# Conversion of Dinitrogen in its Molybdenum and Tungsten Complexes into Ammonia and Possible Relevance to the Nitrogenase Reaction

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Treatment of *trans*-$[M(N_2)_2(dppe)_2]$ (A) (dppe = $Ph_2PCH_2CH_2PPh_2$, M = Mo or W) with $H_2SO_4$ gives $[M(HSO_4)(NNH_2)(dppe)_2][HSO_4]$ and no ammonia or hydrazine. However, the complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (B) and *trans*-$[M(N_2)_2(PMePh_2)_4]$ (C) (M = Mo or W) react with $H_2SO_4$ in methanol at 20 °C to give ammonia (*ca.* 1.9 $NH_3$ per W atom and *ca.* 0.7 $NH_3$ per Mo atom), together with a little hydrazine for (B; M = W) but not for (B; M = Mo). Treatment of (B; M = Mo and W) with a variety of other acids gives ammonia, but less effectively than with $H_2SO_4$. Anhydrous $HBF_4$ also gives ammonia from (B; M = Mo or W), but (A; M = Mo or W) gives only *trans*-$[MF(NNH_2)(dppe)_2][BF_4]$. Ammonia (1.6 $NH_3$ per W atom) is also obtained when (B; M = W) but not (B; M = Mo) is treated with methanol alone, either at reflux or on irradiation at 20 °C for several hours. The mechanism of these reactions and their relevance to the action of nitrogenase is discussed.

WE have previously described the diprotonation and reduction of a ligating dinitrogen molecule in the complexes *trans*-$[M(N_2)_2(dppe)_2]$ (A; M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$) to give complexes of diazenido-$(N_2H)$,[1] diazine $(N_2H_2)$, and hydrazido(2−) $(NNH_2)$ ligands.[2] These reactions occur when complexes (A) are treated with halogen acids and neither ammonia nor hydrazine are produced.[2] In contrast, ammonia is obtained in good yield when the analogous complexes with unidentate tertiary phosphine ligands, *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (B; M = Mo or W) or *trans*-$[M(N_2)_2(PMePh_2)_4]$ (C; M = Mo or W), are treated with sulphuric acid in methanol, as already reported briefly.[3] This is

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[1] J. Chatt, A. J. Pearman, and R. L. Richards, *J.C.S. Dalton*, 1976, 1520.

[2] J. Chatt, G. A. Heath, and R. L. Richards, *J.C.S. Dalton*, 1974, 2074.

[3] J. Chatt, A. J. Pearman, and R. L. Richards, *Nature*, 1975, **253**, 39.

accompanied by a little hydrazine when M = W. Here we describe in detail these reactions to give ammonia and the reactions of a variety of other acids which give ammonia from ligating dinitrogen in various protic solvents, including aqueous methanol and water.

## RESULTS

*Production of Ammonia by Reaction with Acids.*—When treated with an excess of $H_2SO_4$ in methanol, complexes (B) and (C) react rapidly at 20 °C with evolution of *ca.* 1 mol of dinitrogen. Thereafter the course of the reaction differs somewhat, depending on the metal.

TABLE 1

Protonation of tungsten complexes

| Mass of complex ($m$/g)[a] | Acid (amount)[b] | Solvent ($V$/cm$^3$) | $t$/h | Yield[b] | | | | $N_2$ balance[b,c] |
|---|---|---|---|---|---|---|---|---|
| | | | | $N_2$ evolved | $NH_3$ | $N_2H_4$ | $N_2$ (NaOBr) | |
| (B; M = W) | | | | | | | | |
| 0.307[d] | $H_2SO_4$ (14.9) | thf (30) | 24 | 0.98 | 0.89 | 0.18 | 0.61 | 1.61 (1.59) |
| 0.268 | $H_2SO_4$ (14.9) | MeOH (30) | 18 | 0.97 | 1.83 | 0.02 | 0.95 | 1.91 (1.92) |
| 0.310[d] | $H_2SO_4$ (14.9) | MeOH (30) | 24 | 0.95 | 1.76 | 0.02 | 0.92 | 1.85 (1.87) |
| 0.150[e] | $H_2SO_4$ (14.9) | MeOH (30) | 20 | n.d.[f] | 1.98 | 0.03 | 1.00 | 1.02 (1.00) |
| 0.149[g] | $H_2SO_4$ (15.0) | MeOH (30) | 20 | n.d. | 1.88 | 0.02 | 0.90 | 0.96 (0.90) |
| 0.153[h] | $H_2SO_4$ (15.0) | MeOH (30) | 20 | n.d. | 1.94 | 0.02 | 0.98 | 0.99 (0.98) |
| 0.150 | $H_2SO_4$,$TiCl_3$ (15.0, 12.0) | MeOH (30) | 20 | 0.98 | 1.4 | 0.06 | 0.75 | 1.74 (1.73) |
| 0.357[d] | $H_2SO_4$ (14.6) | MeOH,$H_2O$ (15, 15) | 40 | 0.98 | 1.26 | 0.03 | 0.67 | 1.64 (1.65) |
| 0.248 | $H_2SO_4$ (18.2) | $H_2O$ (30) | 400 | n.d. | 1.50 | 0.00 | 0.76 | 0.75 (0.76) |
| 0.127 | $H_2SO_4$ (17.6) | $Me_2CO$ (30) | 20 | 0.99 | 0.20 | n.d.[i] | 0.44 | 1.09[i] (1.43) |
| 0.127[j] | $H_2SO_4$ (15.2) | $Me_2CO$ (30) | 20 | 0.96 | 1.18 | 0 | n.d. | 1.55 (n.d.) |
| 0.127 | $H_2SO_4$ (15.2) | $C_6H_6$ (30) | 50 | 1.07, 0.08[k] | 0.60 | 0.25 | 0.57 | 1.62 (1.64) |
| 0.100[l] | $H_2SO_4$ (14.9) | *m* (30) | 40 | 1.00 | 0.74 | 0.32 | 0.72 | 1.69 (1.72) |
| 0.105[l] | $H_2SO_4$ (15.6) | *n* (30) | 20 | 1.00 | 1.42 | *o* | 0.69 | 1.71 (1.69) |
| 0.141[d] | $H_2SO_4$ (14.8) | $CH_2Cl_2$ (40) | 48 | 1.09 | 0.90 | 0.13 | 0.50 | 1.67 (1.59) |
| 0.191 | $H_2SO_4$ (14.8) | $CH_2Cl_2$ (40) | 96 | 1.08 | 0.86 | 0.13 | 0.50 | 1.64 (1.58) |
| 0.133 | $H_3PO_2$ (16.0) | MeOH (30) | 42 | 1.02, 0.04[k] | 1.00 | 0.09 | 0.60 | 1.61 (1.62) |
| 0.125[e] | $H_3PO_2$ (16.0) | MeOH (30) | 42 | n.d. | 0.90 | 0.09 | 0.52 | 0.54 (0.52) |
| 0.274 | $H_3PO_4$ (13.5) | MeOH (30) | 48 | 0.98 | 1.51 | 0.07 | 0.90 | 1.80 (1.88) |
| 0.209[d] | $HBF_4$ (15.0) | MeOH (30) | 70 | 1.00 | 1.74 | 0.04 | 0.97 | 1.91 (1.97) |
| 0.221 | $MeSO_3H$ (16.5) | MeOH (30) | 42 | 1.00, 0.04[k] | 1.40 | 0.06 | 0.83 | 1.76 (1.83) |
| 0.219 | $(CO_2H)_2$ (11.1) | MeOH (30) | 87 | 0.97 | 1.00 | 0.11 | 0.68 | 1.58 (1.65) |
| 0.272 | $CH_2(CO_2H)_2$ (14.1) | MeOH (30) | 40 | 1.10, 0.12[k] | 1.14 | 0.07 | 0.71 | 1.74 (1.81) |
| 0.272 | $(CH_2CO_2H)_2$ (14.3) | MeOH (30) | 7 (60 °C) | n.d. | 0.38 | 0.01 | 0.23 | 0.20 (0.23) |
| 0.266 | $MeCO_2H$ (15.0) | MeOH (30) | 3 (60 °C) | 1.20, 0.22[k] | 0.94 | 0.03 | 0.56 | 1.70 (1.76) |
| 0.195 | $CF_3CO_2H$ (16.0) | MeOH (30) | 23 | 1.20, 0.07[k] | 0.16 | 0.01 | n.d. | 1.29 |
| 0.121 | $CF_3CO_2H$ (15.2) | MeOH (30) | 43 | 1.00 | 1.26 | 0.10 | 0.74 | 1.73 (1.74) |
| 0.215 | Catechol (16.6) | MeOH (30) | 1 (60 °C) | 1.02, 0.05[k] | 0.66 | 0.03 | 0.42 | 1.38 (1.44) |
| 0.175[l] | HBr (100)[p] | *n* (30) | 48 | n.d. | 1.14 | 0.02 | 0.63 | 0.59 (0.63) |
| 0.115 | | MeOH (30) | 4 (60 °C) | 1.00, 0.04[k] | 1.64 | 0.02 | 0.84 | 1.84 (1.84) |
| 0.971 | | MeOH (30) | 42[q] | 1.03 0.02[k] | 1.56 | 0.03 | 0.78 | 1.84 (1.81) |
| 0.139 | | MeOH–NaOMe (30) | 4 (60 °C) | 1.06 , 0.05[k] | 1.38 | 0.08 | 0.73 | 1.85 (1.79) |
| 0.101 | | EtOH (30) | 5 (65 °C) | 1.72, 1.04,[k] 0.13[r] | 0.43 | *o* | 0.21 | 1.94 (1.93) |
| (C; M = W) | | | | | | | | |
| 0.301[d] | $H_2SO_4$ (19.4) | thf (30) | 18 | 1.00 | 0.72 | 0.15 | 0.54 | 1.51 (1.54) |
| 0.059 | $H_2SO_4$ (19.8) | MeOH (30) | 20 | 0.99 | 1.80 | 0.07 | 0.97 | 1.96 (1.96) |
| 0.229 | HCl (10.0) | MeOH (30) | 18 | 1.01, 0.02[k] | 1.90 | 0.03 | 0.96 | 1.99 (1.97) |
| 0.047 | | MeOH (30) | 4 (60 °C) | 0.31 | 0.13 | 0.01 | n.d. | 0.39 |
| 0.050 | | MeOH (30) | 42[q] | 0.21 | 0.06 | 0.01 | n.d. | 0.25 |

[a] Typical weights are given; other data are average values over at least two runs. [b] mol per W atom. [c] Total $N_2$ recovered as nitrogen hydrides (converted into mol equivalents of $N_2$) and $N_2$ from reaction. The numbers in parentheses include mol $N_2$ from NaOBr oxidation rather than mol $N_2$ equivalent to nitrogen hydrides. [d] Residue extracted with distilled water; base distillation on extract. [e] Reaction under $N_2$. [f] Not determined. [g] Reaction under $H_2$. [h] Reaction under 3 : 1 $H_2 : N_2$ mixture. [i] Interference with colour test, value could not be obtained. [j] Kjeldahl reduction on residue before base distillation. [k] $H_2$ evolved. [l] Solvent removal at 140 °C *in vacuo* (see text). [m] *N*-Methylpyrrolidone. [n] Propylene carbonate. [o] Less than 0.005 mol per W atom. [p] Aqueous HBr used; reaction under argon (see text). [q] Under irradiation (see text). [r] $CH_4$ evolved.

Complexes (B and C; M = W) rapidly form a red solution on addition of the acid (*ca.* 1 min), which slowly darkens and gives a blue precipitate after *ca.* 1 h. This solution contains ammonia (presumably as ammonium sulphate) which, after removal of solvent, can be extracted with water or, after treatment with potassium hydroxide solution, distilled from the residue and determined with indophenol or by oxidation with hypobromite solution (see Experimental section). About 1.8—1.9 mol of $NH_3$ per W atom are produced by the reaction together with a trace amount of hydrazine (see Table 1). More hydrazine (*ca.* 0.2 mol per W atom, see Table 1) is obtained, but less ammonia, if tetrahydrofuran (thf), benzene, *N*-methylpyrrolidone, or dichloromethane is used as solvent. The blue solid product was not identified, but since it contained little carbon, hydrogen, or sulphur (microanalysis) it is probably essentially a tungsten(VI) oxide or a related substance. Thus the reaction may be represented by (1) (L = $PMe_2Ph$ or $PMePh_2$).

$$(\text{B or C};\ M = W) \xrightarrow[\text{MeOH, 20 °C}]{H_2SO_4} \text{tungsten(VI) oxide} + 2[NH_4]^+ + N_2 + 4[HL][HSO_4] \qquad (1)$$

When complexes (B or C; M = Mo) are similarly treated with $H_2SO_4$, dinitrogen is again rapidly evolved (*ca.* 1—2 min) with the formation of a transient red colour followed by a brown-yellow solution which does not change further after *ca.* 5 min. If solvent is removed under low pressure at 25 °C the resulting brown oil is soluble in water and gives *ca.* 0.7 mol $NH_3$ per Mo atom, together with some dinitrogen, by distillation from a concentrated aqueous solution of KOH. This gives a reasonably close nitrogen balance for the reaction (see Table 2 and Experimental section). The reaction thus differs from that of (B or C; M = W) both in the yield of ammonia and in the nature of the final metal product. No solid could be isolated from the reaction product of (B or C; M = Mo). A further difference is the

TABLE 2

Protonation of molybdenum complexes

| Mass of complex ($m$/g) [a] | Acid (amount) [b] | Solvent ($V$/cm$^3$) | $t$/h | Yield [b] | | | | N$_2$ balance [b,c] |
|---|---|---|---|---|---|---|---|---|
| | | | | $N_2$ evolved | $NH_3$ | $N_2H_4$ | $N_2$(NaOBr) | |
| (B; M = Mo) | | | | | | | | |
| 0.271 | $H_2SO_4$ (7.0) | thf (50) | 18 | 1.06 ,<br>0.01 [d] | 0.55 | *e* | 0.30 | 1.34 (1.36) |
| 0.150 | $H_2SO_4$ (12.7) | MeOH (40) | 0.25 | 1.23,<br>0.21 [d] | 0.64 | *e* | 0.34 | 1.98 [f] (2.02) [f] |
| 0.094 | $H_2SO_4$ (13.0) | MeOH (50) | 2<br>(57 °C) | 1.41,<br>0.42 [d] | 0.68 | *e* | n.d. [g] | 2.04 [f] |
| 0.222 | $H_2SO_4$ (12.2) | MeOH (50) | 2<br>(−10 °C) | 1.12,<br>0.40 [d] | 0.66 | *e* | 0.35 | 1.45 (1.47) |
| 0.129 [h] | $H_2SO_4$ (12.0) | MeOH (50) | 24 | n.d. | 0.04 | *i* | n.d. | n.d. |
| 0.100 [j] | $H_2SO_4$ (12.0) | MeOH (50) | 16 | n.d. | 0.03 | *i* | n.d. | n.d. |
| 0.137 [k] | $H_2SO_4$ (10.6) | *l* (50) | 18 | 1.0,<br>0.1 [d] | 0.44 | *i* | 0.25 | 1.22 (1.25) |
| 0.111 [k] | $H_2SO_4$ (17.0) | *m* (50) | 24 | 1.50 | 0.80 | *i* | 0.45 | 1.90 (1.95) |
| 0.060 | $H_2SO_4$ (13.0) | $Me_2CO$ (50) | 18 | 0.9,<br>0.01 [d] | 0—0.4 | n.d. [n] | 0—0.4 | 0.9—1.3 |
| 0.115 | $H_2SO_4$ (12.5) | $Me_2SO$ (50) | 18 | 1.92 | *i* | *i* | *i* | 1.92 |
| 0.072 | $H_3PO_4$ (13.0) | MeOH (30) | 18 | 1.24,<br>0.26 [d] | 0.34 | *i* | 0.18 | 1.40 (1.42) |
| 0.195 [o] | $H_3PO_2$ (11.5) | MeOH (50) | 48 | n.d. | 0.06 | *i* | *i* | n.d. |
| 0.496 | $HBF_4$ (14.0) [p] | MeOH (50) | 56 | 1.26,<br>0.26 [d] | 0.68 | *e* | 0.34 | 1.60 (1.60) |
| 0.132 [k] | HBr (100) [q] | *m* (30) | 48 | n.d. | 0.88 | *e* | 0.46 | n.d. |
| 0.132 | HCl (10) | MeOH (50) | 48 | 1.80 | 0.10 | *e* | n.d. | 1.86 |
| 0.136 | HBr (10) | MeOH (50) | 18 | 1.80 | 0.12 | *e* | 0.06 | 1.86 (1.86) |
| 0.117 | $MeCO_2H$ (10) | MeOH (40) | 20 | n.d. | *i* | 0 | 0 | n.d. |
| 0.119 | | MeOH (50) | 5<br>(50 °C) | 1.9,<br>0.9 [d] | *i* | 0 | 0 | 1.9 |
| 0.120 | | MeOH (50) | 18 [r] | n.d. | *i* | 0 | 0 | n.d. |
| 0.273 [s] | $H_2SO_4$ (12.2) | MeOH (50) | 18 | n.d. | *i* | *i* | *i* | n.d. |
| (C; M = Mo) | | | | | | | | |
| 0.235 | $H_2SO_4$ (14.0) | thf (50) | 24 | 1.87 | 0.08 | 0.02 | 0.06 | 1.93 (1.93) |
| 0.178 | $H_2SO_4$ (13.5) | MeOH (30) | 18 | 1.64 | 0.66 | *i* | 0.35 | 1.97 (1.99) |
| 0.60 | $H_2SO_4$ (15) | $Me_2CO$ (30) | 18 | 0.60 | *i* | *i* | *i* | 0.50 (0.60) |
| 0.196 [n] | $H_3PO_2$ (13.2) | MeOH (50) | 48 | n.d. | *i* | *i* | *i* | n.d. |
| *trans*-[Mo($N_2$)$_2$($PMePh_2$)$_2$(dppe)] | | | | | | | | |
| 0.135 | $H_2SO_4$ (12.5) | MeOH (15) | 18 | 1.2,<br>0.2 | 0.56 | *i* | 0.32 | 1.48 (1.52) |

[a] Typical weights are given; other data are mean values of at least two runs in most cases and at least four runs where high yields of ammonia are obtained. [b] Mol per Mo atom. [c] Total $N_2$ removed as nitrogen hydrides ($N_2$ equivalent) and $N_2$ from reaction. Values in parentheses use NaOBr oxidation value rather than nitrogen hydride ($N_2$ equivalent) value. [d] $H_2$ value. [e] Less than 0.005 mol per Mo atom. [f] Includes $N_2$ evolved during base distillation (see text). [g] Not determined. [h] With added Zn (0.5 g). [i] Negligible. [j] With added Mg (0.2 g). [k] Solvent removed at 140 °C *in vacuo*. [l] *N*-Methylpyrrolidone. [m] Propylene carbonate. [n] Interference with colour test; value could not be determined. [o] Reaction under $N_2$. [p] Aqueous acid used. [q] Aqueous HBr used; reaction under argon (see text). [r] Irradiated (see text). [s] Reaction under $H_2$. [t] Prepared from *trans*-[Mo($N_2$)$_2$($PMePh_2$)$_4$] and dppe (J. Chatt and R. L. Richards, unpublished work).

point at which free ammonium ion is produced. The acid solutions from the tungsten complexes (B) or (C) contain ammonium sulphate and give the indophenol test directly, but those from the molybdenum complexes do not. The ammonia is obtained at the KOH distillation stage. This implies that some intermediate is formed in the molybdenum case which gives ammonia (and some dinitrogen) on base hydrolysis. Attempts to isolate the intermediate provided only uncharacterisable oils.

A variety of other acids also gives ammonia (with a trace amount of hydrazine in some cases) from (B and C; M = W or Mo). The results are shown in the Tables which give the yields of ammonia and hydrazine as determined by colour tests (see Experimental section), the yield of dinitrogen obtained after oxidation by sodium hypobromite solution of the product ammonia (and hydrazine)-containing solution, and the total nitrogen balance as far as it could be determined. The oxidation with hypobromite was carried out to ensure that the positive colour tests were indeed due to ammonia and hydrazine, and not to some interfering reaction product such as the phosphine. As additional evidence, $^{15}NH_3$ was produced from *cis*-$[M(^{15}N_2)_2(PMe_2Ph)_4]$ and $H_2SO_4$–MeOH (see Experimental section).

In some cases (Tables), especially when organic acids were used, or acetone was used as solvent, a large proportion (up to 0.7—0.9 mol) of dinitrogen could not be accounted for. These reactions are still under investigation, but they may involve the formation of organic nitrogen-containing products or the loss of dinitrogen at some stage of the work-up. Experiments in which hydrazine was distilled from a solution of KOH containing tungsten or molybdenum showed that oxidation of hydrazine to dinitrogen occurs and thus the measured yield of hydrazine may be rather low.

The highest yields of ammonia were obtained for both molybdenum and tungsten complexes when $H_2SO_4$ was used as reagent. In the tungsten case the maximum yield of ammonia (*ca.* 1.9 mol per W atom) was obtained when methanol was the solvent. High yields (1.5 mol per W atom) were also obtained even when water was used as the reaction medium, although the reaction time was greatly increased, probably as a consequence of the insolubility of the dinitrogen complex. In the molybdenum case the highest yield (*ca.* 0.9 mol $NH_3$ per Mo atom) was obtained with propylene carbonate as solvent. This solvent was inconvenient because its high boiling point made it difficult to remove and methanol, which gave somewhat lower yields (*ca.* 0.7 mol per Mo atom), was preferred. Water as reaction medium lowered the yield. The acids $H_3PO_4$ or $HBF_4$ gave almost as high yields from both the molybdenum and the tungsten complexes as did $H_2SO_4$, but other acids generally gave much lower yields (Tables). Increasing (to 55 °C) or decreasing (to −10 °C) the temperature at which the $H_2SO_4$–MeOH reaction took place had little effect on yield, as did using a dinitrogen atmosphere instead of a vacuum over the reaction mixture. Dihydrogen (used as a 3 : 1 mixture with dinitrogen as a reaction atmosphere) had little effect on the yield from the tungsten complexes but prevented the formation of ammonia from the molybdenum ones, perhaps because dihydrogen displaced dinitrogen from the more labile molybdenum complexes. Similarly, addition of $TiCl_3$ (B; M = W) or zinc or magnesium (B; M = Mo) to the acid reaction medium had an adverse effect on the yield of ammonia (Tables and Experimental section). Acetone as a solvent lowered the yields of ammonia and possibly gave increased trace amounts of hydrazine from (B; M = Mo), but, because acetone interferes with the *p*-dimethylaminobenzaldehyde colour test, yields of hydrazine could not be accurately determined. Also, *ca.* 0.5 mol of $N_2$ could not be accounted for in the reactions in acetone, possibly owing to the formation of 2-diazopropane complexes.[4]

*Reaction in Methanol.*—The tungsten, but not the molybdenum, complexes produce ammonia by reaction with methanol alone.[5] The reaction is slower than in the presence of $H_2SO_4$ and requires heating (3—4 h at reflux) or irradiation (2 × 150-W tungsten-filament lamps at 20 °C for 42 h), but it gives almost as high a yield of ammonia (*ca.* 1.6 mol per W atom) as when acid is present. Ethanol, at the boil, gives only 0.4 mol $NH_3$ per W atom. Surprisingly, (C; M = W) gave little ammonia when treated as (B; M = W) above, perhaps because it is more labile than (B; M = W).

*Reaction of Complexes* (A) *with* $H_2SO_4$ *and* $HBF_4$.—In contrast to (B) and (C), complex (A), which contains two chelating ditertiary phosphine ligands, reacts with acids with only partial reduction of a dinitrogen ligand. Thus $HBF_4$ produces a hydrazido(2−)-ligand and a fluoride ion is transferred from $[BF_4]^-$ to the metal, presumably with the formation of thf·$BF_3$ [reaction (2)]. Complex (D; M = Mo) has been independently prepared from (A; M = Mo) and $[OEt_3][BF_4]$ and its crystal structure determined.[6]

$$\textit{trans}\text{-}[M(N_2)_2(dppe)_2] + 2HBF_4 \xrightarrow{\text{thf}} \textit{trans}\text{-}[MF(NNH_2)(dppe)_2][BF_4]\ (D) + N_2 + \text{thf}\cdot BF_3 \quad (2)$$

Hydrazido(2−)-complexes are also produced by the reactions of (A; M = Mo or W) with an excess of concentrated $H_2SO_4$ in thf. Their assignment as ($NNH_2$) complexes follows from their characteristic NH pattern in their i.r. spectra and because they are 1 : 1 electrolytes in methanol solution. They are insufficiently soluble in non-protic solvents for the determination of N–H n.m.r. resonances, but they contain the elements of 2 mol of $H_2SO_4$ and are formulated as hydrogensulphato-complexes [reaction (3)].

$$\textit{trans}\text{-}[M(N_2)_2(dppe)_2] + 2H_2SO_4 \xrightarrow{\text{thf}} [M(HSO_4)(NNH_2)(dppe)_2][HSO_4]\ (E) + N_2 \quad (3)$$

Bands in the 900—1 200 cm$^{-1}$ region of the i.r. spectra of (E) are attributed to the S=O bands of the hydrogensulphate ligands.

No appreciable amount of ammonia was detected from reactions (2) or (3), run at 20 °C, even when methanol was used as solvent, but the presence of only two monophosphine ligands, as in *trans*-$[Mo(N_2)_2(PMePh_2)_2(dppe)_2]$,[7] is sufficient to allow the production of ammonia on treatment with $H_2SO_4$ in methanol (0.56 mol per Mo atom) (Table 2).

## DISCUSSION

Two points emerge from the above work: (*a*) ammonia is produced at room temperature only when at least two monotertiary phosphines as opposed to diphosphines

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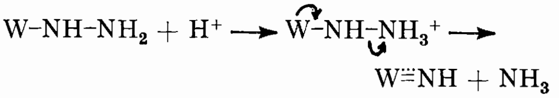
[6] M. Hidai, T. Kodoma, M. Sato, M. Harakawa, and Y. Uchida, *Inorg. Chem.*, 1976, **15**, 2694.

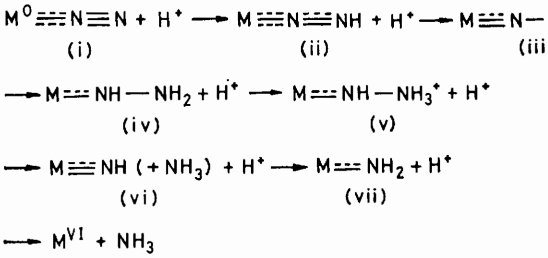
[7] J. Chatt and R. L. Richards, unpublished work.

ligate the metal; and (*b*) oxygen-containing solvents or oxo-anions assist the reduction. When two chelating diphosphine ligands are attached to the metal, protonation and reduction of dinitrogen at room temperature stops at the $N_2H_2$ stage in either methanol or thf as in (D) and (E). For the protonation to proceed further the metal must release more electron density mesomerically into the $N_2H_2$ ligand. In our tetrakis(monotertiary phosphine) complexes we believe this release to be caused by the replacement of the neutral, mildly electron $\pi$-accepting, tertiary phosphine ligands by strong $\pi$-donor ligands, preferably oxo-anionic ones such as the sulphate, hydrogensulphate, or phosphate anions which also carry negative charge into the complex. Fluoride, methanol (or methoxide), and other oxygen-containing solvents and halide ions are less effective. The oxo-$\pi$ donors will raise the energy level of the filled non-bonding *d* electrons of the metal, so causing greater mesomeric electron release into the $N_2H_2$ ligand and its further protonation and reduction to ammonia. Evidence that the tertiary phosphine is displaced from the tetrakis(monotertiary phosphine) complexes comes from the isolation of $[WCl_3(N_2H_3)(PMePh_2)_2]$ from the reaction of *trans*-$[W(N_2)_2(PMePh_2)_4]$ with HCl in dichloromethane at room temperature.[8] It seems clear that the $N_2H_2$ ligand in the bis(diphosphine) complexes (D) or (E) is not protonated and reduced because the chelate diphosphine ligands are not displaced under the reaction conditions used. However, by the use of a suitable solvent, *e.g.* propylene carbonate and acid at higher temperatures, the chelating ligands can be displaced and ammonia is obtained. Brûlet and van Tamelen[9] observed this reaction but considered that both a long reaction time (30 h) at room temperature followed by an aqueous HCl–$[NH_4]$Cl hydrolysis step at 100 °C was necessary to produce ammonia (0.37 mol per Mo atom). Dr. J. R. Dilworth in our laboratory has repeated their work and finds that the long reaction time at room temperature is not necessary. Within a few minutes of mixing the reagents, (A; M = Mo) and HBr in propylene carbonate, he removed the solvent by evaporation *in vacuo* at *ca.* 150 °C and then by alkaline distillation of the residue obtained 0.36 mol of $NH_3$ per Mo atom. The use of high-boiling oxygen-containing solvents had the fortuitous result that in the work-up stage the reaction mixture was heated to such a temperature that the diphosphine was displaced by solvent or halide ion, so allowing the reaction to proceed analogously to that of complexes (B) or (C) in methanol at room temperature.

Methanol alone at reflux is sufficiently acidic to cause the reduction of dinitrogen in (A; M = W) to ammonia but not in (A; M = Mo).[5] Presumably in these reactions one dinitrogen ligand is lost, giving an intermediate methanol or hydridomethoxo-complex. This intermediate is probably less stable when M = Mo than W, in keeping with the general chemistry of these metals, so that the second dinitrogen molecule may be lost from the molybdenum intermediate whereas it remains bound in the tungsten one sufficiently strongly to allow its further protonation and reduction. Since tungsten complexes of types (B) and (C) give 90% yields of ammonia (1.8 mol per atom), the ligating dinitrogen is most probably reduced at the single metal centre by successive protonations and progressive oxidation of the metal through six oxidation states (0—VI). A complex containing the $N_2H_3$ ligand, $[WCl_3(N_2H_3)(PMePh_2)_2]$, has been prepared from (C; M = W),[8] but none containing $N_2H_4$. Since $N_2H_4$ is only a very minor product of the reduction by acid with (B; M = W) or (C; M = W), it seems likely that the N–N bond is split at the fourth protonation by a simple mechanism as illustrated in reaction (4). This leads to a simple mechanism of six successive protonation and reduction steps. If the reduction of dinitrogen to ammonia occurs at a single molybdenum atom site in nitrogenase, this mechanism could well serve as a model for the reduction at the atomic level. The stages of the reduction may be represented by formal valence changes as in the series of reactions (5). At each stage, donor $\pi$ bonding, first from metal to nitrogen and later from nitrogen to metal, will be strong and (i)—(iii) will have linear M–N–N structures. This sequence demonstrates how the strong triple bond of dinitrogen can be progressively degraded by the transfer of its $\pi$-electron density into a multiple M–N bond and to N–H $\sigma$ bonds. Finally, as a weak single N–N bond, it undergoes spontaneous cleavage to ammonia and a readily hydrolysable M$\equiv$NH, or perhaps M≡N, moiety.



$$\mathrm{W{-}NH{-}NH_2 + H^+ \longrightarrow W{-}NH{-}NH_3{}^+ \longrightarrow W{\equiv}NH + NH_3} \qquad (4)$$



$$\mathrm{M^0{\equiv}N{\equiv}N + H^+ \longrightarrow M{\equiv}N{\equiv}NH + H^+ \longrightarrow M{\equiv}N{-}NH_2 + H^+}$$
(i) (ii) (iii)

$$\mathrm{\longrightarrow M{=}NH{-}NH_2 + H^+ \longrightarrow M{=}NH{-}NH_3{}^+ + H^+}$$
(iv) (v)

$$\mathrm{\longrightarrow M{\equiv}NH\ (+NH_3) + H^+ \longrightarrow M{=}NH_2 + H^+}$$
(vi) (vii)

$$\mathrm{\longrightarrow M^{VI} + NH_3} \qquad (5)$$

Where we have *X*-ray structures, *e.g.* for (i) and (iii), the M–N–N system is linear and the N–N distances show the progress of degradation of the $N_2$ molecule {N–N 1.10(2) Å in (A; M = Mo)[10] and 1.37(2) Å in *trans*-$[WCl(NNH_2)(dppe)_2][BPh_4]$[11]}. The above scheme may represent the degradation of dinitrogen at the atomic level on nitrogenase. Nevertheless, it is very unlikely that a change of oxidation state of six units occurs in the molybdenum of the enzyme but rather that it takes

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[8] J. Chatt, A. J. Pearman, and R. L. Richards, *J. Organometallic Chem.*, 1975, **101**, C45.

[9] C. P. Brûlet and E. E. van Tamelen, *J. Amer. Chem. Soc.*, 1975, **97**, 911.

[10] T. Uchida, Y. Uchida, M. Hidai, and T. Kodoma, *Bull. Chem. Soc. Japan*, 1971, **44**, 2883.

[11] G. A. Heath, R. Mason, and K. M. Thomas, *J. Amer. Chem. Soc.*, 1974, **96**, 259.

up dinitrogen at an intermediate oxidation state, say III or IV, and as protonation proceeds electrons are passed through the molybdenum from the iron–sulphur cluster centres contained in the enzyme,[12] as required.

A great many 'mechanisms' for the reduction of dinitrogen at a metal site or sites in nitrogenase have been suggested and that above is very similar to one proposed by one of us some years ago when iron was considered to be the likely metal site.[13] The above proposal has the merit that all its stages except (v) have been recognised in stable complexes.[8] The conversion (v) ⟶ (vi) will probably be spontaneous except when the metal is in so high an oxidation state that it is unable to undergo the one oxidation step necessary for the conversion. The important initial stages (i)—(iv) have all been prepared from molecular nitrogen and their interconversions and conversions to ammonia studied. The group (vi) has been recognised in a stable complex (incidentally of molybdenum) only recently,[14] but (vii) is of long standing. The complex *trans*-$[MoCl_2N(PMe_2Ph)_2]$, related to (vi) by a single protonation, hydrolyses quantitatively to ammonia.[14] Thus all the steps have been realised except that represented by reaction (4). Some evidence for it comes from the isolation of a complex containing one atom of nitrogen (in an $NH_n$ group) to two of molybdenum from the reaction of (C; M = Mo) with HI in thf.[7] It accords with the suggested splitting of the $N_2$ molecule to give a complex containing a $Mo\overset{\cdot\cdot}{=}NH_n$ group, and this has then become attached to another, non-nitrogenous, complex molybdenum product of the reaction.

We have noted that complex (B; M = Mo) reacts differently from (B; M = W) in $H_2SO_4$–MeOH. The main difference between these complexes is in the stage at which ammonia is released and probably indicates a difference of mechanism caused by the poorer reducing power of molybdenum. When (B; M = W) is treated with $H_2SO_4$ in methanol the product ammonia is produced as ammonium sulphate, but its molybdenum analogue does not produce the ammonium salt directly. The ammonia is produced only after removal of the methanol at low pressure and subjecting the residue to alkaline distillation. The yield is *ca.* 0.67 mol $NH_3$ per Mo atom, which may be fortuitous, but it is consistent with the disproportionation of the $N_2H_2$ ligand at the hydrazido(2−) stage of reduction (6).

$$3N_2H_2 \longrightarrow 2NH_3 + 2N_2 \qquad (6)$$

The complexes $[MX_2(NNH_2)(PMe_2Ph)_3]$ (M = Mo or W; X = Cl, Br, or I) [8] each give yields of ammonia close to those obtained directly from their parent bis(dinitrogen) complexes (B; M = Mo or W), *i.e.* 0.65—0.9 mol $NH_3$ per Mo atom and 1.4—1.9 mol $NH_3$ per W atom (depending on X), on treatment with $H_2SO_4$–MeOH. This indicates that the mechanisms of reduction differ for the complexes of the two metals after the $N_2H_2$ stage. The tungsten complexes protonate further to give good yields of ammonia and some hydrazine, but the molybdenum ones appear to stop at the $N_2H_2$ stage, perhaps because the metal is not sufficiently reducing. In work-up the attack by alkali causes disproportionation of the $N_2H_2$ ligand to ammonia [reaction (6)] with only the faintest traces of hydrazine. The high yield of ammonia obtained from the molybdenum complex in propylene carbonate may indicate the attainment of a greater degree of reduction in this high-boiling solvent.

There are other differences between the reaction of the tungsten and molybdenum complexes relating to the mechanism, but we do not think they are so fundamental as to indicate that one goes *via* a mononuclear and the other by a binuclear intermediate. They are currently under investigation.

Oxygen ligands are evidently important in promoting the protonation and reduction of ligating dinitrogen in our molybdenum and tungsten complexes. Thus one might question whether, in nitrogenase the molybdenum, generally assumed to be at the active site,[12] is in an oxygen environment. The above evidence, and the observation that dinitrogen can be converted into hydrazine by $V(OH)_2$ in alkaline solution with catechol or alkaline suspension with $Mg(OH)_2$,[15] certainly suggest that this environment is a relevant one, and that dinitrogen can interact effectively with early transition-metal ions in an open-shell state in the presence of oxygen ligands. Molybdenum, in its higher oxidation states, is usually found associated with oxygen ligands.[16]

It has been considered for some time that a sulphur environment is crucial for the function of molybdenum in nitrogenase but it now appears that oxygen ligands are just as likely to play a major role.

## EXPERIMENTAL

Experiments with air-sensitive materials were carried out under dinitrogen; gases were manipulated by standard high-vacuum techniques and dinitrogen–dihydrogen mixtures were determined by difference after removal of dihydrogen from the measured mixture with B.T.S. catalyst. Ammonia and hydrazine yields were determined using indophenol and *p*-dimethylaminobenzaldehyde reagents respectively. Sodium hypobromite, used to oxidise nitrogen hydrides to dinitrogen, was prepared by a standard technique.[17] The complexes *cis*-$[W(N_2)_2(PMe_2Ph)_4]$,[2] *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$,[18] and *trans*-$[Mo(N_2)_2(PMePh_2)_4]$ [18] were prepared by published methods. Infrared spectra were determined with a Unicam SP 2000 instrument and n.m.r. measurements were taken with a Jeol P.S. 100 spectrometer. Conductivities were measured using a Portland electronics conductivity bridge and analyses were by Mr. and Mrs. A. G. Olney of the University of Sussex. All the reagents were of analytical grade unless otherwise stated. Irradiation experiments were carried out using

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[12] R. R. Eady and J. R. Postgate, *Nature*, 1974, **249**, 805.

[13] J. Chatt, *Proc. Roy. Soc.*, 1969, **B172**, 327.

[14] J. Chatt and J. R. Dilworth, *J.C.S. Chem. Comm.*, 1975, 983.

[15] A. E. Shilov, *Russ. Chem. Rev.*, 1974, **43**, 378.

[16] B. Spivack and Z. Dori, *Co-ordination Chem. Rev.*, 1975, **17**, 99; R. A. D. Wentworth, *ibid.*, 1976, **18**, 1.

[17] A. san Pietro in 'Methods in Enzymology,' eds. S. P. Colowick and N. O. Kaplan, Academic Press, New York, 1957, vol. IV, p. 485.

[18] T. A. George and C. D. Seibold, *Inorg. Chem.*, 1973, **12**, 2544.

2 × 150-W tungsten-filament lamps at a distance of 30 cm from the reaction flask. Mass-spectral measurements were with an A.E.I. MS10 instrument.

trans-*Bis(dinitrogen)tetrakis(methyldiphenylphosphine)-tungsten, trans*-$[W(N_2)_2(PMePh_2)_4]$ (C; M = W).—Tetrahydrofuran (150 $cm^3$) was added to *trans*-$[WCl_4(PMePh_2)_2]$ (3 g) and magnesium (5 g) in a flask (250 $cm^3$) under dinitrogen, followed by $PMePh_2$ (1.6 g) and two crystals of iodine. The mixture was stirred under dinitrogen for 48 h giving a brown-orange solution which was filtered then concentrated *in vacuo* to a quarter of its volume. Addition of isopropyl alcohol and diethyl ether gave red crystals of the product which were filtered off and recrystallised (toluene–methanol) as red-orange prisms [1.4 g, $\nu(N_2)$ at 1 905 $cm^{-1}$] (Found: C, 59.7; H, 5.4; N, 5.2. $C_{52}H_{52}N_4P_4W$ requires C, 60.0; H, 5.0; N, 5.4%). The n.m.r. spectrum of this complex showed a P*Me* singlet at 1.95 p.p.m. ($CD_2Cl_2$ solution relative to tetramethylsilane); this and the single i.r. $\nu(N_2)$ band indicates the *trans* configuration.

*Bis*[1,2-*bis(diphenylphosphino)ethane*][*hydrazido*(2—)-N]-(*hydrogensulphato*)*tungsten Hydrogensulphate*, $[W(HSO_4)(NNH_2)(dppe)_2][HSO_4]$.—Concentrated sulphuric acid (1.0 $cm^3$) was added *in vacuo* at 20 °C to a solution of *trans*-$[W(N_2)_2(dppe)_2]$ (0.79 g) in thf (60 $cm^3$) with stirring. There was vigorous effervescence, complete in *ca.* 1—2 min, and the solution became dark red-brown, then yellow-brown. Dinitrogen (17.0 $cm^3$, 0.99 mol) was evolved but no dihydrogen. The solvent was removed *in vacuo* giving a brown oil which was dissolved in methanol. Addition of diethyl ether gave the crude product which was recrystallised from methanol–diethyl ether as orange-yellow *needles* (0.8 g) [$\nu$(NH) at 3 240 and 3 100—3 280 $cm^{-1}$; n.m.r. in $CD_3OD$, $CH_2$ multiplet at 3.0 p.p.m. and Ph multiplet at 6.8—7.7 p.p.m. (relative to $SiMe_4$); $\Lambda$ = 87 S $cm^2$ $mol^{-1}$ (*ca.* $10^{-3}$ mol $dm^{-3}$ solution in $MeNO_2$)] (Found: C, 51.6; H, 4.6; N, 2.4; S, 5.5. $C_{52}H_{52}N_2O_8P_4S_2W$ requires C, 51.9; H, 4.2; N, 2.3; S, 5.3%).

*Bis*[1,2-*bis(diphenylphosphino)ethane*][*hydrazido*(2—)-N]-(*hydrogensulphato*)*molybdenum Hydrogensulphate*, $[Mo(HSO_4)(NNH_2)(dppe)_2][HSO_4]$.—This was prepared similarly to the tungsten analogue, from *trans*-$[Mo(N_2)_2(dppe)_2]$ (0.42 g) and $H_2SO_4$ (0.4 $cm^3$) in thf (50 $cm^3$) with the evolution of dinitrogen (11.0 $cm^3$, 1.1 mol), as yellow-brown *prisms* (MeOH–$Et_2O$) (0.4 g) : $\nu$(NH) at 3 190 $cm^{-1}$, $HSO_4$ bands at 1 150, 1 050, and 850 $cm^{-1}$; n.m.r. in $CD_3OD$, $CH_2$ multiplet at 3.0 p.p.m. and Ph multiplet at 6.8—7.8 p.p.m. (relative to $SiMe_4$); $\Lambda$ = 89 S $cm^2$ $mol^{-1}$ (*ca.* $10^{-3}$ mol $dm^{-3}$ solution in $MeNO_2$) (Found: C, 55.5; H, 4.7; N, 2.7. $C_{52}H_{52}MoN_2O_8P_4S_2$ requires C, 56.0; H, 4.5; N, 2.5%).

*Bis*[1,2-*bis(diphenylphosphino)ethane*]*fluoro*[*hydrazido*-(2—)-N]*tungsten Tetrafluoroborate*, $[WF(NNH_2)(dppe)_2][BF_4]$.—The salt $[OEt_2H][BF_4]$ (0.5 $cm^3$) was added to a solution of *trans*-$[W(N_2)_2(dppe)_2]$ (0.53 g) in thf (60 $cm^3$) *in vacuo*. Dinitrogen (10.3 $cm^3$, 0.9 mol) was rapidly evolved with formation of a clear yellow solution after *ca.* 20 min. The solution was stirred for another 3 h and then concentrated *in vacuo* to about a quarter of its volume. Addition of diethyl ether gave the product which crystallised as yellow *prisms* (MeOH–$Et_2O$) (0.3 g): $\nu$(NH) at 3 220 and 3 295 $cm^{-1}$, B–F bands at 1 010—1 100 $cm^{-1}$; $\Lambda$ = 90 S $cm^2$ $mol^{-1}$ in a $10^{-3}$ mol $dm^{-3}$ solution in $MeNO_2$; n.m.r. data are reported elsewhere [1] (Found: C, 55.8; H, 4.6; N, 2.5. $C_{52}H_{52}BF_5N_2P_4W$ requires C, 55.9; H, 4.5; N, 2.5%).

*Bis*[1,2-*bis(diphenylphosphino)ethane*]*fluoro*[*hydrazido*-(2—)-N]*molybdenum Tetrafluoroborate*, $[MoF(NNH_2)(dppe)_2][BF_4]$.—This was prepared similarly to the tungsten analogue from *trans*-$[Mo(N_2)_2(dppe)_2]$ (0.48 g) and $[OEt_2H][BF_4]$ (0.3 $cm^3$) in thf (100 $cm^3$) with evolution of dinitrogen (9.6 $cm^3$, 0.85 mol), and crystallised as pink *prisms* (MeOH–$Et_2O$) (0.3 g): $\nu$(NH) at 3 270 and 3 340 $cm^{-1}$, B–F bands at 1 000—1 100 $cm^{-1}$; $\Lambda$ = 80 S $cm^2$ $mol^{-1}$ in a *ca.* $10^{-3}$ mol $dm^{-3}$ solution in $MeNO_2$; n.m.r. data are reported elsewhere [1] (Found: C, 60.1; H, 5.2; N, 2.4. $C_{52}H_{52}BF_5MoN_2P_4$ requires C, 55.9; H, 4.5; N, 2.5%).

*Reactions of cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (B) *and trans*-$[M(N_2)_2(PMePh_2)_4]$ (C) *with Sulphuric Acid*.—Since the methods adopted were generally applied, only typical examples are described in detail. Yields, reaction times, solvents, *etc.*, of all the protonation reactions are shown in Tables 1 and 2.

(*i*) M = W. Volatile solvents (thf, acetone, methanol, water, or benzene; *ca.* 30 $cm^3$) were condensed *in vacuo* at −196 °C on to (B) or (C). The mixture was then warmed to 20 °C, $H_2SO_4$ was added by means of a side-tube which could be rotated, and the mixture was stirred. Dinitrogen (0.99—1.02 mol) was rapidly evolved with formation of a red solution. On further stirring the solution darkened and deposited a blue solid [(B), 2—3 h; (C), 20 min]. The mixture was stirred for another 20 h [400 h in the case of water, the reaction being slower because of the insolubility of (B)], the solvent was removed *in vacuo*, and the residue was extracted with water (4 × 10 $cm^3$). Potassium hydroxide solution (30 $cm^3$, 40% w/v) was then added and the mixture distilled under argon into dilute $H_2SO_4$ (10 $cm^3$, 0.1N) which was then diluted to a known volume with distilled water. Aliquot portions of this solution were then tested for ammonia (indophenol) and hydrazine (*p*-dimethylaminobenzaldehyde), or oxidised to dinitrogen with sodium hypobromite solution and the gas thus obtained quantitatively measured by means of a Töpler pump. All the experiments were performed at least in duplicate with appropriate blanks using $[MCl_n(PR_3)_2]$-type complexes in place of bis(dinitrogen) complexes. Experiments using dinitrogen or dinitrogen–dihydrogen (1 : 3 v/v atmosphere) gave essentially the same yields of ammonia. Treating the residue after removal of solvent directly with base and distilling gave rather higher yields of ammonia than by aqueous extraction and so this technique was the one usually adopted.

Involatile solvents such as *N*-methylpyrrolidone or propylene carbonate were added to the solid tungsten complex, then the mixture was degassed by standard techniques before addition of acid as described above. These solvents were subsequently removed *in vacuo* at *ca.* 140 °C.

Some other reactions in which $TiCl_3$ was added (1—0.75 mol per mol $H_2SO_4$), either *in vacuo* or under dinitrogen or dihydrogen–dinitrogen mixtures, in the hope of increasing the yield of ammonia in fact gave rather lower yields (see Table 1 for an example) A brown solid was produced which was isolated and shown to be $[WCl_2(NNH_2)(PMe_2Ph)_3]$.[8] On base distillation, this complex gives ammonia but only 1.4 mol per W atom.[8]

(*ii*) M = Mo. The technique was the same as for (*i*) but the course of reaction was somewhat different. Addition of $H_2SO_4$ caused rapid evolution of dinitrogen (*ca.* 1—1.4 mol) and dihydrogen (variable amounts, see Table 2), and a yellow-brown solution resulted after *ca.* 5 min which showed no further change on stirring for another 18 h.

Removal of solvent gave a brown water-soluble oil, which could not therefore be extracted with water but was distilled from base as above, giving the yields of ammonia shown in Table 2. Separate experiments in a sealed vessel which could be subsequently opened *via* a break seal showed that dinitrogen (0.3—0.7 mol) was evolved at the base-distillation stage so that all the original dinitrogen could be accounted for (Table 2). Attempts to isolate a complex from the brown residual oil obtained after removal of solvents were unsuccessful. Repeated experiments using a dinitrogen atmosphere gave no change of ammonia yield, but addition of hydrogen, magnesium, or zinc gave greatly decreased yields (Table 2). Duplication of results and the determination of blanks were carried out as above.

*Preparation of* $^{15}$N-*labelled Dinitrogen Complexes and their Reactions with Sulphuric Acid.*—(*a*) *Tungsten.* The complex *cis*-$[W(^{15}N_2)_2(PMe_2Ph)_4]$ (F) was prepared from $[WCl_4(PMe_2Ph)_3]$ (1.7 g) and $^{15}N_2$ (20 cm$^3$, 92% enriched gas) by the published method[2] (the reaction atmosphere being $^{15}N_2$, argon, or a vacuum as appropriate) as yellow *prisms* (0.3 g) [$\nu(^{15}N_2)$ at 1 928 and 1 850 cm$^{-1}$]. Complex (F) (0.084 g) was then treated with $H_2SO_4$ (0.1 cm$^3$) in methanol (30 cm$^3$) as described above. The yield of ammonia obtained was 1.87 mol per W atom and mass spectrometry of the gas obtained after hypobromite oxidation showed it to be *ca.* 85% $^{15}N_2$. Evidently a little $^{14}$N entered the system during the experiments.

(*b*) *Molybdenum.* Complex (B; M = Mo) was labelled by exchange. Thus (B; M = Mo) (0.15 g) in thf (15 cm$^3$) was stirred under $^{15}N_2$ (20 cm$^3$, 92% enriched) for 20 min, then the solution was frozen and the gas removed and stored. Methanol (40 cm$^3$) was condensed on to the solution at −196 °C and, on warming to 20 °C and stirring the mixture *in vacuo*, yellow *crystals* of (G) deposited which were filtered under argon and dried (vacuum) (0.04 g): i.r. bands at 2 015 and 1 973 cm$^{-1}$ [$\nu(^{14}N_2)$], 1 935 and 1 870 cm$^{-1}$ [$\nu(^{15}N_2)$], and 1 955 and 1 915 cm$^{-1}$ [$\nu(^{14}N_2)$ and $\nu(^{15}N_2)$ of partially exchanged complex]. Complex (G) (0.02 g) was treated with $H_2SO_4$ (0.1 cm$^3$) in methanol (20 cm$^3$) as above, giving dinitrogen gas (1.57 mol, 32.5% enriched in $^{15}N_2$) and ammonia (0.66 mol per Mo atom) which was oxidised as above to give dinitrogen (0.35 mol per Mo atom) containing 31% $^{15}$N (as $^{15}N_2$, $^{15}N{\equiv}^{14}N$, and $^{14}N_2$ in near-statistical distribution) in good agreement with the labelled N in (G).

These two experiments leave no doubt that the ammonia produced in these reactions is from ligating dinitrogen.

*Reactions of Other Acids with* (B) *and* (C) (M = Mo *or* W). —The technique used in these reactions was essentially the same as for $H_2SO_4$ and yields, *etc.*, are shown in Tables 1 and 2. Some differences which occurred are noted below, the reactions being in methanol unless otherwise stated.

(B; M = W). Hypophosphorous acid gave a green-black solution after a few minutes but no precipitated solid. Orthophosphoric acid, after initial formation of a red-green solution, gave a very dark green solution after 24 h, but no precipitate. Methanesulphonic acid gave a red-black solution after 42 h and no precipitate. With oxalic acid dihydrate, dinitrogen was slowly evolved and a red solution formed, which did not change noticeably on stirring for 87 h. With malonic acid, dinitrogen and dihydrogen were slowly evolved giving a red-orange solution which did not change on stirring for 40 h. Mixtures of the complex with succinic or acetic acids were warmed to 60 °C to initiate reaction. Red solutions were obtained after 7 and 3 h with evolution of dinitrogen and dihydrogen. With trichloroacetic acid, dinitrogen and dihydrogen were rapidly evolved with formation of a yellow solution which did not change over 24 h. Trifluoroacetic acid slowly gave a red-orange solution which darkened slightly over 43 h. With catechol, the mixture was heated to 60 °C to initiate reaction and a red solution formed during 1 h with evolution of dinitrogen and dihydrogen. With tetrafluoroboric acid, dinitrogen was rapidly evolved with formation of an orange solution which became red over 45 min then deep burgundy-red over 12 h. After another 24 h a blue-black solid precipitated. Finally, with aqueous hydrobromic acid in propylene carbonate, dinitrogen was rapidly evolved and a red solution was obtained after 2 min which became brown on stirring for 48 h. Following van Tamelen's procedure,[9] HCl (20 cm$^3$, $10^{-5}$N) was added and the mixture was distilled *in vacuo* to near dryness at 140 °C and worked-up in the usual way.

(C; M = W). Anhydrous hydrogen chloride was condensed on to the reagents at −196 °C *in vacuo*. On warming to 20 °C, dinitrogen and dihydrogen were evolved and a red solution was produced after 4 min which slowly became pale golden-yellow during 18 h.

(B; M = Mo). After addition of $H_3PO_2$ in a dinitrogen atmosphere, a yellow precipitate formed during 24 h which slowly redissolved over a further 48 h leaving a yellow solution. With $H_3PO_4$, dinitrogen and dihydrogen were rapidly evolved and a yellow-brown solution was obtained. Acetic acid slowly gave a dark brown solution with evolution of dinitrogen and dihydrogen over 20 h. Hydrogen chloride in thf was condensed on to the reagents at −196 °C *in vacuo*. On warming to 20 °C dinitrogen and dihydrogen were rapidly evolved with formation of a yellow solution and a khaki precipitate which was not examined but worked-up in the usual way, the yield of ammonia being poor (Table 2). With $HBF_4$, dinitrogen and dihydrogen were rapidly evolved at 20 °C with formation of a dark brown solution which deposited a very dark brown solid during another 56 h.

*Reactions of* (B; M = W).—*With methanol.* (*i*) *With heating.* Methanol (30 cm$^3$) was condensed on to the complex (0.115 g) *in vacuo* at −196 °C. The mixture was then heated, with stirring, under reflux whereupon dinitrogen and dihydrogen were evolved and a deep red solution formed. The solution was stirred at reflux for 4 h then cooled to 20 °C. The volatiles were distilled into $H_2SO_4$ *in vacuo* at −196 °C. The residue was distilled from base and worked-up in the usual way. The sulphuric acid extract was stirred for 1 h, the solvent removed *in vacuo*, and the residue worked-up with base as usual.

(*ii*) *With irradiation.* Methanol (30 cm$^3$) was condensed on to the complex (0.97 g) *in vacuo* at −196 °C and the mixture was warmed to 20 °C and irradiated, with stirring, with 2 × 150-W tungsten-filament lamps for 42 h. A brown solution slowly formed (24 h) and dinitrogen and dihydrogen were evolved. The solvent and volatiles were condensed on to $H_2SO_4$ (0.5 cm$^3$) and the work-up then followed procedure (*i*).

*With methanol–sodium methoxide.* Methanol (30 cm$^3$) was condensed on to sodium metal (0.024 g) *in vacuo* at −196 °C and the mixture was warmed to 20 °C and stirred until reaction was complete. The solution was then degassed *in vacuo* and (B; M = W) (0.139 g) was added *in vacuo* to give a pale yellow-brown solution which was then warmed at 60 °C for 4 h. Dinitrogen and dihydrogen were evolved and the solution was then cooled to 20 °C and worked-up as for the methanol reactions above.

*With ethanol.* Ethanol (30 $cm^3$) was condensed on to the complex *in vacuo* at $-196$ °C and the mixture was warmed to 65 °C and stirred for 5 h. Dinitrogen, dihydrogen, and methane were evolved and the solution changed from orange to dark red-brown in *ca.* 1 h. Work-up then followed the procedure above.

*Reaction of* (B; M = Mo) *with Methanol.*—Methanol (40 $cm^3$) was condensed on to the complex (0.137 g) and the mixture was warmed to 50 °C then stirred for 5 h. A brown solution formed and dinitrogen and dihydrogen were evolved. Work-up then followed the usual procedure.

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