From Metal Imides and Molecular Nitrogen to Ammonia and Dinitrogen Complexes

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Reduction of a molybdenum imide under molecular nitrogen gives ammonia and a dinitrogen complex.

Biological and electrochemical nitrogen fixation systems are envisaged as involving metallo-imide groups in the common reaction sequence shown by Scheme 1.[1—5]

For example, it has been shown that the protolysis of the N–N bond in a reduced organo-hydrazide can give an imide and an amine[6,7] and the degradation of such imides in conditions gives some ammonia[8—10] but, as is indicated in Scheme 1 (box), nitrogen fixation *via* (M=NH) intermediates requires the release of the second molecule of ammonia by reactions which conserve, or at least allow the reassembly of, a metal site at which dinitrogen can again bind.
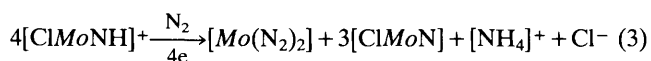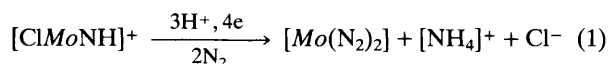
A chemical precedent for this stage in the fixation sequence has hitherto been lacking.

We now report that under molecular nitrogen the electrochemical reduction of certain imido-species can give dinitrogen complexes and ammonia. We suggest that metallo-amides (M–NH$_2$) are key intermediates in the reduction.

Electrolysis of *trans*-[Mo(NH)Cl(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]$^+$ at a mercury pool cathode (-2.6 V *versus* ferrocinium/ferrocene couple, fc$^+$/fc; 1.2 F mol^{-1}) in tetrahydrofuran (thf) containing 0.2 M[NBu$_4$][BF$_4$] and saturated with molecular nitrogen (1 atm.) produces free ammonia in a yield of *ca.* 15 mol% mol^{-1} imide, the dinitrogen complex *trans*-[Mo(N$_2$)$_2$(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] *ca.* 35 mol% mol^{-1} imide, and the nitride complex *trans*-[Mo(N)Cl(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] *ca.* 65 mol% mol^{-1} imide; a typical ^{31}P-{^{1}H} n.m.r. spectrum

obtained after exhaustive electrolysis shows only the resonances of these two metal products at 75.1 and 85.4 p.p.m., respectively, relative to trimethylphosphite.

The data are consistent with the imide behaving as both the electroactive species and as a source of proton, equations (1)—(3). The acid–base behaviour of the imide–nitride system is well established[8—10] and such coupling of electronation with protonation is akin to the 'father–son' reactions of related hydrazide species[4,5] but the yield of ammonia is somewhat lower than that required by the stoicheiometry (ca. 60% of the theoretical value of 25 mol% NH_3 mol^{-1} imide). Ammonia, the dinitrogen complex, and the nitride are also produced on reduction of related imide cations as listed in Table 1.

$$[ClMoNH]^+ \xrightarrow[2N_2]{3H^+,4e} [Mo(N_2)_2] + [NH_4]^+ + Cl^- \quad (1)$$

$$[ClMoNH]^+ \rightleftharpoons [ClMoN] + H^+ \quad (2)$$

$$4[ClMoNH]^+ \xrightarrow[4e]{N_2} [Mo(N_2)_2] + 3[ClMoN] + [NH_4]^+ + Cl^- \quad (3)$$

The mechanism of reduction of the imide involves an initial irreversible electron-transfer ($^IE_p{}^{red} = -2.1$ V vs. fc$^+$/fc)
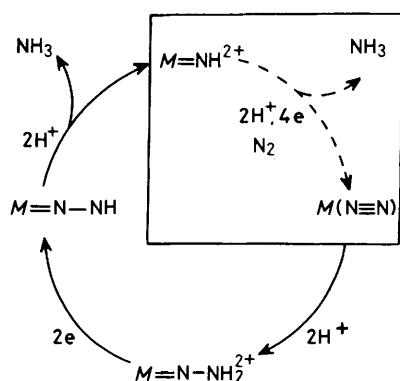

Scheme 1. M represents a transition-metal centre and its conserved ligands.

which gives two primary products: the stable nitride and an unstable intermediate (Figure 1). The intermediate is oxidised reversibly in a one-electron step ($E_{1/2}{}^{ox} = -1.58$ V vs. fc$^+$/fc) and also undergoes an irreversible one-electron reduction ($^{II}E_p{}^{red} = -2.58$ V vs. fc$^+$/fc), as shown by the voltammogram (Figure 1). Bulk electrolysis performed at a potential negative of $^IE_p{}^{red}$ but positive of $^{II}E_p{}^{red}$ consumes 1 F mol^{-1} and gives the nitride as the major product; only small amounts of the dinitrogen complex are produced and less than 1% ammonia.

In the absence of a pathway for its reduction, the intermediate must decay to the stable nitride, and it is only when electrolyses are carried out at potentials at or just negative of $^{II}E_p{}^{red}$ that the dinitrogen complex and ammonia are formed in significant amounts. That the reduction of the intermediate leads directly and rapidly to the formation of trans-$[Mo(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ is clearly shown by the comparative voltammetry under argon and dinitrogen (Figure 1): the substrates H_2, CO, and Bu^{t}NC produce effects on the voltammetry parallel to that of N_2,[11] for example, in the presence of the isocyanide, trans-$[Mo(Bu^tNC)_2(Ph_2PCH_2-CH_2PPh_2)_2]$ is formed.

The intermediate is too unstable to isolate but substitutions on the parent imide allow us to infer something about its structure. Replacing the chloride ligand on the metal by other halide ligands alters $E_{1/2}{}^{ox}$ and $^{II}E_p{}^{red}$ of the electrogenerated intermediate and this indicates that Cl is retained at Mo after the primary electron-transfer (Table 1). Replacing the hydrogen of the imide group by CH_3 stabilises the intermediate. At $-15\,°C$ solutions containing the methylated intermediate can be prepared by bulk electrolysis and these solutions
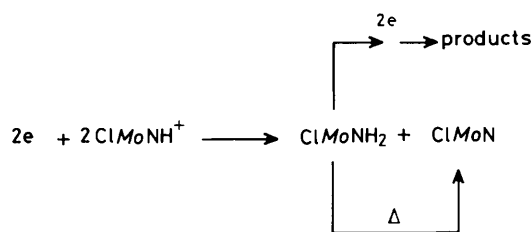
Scheme 2. Mo represents the square-planar $Mo(Ph_2PCH_2CH_2PPh_2)_2$ assembly.

Table 1.

Imide[a] complex	Primary reduction[b] potential $^IE_p{}^{red}$/V	Oxidation potential[b] of intermediate $E_{1/2}{}^{ox}$/V	Products[c] (Yield/mol% mol^{-1} imide)
[FMoNH]$^+$	−2.51	−1.85	NH_3 (10.5) $[Mo(N_2)_2]$(22) [FMoN](78)
[ClMoNH]$^+$	−2.09	−1.57	NH_3 (15.0) $[Mo(N_2)_2]$(27) [ClMoN](73)
[BrMoNH]$^+$	−2.02	−1.49	NH_3 (14.5) $[Mo(N_2)_2]$(22) [BrMoN](65)
[IMoNH]$^+$	−2.00	−1.36	NH_3 (6.0) $[Mo(N_2)_2]$ free diphosphine and unidentified products
[N$_3$MoNH]$^+$	−2.15	−1.25	n.d.
[MeOMoNH]$^+$	−2.62	−1.65	n.d.
[ClMoN]$^+$	−2.36	−1.48	NH_2Me(43)[d]
[ClWNH]$^+$	−2.35	−1.33	NH_3 (4.5) $[W(N_2)_2]$(20) [ClWN](80)

[a] Mo represents trans-$Mo(Ph_2PCH_2CH_2PPh_2)_2$. [b] Potentials are versus fc$^+$/fc and were measured at a glassy carbon electrode in 0.2 M [NBu$_4$][BF$_4$]–thf. [c] Exhaustive electrolyses were performed at potentials ca. ($^{II}E_p{}^{red} - 0.1$)V; see text. Yields of ammonia were determined by the indophenol test[5] and methylamine with 2,4-dinitrofluorobenzene.[13] Complexes were identified and estimated by cyclic voltammetry and ^{31}P-$\{^1H\}$ n.m.r. The formation of $[Mo(N_2)_2]$ was confirmed by i.r. spectroscopy. [d] Electrolyses were performed at $-15\,°C$ to stabilise the methylated intermediate. Examination of the catholyte after exhaustive electrolysis by ^{31}P-$\{^1H\}$ n.m.r. showed the presence of the parent methylimide (singlet, -97.4 p.p.m. relative to trimethylphosphite, tmp), the methylene imide (singlet, 83.4 p.p.m. relative to tmp) and a singlet resonance at -53.2 p.p.m. relative to tmp which we assign to the methylated intermediate. Treatment of the catholyte after electrolysis with aqueous HCl (0.1 M) gave methylamine. Under the same conditions the methyleneimide reacts with aqueous HCl to give the parent alkylimide.
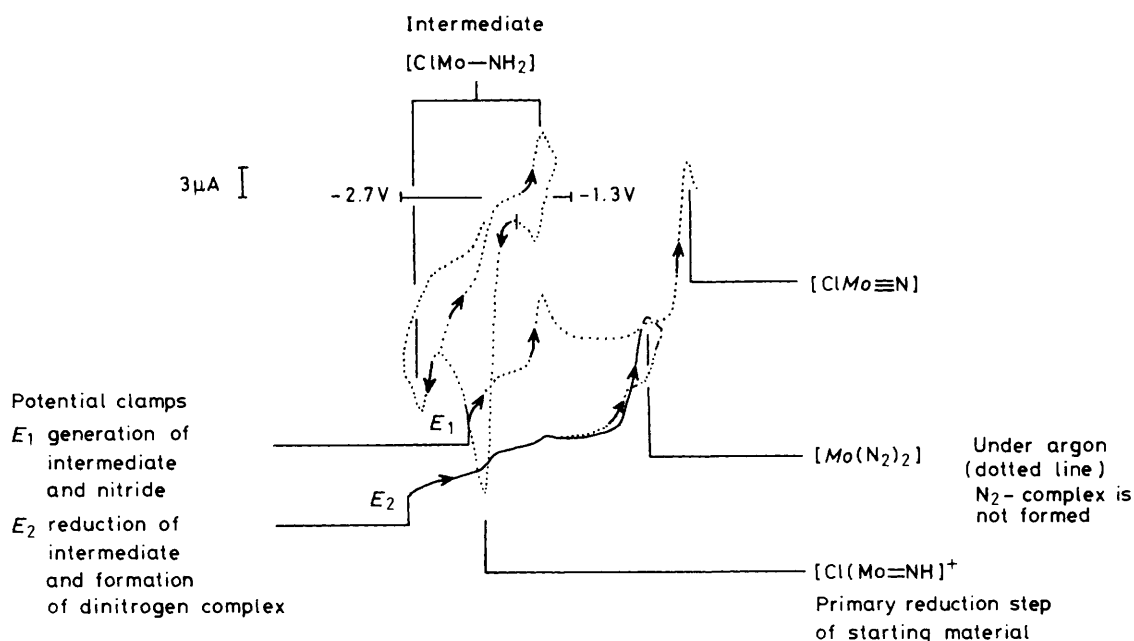
Intermediate

[ClMo—NH₂]

Figure 1. Cyclic and clamp voltammograms of *trans*-[Mo(NH)Cl(Ph₂PCH₂CH₂PPh₂)₂]⁺ (5.8 mM) recorded at a glassy carbon electrode (area = 5.4 mm²). The potential scale is relative to fc⁺/fc and the scan-rates are 0.10 Vs⁻¹.

also contain a product formed by de-protonation of the parent methylimide, *trans*-[MoCl(NCH₂)(Ph₂PCH₂CH₂PPh₂)₂].[12] This parallels the co-production of nitride and intermediate when the imide is reduced.

On the basis of these observations we suggest that the key intermediate is an amide complex [MoCl(NH₂)(Ph₂PCH₂-CH₂PPh₂)₂] and that it is formed in the primary electrode reaction by coupled electron and proton transfer (Scheme 2). The observed $n_{apparent}$ [close to one on the time-scale of the cyclic voltammetry (seconds)] is consistent with this. Reduction of the amide provides the route to ammonia and the dinitrogen complex whilst its thermal decay provides a pathway to further nitride. The difference in stability of the methylamide and amide intermediates is presumably because the latter can lose H₂ but the former cannot.

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