Towards a Nitrogen-fixing Cycle: Electrochemical Reduction of a Hydrazido-complex of Molybdenum(IV) under N_2 to Yield the Dialkylhydrazine and a Molybdenum(0) Dinitrogen Complex

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Summary Electrochemical reduction of *trans*-$[MoBr(\overline{N_2CH_2[CH_2]_3CH_2})(dppe)_2]^+$, (**5**) (dppe = $Ph_2PCH_2CH_2PPh_2$) at a Pt electrode in tetrahydrofuran–0·2 M $[NBu_4][BF_4]$ under N_2 yields the free organohydrazine and *trans*-$[Mo(N_2)_2(dppe)_2]$, (**1**), under CO yields *cis*- and *trans*-$[Mo(CO)_2(dppe)_2]$ and *N*-aminopiperidine, and under Ar yields the reduction product *trans*-$[Mo^{II}(\overline{N_2CH_2[CH_2]_3CH_2})(dppe)_2]$; the product (**1**) is readily converted into (**5**), thus a cycle for the fixation of N_2 as an organohydrazine is plausible.

WE have shown previously how co-ordinated dinitrogen can be converted into dialkylhydrazido(2−)-ligands by reaction with alkyl bromides, RBr,[1,3] equation (1) (dppe = $Ph_2PCH_2CH_2PPh_2$). Hitherto, it has only been possible

$$\begin{tikzcd}
\textit{trans}\text{-}[Mo(N_2)_2(dppe)_2] \arrow[r, "RBr"] & \textit{trans}\text{-}[MoBr(N_2R)(dppe)_2] \arrow[d, "RBr"] \\
\mathbf{(1)} & \mathbf{(2)} \\
 & \textit{trans}\text{-}[MoBr(N_2R_2)(dppe)_2]^+ \quad \mathbf{(3)} \qquad (1)
\end{tikzcd}$$

to liberate organonitrogen compounds from complexes (**3**) by destructive reduction.[3] We show here how electrochemical reduction[4] of a complex of type (**3**) can produce a dialkylhydrazine and regenerate the initial dinitrogen complex (**1**), *via* equation (2). This opens the possibility of an electrochemical cycle to produce organohydrazines from dinitrogen.

$$\begin{tikzcd}
\textit{trans}\text{-}[MoBr(N_2R_2)(dppe)_2]^+ \arrow[r, "2e"'] & \textit{trans}\text{-}[Mo(N_2R_2)(dppe)_2] + Br^- \\
\mathbf{(3)} & \mathbf{(4)} \arrow[d, "N_2"', "H^+,\ 2e"] \\
 & H_2NNR_2 + \textit{trans}\text{-}[Mo(N_2)_2(dppe)_2] \quad \mathbf{(1)} \qquad (2)
\end{tikzcd}$$

Controlled potential electrolysis (c.p.e.) and cyclic voltammetry (c.v.) of *trans*-$[MoBr(Q)(dppe)_2]^+$ (**5**) (Q = $\overline{NNCH_2[CH_2]_3CH_2}$) under an atmosphere of *argon*, in tetrahydrofuran (THF) or MeCN–0·2 M $[NBu_4][BF_4]$, shows that the complex undergoes an irreversible diffusion-controlled two-electron reduction at a Pt electrode, $E_p^{RED}(\mathbf{5}) = -1{\cdot}62$ V *vs.* the saturated calomel electrode, (S.C.E.) to give a single, stable dark-red solution species (**6**). The complex (**5**) is also reduced to (**6**) by $LiBu^t$ in Et_2O; (**6**) is stable in the presence of an excess of $LiBu^t$ and is therefore unlikely to possess N–H bonds. A solution of (**6**) in THF shows a single phosphorus resonance and therefore the dppe ligands are retained in a square plane. The oxidation potential of (**6**) is essentially solvent-independent (THF or MeCN); it is therefore unlikely that (**6**) contains a co-ordinated solvent molecule.

The product of oxidation of (**6**), in contrast with its oxidation potential, shows a solvent-dependent reduction potential. C.p.e. and c.v. of an electrochemically generated solution of (**6**) in THF–0·2 M $[NBu_4][BF_4]$ show that (**5**) is regenerated in a diffusion-controlled two-electron process

TABLE

Species[a]	E_p^{RED}/V[b]	Comment
trans-$[\mathrm{MoBr(Q)(dppe)_2}]^+$	$-1{\cdot}63$	(5)
trans-$[\mathrm{MoBr(N}\overline{\mathrm{NCH_2[CH_2]_2CH_2}}\mathrm{)(dppe)_2}]^+$	$-1{\cdot}61$	Reduction under CO gives *N*-aminopyrollidine
trans-$[\mathrm{MoBr(Q)(depe)_2}]^+$	$-1{\cdot}86$	
trans-$[\mathrm{MoBr(NN}\begin{smallmatrix}\diagup\mathrm{Me}\\ \diagdown\mathrm{Me}\end{smallmatrix}\mathrm{)(depe)_2}]^+$	$-1{\cdot}79$	
$[\mathrm{Mo(NN}\begin{smallmatrix}\diagup\mathrm{Me}\\ \diagdown\mathrm{Me}\end{smallmatrix}\mathrm{)(dtc)_3}]^+$	$-0{\cdot}81$	See ref. 4
trans-$[\mathrm{MoBr(NNMe)(dppe)_2}]$	no reduction	Oxidises in reversible 1e step at 0·00 V
trans-$[\mathrm{WBr(Q)(dppe)_2}]^+$	$-1{\cdot}97$	
trans-$[\mathrm{WBr(NN}\begin{smallmatrix}\diagup\mathrm{Me}\\ \diagdown\mathrm{Me}\end{smallmatrix}\mathrm{)(dppe)_2}]^+$	$-1{\cdot}75$	
trans-$[\mathrm{WBr(NNMe)(dppe)_2}]$	no reduction	Oxidises in reversible 1e step at +0·03 V

[a] depe = $\mathrm{Et_2PCH_2CH_2PEt_2}$, dtc = $\mathrm{S_2CNMe_2}$.

[b] E_p^{RED} are quoted *vs.* S.C.E. in THF–0·2 M $[\mathrm{NBu_4}][\mathrm{BF_4}]$ and were measured by c.v. at 0·3 V $\mathrm{s^{-1}}$ at a Pt electrode, E_p^{OX} (ferrocene) = 0·55 V under these conditions.

at potentials positive of $E_p^{\mathrm{OX}}(\mathbf{6}) = -0{\cdot}82$ V. Therefore (**6**) must retain the essential co-ordination environment of (**5**) and the reduction of (**5**) is *chemically* reversible.

Oxidation of (**6**) in THF containing *ca.* 1% MeCN or in MeCN–0·2 M $[\mathrm{NBu_4}][\mathrm{BF_4}]$ produces a single product which is some 500 mV easier to oxidise than is (**5**) and must contain co-ordinated MeCN. Bromide cannot be removed from (**5**) even when it is heated in MeCN under reflux in the presence of $\mathrm{Tl[BF_4]}$. *If* the product (**6**) contained co-ordinated $\mathrm{Br^-}$ then re-oxidation of (**6**) in both THF and MeCN should have given (**5**). This strongly suggests that $\mathrm{Br^-}$ loss follows the 2e reduction of (**5**) in THF or MeCN containing 0·2 M $[\mathrm{NBu_4}][\mathrm{BF_4}]$. We therefore conclude that under Ar, two-electron reduction of (**5**) gives the five-co-ordinate closed-shell complex $[\mathrm{Mo^{II}(Q)(dppe)_2}]^0$ according to equation (3). This is the first example of a $\mathrm{Mo^{II}}$-hydrazido(2−)-complex. We suggest that oxidation of (**6**) in the presence of MeCN produces (**7**), equation (3).

$$\begin{array}{ccc}
[\mathrm{MoBr(Q)(dppe)_2}]^+ & \underset{\mathrm{THF,\ 2e}}{\rightleftharpoons} & \mathit{trans}\text{-}[\mathrm{Mo(Q)(dppe)_2}]^0 + \mathrm{Br^-} \\
(\mathbf{5}) & & (\mathbf{6}) \\
 & & \Big\downarrow{\scriptstyle -2\mathrm{e,\ MeCN}} \\
 & & [\mathrm{Mo(MeCN)(Q)(dppe)_2}]^{2+} \\
 & & (\mathbf{7})
\end{array} \qquad (3)$$

Complexes (**3**), related to (**5**) but containing other $\mathrm{N_2R_2}$ ligands, (R = alkyl), also undergo 2e-reduction in THF–0·2 M $[\mathrm{NBu_4}][\mathrm{BF_4}]$ under Ar, at a Pt electrode, forming species analogous to (**6**). The Table lists redox potential data for the complexes.

Reduction of (**5**) under an atmosphere of CO rather than of argon in THF–0·2 M $[\mathrm{NBu_4}][\mathrm{BF_4}]$ at a Pt electrode proceeds according to equation (4). *N*-Aminopiperidine was determined by g.l.c. (3% KOH; 6% Carbowax; Chromosorb) and also by *in situ* cyclic voltammetry on the catholyte following c.p.e., E_p^{OX}, $\mathrm{QH_2}$ = +0·45 V, Pt electrode, *vs.* S.C.E.). The latter technique established that the hydrazine was formed as a solution-free species. Yields of the hydrazine estimated by both methods were concordant. The $\mathrm{Mo^0}$ *cis-* and *trans*-dicarbonyl products were identified by isolation and i.r. spectroscopy [ν(CO), *trans*-isomer, 1825; *cis*-isomer, 1860 and 1780 $\mathrm{cm^{-1}}$; Nujol] and by their characteristic oxidation potentials measured by *in situ* c.v. on the catholyte $\{E_{\frac{1}{2}}^{\mathrm{OX}}$, *trans*-$[\mathrm{Mo(CO)_2(dppe)_2}]$ = −0·11 V; *cis*-$[\mathrm{Mo(CO)_2(dppe)_2}]$ = +0·19 V$\}$.

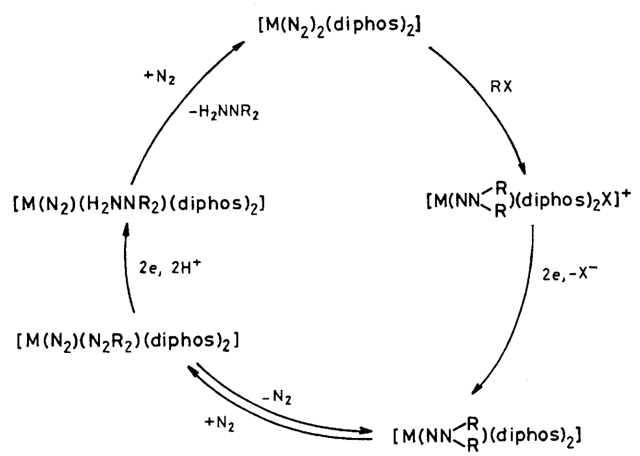
$$(\mathbf{5}) \xrightarrow{\mathrm{CO}} \underset{(65\%)}{\mathrm{QH_2}} + \underset{(75\%)}{\mathit{cis}\text{- and }\mathit{trans}\text{-}[\mathrm{Mo(CO)_2(dppe)_2}]} \qquad (4)$$

Yields of the carbonyls were determined by peak current measurements. The charge passed, *q*, during electrolysis was measured coulometrically; current *vs. q* plots were non-linear under carbon monoxide and tended towards 4e. C.v. of the catholyte during electrolysis showed that (**6**) is an intermediate in the reduction of (**5**) under CO. C.v. experiments also showed that (**6**) reacts slowly with CO to produce a species (**8**) which is electro-reducible at a potential *ca.* 60 mV positive of (**5**). The change in overall reduction pathway and electron stoicheiometry under CO from that under argon is a consequence of co-ordination of the π-acid ligand to the electron-rich primary reduction product (**6**).

A plausible reduction pathway to the free organohydrazine and $\mathrm{Mo^0}$ products is outlined in equation (5).

$$\begin{array}{ccc}
 & (\mathbf{5}) \underset{-\mathrm{Br^-}}{\overset{2\mathrm{e}}{\longrightarrow}} (\mathbf{6}) \overset{\mathrm{CO}}{\rightleftharpoons} & [\mathrm{Mo(CO)(Q)(dppe)_2}]^0 \\
 & & (\mathbf{8}) \\
 & & \Big\downarrow{\scriptstyle 2\mathrm{e},2\mathrm{H^+}} \\
\mathrm{QH_2} + \underset{\mathit{cis}\text{ and }\mathit{trans}}{[\mathrm{Mo(CO)_2(dppe)_2}]} & \xleftarrow{\mathrm{CO}} & [\mathrm{Mo(CO)(QH_2)(dppe)_2}]
\end{array} \qquad (5)$$

C.p.e. of (**5**) under *dinitrogen* rather than argon in THF–0·2 M $[\mathrm{NBu_4}][\mathrm{BF_4}]$ at Pt or Hg electrodes and at −1·8 V *vs.* S.C.E. leads to the rapid formation of (**6**) *via* the two-electron reduction process (3). Further reduction takes place at a much slower rate, and current *vs. q* plots show that the process tends towards a 4e reduction. At the end of such electrolysis we have isolated (**1**) [$\nu(\mathrm{N_2})$ = 1975 $\mathrm{cm^{-1}}$] in yields of up to 45% based upon (**5**) and have detected the free hydrazine by g.l.c. and c.v. in yields of 60—70% based upon charge passed. The current yield of (**1**) is variable, 15—45%, and we have not optimised conditions for its formation. We assume the dinitrogen complex is formed *via* a pathway which parallels the reduction of (**5**) under CO, equation (6).



SCHEME. M = Mo or W; diphos = $R'_2PCH_2CH_2PR'_2$, R′ = alkyl or aryl; R = alkyl; X = Br or I.

$$\begin{array}{c} (\mathbf{5}) \xrightarrow{2e} (\mathbf{6}) \overset{N_2}{\rightleftharpoons} [Mo(N_2)(Q)(dppe)_2] \\ N_2 \big\downarrow 2e, H^+ \\ (\mathbf{1}) + QH_2 \end{array} \qquad (6)$$

The formation of (**1**) *via* the electrochemical reduction of (**5**) under N_2 suggests that we might achieve an electrochemical reduction of N_2 to the organohydrazine, according to equation (7), by a cycle such as is illustrated in the Scheme.

$$N_2 + Br[CH_2]_5Br + 2H^+ + 4e \rightarrow QH_2 + 2Br^- \qquad (7)$$

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