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# ELECTROCHEMISTRY OF LIGANDS MULTIPLY BONDED TO MOLYBDENUM AND TUNGSTEN

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**Abstract**—This paper describes some new electrochemically driven reactions of ligands which are multiply bonded to molybdenum or tungsten.

We describe some new electrochemical reactions of ligands which are multiply bonded to molybdenum and tungsten. Our interest was initially focused on the electrochemistry of imide ligands for the following reasons.

First, electron-transfer reactions involving MoNH or WNH groups are plausible steps in electrochemical[1] and biochemical[2] nitrogen fixation pathways, as outlined in Scheme 1 (Box).[3]

Secondly, oxidation reactions involving imide or alkylimide groups might provide a means of diversifying the nitrogen products which can be made from molecular nitrogen, via chemistry at the square-planar $\{M(dppe)_2\}$ assembly (M = Mo or W; dppe = $Ph_2PCH_2CH_2PPh_2$).[4]

However, work with imides has led us to explore the electrochemistry of oxide, methyleneamide, cyanide and aminocarbyne ligating molybdenum or tungsten and has provided some new ligand-centred chemistry.

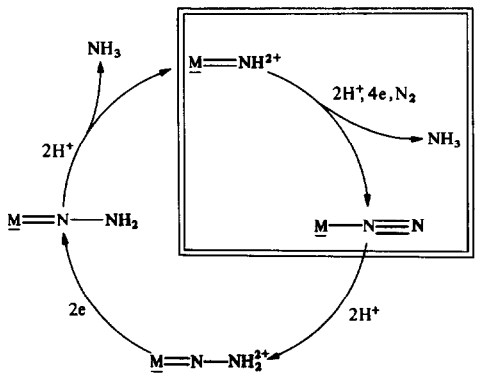
## IMIDE AND OXIDE REDUCTION

Simple imide complexes such as *trans*-$[Mo(NH)Cl(dppe)_2]^+$ are reduced under molecular nitrogen to dinitrogen complexes and ammonia,[3] and this provides some support for a role of the {MNH} group in both electrochemical and biological fixation pathways, Scheme 2.

However, it is also possible to obtain ammonia by hydrolysis of an imide which produces an oxide via a prototropic rearrangement, Scheme 3.[5]

What is rather interesting here is that the primary reversible reduction of the oxides, *trans*-$[MOCl(dppe)_2]^+$, occurs at potentials more than 300 mV positive of those of their imido analogues. Moreover, in the presence of a source of protons, the reduction of the oxide becomes irreversible and, under molecular nitrogen, *trans*-$[M(N_2)_2(dppe)_2]$ is produced in an overall 4F $mol^{-1}$ process. The effect of molecular nitrogen on the voltammetry of the molybdenum oxide is illustrated in Fig. 1; the intermediate detected as peak (i) in the voltammogram is the hydroxide intermediate, *trans*-[Mo(OH)Cl $(dppe)_2$], and that labelled (ii) is of the product, *trans*-$[M(N_2)_2(dppe)_2]$, Scheme 4.[5,6]

The relative ease of the multi-electron reduction of the Mo=O group, compared to that of




Scheme 1. In this scheme and Scheme 5, M represents a metal centre and conserved co-ligands. Elsewhere it represents the specific assemblies *trans*-{Mo or $W(dppe)_2$}.

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$$Cl—\underline{Mo}{=}NH^{+} \xrightarrow{2e,H^{+}} Cl—\underline{Mo}—NH_2 \xrightarrow[2N_2,\,-Cl^{-}]{2e,H^{+}} N_2—\underline{Mo}—N_2 + NH_3$$

Scheme 2.

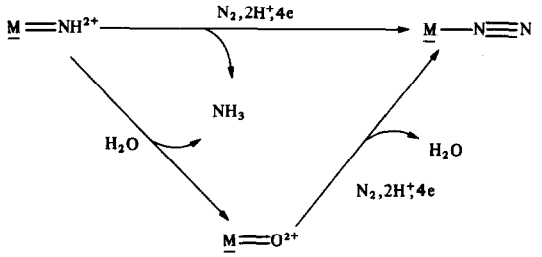
$$MeO—\underline{W}{=}NH^{+} \xrightarrow[-MeOH]{H^{+},H_2O} H_2O—\underline{W}{=}NH^{2+} \longrightarrow O{=}\underline{W}—NH_3^{2+} \xrightarrow{Cl^{-}} O{=}\underline{W}—Cl^{+} + NH_3$$

Prototropic rearrangement

Scheme 3.

$$Cl—\underline{M}{=}O^{+} \xrightarrow{2e,H^{+}} Cl—\underline{M}—OH \xrightarrow[2N_2,\,-Cl^{-}]{2e,H^{+}} N_2—\underline{M}—N_2 + H_2O$$

Scheme 4.




Scheme 5.

Mo=NH, suggests that a sequence involving hydrolysis and oxide reduction might be more favourable in an enzymic nitrogen fixation pathway than direct imide reduction, Scheme 5.[3,5]

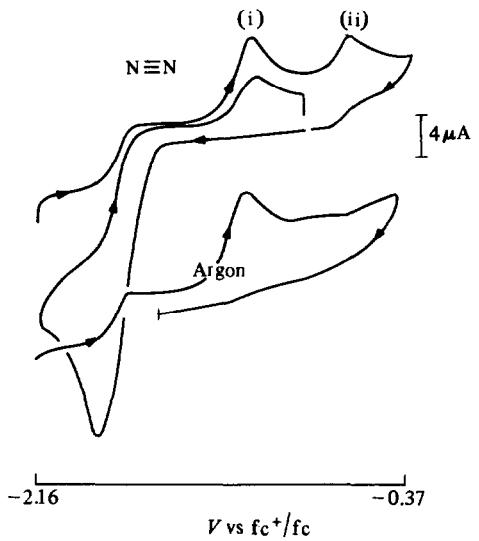


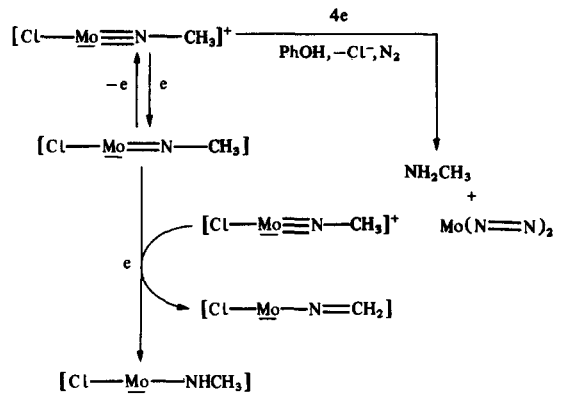

Fig. 1. Clamp voltammograms of *trans*-[MoOCl(dppe)$_2$]$^+$, in a tetrahydrofuran electrolyte containing phenol, showing the detection of the hydroxide (i) and the product (ii), *trans*-[Mo(N$_2$)$_2$(dppe)$_2$]. Potentials are relative to ferrocinium/ferrocene, fc$^+$/fc, here and in Scheme 7. For details see ref. 3.

## METHYLIMIDE REDUCTION: GENERATION OF A STRONG BASE

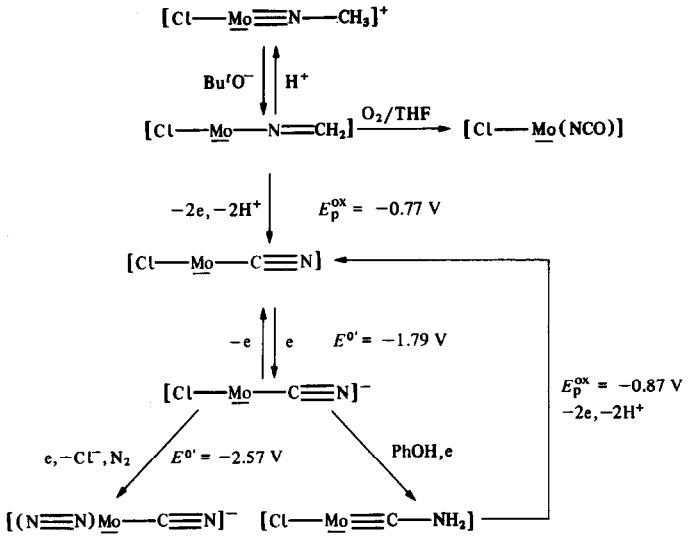
In detail, the electrochemical reduction of *trans*-[Mo(NH)Cl(dppe)$_2$]$^+$ is an irreversible process which initially produces two products viz. the unstable amide, *trans*-[Mo(NH$_2$)Cl(dppe)$_2$], and the nitride, *trans*-[Mo(N)Cl(dppe)$_2$].[2,3] This occurs as an apparent one-electron process, because the primary reduction product removes a proton from the reactant to give the nitride and a cation, the latter is then rapidly reduced to the neutral amide, Scheme 2.[3]

That the primary reduction step involves a single electron-transfer step is suggested by the behaviour of the methylimide analogue, *trans*-[Mo(NMe)Cl(dppe)$_2$]$^+$, which at low temperature displays an electrochemically reversible one-electron reduction, Scheme 6.

We might expect that the reactant, *trans*-[Mo(NMe)Cl(dppe)$_2$]$^+$, would be incapable of furnishing a proton to the neutral one-electron intermediate, but this is not the case. At ambient tem-




Scheme 6. Oxidation of methylimide and methyleneamide ligands: a radical di-cation and a cyanide.




Scheme 7.

peratures, the reduction becomes less reversible and we detect *trans*-[Mo(NHMe)Cl(dppe)$_2$] and the methyleneamide species, *trans*-[Mo(NCH$_2$)Cl(dppe)$_2$], Scheme 6.

Deprotonation of the methylimide by K[OBu$^t$] affords the methyleneamide by an independent route, and the complex has been isolated and fully characterized.[7] Its formation during electro-reduction is circumvented when phenol is present as a source of protons; a clean four-electron reduction to the amine and *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] is possible on a preparative scale using a mercury cathode and a THF electrolyte, Scheme 6.

Whether the "19-e" primary intermediate adopts a "17-e" bent MoNC configuration remains a matter of speculation, the important message is that we generate a metallo-nitrogen base that is capable of deprotonating the parent carbon acid, the methylimide. Such "father–son" reactions appear to be a common feature of the electrochemistry of imide, alkylimide, hydrazide and diazoalkane cations.[1,3]

Cyclic voltammetry showed that *trans*-[Mo(NMe)Cl(dppe)$_2$]$^+$ undergoes a partially reversible one-electron oxidation in common non-aqueous electrolytes, but our attempts to electrosynthesize clean products in such solvents were unsuccessful.

However, in trifluoroacetic acid containing 0.2 M [NBu$_4$][BF$_4$] and trifluoroacetic anhydride, a medium of low nucleophilicity, the radical di-cation *trans*-[Mo(NMe)Cl(dppe)$_2$]$^{2+}$ is reasonably stable and can be prepared as a solution species by either electro-oxidation at platinum, or by chemical oxidation with [NO][PF$_6$]. We have characterized the di-cation, certain of its isotopically substituted derivatives and a minor co-product, by EPR and ENDOR spectroscopy. This has enabled us to establish that the radical retains the essential structure of the 18-electron parent.[8]

As a means of transforming a methylimide ligand, direct electro-oxidation appeared unpromising, we therefore looked at the oxidation of the de-protonated species, the methyleneamide, *trans*-[Mo(NCH$_2$)Cl(dppe)$_2$].

Electrochemical or iodine oxidation of this complex afforded the cyanide *trans*-[Mo(CN)Cl(dppe)$_2$], which was characterized by an X-ray crystallographic analysis of green prisms isolated in low yield from an anolyte.[7] Labelling studies suggest that the rearrangement of the MoNC framework to MoCN is an intramolecular process, Scheme 7.[7]

## THE REDUCTION OF A MOLYBDENUM CYANIDE TO AN AMINOCARBYNE AND TO A DINITROGEN COMPLEX

Cyclic voltammetry shows that *trans*-(Mo(CN)Cl(dppe)$_2$] undergoes two successive one-electron reduction steps in a dry THF electrolyte at a vitreous carbon electrode. The first of these is reversible, the second leads to the irreversible loss of Cl$^-$ and to the formation of the known anionic dinitrogen complex *trans*-[Mo(N$_2$)(CN)(dppe)$_2$]$^-$, Scheme 7. The cyanide also undergoes a reversible one-electron oxidation.

In the presence of a proton source, phenol, the primary reduction of the cyanide becomes an irreversible two-electron process and at a mercury pool cathode the aminocarbyne *trans*-[Mo(CNH$_2$)Cl(dppe)$_2$] is formed in good yield. As far as we

are aware, this is the first example of the partial reduction of a cyanide ligand to aminocarbyne; the complex has an isostructural rhenium analogue, the hitherto unique *trans*-$[Re(CNH_2)Cl(dppe)_2]^+$.[9] In formal terms, the 16-electron $Mo^{II}$–cyanide is "reduced" to an 18-electron $Mo^{IV}$ product, a process which is chemically reversible, Scheme 7.[7]

The reduction of the cyanide to a molybdo–aminocarbyne provides a chemical precedent for a plausible step in enzymic reduction of $CN^-$ by molybdenum nitrogenase.[10]

## CONCLUSIONS

We summarize our conclusions as follows:

(1) In the presence of a proton source, cathode reactions can provide a means of releasing multiply-bonded ligands from $\{M(dppe)_2\}$ assemblies and of exposing a site at which dinitrogen (and other $\pi$-acid ligands) can then bind. This is important in the construction of nitrogen fixing pathways and also bears upon possible mechanisms of enzymic fixation.

(2) In the *absence* of a proton source, the primary products of electron-transfer to closed-shell hydrazides, imides or alkylimides can be sufficiently basic to remove a proton from the parent cation. Indeed metallo–nitrogen bases can be electrogenerated which are capable of deprotonating a methylimide ligand.

(3) Electro-oxidation of the methyleneamide to a cyanide and reduction of this cyanide to an aminocarbyne provides a pathway for the isomerization of the $\{MoNCH_2\}$ group to $\{MoCNH_2\}$.

(4) The partial reduction of $CN^-$ at a simple mononuclear molybdenum to a bound aminocarbyne suggests that the generation of a $\{MoCNH_2\}$ group is a plausible stage in cyanide metabolism by molybdenum nitrogenase.

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