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Metallo-oxides in Nitrogen Fixation

D. L. Hughes, M. Y. Mohammed, and C. J. Pickett*

AFRC Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, U.K.

Ammonia is released from the metallo-imide *trans*-$[W(NH)(OMe)(Ph_2PCH_2CH_2PPh_2)_2]^+$ without degradation of the phosphine ligand assembly by a hydrolysis reaction which gives the oxide *trans*-$[WOCl(Ph_2PCH_2CH_2PPh_2)_2]^+$; and this oxide and its Mo analogue are reduced at a mercury cathode in the presence of molecular nitrogen with phenol as a proton source to give *trans*-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (M = Mo or W); the primary reduction potentials of the Mo and W oxides are substantially positive of those of their isostructural imide counterparts and this suggests a possible role for oxides in biological nitrogen fixation.

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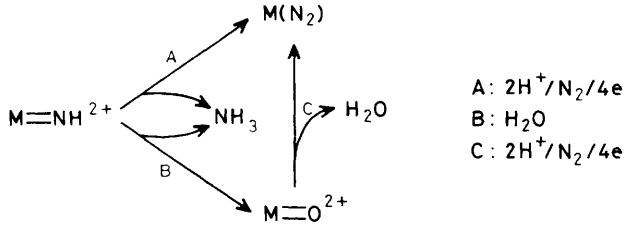
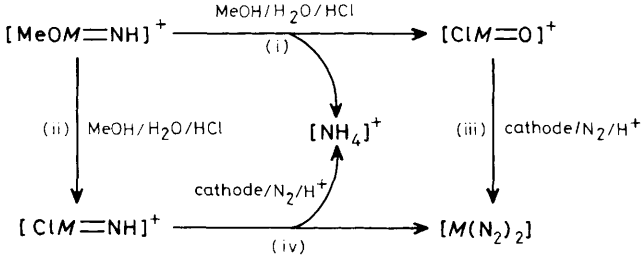
The direct electronation of simple molybdenum and tungsten imides under molecular nitrogen can give ammonia and dinitrogen complexes, and this might parallel a reaction sequence in biological nitrogen fixation (Scheme 1, pathway A).[1,2] We now provide a chemical example which shows that an alternative route involving a metal oxide is also viable (Scheme 1, pathways B + C). Electronation in the latter pathway is driven at a substantially less negative potential than that demanded by the former process and this suggests that water-oxide interconversions could play a key role in imide metabolism at an enzymic fixation site.



Scheme 1. Conversion of an imide to free ammonia at a metal site M with binding of molecular nitrogen. Pathway A involves direct electronation and protic attack whereas pathways B + C require an initial hydrolysis (B) to give ammonia followed by reduction of the oxide in a step (C) which parallels (A).

The acid hydrolysis of the imide group of the tertiary phosphine complex *trans*-$[W(NH)(OMe)(Ph_2PCH_2CH_2PPh_2)_2]^+$ gives ammonia without the destruction of the metal–P_4 assembly, Scheme 2(i). The oxide *trans*-$[WOCl(Ph_2PCH_2CH_2PPh_2)_2]^+$ was isolated and fully characterised as its HCl_2^- salt.[3] Hitherto ammonia has only been obtained chemically from such imides by degradative routes that give free diphosphine and unidentified metal products.[4]



Scheme 2. Two pathways from imides to ammonia *via* reactions at the $\{M(Ph_2PCH_2CH_2PPh_2)_2\}$ assembly (*M*) which yield dinitrogen complexes. Hydrolysis (i) gives the tungsten oxide and ammonia and, by a competing reaction, (ii), the substitution product. Optimum conditions give yields of oxide and ammonia of about 50—55%. When M = Mo or with anhydrous HCl–MeOH *only* the substitution products are obtained. Electrolysis of either the Mo or W oxide gives the respective dinitrogen complex (iii) as does reduction of the imides (iv) (see ref. 1).

The initial steps in the formation of the tungsten oxide and ammonia are probably the same as those established for the mechanism of substitution,[5] *i.e.* protonation of methoxide, liberation of methanol, and subsequent attack at the metal by the nucleophile, H_2O in this case. We envisage subsequent prototropic rearrangement (1) followed by release of ammonia and ligation of chloride. *trans*-$[Mo(NH)(OMe)(Ph_2PCH_2CH_2PPh_2)_2]^+$ gives only the chloride substituted product [Scheme 2 (ii)] when treated with aqueous hydrochloric acid, presumably because prototropic rearrangement is less favourable than irreversible substitution of water or methanol by Cl^-.

$$[(H_2O)M{=}NH]^{2+} \rightarrow [O{=}M(NH_3)]^{2+} \quad (1)$$

The reversible one-electron reduction of the oxides *trans*-$[MOCl(Ph_2PCH_2CH_2PPh_2)_2]^+$ (M = Mo or W) generates reactive M^{III} intermediates which in the presence of a proton

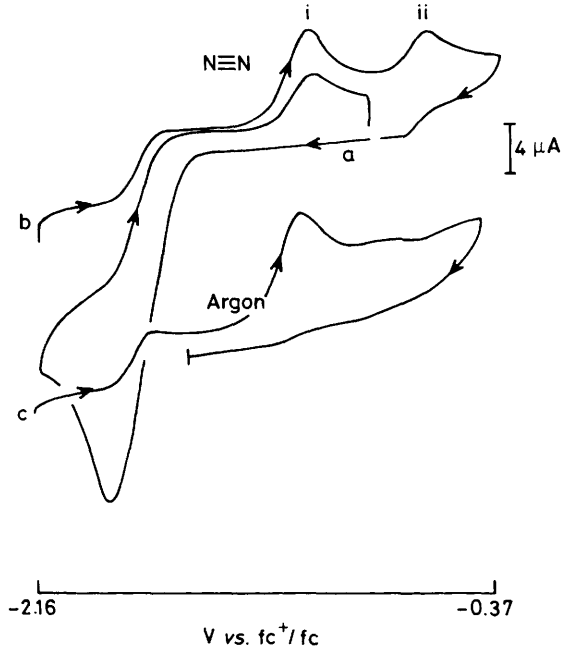


Figure 1. Voltammetry of *trans*-$[MoOCl(Ph_2PCH_2CH_2PPh_2)_2]^+$ in a thf electrolyte at a vitreous carbon electrode in the presence of PhOH, scan-rate 200 mV s^{-1}. Curve a shows the primary reduction of the oxide, and is irreversible in the presence of phenol; curve b shows the effect of clamping at a potential negative of the primary reduction process under dinitrogen; and curve c the effect of clamping under argon. The product peak labelled (i) we assign to the oxidation of *trans*-$[Mo(OH)Cl(Ph_2PCH_2CH_2PPh_2)_2]$: the product peak (ii) is *only* present under molecular nitrogen and its potential corresponds to the (reversible) oxidation of *trans*-$[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$.

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source and molecular nitrogen undergo further electron-transfer chemistry to give the dinitrogen complexes *trans*-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$, as illustrated by the voltammogram (Figure 1). This was confirmed by bulk electrolysis in the following way. Reduction of *trans*-$[MoOCl(Ph_2PCH_2CH_2PPh_2)_2]^+$ at a Hg-pool cathode held at −1.9 V relative to ferrocinium–ferrocene (fc^+–fc) in a tetrahydrofuran (thf) electrolyte containing 0.2 M $[NBu_4]$, $[BF_4]$, *ca.* 10 mM PhOH, and saturated with N_2 (1 atm), gives a quantitative yield of the molybdenum–dinitrogen complex with the consumption of about 4 F mol^{-1} of oxide. The dinitrogen complex was isolated as an orange solid and its identity was confirmed by ^{31}P n.m.r. and i.r. spectroscopy and cyclic voltammetry. Because reductions were carried out in the presence of a proton source we looked for evidence for the formation of the hydride *trans*-$[MoH_4(Ph_2PCH_2CH_2PPh_2)_2]$ but found none.

The primary reduction potentials of the molybdenum and tungsten oxides are respectively −1.80 and −1.99 V *vs.* fc^+–fc and these values are substantially positive (> +300 mV) of those for their isostructural imide analogues.[1] In biological systems where the free energy to drive direct electron-transfer is limited, a pathway similar to B + C might be more favourable than one analogous to A (Scheme 1); the former pathway requires access of water to the fixation site, whereas the latter does not.

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