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Preliminary communication

THE MECHANISM OF THE CONVERSION OF A COORDINATED DINITROGEN TO A HYDRAZIDO(2—) LIGAND

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Summary

Elucidation of the mechanism of the reaction between *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) and HCl, HBr and H_2SO_4 in methanol, to yield $[M(NNH_2)(OCH_3)_2(PMe_2Ph)_3]$, has shown that protic solvents play a unique role in this reaction.

The factors which influence the reduction of coordinated dinitrogen to ammonia are of fundamental importance in relation to the structure and function of the enzyme nitrogenase [1]. The first mechanistic study of the conversion of a coordinated dinitrogen to a hydrazido(2—)-ligand (NNH_2^{2-}) is now reported. This mechanism demonstrates the unique role played by a protic solvent in this reaction.

Treatment of *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) in methanol with an excess of acid ultimately yields ammonia [2], via complexes of the type $[M(NNH_2)X_2(PMe_2Ph)_3]$ (isolated when X = Cl, Br or I) [3]. These hydrazido(2—)-complexes are isolated under conditions where they are precipitated from solution. However, spectrophotometric titration of a dilute solution of *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ with HX (X = Cl, Br or HSO_4) in methanol shows that, for a given metal, a common product is formed in the reaction with all three acids, and that one mole-equivalent of acid is consumed per mole-equivalent of complex ($[M]/[H^+] = 1/1$). The product of the reaction is $[M(NNH_2)(OCH_3)_2(PMe_2Ph)_3]$ which can also be obtained upon treatment of $[M(NNH_2)X_2(PMe_2Ph)_3]$ (X = Cl or Br) with $TlBF_4$ in methanol. Thus the stoichiometry corresponds to the equation:

$$cis\text{-}[M(N_2)_2(PMe_2Ph)_4] + H^+ + 2CH_3OH \rightarrow [M(NNH_2)(OCH_3)_2(PMe_2Ph)_3] + N_2 + \overset{+}{H}PMe_2Ph \quad (1)$$

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The kinetics of reaction 1 exhibit a first-order dependence in complex concentration and a second-order dependence in acid concentration $[H^+]_{total}$ = 1.0—30.0 m*M* (Mo); $[H^+]_{total}$ = 0.25—1.0 m*M* (W), but are independent of the nature of the anion ($k_{Mo}^{app.}$ = 3.9 (±0.4) × 10^5 $[H^+]^2 M^{-2} s^{-1}$ and $k_W^{app.}$ = 3.6 (±0.4) × 10^8 $[H^+]^2$ M^{-2} s^{-1}, at 25°C, μ_{total} = 30 m*M* ($LiClO_4$))*. Exponential absorbance-time traces are obtained even when the concentration of acid is only slightly in excess of the complex concentration (see Fig. 1), the initial and final absorbances corresponding to *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ and $[M(NNH_2)(OCH_3)_2(PMe_2Ph)_3]$, respectively. These observations are consistent with the mechanism shown in Scheme 1. In this Scheme, diprotonation of a coordinated dinitrogen in *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (A) labilises the *cis*-dinitrogen to yield the five-coordinate intermediate $[M(NNH_2)(PMe_2Ph)_4]^{2+}$ (D). Rapid attack of methanol on D yields *cis*-$[M(NNH_2)(OCH_3)(PMe_2Ph)_4]^+$ (E) and a mole-equivalent of protons. Subsequent dissociation of a phosphine results in the five-coordinate $[M(NNH_2)(OCH_3)(PMe_2Ph)_3]^+$ (F) which is rapidly attacked by methanol to yield $[M(NNH_2)(OCH_3)_2(PMe_2Ph)_3]$ (G)

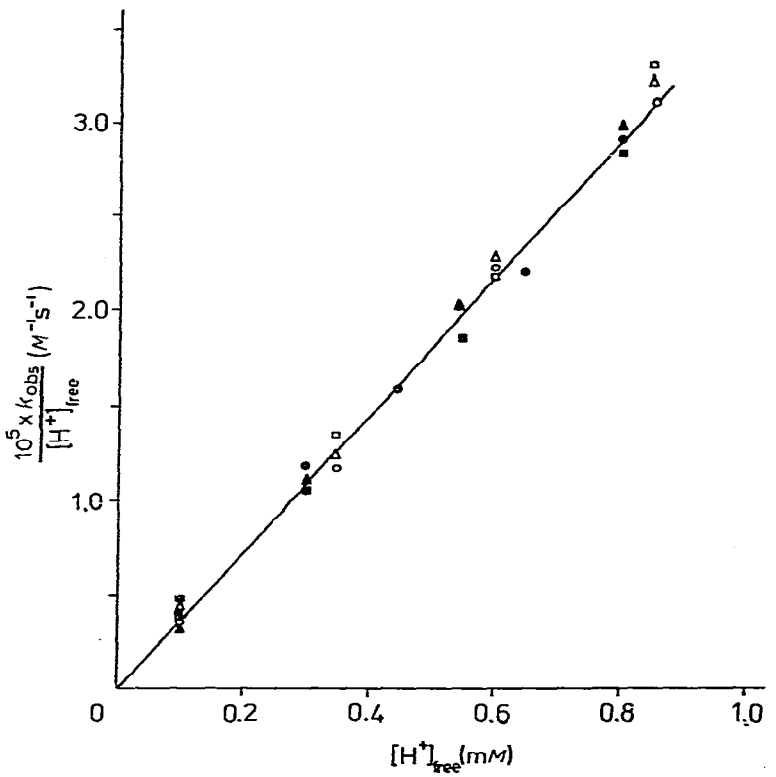
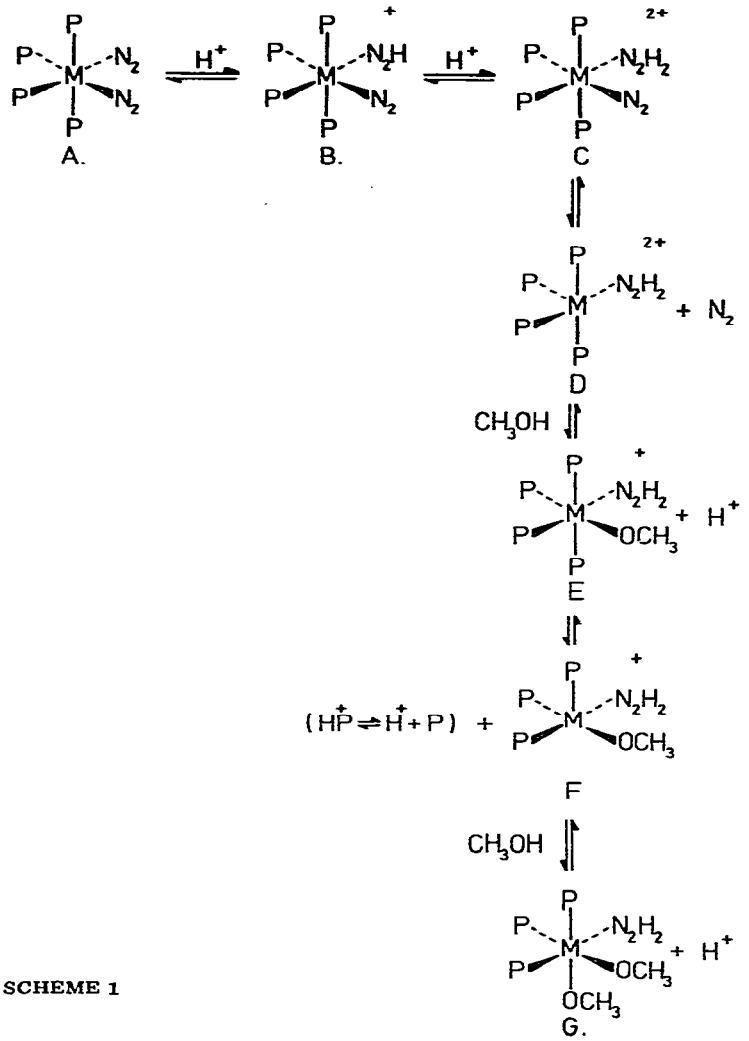


Fig. 1. Variation of $k_{obs}/[H^+]_{free}$ with $[H^+]_{free}$ ($[H^+]_{free} = [H^+]_{total} - [W]$) for the reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with HCl (▲, [W] = 0.2 m*M*; △, [W] = 0.15 m*M*), HBr (■, [W] = 0.2 m*M*; □, [W] = 0.15 m*M*), and H_2SO_4 (●, [W] = 0.2 m*M*; ○, [W] = 0.15 m*M*) in methanol at 25°C.

*k^{app} = apparent rate constant.



SCHEME 1

and a further mole-equivalent of protons. Thus both the protons employed to diprotonate A are subsequently regenerated, but the liberated phosphine consumes one mole-equivalent of protons resulting in the observed stoichiometry. It is not clear whether loss of dinitrogen or phosphine is rate-limiting, however the latter seems the more probable, and this is consistent with the kinetics if E is a steady-state intermediate.

Of further interest is, (i) the greater reactivity of *cis*-[$W(N_2)_2(PMe_2Ph)_4$] compared with its molybdenum analogue ($k_W/k_{Mo} = 9.2 \times 10^2$). This is a consequence of the greater basicity of dinitrogen when coordinated to tungsten, and similar behaviour has previously been observed [4,5]. (ii) The isotope effect observed in the reaction of *cis*-[$Mo(N_2)_2(PMe_2Ph)_4$] ($k_H/k_D = 0.3$), although complicated by a secondary- and solvent-isotope effect, is consistent with a mechanism involving protolytic-equilibria prior to the rate-limiting step [6].

In conclusion, this mechanism shows that a protic solvent is advantageous for the protonation of coordinated dinitrogen in these complexes. The facile release of a proton upon coordination of a molecule of solvent is a process which is unique to protic solvents and has the result, in the mechanism described above that protons are only consumed in the neutralisation of liberated phosphine.

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