |
| W–P(2) | 2.532(5) | W–P(4) | 2.522(5) |
| W–Cl(5) | 2.463(4) | W–N(6a) | 1.785(15) |
| P(1)–W–P(2) | 88.7(2) | P(2)–W–P(3) | 176.8(2) |
| P(1)–W–P(3) | 90.6(2) | P(2)–W–P(4) | 90.8(2) |
| P(1)–W–P(4) | 158.4(2) | P(3)–W–P(4) | 91.0(2) |
| P(1)–W–Cl(5) | 78.8(2) | P(1)–W–N(6a) | 101.3(4) |
| P(2)–W–Cl(5) | 91.2(2) | P(2)–W–N(6a) | 88.8(4) |
| P(3)–W–Cl(5) | 91.7(2) | P(3)–W–N(6a) | 88.7(4) |
| P(4)–W–Cl(5) | 79.6(2) | P(4)–W–N(6a) | 100.3(4) |
| Cl(5)–W–N(6a) | 179.5(3) | | |
| (*b*) In the hydrazine ligand and its hydrogen bonds | | | |
| N(6a)–N(6b) | 1.396(20) | N(6b) • • • Cl(62) | 3.101(13) |
| N(6b) • • • Cl(61) | 3.009(13) | N(6b) • • • Cl(62′) | 3.034(13) |
| N(6a)–N(6b)–Cl(61) | 114.9(8) | Cl(61)–N(6b)–Cl(62) | 115.1(4) |
| N(6a)–N(6b)–Cl(62) | 110.0(8) | Cl(61)–N(6b)–Cl(62′) | 110.2(4) |
| N(6a)–N(6b)–Cl(62′) | 108.9(8) | Cl(62)–N(6b)–Cl(62′) | 96.1(4) |
| N(6b)–N(6a)–W | 179.2(10) | N(6b)–Cl(62)–N(6b′) | 83.9(3) |
| (*c*) In the phosphine ligands | | | |
| P(1)–C(11) | 1.791(15) | P(3)–C(31) | 1.798(17) |
| P(1)–C(12) | 1.816(16) | P(3)–C(32) | 1.793(18) |
| P(1)–C(13) | 1.785(16) | P(3)–C(33) | 1.814(18) |
| P(2)–C(21) | 1.847(16) | P(4)–C(41) | 1.817(18) |
| P(2)–C(22) | 1.819(17) | P(4)–C(42) | 1.836(18) |
| P(2)–C(23) | 1.848(17) | P(4)–C(43) | 1.858(19) |
| W–P(1)–C(11) | 118.2(6) | W–P(3)–C(31) | 115.7(6) |
| W–P(1)–C(12) | 116.8(7) | W–P(3)–C(32) | 119.0(8) |
| W–P(1)–C(13) | 115.1(6) | W–P(3)–C(33) | 114.8(8) |
| C(11)–P(1)–C(12) | 99.5(9) | C(31)–P(3)–C(32) | 103.3(10) |
| C(11)–P(1)–C(13) | 103.1(8) | C(31)–P(3)–C(33) | 97.9(9) |
| C(12)–P(1)–C(13) | 101.5(10) | C(32)–P(3)–C(33) | 103.3(11) |
| W–P(2)–C(21) | 117.3(7) | W–P(4)–C(41) | 117.1(8) |
| W–P(2)–C(22) | 118.0(8) | W–P(4)–C(42) | 112.9(6) |
| W–P(2)–C(23) | 116.8(7) | W–P(4)–C(43) | 117.7(7) |
| C(21)–P(2)–C(22) | 101.9(10) | C(41)–P(4)–C(42) | 104.5(10) |
| C(21)–P(2)–C(23) | 102.1(10) | C(41)–P(4)–C(43) | 98.6(11) |
| C(22)–P(2)–C(23) | 97.7(10) | C(42)–P(4)–C(43) | 104.1(10) |

The primed numbers indicate atoms related by a centre of symmetry.

from the equatorial 'plane' towards Cl(5), because of Me • • • Me interactions and the proximity of the chloride ions. The phosphine groups are tightly meshed together, and show a pseudo-mirror plane of symmetry through P(2), P(3), Cl(5), and the nitrogen atoms. Atom Cl(61) lies close to this plane and makes close contact with the methyl group of P(3), *e.g.* Cl(61) • • • C(33) 3.66(2) Å; Cl(62) and Cl(62′), on either side of the plane, interact strongly with the methyl groups of P(2).

Contacts between dimer units in the crystal are at normal van der Waals distances.

*Properties.* Compound (**A**) is poorly soluble except in polar solvents such as MeOH, no doubt a consequence of the extensive hydrogen bonding discussed above, and consequently N–*H* n.m.r. resonances could not be determined. It is also stable to further attack by HCl–MeOH and in this regard it is analogous to the diphosphine complex $[WX(NNH_2)(Ph_2PCH_2CH_2PPh_2)_2]X$, which will only show further reaction of the hydrazide ligand under conditions sufficiently drastic to disrupt the diphosphine chelation [1–9] or if a labile anion allows addition of electrons to the complex.[16] Thus, in this particular situation, the $\{W(PMe_3)_4\}$ unit appears to be not only particularly stable, but also sufficiently electron-releasing to induce further protonation of the hydrazido(2−) ligand. Nevertheless, it appears that disruption of the co-ordination sphere (with loss of $PMe_3$ or an anionic ligand) is necessary to allow the cleavage of the N–N bond to occur, and from the above $^{31}P$ n.m.r. study this appears to be what happens in reactions of the molybdenum analogue.

In order to gain more information on the detail of these reactions, a $^{15}N$ n.m.r. study was undertaken.

$^{15}N$ *N.M.R. Experiments.*—(*a*) *Preparation and nitrogen n.m.r. properties of* $^{15}N$*-labelled complexes.* The $^{15}N$ n.m.r. properties given in Table 4 were measured for the monitoring of protonation reactions of $^{15}N_2$ complexes, as described below. The complexes *cis*-$[M(^{15}N_2)_2(PMe_3)_4]$, with M = Mo (**B**) or W, and $[Mo(^{15}N_2)(PMe_3)_5]$ (**C**) were prepared by exchange (Experimental section). Of interest is the crossover of the $N_\alpha$ and $N_\beta$ resonances in (**B**) compared to (**C**), the $N_\alpha$ resonance being assigned by the coupling to phosphorus; such crossovers with change in the nature of the metal site have been observed for other dinitrogen complexes.[17] In dinitrogen complexes of molybdenum the $N_\alpha$ and $N_\beta$ resonances are close together, and the replacement of $PMe_3$ *cis* to $N_2$ in (**C**) by a second $N_2$ to give (**B**) increases the $N_\alpha$ shielding by about 6 p.p.m., and deshields $N_\beta$ by a similar amount. The nitrogens in *cis*-$[M(^{15}N_2)_2(PMe_3)_4]$ complexes are shielded by about 2.5 p.p.m. (Mo) and 4 p.p.m. (W) relative to those in the analogous $PMe_2Ph$ complexes.[17]

The hydrazido(2−) and hydrazidium complexes *trans*-$[MoCl(^{15}N^{15}NH_2)(PMe_3)_4]Cl$ (**D**) and *trans*-$[WCl(^{15}N^{15}NH_3)(PMe_3)_4]Cl_2$ ($[^{15}N]$**A**) were prepared also, and their $^{15}N$ n.m.r. parameters are shown in Table 4. For these compounds the $N_\beta$ signal is inverted, on broad-band proton decoupling, by a strong nuclear Overhauser effect (n.O.e.). Unusually, the $N_\beta$ resonance of the molybdenum hydrazide (**D**) shows no NH coupling, presumably due to fast exchange; this may perhaps be related to the ready protonation of the analogous tungsten hydrazide to give a stable hydrazidium complex.

(*b*) $^{15}N$ *N.m.r. monitoring of protonation reactions.* The $^{15}N$ n.m.r. spectrum of the reaction of *cis*-$[W(^{15}N_2)_2(PMe_3)_4]$ with HCl in MeOH at 243 K showed rapid degradation of the

**Table 4.** Nitrogen-15 n.m.r.[a] and i.r. data for $^{15}N$-labelled complexes

| Complex | $\delta(^{15}N_{\alpha})$ | $\delta(^{15}N_{\beta})$ | $^{1}J(^{15}N^{15}N)$ | $^{2}J(^{15}NP)$ | Solvent | $\nu(^{15}N_2)$[b]/cm$^{-1}$ |
|---|---|---|---|---|---|---|
| **(B)** *cis*-$[Mo(^{15}N_2)_2(PMe_3)_4]$ | −41.5 | −34.3 | 6 | n.r. | thf | 1 945, 1 880 |
| **(C)** $[Mo(^{15}N_2)(PMe_3)_5]$ | −35.1 | −41.2 | 6 | n.r. | thf | 1 890 |
| *cis*-$[W(^{15}N_2)_2(PMe_3)_4]$ | −61.9 | −36.8 | 6 | 17 (*trans*) | MeOH | 1 930, 1 870 |
| **(D)** *trans*-$[MoCl(^{15}N^{15}NH_2)(PMe_3)_4]Cl$ | −62.9 | −236.5 | 10 | 8 | MeOH | |
| ($[^{15}N]$**A**) *trans*-$[WCl(^{15}N^{15}NH_3)(PMe_3)_4]Cl_2$ | −91.3 | −253.4 | n.r. | n.r. | MeOH | |

[a] $\delta(^{15}N)$ in p.p.m. relative to external $C^2H_3NO_2$, coupling constants in Hz. n.r. = Not resolved. [b] In Nujol mull.

**Table 5.** $^{15}N$ N.m.r. parameters and assignments of intermediates in the reactions of dinitrogen complexes with HCl (generated by $SiClMe_3$) in MeOH

| | Products: $\delta(^{15}N)$/p.p.m., $J$/Hz | | |
|---|---|---|---|
| Reactant[a] | $N_{\alpha}$ | $N_{\beta}$ | Assignment |
| *cis*-$[W(^{15}N_2)_2(PMe_3)_4]$ | −91.3 | −253.4[b] | *trans*-$[WCl(^{15}N^{15}NH_3)(PMe_3)_4]Cl_2$ ($[^{15}N]$**A**) |
| (243 K) | | −234.8[b,c] | $W{-}^{15}N_{\alpha}{-}^{15}N_{\beta}H_2$ |
| | | −237.1[b,c] | $W{-}^{15}N_{\alpha}{-}^{15}N_{\beta}H_2$ |
| $[Mo(^{15}N_2)(PMe_3)_5]$ **(C)** | −62.9 | −236.5[b] | *trans*-$[MoCl(^{15}N^{15}NH_2)(PMe_3)_4]Cl$ **(D)** |
| (213 K) | $^{2}J(PN) = 8$ | $^{1}J(^{15}N^{15}N) = 10$ | |
| | −48.2 | −223.6[b] | $Mo{-}^{15}N_{\alpha}{-}^{15}N_{\beta}H_2$ **(E)** |
| | | $^{1}J(^{15}NH) = 92$ | |
| | −36.0 | −123.2[b] | $Mo{-}^{15}N_{\alpha}{-}^{15}N_{\beta}H$ |
| | −322.1[b] | | See text |
| | −278[b] | | See text |
| *cis*-$[Mo(^{15}N_2)_2(PMe_3)_4]$ **(B)** | −35.8 | −218.4[b] | $Mo{-}^{15}N_{\alpha}{-}^{15}N_{\beta}H_2$ **(F)** |
| | | $^{1}J(^{15}NH) = 87$ | |

[a] For reaction conditions see text. [b] Inverted by n.O.e. on proton decoupling. [c] Low intensity.

resonances of the starting complex (Table 4), appearance of free $^{15}N_2$ (≈74 p.p.m.), and the characteristic resonances of $[WCl(^{15}N^{15}NH_3)(PMe_3)_4]^{2+}$ (Tables 4 and 5). There were also minor (<5%) resonances in the region for $^{15}N_{\beta}$ of hydrazide ligands at −234.8 and −237.1 p.p.m. which had essentially disappeared after 20 min, leaving only the resonances of the hydrazidium complex. These data are consistent with the earlier observation that only the hydrazidium complex was the final product of this reaction.

The weaker lines at −234.8 and −237.1 p.p.m. were assigned to N-*N*H$_2$ groups, on the evidence of the n.O.e. and the comparison with *trans*-$[WCl(NNH_2)(Ph_2PCH_2CH_2PPh_2)_2]Cl$, for which the $N_{\alpha}$ and $N_{\beta}$ shifts are −96.2 and −253.4 p.p.m. respectively.[9] These shifts are sensitive to the nature of the solvent and the co-ligands, particularly the *trans* ligand (X = Cl, Br, I, or $HSO_4$ in the series measured).[9] The minor products observed could then be hydrazides with replacements of phosphine by methoxide, or chloride, as described below for the molybdenum systems.

The nitrogen shifts for the hydrazidium complex ($[^{15}N]$**A**) show only a small increase in shielding on protonation of the hydrazide. Protonation of nitrogen in a delocalised system greatly increases the nitrogen shielding, by reducing paramagnetic (*e.g.* $n \longrightarrow \pi^*$) circulations;[18] thus protonation of linear diazenides (M–N=NH) to give hydrazides (M=N–NH$_2$) increases the $N_{\beta}$ shielding by 60—75 p.p.m., and the $N_{\alpha}$ shielding by *ca.* 50 p.p.m.[19] as electrons are delocalised towards the metal. In a σ-bonded system, however, protonation may decrease the nitrogen shielding, as *e.g.* by 40 p.p.m. from gaseous ammonia to aqueous ammonium ion, largely as an effect of the positive charge on the nitrogen. Atom $N_{\beta}$ in the hydrazido(2−) ligand is deshielded relative to hydrazines [which have $\delta(^{15}N_{\beta})$ *ca.* −320 p.p.m.] by flattening of the nitrogen as in amides [*cf.* $\delta(^{15}N)$ −265 p.p.m. for formamide]. The smallness of the increase in shielding on protonation of the hydrazide to hydrazidium suggests localisation of the positive charge on $N_{\beta}$, with back bonding from the electron-rich metal.

The reactions of the molybdenum compounds are more complicated. Addition of $SiMe_3Cl$ to $[Mo(^{15}N_2)(PMe_3)_5]$ in MeOH at 213 K caused evolution of $^{15}N_2$ and formation of a red solution. Spectral accumulation at this temperature gave a number of resonances assigned as follows (see Table 5). First a pair of resonances at −36.0 and −123.2 p.p.m. are assigned to $N_{\alpha}$ and $N_{\beta}$ of a diazenido ligand since this is the typical resonance region for these ligands.[19] The low concentration and rapid (≈15 min) disappearance of these resonances are consistent with the formation of a low steady-state concentration of an –N$_2$H complex which rapidly converts into an =N–NH$_2$ compound, typical behaviour for diazenide ligands.[1–9,19]

Two further sets of resonances are observed which are typical of hydrazido(2−) species.[9] One set is due to the hydrazide $[MoCl(^{15}N^{15}NH_2)(PMe_3)_4]Cl$ **(D)** (*cf.* Tables 1, 4, and 5). The second hydrazide **(E)** shows NH coupling, as is more usual.

After 20 min of reaction at 298 K and further spectral accumulation at 213 K the hydrazide **(D)** resonances were still present, those of **(E)** had disappeared, and a singlet had appeared at −322.1 p.p.m. This showed a large n.O.e., comparable to that of **(D)**, on proton decoupling. After 24 h of reaction at room temperature the hydrazide **(D)** resonances had disappeared but the signal at −322.1 p.p.m. was still present, accompanied by a broader signal at −278 p.p.m., also showing a sizeable n.O.e. These signals must therefore arise from $NH_n$ species with exchanging protons. In these systems, $NH_4^+$ appears at about −365 p.p.m.; $N_2H_5^+$ might be expected to resonate at about −355 p.p.m., but no hydrazine was recovered on base distillation of the product.

Possible candidates for the resonance at −322.1 p.p.m. are $SiMe_3(NH_2)$ [since $SiHMe_3Bu$ and $SiMe_3(NHPh)$ have $\delta(^{15}N)$ −325(3) and −326(3) p.p.m. respectively][20] or $PMe_3(NH_2)^+$ {$[PMe_3(NHPh)]Cl$ has $\delta(^{15}N)$ −322.3 p.p.m. and small $J(P^{15}N)$ 4 Hz};[18] the formation of $PHMe_3^+$ was mentioned in the discussion of the $^{31}P$ spectra. Both of these species would give ammonia on base distillation, and the phosphazene gives phosphine oxides also.[21] The resonance at

$-278$ p.p.m. might represent a hydroxylamine [*cf.* $PhCH_2ONH_2$ has $\delta(^{15}N)$ $-254$ p.p.m.],[20] or possibly some residual hydrazide, since the final yield of ammonia is about 0.4 mol per Mo. The final reduction to ammonia produces paramagnetic species such as $Mo^{III}$, so paramagnetic shifts, broadening, and loss of signal may be present. Work-up of the reaction mixture gave ammonia, phosphine oxide, and other uncharacterised products.

Similar treatment of *cis*-$[Mo(^{15}N_2)_2(PMe_3)_4]$ gave the hydrazide (**D**) and a transient hydrazide (**F**) showing NH coupling (Table 4), but no diazenide signals were evident.

The observation of a number of hydrazido(2−) species in reactions of dinitrogen complexes leading to ammonia has already been reported for $PMe_2Ph$ systems[8] and is in keeping with mechanistic studies,[22] which have shown replacement of phosphine by solvent to be important in allowing the protonation of ligating dinitrogen to pass through the hydrazide stage to ammonia. Loss of phosphine in the molybdenum system has already been noted above in $^{31}P$ n.m.r. spectra.

## Conclusions

Use of the relatively small and strongly basic $PMe_3$ ligand has allowed isolation of a complex of a ligand beyond the hydrazido(2−) stage of reduction of ligating dinitrogen, namely the hydrazidium ligand. It seems reasonable to propose that the isolation of $[WCl(NNH_3)(PMe_3)_4]Cl_2$ is a consequence of the following: favourable basicity of the precursor $=N-NH_2$ complex, resistance of the $(PMe_3)_4$ unit towards loss from the tungsten centre, and insolubility of the hydrazidium complex due to the strong hydrogen bonding of the $NH_3$ and $Cl^-$ ions.

The hydrazidium stage of reduction no doubt occurs in related systems such as in the reactions of the molybdenum analogues above, but it has too short a lifetime to be observed. Nevertheless, we might expect that hydrazidium complexes will be isolated from reactions of analogous hydrazide compounds containing strongly electron-releasing ligands, such as $[MoBr(NNH_2)(Et_2PCH_2CH_2PEt_2)_2]Br$, which does appear to add a third proton.[23]

The hydrazidium ligand is the precursor to N–N bond cleavage in the reduction of dinitrogen to ammonia at metal centres. Together with recent evidence for the reduction of complex cations such as $[MoCl(NH)(Ph_2PCH_2CH_2PPh_2)_2]^+$ to ammonia,[24] the new evidence reported herein adds further credence to the proposed cycle of reduction of dinitrogen shown in the Scheme, which might well apply to the molybdenum centre of nitrogenase.

## Experimental

Air-sensitive materials were handled under dinitrogen, argon, or with vacuum techniques as appropriate, non-condensable gases were manipulated by a Töpler pump. Solvents were dried by standard methods and distilled before use. N.m.r. spectra were obtained using JEOL FX90Q, Bruker WM360, and Varian XL200 instruments, and i.r. spectra using Philips Scientific SP2000 or Perkin-Elmer 577 instruments. Nitrogen-15 chemical shifts of *ca.* $10^{-2}$ mol dm$^{-3}$ solutions were measured relative to standard $CD_3NO_2$.[9] Conductivities were obtained using a Portland Electronics conductivity bridge and microanalyses were by Mrs. G. Olney and Mr. C. Macdonald of the University of Sussex and Nitrogen Fixation Laboratory respectively. The dinitrogen complexes *cis*-$[M(N_2)_2(PMe_3)_4]$ and $[M(N_2)(PMe_3)_5]$ were prepared by published methods.[11] Enriched $^{15}N_2$ (95%) was purchased from Prochem Ltd. and repeatedly passed through a trap cooled in liquid nitrogen before use.

X-*Ray Analysis of* $[WCl(NNH_3)(PMe_3)_4]Cl_2$.—*Crystal data.* $C_{12}H_{39}Cl_3N_2P_4W$, $M = 625.6$, monoclinic, space group $P2_1/c$ (no. 14), $a = 14.370(7)$, $b = 13.684(4)$, $c = 13.318(10)$ Å, $\beta = 101.23(6)°$, $U = 2\,568.6$ Å$^3$, $Z = 4$, $D_c = 1.617$ g cm$^{-3}$, $F(000) = 1\,240$, $\mu$(Mo-$K_\alpha$) = 51.5 cm$^{-1}$, $\lambda$(Mo-$K_\alpha$) = 0.710 69 Å.

Crystals were orange plates; one, *ca.* 0.25 × 0.15 × 0.05 mm, was mounted on a glass fibre and coated with epoxy resin. This sealing merely slowed the decomposition of the sample. After brief photographic examination, the crystal was mounted on our Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for measurement of accurate cell parameters (from the settings of 25 centred reflections having $\theta$ *ca.* 10°) and of diffraction intensities. The intensities of two control reflections dropped more than 40% before the data set to $\theta_{max.} = 20°$ was complete. Corrections for crystal decay, Lorentz polarisation effects, and absorption (from the crystal shape and size) were applied, and 2 214 satisfactory, independent data were used in the structure analysis.

Structure determination was by the heavy-atom method in the SHELX program system.[25,26] Refinement, by full-matrix least-squares methods, was concluded at $R = 0.083$, $R' = 0.054$[25] for all reflections, weighted $w = \sigma_F^{-2}$.

The methyl groups were treated as rigid $CH_3$ groups. Two of the three H atoms of the $NNH_3$ ligand were located in difference maps, but did not refine satisfactorily and were not included in the final refinement cycles. All the non-hydrogen atoms were refined anisotropically; the hydrogen atoms of each methyl group were allowed a common isotropic thermal parameter. In a final difference map, the highest peaks, *ca.* 1.0 e Å$^{-3}$, were all close to the W atom.

Scattering factor curves were taken from ref. 27. Computer programs used in this analysis are as noted above and listed in Table 4 of ref. 28. They were run on the VAX 11/750 machine at IHR (Glasshouse Crops Research Institute), Littlehampton.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

*Chloro[hydrazido(2−)]tetrakis(trimethylphosphine)molybdenum*(IV) *Chloride*, $[MoCl(NNH_2)(PMe_3)_4]Cl$.—Hydrogen chloride (2.3 mol equivalent) was condensed at −196 °C in a vacuum onto *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (0.35 g, 0.75 mmol) in hexane or $Et_2O$ (*ca.* 20 cm$^3$) and the mixture was allowed to warm to room temperature with stirring. Dinitrogen (0.90—1.1 mol per Mo) was evolved and a pale yellow-orange precipitate formed in 2—3 min. The suspension was stirred for 5—6 h and the solid was filtered off, washed with $Et_2O$, and dried. Yield 70%. This complex can also be obtained using $SiClMe_3$ and methanolic suspensions of the bis(dinitrogen) complex. The labelled compound $[MoCl(^{15}N^{15}NH_2)(PMe_3)_4]Cl$ was prepared from *cis*-$[Mo(^{15}N_2)_2(PMe_3)_4]$. The tungsten analogue *trans*-$[WCl(NNH_2)(PMe_3)_4]Cl$ was similarly prepared (yield 65%). Both complexes were also obtained using $[M(N_2)(PMe_3)_5]$ as starting material with lower yields and both can be crystallised from thf–MeOH as *yellow-orange plates.*

*[Hydrazido(2−)]iodotetrakis(trimethylphosphine)molybdenum*(IV) *Iodide*, $[MoI(NNH_2)(PMe_3)_4]I$.—Trimethylsilyl iodide (0.2 cm$^3$, 1:2) was added dropwise to a suspension of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (0.27 g, 0.6 mmol) in MeOH (10 cm$^3$) at 0 °C with stirring. A pale yellow precipitate was immediately formed and dinitrogen was evolved. After 5—6 min the precipitate dissolved and the solution became red. The solution was stirred for 15—20 min then the solvent was removed in a vacuum. The crude product was crystallised from thf–$Et_2O$ at −20 °C as *yellow prisms*, yield 84%. The product can also be obtained using $[Mo(N_2)(PMe_3)_5]$ as starting material.

*Chloro(hydrazidium)tetrakis(trimethylphosphine)tungsten*(IV) *Dichloride*, $[\mathrm{WCl(NNH_3)(PMe_3)_4}]\mathrm{Cl_2}$ (**A**).—(*i*) An excess of hydrogen chloride (1:10) was condensed in a vacuum at −196 °C onto *cis*-$[\mathrm{W(N_2)_2(PMe_3)_4}]$ (0.24 g, 0.44 mmol) in MeOH (30 $\mathrm{cm^3}$). The mixture was allowed to warm to room temperature and dinitrogen (*ca.* 1.0—1.1 mol per W) was rapidly evolved. The red solution formed was stirred for 10 h and then concentrated in a vacuum to about 5—10 $\mathrm{cm^3}$. Diethyl ether (*ca.* 10—15 $\mathrm{cm^3}$) was added and the solution was cooled at − 30 °C for 3 d. *Red Crystals* were obtained, washed with $\mathrm{Et_2O}$, and dried. Yield 75%.

(*ii*) An excess of $\mathrm{SiClMe_3}$ (1:6, 1.25 $\mathrm{cm^3}$) was added to a solution of *trans*-$[\mathrm{WCl(NNH_2)(PMe_3)_4}]\mathrm{Cl}$ (0.94 g, 1.6 mmol) in MeOH (16 $\mathrm{cm^3}$). The solution was stirred for 6—7 h and then the solvent was removed *in vacuo*. The residue was extracted with $\mathrm{Et_2O}$–MeOH (or thf–MeOH) and crystallised at −30 °C. Yield 80%.

*Chloro[hydrazido(2−)]tetrakis(trimethylphosphine)tungsten*(IV) *Tetraphenylborate*, $[\mathrm{WCl(NNH_2)(PMe_3)_4}][\mathrm{BPh_4}]$.—Methanol (20 $\mathrm{cm^3}$) was added to a mixture of complex (**A**) (0.16 g) and $\mathrm{Na[BPh_4]}$ (excess, 0.28 g) and the solution was stirred for 1 h. *Orange microcrystals* precipitated, which were filtered off, washed with MeOH and $\mathrm{Et_2O}$, dried, and recrystallised from MeOH–$\mathrm{CH_2Cl_2}$. Yield 88%.

*Chloro{[$^2\mathrm{H_2}$]hydrazido(2−)}tetrakis(trimethylphosphine)tungsten*(IV) *Tetraphenylborate*, $[\mathrm{WCl(NN^2H_2)(PMe_3)_4}][\mathrm{BPh_4}]$.—$[\mathrm{WCl(NNH_2)(PMe_3)_4}][\mathrm{BPh_4}]$ (0.13 g) was dissolved in dry $\mathrm{C^2H_2Cl_2}$ (5 $\mathrm{cm^3}$) and a few drops of $^2\mathrm{H_2O}$ were added under dinitrogen. The solution was stirred vigorously for 40—50 min and then taken to dryness *in vacuo*. The solid was washed with $\mathrm{Et_2O}$ and dried [i.r. data (KBr): $\nu(\mathrm{N{-}^2H_2})$ 2 380 and 2 330 $\mathrm{cm^{-1}}$].

*Preparation of* $^{15}$N-*Labelled Compounds*.—Hexane (40 $\mathrm{cm^3}$) was condensed *in vacuo* at −196 °C onto *cis*-$[\mathrm{Mo(N_2)_2(PMe_3)_4}]$ (1 g). The flask was filled with an excess of $^{15}\mathrm{N_2}$ (*ca.* 1:3) and then warmed to room temperature. The solution was stirred for 3 h and then taken to dryness *in vacuo*. The exchange occurred in 40—60% yield (from spectroscopic data) with formation of the isotopomers *cis*-$[\mathrm{Mo(^{15}N_2)(^{15}N_2)(PMe_3)_4}]$, *cis*-$[\mathrm{Mo(^{15}N_2)(^{14}N_2)(PMe_3)_4}]$, and *cis*-$[\mathrm{Mo(^{14}N_2)(^{14}N_2)(PMe_3)_4}]$. The same procedure was used to prepare the labelled compounds $[\mathrm{Mo(^{15}N_2)(PMe_3)_5}]$ and *cis*-$[\mathrm{W(^{15}N_2)_2(PMe_3)_4}]$, although the tungsten derivative required a longer reaction time (5 h) and irradiation with a tungsten-filament lamp. The complex $[\mathrm{W(N_2)(PMe_3)_5}]$ does not exchange with $^{15}\mathrm{N_2}$ under these conditions.

$^{15}$N-Labelled hydrazide and hydrazidium complexes were then prepared as for their $^{14}$N analogues, work-up being under argon.

*Reactions of Dinitrogen Complexes with* HCl *monitored by* $^{15}$N *N.M.R. Spectroscopy*.—Chlorotrimethylsilane (10 molar excess) was added to a suspension of the $^{15}$N-labelled dinitrogen complex in MeOH in a n.m.r. tube (diameter 15 mm) under argon at −60 °C. The $^{15}$N spectral accumulation was commenced at this temperature. After a suitable period of accumulation the reaction solution was allowed to warm to room temperature (≈293 °C) and react for a period of choice, then the tube was recooled and accumulation recommenced.

*Estimation of Ammonia and Hydrazine*.—After reaction of the appropriate dinitrogen or hydrazide complex with acid as described above and removal of solvent, the residue was base-distilled and ammonia and hydrazine analysed by colour test, as described in earlier papers.[8]

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