

Remarkably Easy One-electron Reduction of 16-Electron Molybdenum Nitrosyls: Mechanistic Implications for the Formation of Alkoxy, Amido, Hydrazido, and Thiolato Complexes Containing the Tris-3,5-dimethylpyrazolylborato-ligand

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Summary Reduction of $[\text{Mo}\{\text{HB}(3,5\text{-Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{I}_2]$, A, is achieved electrochemically in tetrahydrofuran (Pt or C electrodes), and in basic solvents chemically, giving

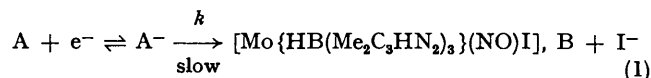
paramagnetic A^- from which I^- dissociates affording paramagnetic $[\text{Mo}\{\text{HB}(\text{Me}_2\text{C}_3\text{NH}_2)_3\}(\text{NO})\text{I}]$; these reduction products are important intermediates in the forma-

tion of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{IQ}]$, where Q = OR, NHR, NHNHR^1R^2 , and SR, from A and ROH, RNH_2 , $\text{R}^1\text{R}^2\text{NNH}_2$, and RSH.

We have described how $[\text{Mo}\{\text{HB}(\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{I}_2]$, A, $[\text{HB}(\text{Me}_2\text{C}_3\text{HN}_2)_3 = \text{tris-3,5-dimethylpyrazolylborate}]$ reacts with alcohols, primary amines, hydrazines, and thiols readily affording the crystalline air- and moisture-stable complexes $[\text{Mo}\{\text{HB}(\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{IQ}]$, where Q = OR, NHR, NHNHR^1R^2 ($\text{R}^1, \text{R}^2 = \text{H, alkyl and/or aryl}$), and SR ($\text{R} = \text{alkyl or aryl}$).¹⁻⁴ Representative members of this series of compounds have been fully characterised crystallographically, and it is quite clear that, as a class, this group of complexes is severely sterically crowded. As a result, the metal in these compounds appears to have a 16-electron configuration, although in $[\text{Mo}\{\text{HB}(\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{IQ}]$, $p\pi \rightarrow d\pi$ donation from the O, N, or S donor of atom of Q to Mo formally increases the electronic configuration of the metal to 18.

A point of considerable interest is how the di-iodide complex A is converted into $[\text{Mo}\{\text{HB}(\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{IQ}]$. Many transition metal nitrosyl complexes undergo ligand substitution *via associative* processes,⁵ but in such sterically hindered species as A it is very difficult to envisage the close approach of a seventh ligand to the metal, even in the transition state. However, if a *dissociative* process occurred, then it should be possible to monitor generation of I^- from A in solution electrochemically. In an attempt to establish, *via electrochemistry*, whether this reaction pathway was possible, we investigated the behaviour of A in tetrahydrofuran (THF) $\{[\text{Bu}_4\text{N}][\text{PF}_6] (0.2 \text{ M})$ as base electrolyte} by cyclic voltammetry (c.v.; Pt or glassy C electrode), controlled potential electrolysis (CPE), and coulometry. We discovered that A undergoes two electrode processes: a reversible one-electron reduction at +0.1 V *vs.* SCE (standard calomel electrode) and a second irreversible reduction at -2.0 V (this has not been further studied). The reversibility of the first process, both chemical and electrochemical, was established by cyclic voltammetry ($E_p^{\text{red}} - E_p^{\text{ox}} = 60 \text{ mV}$) and by comparison with the electrode characteristics of the known reversible couple $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]/[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^+$ under identical conditions. The electrode behaviour of A at +0.1 V thus corresponds to the process $\text{A} + \text{e}^- \rightleftharpoons \text{A}^-$; A^- is green in THF whereas A is dark red-brown.

The heights of the c.v. peaks due to the A/A^- couple, following generation of A^- by CPE, decrease slowly with time until, after 12 h under Ar, they have diminished by 35%. A c.v. of the solution at this time revealed three new anodic peaks (in addition to that of the A/A^- couple), at +0.48, +0.66, and +0.86 V. The two peaks at +0.48 and +0.86 V are irreversible and were identified as the oxidation peaks of free I^- . This was confirmed by the addition of $[\text{NBu}_4]\text{I}$ to the solution, when the heights of the two peaks in question increased significantly. It would



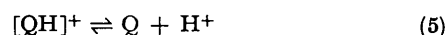
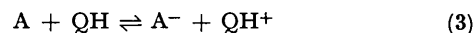
therefore appear that a chemical reaction (1) occurs following formation of A^- . The oxidation peak at +0.66 V, which is reversible, could correspond to the reaction (2).



Immediately after electrolytic generation of A^- , the e.s.r. spectrum of the green solution revealed a signal at $g = 2.206 \pm 0.0005$ [a central strong line with 5 ill defined satellites due to hyperfine coupling with ^{95}Mo ($I = 5/2$) and ^{97}Mo ($I = 5/2$)]. After 12 h under Ar, a second signal had appeared at $g = 1.998$, while the original signal at 2.026 decreased in intensity. We assume that this second signal is due to B. The presence of traces of water seems to facilitate the generation of B since the e.s.r. spectrum of A^- generated in wet solvents shows signals due to both A^- and B.

The value of the redox potential for the couple A/A^- is such that reduction of A should be effected by virtually any basic solvent.⁶ Thus, treatment of A with acetone, alcohols, pyridine, amines, nitriles, thiols, even H_2O but not THF, results in the formation of green species which have e.s.r. spectra very similar to those described above. In many cases, only signals due to B could be detected, since the dissociation of A^- seems to be facilitated by water.

We propose that these observations provide the basis of a mechanism of formation of $[\text{Mo}\{\text{HB}(\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{IQ}]$, as follows in reactions (3)–(7).



In the case of reactions with amines and hydrazines, the reaction proceeds best with two moles of base, since the liberated HI is trapped and isolated as $[\text{RNH}_3]\text{I}$ or $[\text{R}^1\text{R}^2\text{NNH}_3]\text{I}$, and it is known that the Mo–Q bond in $[\text{Mo}\{\text{HB}(\text{Me}_2\text{C}_3\text{HN}_2)_3\}(\text{NO})\text{IQ}]$ is sensitive to acid.

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