Electrochemical Reduction of a Bridging Imide: Generation of Ammonia at a Dimolybdenum Tris(μ-thiolate) Site

Jean-Yves Cabon,[a] Christine Le Roy,[a] Kenneth W. Muir,[b] François Y. Pétillon,[a] François Quentel,[a] Philippe Schollhammer,[a] and Jean Talarmin*[a]

Abstract: The electrochemical reduction of the imide complex $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH)]^+$ ($\mathbf{1}^+$) has been investigated in THF and MeCN electrolytes by cyclic voltammetry, controlled-potential electrolysis and coulometry. In the absence of free protons, the electrochemical reduction produces the amide derivative $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ (**2**) after consumption of 1 F mol^{-1} of $\mathbf{1}^+$. In THF in the presence of acid, the reduction of $\mathbf{1}^+$ occurs through a two-electron process. The presence of acid also results in the shift of the equilibrium between $\mathbf{1}^+$ and amide dication $\mathbf{2}^{2+}$ (MeCN electrolyte) or induces an isomerisation of the imide ligand (THF electrolyte). This allows the electrolysis to be conducted at a potential 600 mV less negative than the reduction potential of $\mathbf{1}^+$. Controlled-potential electrolyses in the presence of acid (2 equiv HTsO) produce the ammine derivative. Ammonia is released from these compounds either by coordination of the solvent (MeCN electrolyte) or by the binding of chloride to the ammine-tosylate complex (electrolyses in THF in the presence of acid and chloride). The final products, isolated almost quantitatively (>95%), are $[Mo_2(cp)_2(\mu\text{-}SMe)_3(MeCN)_2]^+$ and $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$, respectively.

Keywords: ammine complexes · bridging ligands · cyclic voltammetry · molybdenum · nitrogen fixation · nitrogen ligands

Introduction

We have recently described some aspects of the reactivity of dinuclear, thiolate-bridged molybdenum complexes towards hydrazine and substituted hydrazines.[1, 2] Treatment of $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ with hydrazine afforded a complex with a bridging amide ligand, $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$.[1] The two-electron oxidation of this complex[3] produced the imide derivative $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH)]^+$ ($\mathbf{1}^+$), which has now been obtained by the treatment of $[Mo_2(cp)_2(\mu\text{-}SMe)_3(MeCN)_2]^+$ with trimethylsilylazide.

This report discusses the reductive electrochemistry of $\mathbf{1}^+$. It provides the first example of the reduction of a bridging NH ligand to ammonia, via amido and ammine derivatives, at a conserved dinuclear metal-sulfur site, namely $[Mo_2(cp)_2(\mu\text{-}SMe)_3]$. In biological N_2-fixation processes[4, 5] the cleavage of the N≡N triple bond is likely to lead to the formation of imido, amido and ammine complexes, possibly at a di- or polynuclear metal-sulfur site. [6–9] In view of this knowledge, the present work can be seen as modelling certain steps in the reduction of dinitrogen, although it is clear that the site involved in the enzymatic process is not based on a pair of Mo atoms.[6, 7] What is being modelled here is the reduction of an imide ligand, which bridges two metal centres, to ammonia by successive electron and proton transfer steps. This work also permits the comparison of the electron transfer chemistry and reactivity of imide ligands which bridge a pair of transition metals to that of imide ligands bonded to a single metal atom.[4, 5, 10, 11] A partial account of this work has already appeared in a preliminary form.[12]

Results and Discussion

Electrochemical reduction of the imide complex $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH)]^+$ in the absence of acid: Cyclic voltammetry (CV)[13] of $\mathbf{1}^+$ shows that it undergoes an irreversible, diffusion-controlled, one-electron reduction[14] at room temperature in MeCN/or THF/$[NBu_4][PF_6]$ electrolytes (EC process, Table 1).[13, 15] The oxidation of the complex has not yet been investigated. Controlled-potential electrolyses of $\mathbf{1}^+$ at the potential of the first reduction peak are complete after consumption of approximately 1 F mol^{-1} of starting material and produce good yields (>80%) of the amide derivative $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ (**2**).[14] Complex **2** has been

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Table 1. Redox potentials of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}NH)]^+$ ($\mathbf{1}^+$) (CV measurements [V] versus Fc).

solvent	E_p^{red}	Primary product $E_{1/2}^{ox}$	E_p^{red}
THF	– 1.25	– 0.65	– 2.50
MeCN	– 1.21	– 0.64	– 2.49

characterized by comparing the cyclic voltammogram and ^1H NMR spectrum of the solid extracted from the catholyte (THF or MeCN electrolytes) with those of an authentic sample. The electrosynthesis of **2** in more than 80 % yield when no added protons are present indicates that the H atoms necessary for its formation must be provided by the solvent-electrolyte system.[16]

However, complex **2** is not the primary product of the reduction of $\mathbf{1}^+$. The primary product oxidizes at a potential close to that of **2** (Table 1; **2**: $E_{\frac{1}{2}}^{ox1} = -0.64$ V, THF/$[NBu_4][PF_6]$),[3] but no second oxidation is detected around 0 V (Figure 1a), as should be the case if **2** was the primary reduction product (**2**: $E_p^{ox2} = -0.04$ V, THF/$[NBu_4][PF_6]$). Furthermore, the presence of an irreversible reduction at –2.5 V (Figure 1a) in the CV of $\mathbf{1}^+$ is not consistent with **2** being the primary reduction product, since **2** is reduced at a much more negative potential ($E_p^{red} = -3.39$ V, THF/$[NBu_4][PF_6]$).[3] We believe that the redox processes around –0.65 V and –2.5 V arise from a rearranged imide radical.[17] Two coordination modes of the N-H fragment can be envisaged, depending on whether or not the nitrogen lone pair is involved in bonding with the $[Mo_2(cp)_2(\mu\text{-}SMe)_3]$ moiety (Scheme 1, structures **A** and **B**).

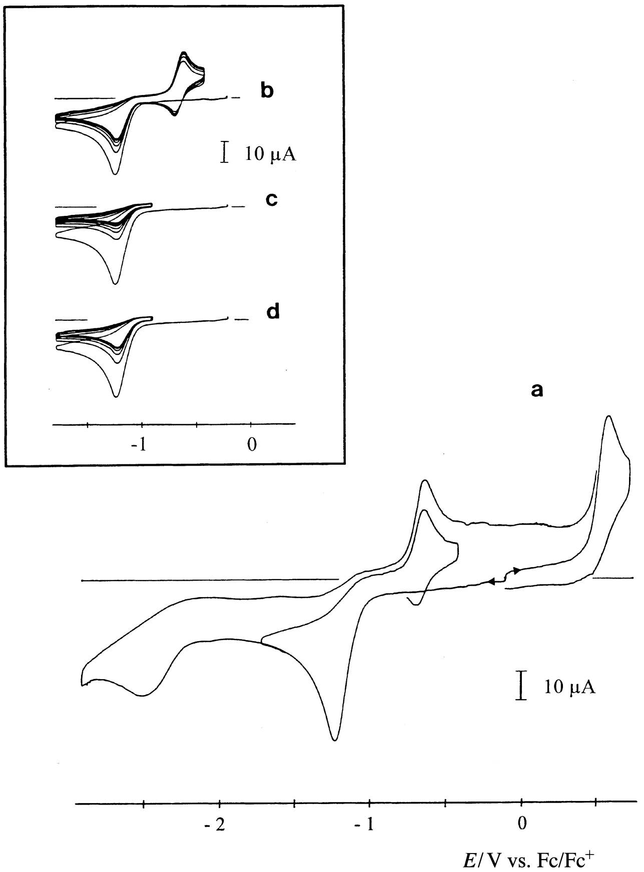
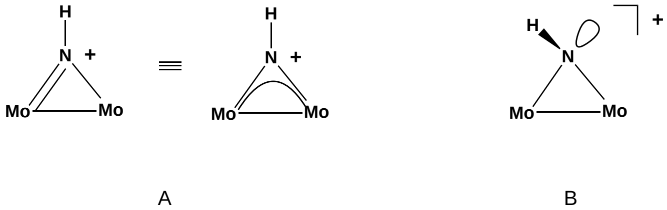


Figure 1. a) Cyclic voltammetry of $\mathbf{1}^+$ (1.5 mM) in MeCN/$[NBu_4][PF_6]$. Inset: Repetitive cyclic scans in the potential range b) – 0.4 V to – 1.8 V, c) and d) – 0.9 V to – 1.8 V. In d), for each scan, the potential is held for 5 s at – 0.9 V before reversal (5 s is the time required to scan from – 0.9 V to – 0.4 V and return at a scan rate $\nu = 0.2$ V s^{-1}). Comparison of the CV in b) and d) shows that $\mathbf{1}^+$ is partially regenerated by the oxidation at – 0.65 V. (Vitreous carbon electrode, scan rate: 0.2 V s^{-1})

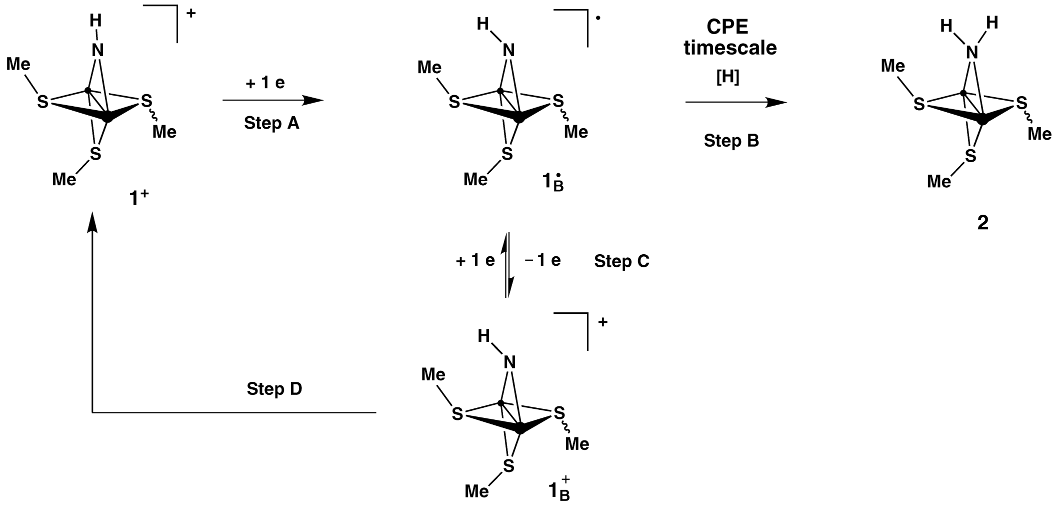


Scheme 1. Coordination modes of the NH fragment.

The ^1H NMR spectrum of $\mathbf{1}^+$, with a resonance at $\delta = 20.4$ which we assigned to the N-H proton,[3] suggests that the positive charge is located on the N atom (structure **A**). The electrochemical reduction of the imide with **A** coordination, that is, $\mathbf{1}^+$ (Scheme 2, Step A), could lead to a radical with a pyramidal nitrogen in a **B**-type ligand, $\mathbf{1}_{\mathbf{B}}^{\bullet}$, with some relief of the electronic strain at the metal centres. This would be consistent with the ability of the product to abstract an H atom from the environment (Scheme 2, Step B), and with its reactivity towards protons (see below). The oxidation of the $\mathbf{1}_{\mathbf{B}}^{\bullet}$ radical at $E_{\frac{1}{2}}^{ox} = -0.65$ V is not fully reversible ($i_p^c/i_p^a < 1$), and the starting material $\mathbf{1}^+$ is at least partially regenerated (compare Figures 1 b–d; see also Scheme 2, Steps C and D).

Similarly, two different geometries of the $[Mo\text{-}N\text{-}R]^+$ linkage have been considered for $[X\text{-}Mo(NR)(dppe)_2]^+$ complexes (X = halide) that undergo an irreversible reduction.[10] In this case, the final product of the electrochemical process was assigned as $[Mo(NR)(dppe)_2]$ (linear Mo-N-R), which

Abstract in French: *La réduction électrochimique du complexe à pont imide $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH)]^+$ ($\mathbf{1}^+$) a été étudiée en l'absence et en présence d'acide, dans le THF et dans l'acétonitrile, par voltammétrie cyclique, électrolyse à potentiel contrôlé et coulométrie. En l'absence d'acide, la réduction produit le dérivé à pont amide, $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ (**2**), après transfert de 1 F mol^{-1} $\mathbf{1}^+$. En milieu acide dans le THF, la réduction de $\mathbf{1}^+$ se produit selon un mécanisme ECE; la présence d'acide se traduit également par le déplacement d'un équilibre entre $\mathbf{1}^+$ et $\mathbf{2}^{2+}$ (dans MeCN) ou par la formation d'un isomère de $\mathbf{1}^+$ (dans le THF), permettant de produire **2** avec un gain de potentiel d'environ 600 mV. Les électrolyses effectuées en présence d'acide (2 équiv HTsO) conduisent au complexe ammine $[Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(X/L)]^{n+}$ (THF: X = TsO, n = 0; MeCN: L = MeCN, n = 1). NH_3 est libéré par réaction de ce complexe avec Cl^- (dans le THF) ou par coordination d'une seconde molécule de solvant (dans l'acétonitrile): les complexes métalliques, respectivement $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ et $[Mo_2(cp)_2(\mu\text{-}SMe)_3(MeCN)_2)]^+$, sont obtenus quantitativement (> 95 %).*



Scheme 2. ● = Mo(cp).

was formed via a 17-electron intermediate with a bent organoimide ligand.[10] The electrochemical reduction of $[\mathrm{X\text{-}Mo(NH)(dppe)_2}]^+$ produced the unstable amide derivative, but this involved proton transfer,[10c] rather than H-atom transfer[16] as is observed here for $[\mathrm{Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH)}]^+$. Although structurally characterised examples of $\mathrm{M_2(\mu\text{-}NR)}$ systems with pyramidal imido nitrogen atoms have been described, especially for iridium,[10d] it should be noted that in all known cases with M = Mo or W, the nitrogen coordination is effectively planar.

The electrochemical synthesis of **2** by reduction of the imide complex $\mathbf{1}^+$, combined with the formation of $[\mathrm{Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(X)}]$ by protonation of $[\mathrm{Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)}]$ (**2**) with HX (X = TsO, $\mathrm{CF_3CO_2}$),[3] suggests that it should be possible to generate ammine derivatives directly by electrochemical reduction of $\mathbf{1}^+$ in the presence of acid. This would result in the reduction of an imide ligand to ammonia at a dinuclear site in which the metal centres are in a sulfur environment.

Electrochemical reduction of $\mathbf{1}^+$ in the presence of acid: The CV of imide complex $\mathbf{1}^+$ in the presence of acid is dependent on the electrolyte. The results for $\mathrm{THF/[NBu_4][PF_6]}$ differ notably from those for $\mathrm{MeCN/[NBu_4][PF_6]}$; the experiments with these electrolytes will now be described.

THF electrolyte

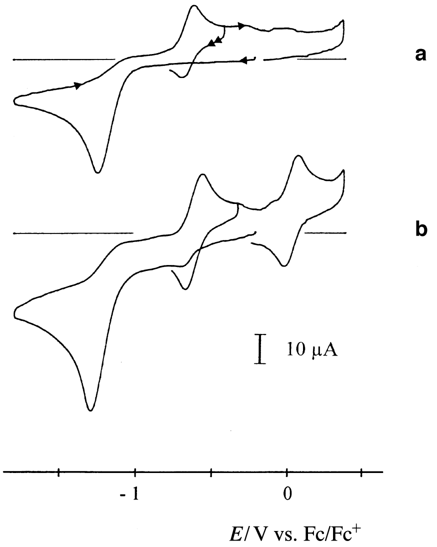
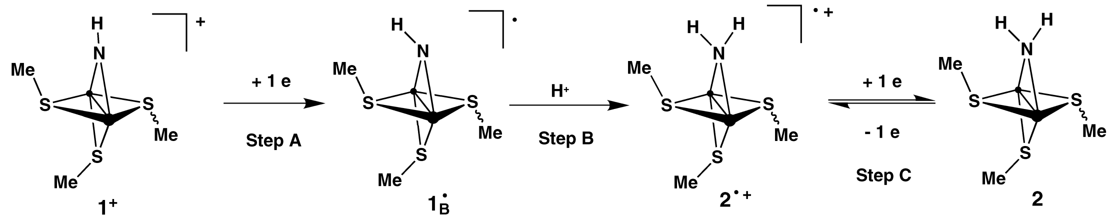


Figure 2. Cyclic voltammetry of $\mathbf{1}^+$ (1.6 mM) in $\mathrm{THF/[NBu_4][PF_6]}$ a) in the absence of acid and b) in the presence of one equivalent of HTsO. The scan directions in b) are the same as in a) (Vitreous carbon electrode, scan rate: 0.2 V s^{-1}).

Cyclic voltammetric studies: After its generation according to Steps A and B in Scheme 2, the protonation of **2** would have no effect on the reduction peak current of $\mathbf{1}^+$ $[i_p^{red}(\mathbf{1}^+)]$. Therefore, the substantial increase of $i_p^{red}(\mathbf{1}^+)$[18] in the presence of one equivalent of H^+ (*p*-toluenesulfonic acid, monohydrate: HTsO, trifluoroacetic acid: $\mathrm{CF_3CO_2H}$ or tetrafluoroboric acid in ether: $\mathrm{HBF_4/Et_2O}$) (Figure 2) demonstrates that **2** is now produced in a two-electron (ECE) process,[13, 15] although the classic criterion for the diagnosis of such processes [deviation of $i_p^{red}(\mathbf{1}^+)/v^{1/2} = f(v)$ from linearity at slow scan rates, v][15] could not be used in this case because of the occurrence of an equilibrium involving $\mathbf{1}^+$ (see below and Figure 6). The chemical step of the ECE process, that is, the protonation of the intermediate, rearranged imide radical $\mathbf{1}^{\bullet}_{\mathrm{B}}$ (Scheme 3, Step B), affords the amide radical cation $\mathbf{2}^{\bullet +}$. The second electrochemical reaction of the ECE process then results in the reduction of $\mathbf{2}^{\bullet +}$ (which has a reduction potential approximately 600 mV less negative than that of $\mathbf{1}^+$) (Scheme 3, Step C).

Consistent with these observations, the oxidation steps of **2** are detected on the reverse scan when the CV is run in the presence of one equivalent of $\mathrm{HBF_4/Et_2O}$, whereas the redox systems of $[\mathrm{Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(X)}]$ are observed when HTsO or $\mathrm{CF_3CO_2H}$ are used (Figure 2b).

We will now discuss how ammine-tosylate complex **3a** is formed. First, $[\mathrm{Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(TsO)}]^{\bullet +}$ ($\mathbf{3a}^{\bullet +}$) does not result from the protonation of $[\mathrm{Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)}]^{\bullet +}$ ($\mathbf{2}^{\bullet +}$). The CV of the amide radical cation



Scheme 3. ● = Mo(cp).

(electrochemically generated from **2**) in the presence of HTsO shows that it does not react with protons, since the reduction and oxidation peaks of $\mathbf{2}^{\cdot+}$ are almost unaffected by the addition of acid (Figure 3a and b). However, the CV in Figure 3c confirms that the reduction of $\mathbf{2}^{\cdot+}$ in the presence of HTsO produces compound **3a**, whose oxidation steps are detected on the reverse scan (EC process, Scheme 4, Steps A and B).[13, 15]

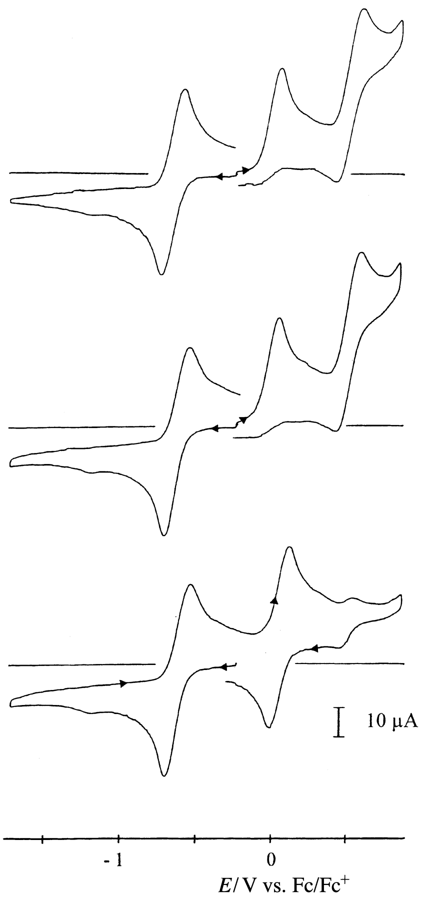
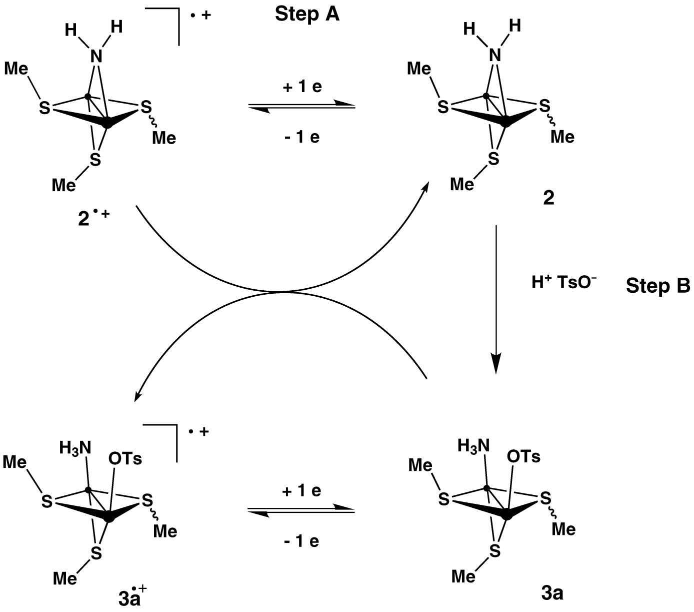


Figure 3. Cyclic voltammetry of $\mathbf{2}^{\cdot+}$ (2 mM) in THF/[NBu$_4$][PF$_6$] a) in the absence of acid and b) in the presence of one equivalent of HTsO. The solution in c) is the same as in b), but CV shows the formation of compound **3a** on the return scan (Vitreous carbon electrode, scan rate: 0.2 V s^{-1}).

Secondly, an electrogenerated mixture of $\mathbf{2}^{\cdot+}$ and **2** is converted into the protonated derivatives **3a** and $\mathbf{3a}^{\cdot+}$ upon addition of one equivalent of HTsO. The more anodic wave in Figure 4, curve 1, which arises from the oxidation of [Mo$_2$(cp)$_2$(μ-SMe)$_3$(μ-NH)]$^+$ generated at the potential of the preceding step, is typical of voltammograms of amide complex **2**. This step is absent in the voltammogram at a rotating-disc electrode in the presence of HTsO, which shows that the starting material has been replaced by the protonated species $\mathbf{3a}^{\cdot+}$ and **3a** (Figure 4, curve 2). Therefore, the presence of **2** is required to convert the amide radical cation $\mathbf{2}^{\cdot+}$ into [Mo$_2$(cp)$_2$(μ-SMe)$_3$(NH$_3$)(TsO)]$^{\cdot+}$ ($\mathbf{3a}^{\cdot+}$).



Scheme 4. ● = Mo(cp).

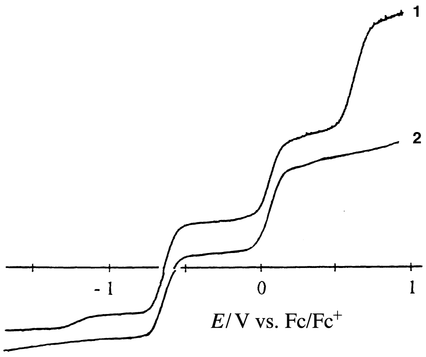


Figure 4. Rotating disc electrode voltammetry of **2** (1.5 mM) in THF/[NBu$_4$][PF$_6$] after partial oxidation at -0.25 V (0.45 F mol^{-1} of **2**, curve 1) and after addition of one equivalent of HTsO to the partially oxidized solution (curve 2) (Vitreous carbon electrode, scan rate: 0.01 V s^{-1}).

Finally, CV monitoring of the electrochemical reduction of $\mathbf{2}^{\cdot+}$ in the presence of 1 equivalent of HTsO shows that after 0.2 F mol^{-1} of $\mathbf{2}^{\cdot+}$ has been consumed, the starting material has been almost completely converted to the protonated form **3a**$^{\bullet+}$.

The above results demonstrate unambiguously that the electrochemical reduction of **1**$^+$ in the presence of HTsO (one or two equivalents) produces $[Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(TsO)]^{\bullet+}$ by the homogeneous cross-redox reaction shown in Scheme 4. The subsequent reduction of $[Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(TsO)]^{\bullet+}$ to the neutral complex is coupled to (or followed by) a chemical step that leads to the formation of a by-product (see section on coulometric studies).

Besides the increase of the reduction peak current of **1**$^+$, another important feature of the CV of this complex in acidic media is the presence of a small reduction peak at a potential less negative than the reduction of **1**$^+$ (Figures 2b and 5). This peak, which is also detected when HBF_4/Et_2O is used instead of HTsO or after electrolysis of $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ at the second oxidation process that produces **1**$^+$ and H$^+$,[3] was not observed in the absence of acid (Figure 2a). Repetitive scans of this system lead to the development of the reversible couple of **3a**/**3a**$^{\bullet+}$ (Figure 5c). Therefore, there is a pathway that allows for the formation of ammine-tosylate complex **3a** by reduction at a potential 0.6 V less negative than the reduction of **1**$^+$. Single-scan CV in the potential range from −0.2 to −1.5 V clearly illustrates the effect of the scan rate on the ratio of the peak currents of the first reduction (i_p^{red1}) and of the reduction of **1**$^+$ [i_p^{red}(**1**$^+$)] (Figure 6); the i_p^{red1}/i_p^{red}(**1**$^+$) ratio is also dependent on the amount of excess acid present (1–3 equiv HTsO). This behaviour is typical of an equilibrium between the species reducible at the first peak and **1**$^+$ involving protons (CE process).[13, 15] As the potential of the first reduction coincides with the reduction potential of **B**-type imide cation $\mathbf{1}_B^+$, we believe that the equilibrium involves a proton-induced isomerisation of **1**$^+$ via the undetected short-lived amide dication **2**$^{2+}$ (Scheme 5, Steps A and B).

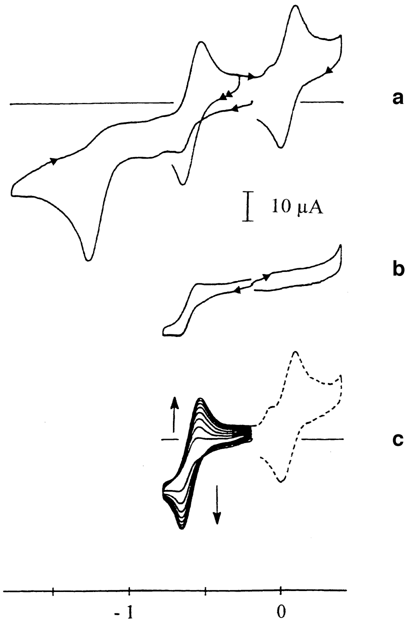


Figure 5. a) Cyclic voltammetry of **1**$^+$ (1.7 mM) in THF/[NBu$_4$][PF$_6$] in the presence of two equivalents of HTsO. The repetitive cyclic scans (c) in the potential range −0.2 V to −0.8 V show the build-up of **3a**/**3a**$^{\bullet+}$. The broken line is the extension of the scan (steady state) to more positive potentials, showing the reversible **3a**$^{\bullet+}$/**3a**$^{2+}$ couple [compare with CV in b)] (Vitreous carbon electrode, scan rate: 0.2 V s^{-1}).

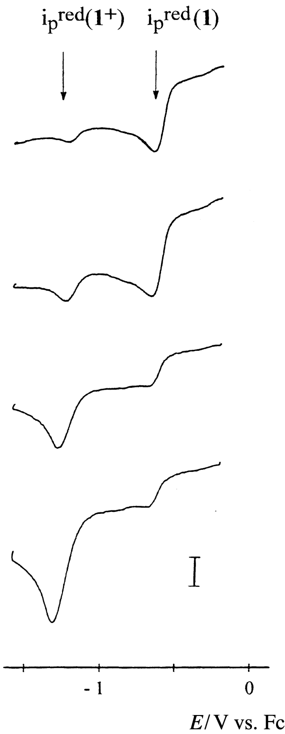
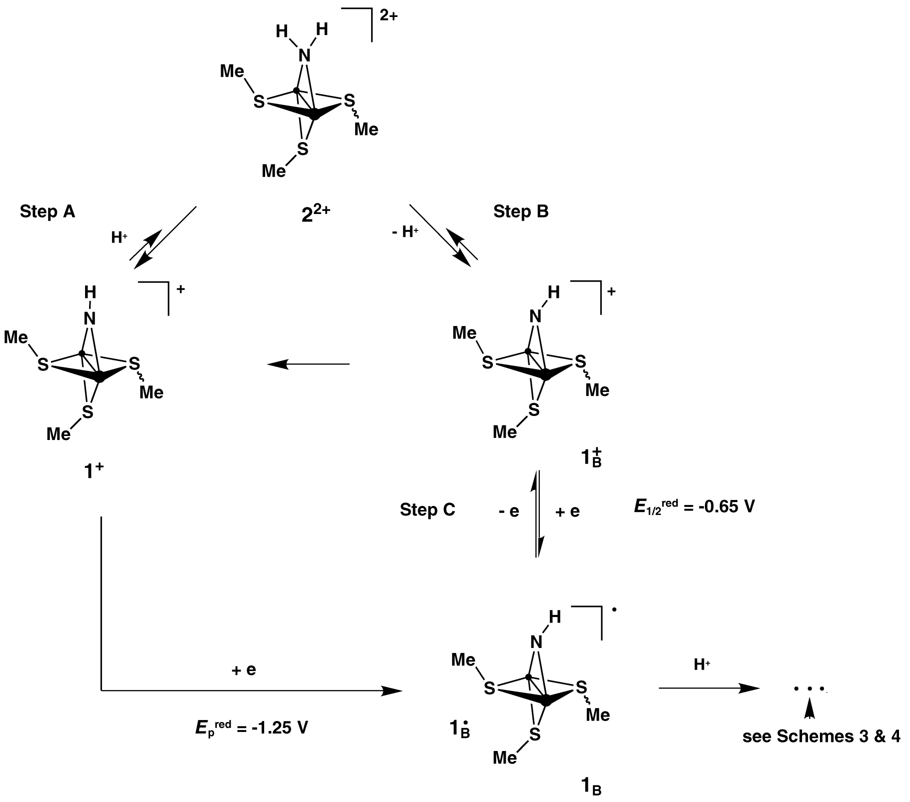


Figure 6. Single-scan cyclic voltammetry of (**1**$^+$) (1.7 mM) in the presence of two equivalents of HTsO in THF/[NBu$_4$][PF$_6$] at different scan rates. From top to bottom: 0.01 V s^{-1} (current scale: 4 μA), 0.02 V s^{-1} (current scale: 4 μA), 0.1 V s^{-1} (current scale: 10 μA), 0.2 V s^{-1} (current scale: 10 μA) (Vitreous carbon electrode).

The equilibrium, which lies towards **1**$^+$ in the absence of acid,[19] is shifted to the right by the reduction of $\mathbf{1}_B^+$; therefore, in the presence of acid, the key-intermediate of the reduction process, that is, the bent imide radical $\mathbf{1}_B^\bullet$, is produced at a potential 0.6 V less negative than that of the reduction of **1**$^+$ (Scheme 5, Step C).

*Coulometric studies: controlled-potential reduction of **1**$^+$ in the presence of p-toluenesulfonic acid (HTsO)*: Controlled-potential electrolyses (CPE) carried out at −1.4 V in the presence of HBF_4/Et_2O (2.1–2.4 F mol^{-1} of **1**$^+$) lead to a mixture of products which have not been identified. Previous studies[3] showed that the protonation of $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ (**2**) by HBF_4/Et_2O or by aqueous HBF_4 was less clean than when HTsO or CF_3CO_2H was used, presumably because THF and/or H_2O are less efficient than TsO$^-$ or $CF_3CO_2^-$ in stabilizing the ammine complex. Therefore, we have focused on the reduction of **1**$^+$ at −1.4 V and −0.8 V in the presence of one and two equivalents of HTsO.

CPE conducted in the presence of one equivalent of HTsO eventually affords amide complex **2** (Table 2), although $[Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(TsO)]^{\bullet+}$ (**3a**$^{\bullet+}$) is detected on the short-CV timescale (Figure 2b), and is formed in the early stage of the experiments (0–1 F mol^{-1} of **1**$^+$, Figure 7a). In



Scheme 5. ● = Mo(cp).

Figure 7a, only one reversible reduction peak is observed at approximately −0.6 V since the reduction potentials of the amido- and ammine-tosylate radical cations are similar ($2^{\bullet+}$: $E_{\frac{1}{2}}^{\text{red}} = -0.64$ V; $3a^{\bullet+}$: $E_{\frac{1}{2}}^{\text{red}} = -0.60$ V);[3] however, the formation of both cations is evident from their distinct oxidation processes ($E_{\text{p}}^{\text{ox}} = -0.04$ V and $E_{\frac{1}{2}}^{\text{ox}} = 0.05$ V, respectively). A by-product with reversible redox couples at $E_{1/2} = -0.83$ V and at approximately 0 V is then produced (Figure 7b) and is reduced when the electrolysis potential is set at −1.4 V (Figure 7c). This minor product, which we have not been able to separate from the supporting electrolyte, could not be identified. It is worth noting that this species is also formed in small amounts along with **2** (major product) when $[Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(TsO)]$ (THF solution) is treated with a base ($[NEt_4][OH]$ in MeOH) or is reduced at −2.6 V. It is therefore likely that the formation of the unknown product is connected to the decay of the ammine-tosylate radical cation $\mathbf{3a}^{\bullet+}$ in the present experiments.[21]

Experimental curves of the cell current versus time during CPE carried out at −0.8 V in the presence of HTsO (1 or 2 equiv) have the unusual shape shown in Figure 8. Diagrams showing the results of CV of the catholyte at different stages of the electrolysis in the presence of two equivalents of HTsO are also shown in Figure 8. The initial rise of the cell current (from the starting point to B) is due to the shift in the equilibrium between $\mathbf{1}^+$ and $\mathbf{1}_{\mathbf{B}}^+$; the reduction of the latter at −0.8 V leads to the build-up of $\mathbf{2}^{\bullet+}$ and $\mathbf{3a}^{\bullet+}$ (Figures 8A and B; note the suppression of the reduction peak of $\mathbf{1}^+$]. As in the case of the electrolyses performed at −1.4 V (2 equiv HTsO), $\mathbf{3a}^{\bullet+}$ is formed quantitatively after 1 F mol^{-1} of $\mathbf{1}^+$ has been consumed (Figure 8C, Scheme 4); therefore, at this stage of the reduction, the initial imide bridge has been converted to a terminal ammine ligand. In the final part of the electrolysis, the ammine-tosylate radical cation is reduced to the neutral form **3a** (Table 2) and a by-product with reversible oxidation processes at $E_{\frac{1}{2}}^{\text{ox1}} = -0.51$ V and $E_{\frac{1}{2}}^{\text{ox2}} = 0.15$ V is also obtained (Figure 8D). That the the by-product has lost its NH_3 ligand is unambiguously demonstrated by its formation when $[Mo_2(cp)_2(\mu\text{-}SMe)_3(MeCN)_2)]^+$ is treated with $[NEt_4][TsO]$ in THF;[20] accordingly, we tentatively assign it as $[Mo_2(cp)_2(\mu\text{-}SMe)_3(H_2O)(TsO)]$ or $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}TsO)]$.[21] Similarly, controlled-potential electrolysis performed in the presence of CF_3CO_2H (2 or 3 equiv) produces a by-product that can be prepared from $[Mo_2(cp)_2(\mu\text{-}SMe)_3(MeCN)_2)]^+$ and $[NEt_4][CF_3CO_2]$. Preliminary results of the X-ray crystal structure of this compound, $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}OCOCF_3)]$ (**4**), indicate the presence of a bridging trifluoroacetate

Table 2. Results of controlled-potential reduction of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}NH)]^+$ ($\mathbf{1}^+$) in the presence of acid in THF/$[NBu_4][PF_6]$.

Conditions	Potential of electrolysis [V/Fc]	n [F mol^{-1} of $\mathbf{1}^+$] (average)	Products (yield[a] [%]) (average)
HTsO (1 equiv)	−1.4	1.82	**2** (ca. 87)[b]
HTsO (1 equiv)	−0.8	1.5	**2** (ca. 65)[b]
HTsO (2 equiv)	−1.4	2	**3a** (>90)[c]
HTsO (2 equiv)	−0.8	1.82	**3a** (ca. 82)[c]
HTsO (3 equiv)	−1.5	2.6	**3a** (ca. 90)[c]
HTsO (3 equiv)	−0.8	1.8	**3a** (ca. 82)[c]
H^+ (2 equiv)[d], Cl^- (>2 equiv)	−1.4	1.7	**5** (80) **2** (10–15)
H^+ (3 equiv)[d], Cl^- (>2 equiv)	−1.4	2.1	**5** (>95), $65 \leq [NH_4]^+ \leq 72$

[a] Yields are estimated by cyclic voltammetry.[14] [b] Other product with reversible redox couples at $E_{1/2} = -0.83$ V and about 0 V. [c] Other product with $E_{1/2}^{\text{ox}} = -0.51$ V and 0.15 V. [d] HTsO or HBF_4/Et_2O.

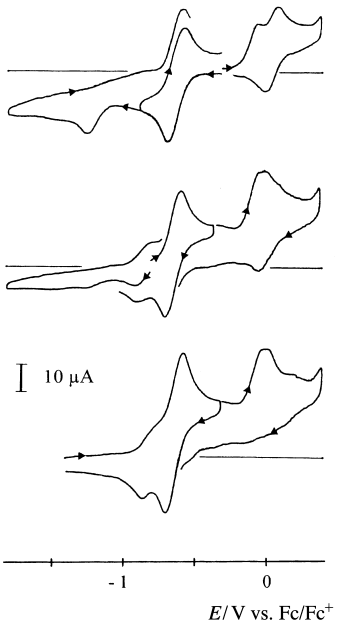


Figure 7. Cyclic voltammetry of the catholyte at different times of the controlled-potential electrolysis of $\mathbf{1}^+$ (1.3 mM) at −1.4 V (Pt cathode) in the presence of one equivalent of HTsO (THF/$[NBu_4][PF_6]$): a) 0.75 F mol^{-1} of $\mathbf{1}^+$, b) 1.5 F mol^{-1} of $\mathbf{1}^+$, c) 1.9 F mol^{-1} of $\mathbf{1}^+$. The CVs in a) and b) are the same as those recorded when the electrolysis is performed at −0.8 V. (Vitreous carbon electrode, scan rate: 0.2 V s^{-1}).

ligand.[22] This species arises from a change of the coordination of the trifluoroacetate anion from terminal to bridging, with the concomitant release of ammonia (Scheme 6).

The reaction of the ammine-trifluoroacetate complex with ammonia produces the μ-NH_2 derivative. The reactions in Scheme 6 have been verified in separate experiments: i) compound **4** could be detected by CV after stirring a solution of $[Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(CF_3CO_2)]$ (**3b**) for approximately 1 h; ii) the addition of NH_3 (aqueous solution) to compound **3b** generates $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ (**2**).

The experiments described above show that ammonia can be released from the ammine complex $[Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(X)]$ when $X = CF_3CO_2$. However, the reaction is not complete since about 80–85% (estimated by CV)[14] of compound **3b** is detected in the final mixture. Electrolyses were therefore performed in the presence of Cl^- in order to control the NH_3-decoordination step by favouring the release of ammonia from the ammine derivatives and by stabilizing the resulting product. We have previously shown that substitution of the tosylate anion by chloride in $[Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(TsO)]$ (**3a**) leads to the formation of $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ and free NH_3.[3]

Reduction of $\mathbf{1}^+$ in the presence of acid and chloride: Controlled-potential reduction of $\mathbf{1}^+$ in the presence of 2–2.5 equivalents of $[NEt_4]Cl$ and two equivalents of HTsO (or HBF_4/Et_2O) effectively affords $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ (**5**) (>80% by CV) and amide complex **2** (10–15% by CV) after consumption of approximately 1.7 F mol^{-1} of $\mathbf{1}^+$ (Table 2). Electrolyses carried out in the presence of approximately 2.5 equivalents of $[NEt_4]Cl$ and three equivalents of HTsO result in almost quantitative formation of compound **5** after 2 F mol^{-1} of $\mathbf{1}^+$ have been consumed (Table 2). The charge

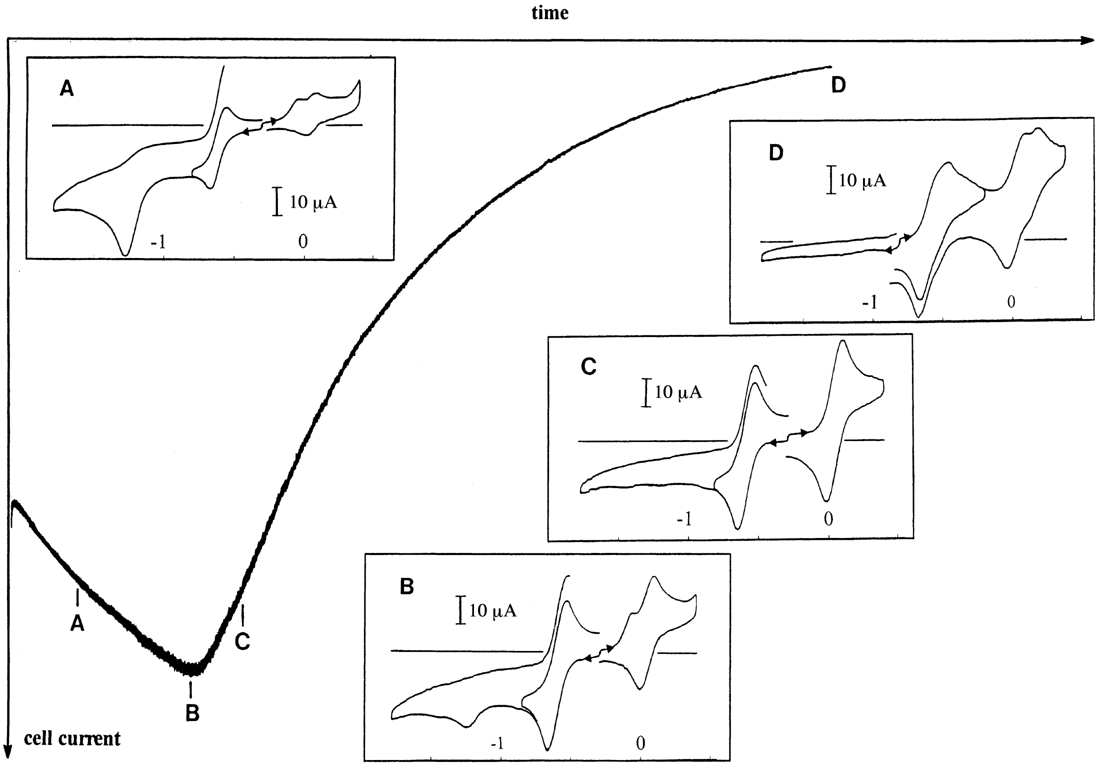
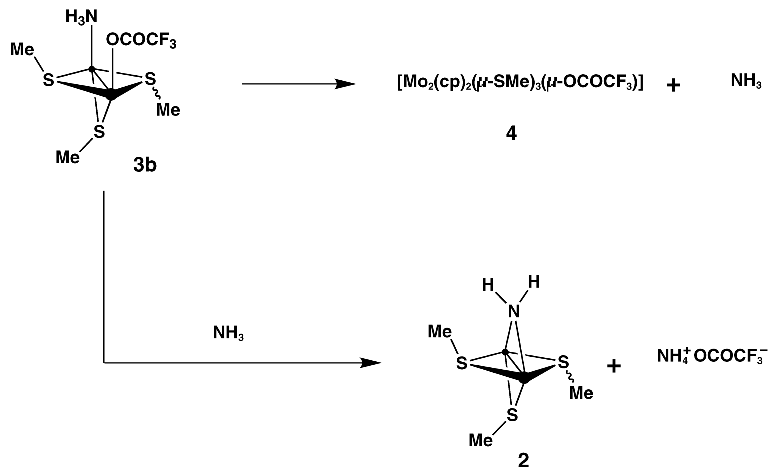
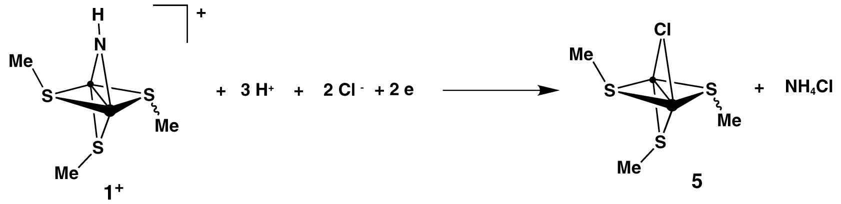


Figure 8. Experimental curve of cell current versus time during a controlled-potential electrolysis of $\mathbf{1}^+$ (1.3 mM) at −0.8 V (Pt cathode) in the presence of two equivalents of HTsO (THF/$[NBu_4][PF_6]$). The CV in A–D are recorded after the passage of 0.25, 0.75, 1.0 and 1.9 F mol^{-1} of $\mathbf{1}^+$, respectively (CV: vitreous carbon electrode, scan rate: 0.2 V s^{-1}).



Scheme 6. ● = Mo(cp).

consumed (ca. 2 F mol^{-1} of **1**$^{+}$), the amount of compound **5** produced (>95 %) and the amount of $[NH_4]^+$ (ca. 70 % mol $[NH_4]^+$ per mole of **1**$^{+}$) detected after CPE in the presence of chloride and three equivalents of HTsO are consistent with the overall reaction shown in Scheme 7.

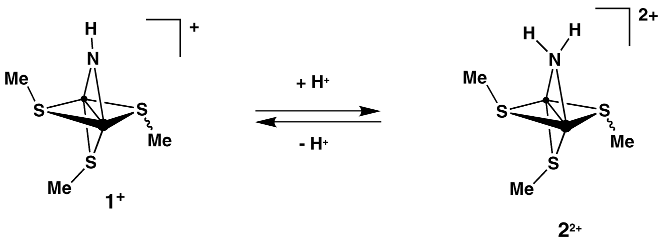


Scheme 7. ● = Mo(cp).

MeCN electrolyte

The CV of **1**$^{+}$ in MeCN/$[NBu_4][PF_6]$ is strongly affected by the presence of acid, which causes the shift of the equilibrium between imide **1**$^{+}$ and amide dication **2**$^{2+}$ (Scheme 8).[3] This is illustrated in Figure 9b and c, which shows the increase of the quasi-reversible reduction of **2**$^{2+}$ at the expense of the irreversible reduction of **1**$^{+}$ (CE mechanism)[13, 15] on addition of acid (1 and 2 equiv HBF_4/Et_2O, respectively).

Similar phenomena are observed when one and two equivalents of HTsO are added, although in this case, the reduction system of **2**$^{2+}$ is broader than when HBF_4/Et_2O is used. The second reduction process is irreversible and generates a product that possesses reversible oxidation couples ($E_{\frac{1}{2}}^{\mathrm{ox1}} = -0.35$ V, Figure 9c; $E_{\frac{1}{2}}^{\mathrm{ox2}} = 0.39$ V, not shown in Figure 9c), which are detected on the reverse and following scans and which are characteristic of the ammine-acetonitrile cation $[Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(MeCN)]^+$. This compound had already been observed when amide complex **2** was protonated in MeCN.[3] The final product of the protonation is $[Mo_2(cp)_2(\mu\text{-}SMe)_3(MeCN)_2]^+$ (**6**$^{+}$), which is a result of the substitution of ammonia by a solvent molecule.[3] In the present case, the detection of $[Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(MeCN)]^+$ confirms that the imide bridge is converted to an ammine ligand by reduction of **1**$^{+}$ in the presence of acid. Controlled-potential electrolyses performed at the potential of the second reduction under these experimental conditions (2 equiv HTsO or HBF_4/Et_2O; Pt cathode) produce the expected bis-acetonitrile complex **6**$^{+}$ almost quantitatively (>90 % by CV) after consumption of approximtely 1.7 F mol^{-1}. This is consistent with the overall reaction shown in Scheme 9.



Scheme 8. ● = Mo(cp).

Conclusion

The results presented herein demonstrate that a bridging imide ligand at a $[Mo_2(\mu\text{-}SMe)_3]$ core can be electrochemically reduced in the presence of protons to ammonia via amido and ammine intermediates. These reactions show two important features. First, the ligand transformation is carried out at a conserved dinuclear sulfur site, which is protected in the final metal product either by two labile acetonitrile ligands or by a chloride bridge. Second, under acidic conditions the reduction processes led to the establishment of equilibria involving the imide complex and either an amide dication (MeCN electrolyte) or a structural isomer of the parent imide (THF electrolyte). These equilibria allow the electrochemical reduction to be performed at a potential that is *approximately 600 mV less negative* than the reduction potential of $[Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH)]^+$.

The imide, amide and ammine complexes described herein are dinuclear counterparts of the mononuclear species involved in the Chatt cycle (at the $M(P)_4$ core)[4] or in the Schrock cycle (at the (cp*)MMe_3 core)[11] (M = Mo, W; $(P)_4$ = tertiary monophosphines or two diphosphines; cp* = C_5Me_5). The above results therefore indicate that several steps of the nitrogen fixation process could take place at a dinuclear metal-sulfur site. We have recently presented preliminary results concerning the electrochemical reduction of substituted diazenido, hydrazido(2-) and diazene ligands coordinated to the $[Mo_2(\mu\text{-}SMe)_3]$ core.[12] These studies will be reported in full detail at a later date.

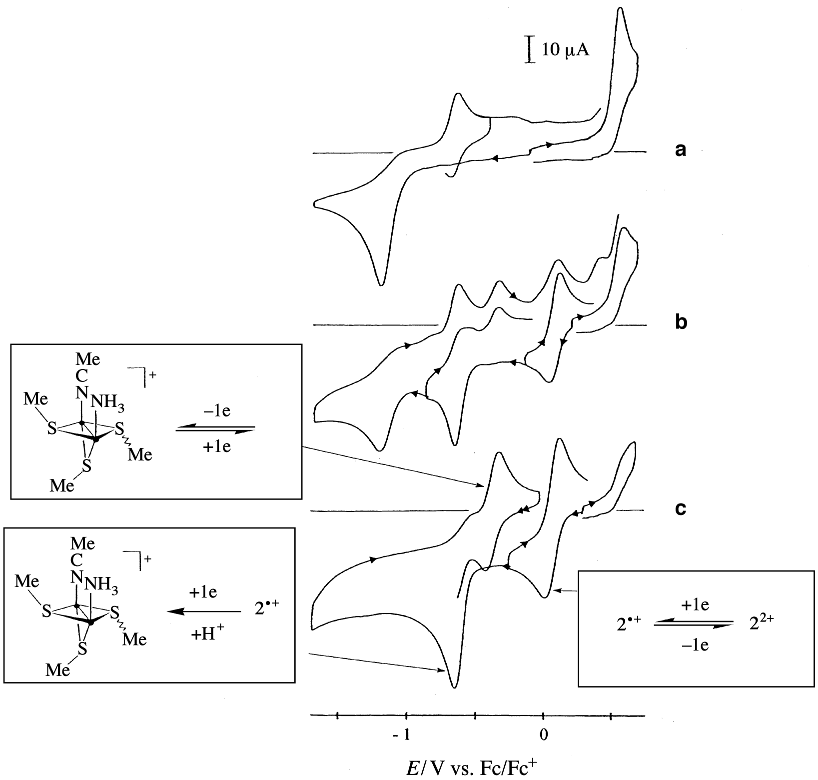
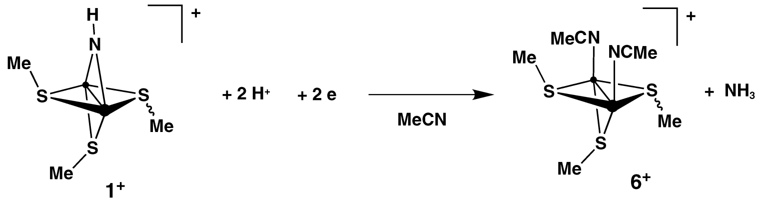


Figure 9. Cyclic voltammetry of 1^+ (1.2 mM) in MeCN/[NBu$_4$][PF$_6$] a) in the absence of acid and in the presence of b) one equivalent and c) two equivalents of HBF$_4$/Et$_2$O (Vitreous carbon electrode, scan rate: 0.2 V s^{-1}).



Scheme 9. ● = Mo(cp).

Experimental Section

Methods and materials: All the experiments were carried out under an inert atmosphere and by using Schlenk techniques for the syntheses. Tetrahydrofuran (THF) was purified as described previously.[23] Acetonitrile (Carlo Erba or BDH, HPLC grade) was used as received. The acids, *p*-toluenesulfonic acid monohydrate (Aldrich), trifluoroacetic acid (Aldrich), tetrafluoroboric acid (diethyl ether complex and aqueous solution (Aldrich)) were used as received. The preparation and purification of the supporting electrolyte [NBu$_4$][PF$_6$] and the electrochemical equipment were described previously.[22] All potentials (text, tables, figures) are quoted against the ferrocene–ferrocenium couple; ferrocene was added as an internal standard at the end of the experiments. NH_4^+ analyses were performed with an Ion Chromatograph Dionex DX-100 and a Dionex AI-450 data acquisition system, and with a Waters Capillary Ion Analyzer. For capillary ion analysis, the UV CAT2 (Waters) electrolyte was used with a 75 μM × 60 cm capillary column. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC300 spectrometer. The complexes [Mo$_2$(cp)$_2$(μ-SMe)$_3$(NH$_2$)][2] and [Mo$_2$(cp)$_2$(μ-SMe)$_3$(MeCN)$_2$]$^+$[23] were synthesized according to literature methods.

Synthesis of [Mo$_2$(cp)$_2$(μ-SMe)$_3$(μ-NH)][BF$_4$] (1^+): N$_3$SiMe$_3$ (0.1 mL, 0.75 mmol) was added to a red solution of [Mo$_2$Cp$_2$(μ-SMe)$_3$(NCCH$_3$)$_2$]BF$_4$ (0.20 g, 0.32 mmol) in acetonitrile (20 mL). The mixture was stirred overnight at room temperature during which time the solution became orange. The volume was then reduced under vacuum and diethyl ether was added to precipitate a brown product, which was washed with pentane (yield: 0.15 g, 83 %). Elemental analysis calcd (%) for C$_{13}$H$_{20}$BF$_4$Mo$_2$NS$_3$: C 27.6, H 3.5, N 2.5; found: C 27.6, H 3.6, N 3.1; spectroscopic data (^{1}H NMR and IR) of 1^+ have been reported previously.[3]

NH_4^+ analyses: In a typical experiment, a THF solution of HTsO (78 μL, 4.7×10^{-7} mol μL^{-1}; 3 equiv) and [NEt$_4$]Cl (0.005 g, 3×10^{-5} mol; 2.5 equiv) were added to a solution of 1^+ (0.0068 g, 1.2×10^{-5} mol) in THF/[NBu$_4$][PF$_6$] (10 mL). The solution was electrolysed at −1.4 V (Pt cathode) under argon. After 2.45 C (2.1 F mol^{-1} of 1^+) were consumed, cyclic voltammetry showed that 1^+ had been converted to [Mo$_2$(cp)$_2$(μ-SMe)$_3$(μ-Cl)] (**5**). The green-yellow catholyte was passed through a cannula into a Schlenk flask. The solvent was evaporated under vacuum and the resulting solid was extracted four times with H$_2$O (10 mL). The filtrates were combined and their volume was brought to 50 mL with water. Samples of this solution were submitted for NH_4^+ analysis by ionic chromatography and by capillary columnn ion analysis.

For ionic chromatography analysis, the ion chromatograph was equipped with a CS12 column and with a cation self-regenerating suppressor CSRS-I. The eluent was 16 mM methanesulfonic acid (Merck) with a 1 mL min^{-1} flowrate. The NH_4^+ concentration was determined from peak area measurements, the instrument was calibrated with the use of standard solutions (Merck).

For capillary column analysis, the NH_4^+ concentration was determined by UV experiments (185 nm, Hg lamp) with peak area measurements. The instrument was calibrated with the use of standard solutions.

The amount of NH_4^+ in the solution was found to be 2.9 ppm (ionic chromatography) and 3.1 ppm (capillary column analysis), that is, 67 % and 72 %, respectively, of the maximum amount possible of NH_4^+.

Acknowledgements

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[1] P. Schollhammer, F. Y. Pétillon, S. Poder-Guillou, J. Y. Saillard, J. Talarmin, K. W. Muir, *Chem. Commun.* **1996**, 2633.

[2] P. Schollhammer, E. Guénin, F. Y. Pétillon, J. Talarmin, K. W. Muir, D. S. Yufit, *Organometallics* **1998**, *17*, 1922.

[3] F. Y. Pétillon, P. Schollhammer, J. Talarmin, *J. Chem. Soc. Dalton Trans.* **1997**, 4019.

[4] C. J. Pickett, *J. Biol. Inorg. Chem.* **1996**, *1*, 601.

[5] a) M. Y. Mohammed, C. J. Pickett, *J. Chem. Soc. Chem. Commun.* **1988**, 1119; b) D. L. Hughes, D. J. Lowe, M. Y. Mohammed, C. J. MacDonald, C. J. Pickett, *Polyhedron* **1989**, *8*, 1653.

[6] a) J. Kim, D. C. Rees, *Science* **1992**, *257*, 1677; b) J. Kim, D. C. Rees, *Nature* **1992**, *360*, 553; c) M. K. Chan, J. Kim, D. C. Rees, *Science* **1993**,

260, 792; d) D. C. Rees, J. Kim, M. M. Georgiadis, H. Komiya, A. J. Chirino, D. Woo, J. Schlessman, M. K. Chan, L. Joshua-Tor, G. Santillan, P. Chakrabarty, B. T. Hsu, *ACS Symp. Ser.* **1993**, *535*, 170.

[7] J. T. Bolin, N. Campobasso, S. W. Muchmore, T. V. Morgan, L. E. Mortenson, *ACS Symp. Ser.* **1993**, 535, 187.

[8] W. H. Orme-Johnson, *Science* **1992**, *257*, 1639.

[9] a) D. Sellmann, *Angew. Chem.* **1993**, *105*, 67, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 64; b) D. Sellmann, J. Sutter, *J. Biol. Inorg. Chem.* **1996**, *1*, 587; c) D. Sellmann, J. Sutter, *Acc. Chem. Res.* **1997**, *30*, 460.

[10] a) M. Y. Mohammed, Ph.D. Thesis, University of Sussex, **1990**; b) M. L. Abasq, Ph.D. Thesis, Université de Bretagne Occidentale, Brest, **1994**; c) Y. Alias, S. K. Ibrahim, M. A. Queiros, A. Fonseca, J. Talarmin, F. Volant, and C. J. Pickett, *J. Chem. Soc. Dalton Trans.* **1997**, 4807; d) D. A. Dobbs, R. G. Bergman , *Organometallics* **1994**, *13*, 4594.

[11] a) T. E. Glassman, M. G. Vale, R. R. Schrock, *Organometallics* **1991**, *10*, 4046; b) R. R. Schrock, T. E. Glassman, M. G. Vale, M. Kol, *J. Am. Chem. Soc.* **1993**, *115*, 1760.

[12] F. Y. Pétillon, P. Schollhammer, J. Talarmin, K. W. Muir, *Inorg. Chem.* **1999**, *38*, 1954.

[13] The parameters i_p and E_p are the peak current and the peak potential of a redox process, respectively; $E_{1/2} = (E_\mathrm{p}^\mathrm{a} + E_\mathrm{p}^\mathrm{c})/2$; E_p^a, i_p^a and E_p^c, i_p^c are the potential and the current of the anodic and of the cathodic peak of a reversible process, respectively; an EC process is comprised of an electron transfer step (E) followed by a chemical reaction (C). CV and CPE stand for cyclic voltammetry and controlled-potential electrolysis, respectively.

[14] CV of equimolar solutions of $\mathbf{1}^+$ and **2** (whose first oxidation is a reversible one-electron step) showed that the ratio of the reduction peak current of $\mathbf{1}^+$ [$i_\mathrm{p}^\mathrm{red}(\mathbf{1}^+)$] to the first oxidation peak current of **2** [$i_\mathrm{p}^\mathrm{ox1}(\mathbf{2})$] was close to one in MeCN/[NBu_4][PF_6] [$0.97 \leq i_\mathrm{p}^\mathrm{red}(\mathbf{1}^+)/i_\mathrm{p}^\mathrm{ox1}(\mathbf{2}) \leq 1.03$]. The same was true for $\mathbf{1}^+$ and $\mathbf{6}^+$ (whose first oxidation is also a reversible one-electron step) in a MeCN electrolyte. In THF/[NBu_4][PF_6], $i_\mathrm{p}^\mathrm{red}(\mathbf{1}^+)/i_\mathrm{p}^\mathrm{ox1}(\mathbf{2})$ was 0.90. These experiments confirm that the reduction of $\mathbf{1}^+$ involves one electron on the CV timescale, with the reasonable assumption that the diffusion coefficients of $\mathbf{1}^+$, **2** and $\mathbf{6}^+$ are similar. On the other hand, the above experiments and the fact that the ratio of the first oxidation peak current of [Mo_2(cp)$_2$-(μ-SMe)$_3$(NH_3)(X)] to that of **2** was (average) 0.74 (X = TsO) and 0.87 (X = CF_3CO_2) show that the yields of controlled-potential electrolyses could be reliably estimated by CV, by comparing the peak current of the reactant complex $\mathbf{1}^+$ to that of the product(s).

[15] a) A. J. Bard, L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, Wiley, New York, **1980**, chapter 11, pp. 429–485; b) E. R. Brown, R. F. Large, in *Techniques of Chemistry, Volume I—Physical Methods of Chemistry, Part IIA*, (Ed.: A. Weissberger), Wiley, **1971**, chapter 6, pp. 423–530.

[16] The possibility of a "father–son" reaction involving proton transfer from the imide cation $\mathbf{1}^+$ to the reduction product $\mathbf{1}^{\bullet}_\mathbf{B}$ was considered. This mechanism, which would result in an overall one-electron reduction of $\mathbf{1}^+$, was rejected since the nitride complex [Mo_2(cp)$_2$(μ-SMe)$_3$(μ-N)] which would be formed along with amide **2** has never been observed.

[17] As suggested by a reviewer, an equally valid interpretation would be to consider the reduction product ($\mathbf{1}^{\bullet}_\mathbf{B}$) as a mixed-valence Mo(III,IV) complex with a bridging NH^{2-} ligand, for example, [$Mo_2^{III,IV}$(cp)$_2$(μ-SMe)$_3$(μ-NH)].

[18] In THF/[NBu_4][PF_6], the oxidation peak of $\mathbf{1}^+$ is essentially unaffected by the addition of acid.

[19] This is shown by the fact that the oxidation of the **B**-type imide radical is not fully reversible [$(i_\mathrm{p}^\mathrm{c}/i_\mathrm{p}^\mathrm{a}) < 1$] and that $\mathbf{1}^+$ is regenerated, see Figures 1b–d.

[20] [NEt_4][TsO] was prepared in solution by the neutralization of a solution of HTsO (monohydrate) in THF by [NEt_4][OH] (in MeOH), so that the resulting solution contained two equivalents of H_2O.

[21] The redox potentials of the unidentified tosylate complex are shifted anodically by about 0.1 V with respect to those of the ammine-tosylate complex**3a** ($E_{\frac{1}{2}}^\mathrm{ox1} = -0.60$ V, $E_{\frac{1}{2}}^\mathrm{ox2} = 0.05$ V, THF [NBu_4][PF_6]),[3] so that the former is more likely to be [Mo_2(cp)$_2$(μ-SMe)$_3$(H_2O)(TsO)] than [Mo_2(cp)$_2$(μ-SMe)$_3$(μ-TsO)].

[22] C. Le Roy, K. W. Muir, F. Y. Pétillon, P. Schollhammer, J. Talarmin, unpublished results.

[23] F. Barrière, Y. Le Mest, F. Y. Pétillon, S. Poder-Guillou, P. Schollhammer, J. Talarmin, *J. Chem. Soc. Dalton Trans.* **1996**, 3967.

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