Nitrate- and Nitrite-Assisted Conversion of an Acetonitrile Ligand Into an Amidato Bridge at an $\{Mo_2(Cp)_2(\mu\text{-}SMe)_3\}$ Core: Electrochemistry of the Amidato Complex $[Mo_2(Cp)_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1,\eta^1\text{-}OC(Me)NH\}]^+$

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Treatment of $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(MeCN)_2]^+$ (**1⁺**) with NO_3^- or NO_2^- results in the conversion of one terminally bound acetonitrile ligand into an amidato bridge. The reaction produces $[Mo_2(Cp)_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1,\eta^1\text{-}OC(Me)NH\}]^{0/+}$ ($\mathbf{2^{0/+}}$) and involves the formation of an intermediate, which was detected by cyclic voltammetry but which could not be isolated, and which likely arises from the substitution of the NO_x anion for one MeCN ligand. The electrochemical behaviour of $\mathbf{2^+}$ was studied by cyclic voltammetry in THF and MeCN. The reduction of $\mathbf{2^+}$ in the presence of acid (HBF_4/H_2O or HBF_4/Et_2O) in these solvents leads to the release of the amidate bridge. Controlled-potential electrolysis of $\mathbf{2^+}$ in MeCN in the presence of acid produces $\mathbf{1^+}$ quantitatively; the charge consumed (>1 F mol^{-1} of $\mathbf{1^+}$) indicates that electrons are also used to reduce protons. This was confirmed by the formation of $\mathbf{2^+}$ (in variable amounts depending on the conditions) on treating **2** with acid.

Introduction

Complexes with the $\{Mo_2(Cp)_2(\mu\text{-}SMe)_3\}$ core have been shown to sustain transformations of various unsaturated substrates.[1–3] The electrochemical reduction of a complex containing a $\mu\text{-}\eta^1,\eta^1$-coordinated phenyldiazene ligand in the presence of acid results in the cleavage of the N=N bond and the release of ammonia and aniline.[2] During this reduction, the nitrogenous moiety undergoes a coordination change, most probably at the hydrazido(1–) stage, from a $\mu\text{-}\eta^1,\eta^1$ to a $\mu\text{-}\eta^1$ geometry.[2] This has been recently confirmed by a theoretical study of the different steps of the reduction process.[4] Similarly, the electrochemical reduction in the presence of protons of a complex bearing a $\mu\text{-}\eta^1,\eta^2$-vinylidene ligand affords a $\mu\text{-}\eta^1$-coordinated carbyne derivative.[3]

These examples, which illustrate the ability of the $\{Mo_2(Cp)_2(\mu\text{-}SMe)_3\}$ entity to adjust to the electronic properties of various unsaturated ligands in different coordination modes, prompted us to examine the possibility of reducing nitrate and nitrite at this site. Nitrate and nitrite are known to adopt various modes of coordination to metal centres,[5–8] including, respectively, $\mu\text{-}\eta^1,\eta^1\text{-}(O,O)$ and $\mu\text{-}\eta^1,\eta^1\text{-}(N,O)$ binding to bimetallic units. It has been suggested that the nature of the metal-coordinated atom(s) may influence the nature of the reduction products of nitrate and nitrite.[9] In the case of the nitrite ion, the possibility of an asymmetrical $\mu\text{-}\eta^1,\eta^1\text{-}(N,O)$ coordination to a bimetallic fragment is particularly attractive since this might allow the reductive cleavage of an N–O bond, with conservation of an M–O bond and *without* the release of NO, which would circumvent the difficulty of re-binding this molecule for further reduction. Several examples of $\mu\text{-}\eta^1,\eta^1\text{-}(N,O)$ coordination of NO_2^- have been reported,[5,6,7a] and in some cases the nitrite (nitrate) complex was obtained by substitution of NO_2^- (NO_3^-) for MeCN ligands.[5,6] We therefore examined the reaction of the bis(acetonitrile) complex $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(MeCN)_2]^+$ (**1⁺**)[10] with nitrate and nitrite. However, these reactions did not produce NO_3^- or NO_2^- derivatives, but the amidato complex, $[Mo_2(Cp)_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1,\eta^1\text{-}OC(Me)NH\}]^{0/+}$ ($\mathbf{2^{0/+}}$), which we already knew to arise from hydration of one acetonitrile ligand in **1⁺**, and which we fully characterized in a previous study.[11] An example of a nitrite-promoted hydration of acetonitrile has previously been reported.[12] In this case, coordination of the nitrite anion to a $\{Cr(\mu\text{-}OH)_2Cr\}$ core resulted in the cleavage of one hydroxy bridge and attack of this on a noncoordinated acetonitrile molecule. The coordinated nitrite was released upon formation of the amidato bridge.[12]

In this paper, we report the reactions of **1⁺** with NO_3^- and NO_2^- as well as the electrochemical behaviour of the reaction product, the amidato complex $\mathbf{2^{0/+}}$.

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Results and Discussion

Reaction of NO_3^- or NO_2^- with $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(MeCN)_2]^+$ (1^+)

The bis(acetonitrile) complex $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(MeCN)_2]^+$ (**1**$^+$) undergoes two diffusion-controlled, reversible, one-electron oxidation steps ($E_{1/2}^{ox1}$ = –0.20 V; $E_{1/2}^{ox2}$ = 0.45 V) and an irreversible reduction (E_p^{red} = –2.2 V) in $MeCN/[NBu_4][PF_6]$.[10,13] $\mathbf{1^+}$ is stable in this electrolyte, as shown by control CVs[13] over a period of several hours. Addition of a large excess of NO_3^- to a solution of $\mathbf{1^+}$ in $MeCN/[NBu_4][PF_6]$ leads to drastic changes of the cyclic voltammogram: the two reversible oxidations and the irreversible reduction of $\mathbf{1^+}$ are replaced by two oxidation and two reduction steps, the relative intensities of which change with time. After several minutes, two couples with $E_{1/2}^{ox}$ = 0 V and $E_{1/2}^{red}$ = –0.81 V have developed at the expense of the other two redox systems with $E_{1/2}^{ox}$ = 0.27 V and E_p^{red} = –1.3 V.

In $THF/[NBu_4][PF_6]$, a solution of $\mathbf{1^+}$ instantly turns from red-orange to yellow upon addition of one equivalent of NO_3^-. The CV recorded immediately after mixing (Figure 1a) shows that the reversible oxidations of $\mathbf{1^+}$ ($E_{1/2}^{ox1}$ = –0.25 V; $E_{1/2}^{ox2}$ = 0.37 V in $THF/[NBu_4][PF_6]$) are replaced by two oxidation ($E_{1/2}^{ox}$ = 0.01 V; $E_{1/2}^{ox}$ = 0.24 V) and two reduction steps ($E_{1/2}^{red}$ = –0.80 V; E_p^{red} = –1.37 V), very similar to those observed in MeCN. After about two hours stirring, the redox systems with $E_{1/2}^{ox}$ = 0.24 V and E_p^{red} = –1.37 V have almost completely disappeared (Figure 1b). The metal-containing product, which possesses the same redox potentials as the amidato complex $[Mo_2(Cp)_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1,\eta^1\text{-}OC(Me)NH\}]^+$ ($\mathbf{2^+}$; $E_{1/2}^{ox}$ = 0 V; $E_{1/2}^{red}$ = –0.80 V) [11] in THF and MeCN electrolytes, could not be separated from the supporting electrolyte. However, the nature of the product was confirmed by the ^1H NMR spectrum of the compound obtained by reaction of $\mathbf{1^+}$ with NO_3^- in THF without supporting electrolyte, and treatment of the reaction mixture with $NaBH_4$ before work-up. The ^1H NMR spectrum showed that the reduced amidato complex **2**[11] had formed under these conditions.

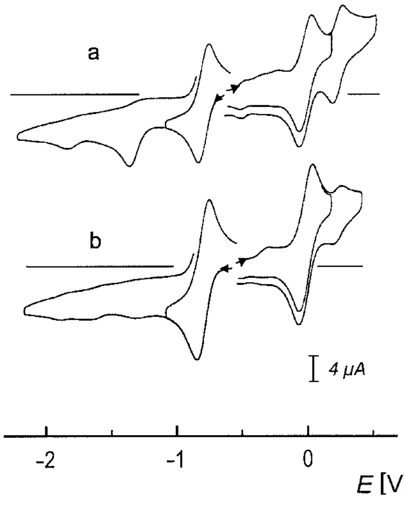


Figure 1. Cyclic voltammetry of $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(MeCN)_2]^+$ ($\mathbf{1^+}$; 1.1 mM) in $THF/[NBu_4][PF_6]$ a) immediately after addition of 1 equiv. of $[NBu_4][NO_3]$, and b) after 2 h stirring (vitreous carbon electrode, v = 0.2 V s^{-1}; potentials are against ferrocene/ferrocenium).

Similar experiments were performed with nitrite (Figure 2). Although the reaction of $\mathbf{1^+}$ with NO_2^- is faster than with NO_3^-, a CV recorded immediately after addition of one equivalent of $\mathbf{1^+}$ to a THF solution of NO_2^- (Figure 2, a) allowed the detection of an intermediate with $E_{1/2}^{ox}$ = 0.21 V and E_p^{red} = –1.39 V, in addition to the final product $\mathbf{2^+}$ (Figure 2, b). Different to the reaction with NO_3^-, the amidato complex formed upon reaction of $\mathbf{1^+}$ with nitrite is present as a mixture of the neutral and cationic forms (**2**/$\mathbf{2^+}$; Figure 2, b). Voltammetry at a rotating disc electrode confirmed this. The nature of the metal product was again ascertained by comparison of the ^1H NMR spectrum of the complex isolated (after reduction by $NaBH_4$) from the reaction carried out in THF in the absence of supporting electrolyte, with that of an authentic sample of **2**. The reaction of $\mathbf{1^+}$ with NO_3^- or NO_2^- can be represented as shown in Scheme 1. The CVs in Figures 1b and 2b show that minor co-products, which we have not attempted to characterize, are also present.

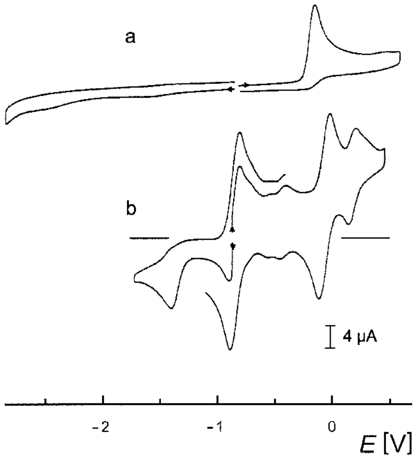
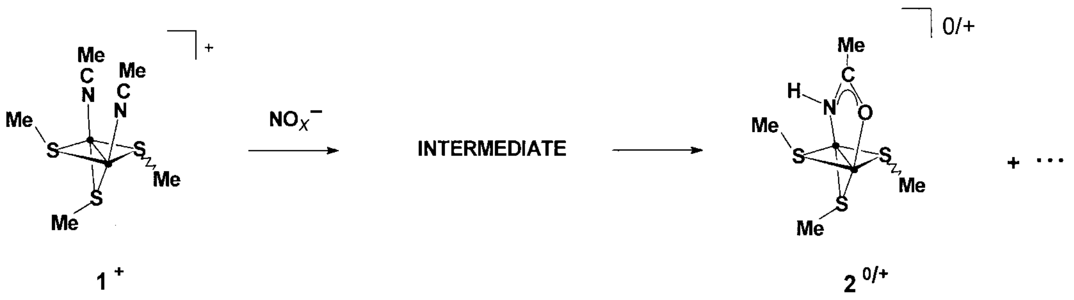


Figure 2. Cyclic voltammetry of a solution of $[NBu_4][NO_2]$ (1 mM) in $THF/[NBu_4][PF_6]$ a) before, and b) immediately after addition of $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(MeCN)_2]^+$ ($\mathbf{1^+}$; 1 mM, 1 equiv.) (vitreous carbon electrode, v = 0.2 V s^{-1}; potentials are against ferrocene/ferrocenium).

In THF, $\mathbf{2^+}$ (or **2**) is not formed from $\mathbf{1^+}$ in the absence of NO_x^- on the timescale of the experiments described above. Therefore, these ions clearly promote the formation of the amidato complex $\mathbf{2^+}$ (or **2**). Two different properties of NO_x^- might explain their role in the reaction. The first possibility is that NO_x^- acts as a ligand, replacing one of the MeCN groups of $\mathbf{1^+}$. Coordination and reduction of nitrate or nitrite ions by oxo transfer to a metal centre have been reported.[14] In the case of transition-metal nitrite complexes, transfer of an oxygen atom to an organic substrate has also been observed, the NO_2^- ligand being N-bound (*nitro* coordination) to the metal.[15] In the present study, the similarity of the redox potentials of the intermediates



Scheme 1. ● = MoCp; x = 2 or 3.

detected during the course of the reaction of 1^+ with either nitrate or nitrite suggests that the intermediates should be similar, that is with a *nitrito* coordination of NO_2^-. The amidato complex would then result from a sequence of reactions that includes the release of an $NO_{(x-1)}$ species (neutral or anionic) and the transfer of a proton or of a H atom from the environment. The release of a nitrite *anion* in the reaction of 1^+ with NO_3^- is unlikely since we did not detect the oxidation peak of NO_2^- (see Figure 2, a) by CV after completion of the reaction of 1^+ with NO_3^- (Figure 1, b). The fact that 2^+ is formed by treating 1^+ with NO_3^- while a mixture of $2/2^+$ results from the reaction of 1^+ with NO_2^- might arise from homogeneous redox steps involving nitrogen oxides released in the reactions.

The second possibility is that the NO_x^- anion acts as a base [HNO_3/NO_3^-: pK_a = 8.89 in MeCN].[16] Since the experiments were not conducted under rigorously anhydrous conditions, residual water in the solvent might be involved. Thus, deprotonation of $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(MeCN)(H_2O)]^+$, a possible precursor of 2^+, by nitrate or nitrite would lead to a hydroxo ligand and thus promote the formation of 2^+ (or **2**). This would be similar to the postulated mechanism of hydrolytic reactions catalysed by enzymes possessing two metal ions in close proximity at the active site. It is thought that the metal centres in these enzymes act cooperatively, the role of one of them being to modify the pK_a of a bound water molecule, thus generating a hydroxide ligand that attacks the substrate present at the neighbouring metal centre.[17,18] Similar reactions can involve mononuclear complexes. The metal-promoted hydrolysis of a nitrile ligand in the side chain of a tetrazamacrocyclic Cu complex has been reported recently.[19]

If this is the case in our study, the intermediate detected in the reaction of 1^+ with NO_x ions would be either a hydroxo complex or a species derived therefrom. However, it is not clear why such an intermediate would be longer-lived when generated by the reaction of 1^+ with NO_3^- than when it arises from the reaction of 1^+ with nitrite.

In order to discriminate between the above possibilities, we conducted two types of experiments, namely the reaction of 1^+ with a base (Et_3N: pK_a = 18.5 in MeCN)[20] and, the reaction of 1^+ with a weakly basic, oxygen-containing anion ClO_4^- [$HClO_4/ClO_4^-$: pK_a = 1.6 in MeCN].[21]

The reaction of 1^+ with Et_3N (1.2 equiv.) was monitored by cyclic voltammetry in THF/$[NBu_4][PF_6]$. Although the characteristic couples of 1^+ were replaced by reversible systems at –0.67 V and 0.67 V on addition of Et_3N, the CV did not show the formation of an intermediate such as the one observed on treatment with nitrate or nitrite. Small reversible couples around –0.8 V and 0 V suggested that only a small amount of the amidato complex might be produced. Therefore, it appears unlikely that $2^{+/0}$ results from the deprotonation of an aqua precursor. It is worth noting that reaction of 1^+ with chloride, the basicity of which is very similar to that of nitrate (HCl/Cl^-: pK_a = 8.94 in MeCN),[16] produces the known $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ complex by the substitution of Cl^- for a MeCN ligand.[10]

The CV of 1^+ in MeCN is not affected by the presence of a large excess of ClO_4^- (supporting electrolyte: $[NEt_4][ClO_4]$). On the contrary, the CV of 1^+ recorded in THF/$LiClO_4$ or in THF/$[NBu_4][PF_6]$ in the presence of ClO_4^- is totally different from that obtained in the absence of perchlorate. The characteristic redox couples of 1^+ are not observed in the presence of ClO_4^-. Instead, redox systems similar to those present after addition of NO_x^- to a solution of 1^+ are detected. A small amount of 2^+, characterized by a reduction around –0.8 V and an oxidation at 0 V, is present in solution (Figure 3, a), and its concentration increases slowly with time.

The major compound present in a THF solution of 1^+ in the presence of ClO_4^- could not be isolated. It clearly arises from a reaction between the metal complex and perchlorate. That the redox potentials of this species ($E_{1/2}^{ox}$ = 0.23 V, E_p^{red} = –1.27 V in THF/Li[ClO_4]; $E_{1/2}^{ox}$ = 0.23 V, E_p^{red} = –1.4 V in THF/$[NBu_4][PF_6]$ + 2 equiv. ClO_4^-) are close to those of the intermediate observed upon addition of NO_x^- to 1^+ suggests that the nature of the metal compound responsible for these couples is similar in each case. However, whereas the amidato complex is formed essentially quantitatively from the intermediate observed upon treating 1^+ with NO_3^- or with NO_2^- (**2** is also formed in the latter case) within a few minutes (NO_2^-) or a few tens of minutes (NO_3^-), formation of the amidato complex 2^+ from the perchlorate intermediate is very much slower, while that of **2** requires an electrochemical reduction step.

The control experiments with Et_3N and ClO_4^- demonstrate that the basic properties of the reactant, that is its ability to deprotonate coordinated water, are not essential to the formation of $2^{+/0}$. It is therefore unlikely that the residual water of the solvent plays a pivotal part in the pro-

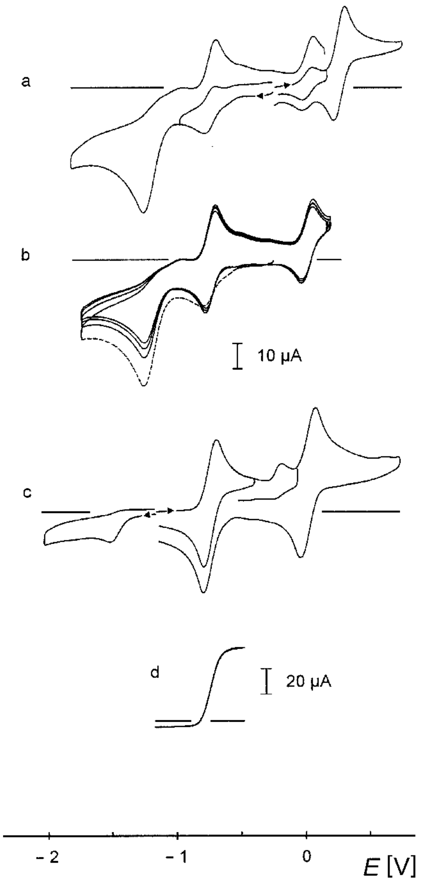


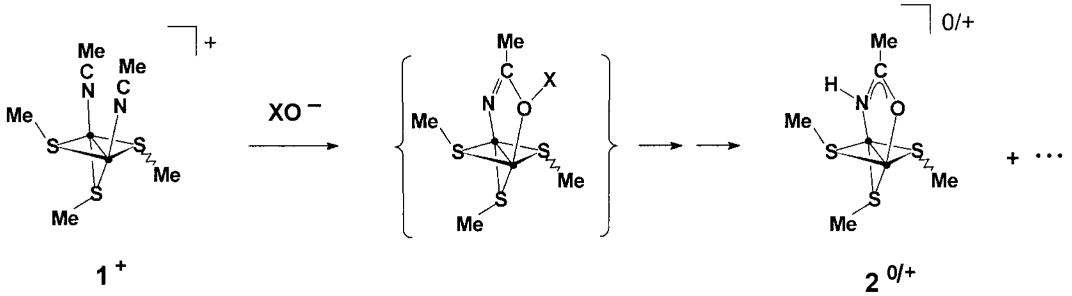
Figure 3. Cyclic voltammetry of $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(MeCN)_2]^+$ ($\mathbf{1}^+$; 2 mM) in THF/$LiClO_4$ recorded immediately after the addition of the metal complex (a); the curve in b) represents repetitive scans in the potential range –1.8/0.2 V and the dashed curve is the first negative-going scan; the cyclic voltammogram in (c) and the RDE voltammogram in (d) were obtained after controlled-potential electrolysis of the solution in b) at –1.4 V on a graphite cathode (n = 2 F per mol of $\mathbf{1}^+$) (vitreous carbon electrode, v = 0.2 V s^{-1}; potentials are against ferrocene/ferrocenium).

cess on the timescale of the electrochemical experiments.That the amidate derivative was obtained upon treatment of $\mathbf{1}^+$ with different oxo anions strongly suggests that the oxygen atom in $\mathbf{2}^{+/0}$ comes from the XO$^-$ moiety bound to a metal centre (X = NO, NO_2 or ClO_3).

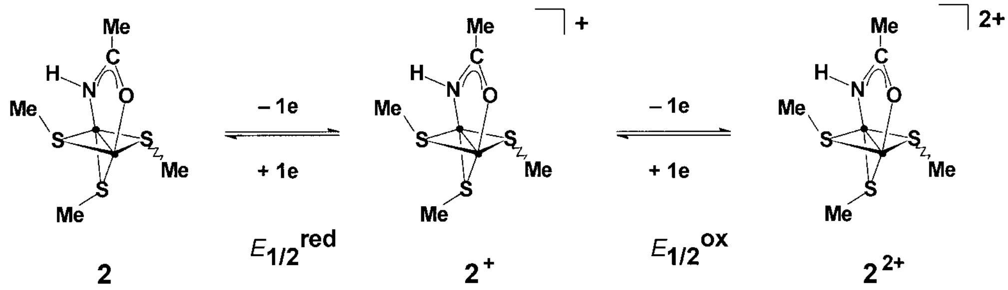
Metal complexes containing perchlorate ligands have been reported.[18,22] However, in these compounds ClO_4^- can generally be substituted by a variety of ligands, in contrast to what is observed here: addition of a large excess of acetonitrile has no effect on the CV shown in Figure 3a. Therefore, it is unlikely that the species observed in THF in the presence of perchlorate arises from the simple substitution of ClO_4^- for one MeCN ligand in $\mathbf{1}^+$. Rather, an intermediate such as the one shown in Scheme 2 can be envisaged. The absence of a perchlorate derivative in MeCN/$[NEt_4][ClO_4]$ would then arise from the worse coordinating ability of ClO_4^- as compared to acetonitrile.

The reduced amidato complex **2** is generated from the intermediate formed in the reaction of $\mathbf{1}^+$ with perchlorate by reduction at –1.3 V (Figures 3a and b). This was confirmed by voltammetry of the catholyte after controlled-potential electrolysis (E_{el} = –1.4 V, graphite cathode), as shown in Figures 3c and 3d. However, the charge consumed to produce **2** was between 1.4 and 2 F per mol of $\mathbf{1}^+$, while $\mathbf{2}^+$ was the major product formed after the transfer of about 1 F per mol of $\mathbf{1}^+$. Assuming that the intermediate is as shown in Scheme 2, the formation of $\mathbf{2}^+$ in the early stage of the electrolysis would be consistent with a (one-electron) reductive elimination of X$^-$ (e.g. ClO_3^-) accompanied (or followed) by a protonation step. The reduction of $\mathbf{2}^+$ ($E_{1/2}^{red}$ = –0.8 V) at the electrolysis potential completes the reduction process. A small amount of an unknown product is also present after electrolysis (Figure 3c).

It has been shown that coordinated nitriles can be attacked by carbonate to produce an amide derivative with the release of CO_2.[23] Oxyfunctionalizations of coordinated nitriles with various oxygen-containing substrates have also been reported.[24] A direct attack of XO$^-$ (X = NO, NO_2 or ClO_3) on one of the MeCN ligands of $\mathbf{1}^+$ could also take place. However, this possibility appears less likely on the basis of the experiments carried out in MeCN, since the formation of $\mathbf{2}^+$ from $\mathbf{1}^+$ and NO_3^- is slower than in THF or requires a large excess of nitrate, while no reaction occurred in the presence of ClO_4^-, even when used in very large excess (supporting electrolyte). The fact that the redox potentials of the intermediates detected in the reactions of $\mathbf{1}^+$ with NO_2^-, NO_3^- or ClO_4^- are very similar in THF suggests that they must be closely related. While the intermediate formed by treating $\mathbf{1}^+$ with nitrate and nitrite produces $\mathbf{2}^{+/0}$ within a relatively short time, it appears longer-lived when obtained by reaction of $\mathbf{1}^+$ with perchlorate. As the intermediate could not be isolated from the solution, its nature is not known and the reason for this difference could



Scheme 2. Postulated intermediate in the reaction of $\mathbf{1}^+$ with XO$^-$ (X = NO_2, NO or ClO_3). ● = MoCp.



Scheme 3. ● = MoCp.

not be elucidated. However, if the precursor of the amidato complex is as shown in Scheme 2, the different lifetimes might indicate that the X–O bond is stronger for X = Cl than for X = N.

The reactivity of $\mathbf{1}^+$ reveals the occurrence of a bimetallic effect in the $\{Mo_2(Cp)_2(\mu\text{-}SMe)_3\}$ moiety. Treatment of $\mathbf{1}^+$ with chloride or trifluoroacetate produces complexes where the anion occupies a bridging position.[10,32] This indicates that the remaining MeCN ligand in the likely intermediate $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(MeCN)X]$ (X = Cl, CF_3CO_2) is released upon X bridging. Despite the ability of NO_3^- and NO_2^- to adopt bridging coordination modes,[5,6,7a] this was not observed at the $\{Mo_2(Cp)_2(\mu\text{-}SMe)_3\}$ core, and the amidato complex $\mathbf{2}^+$ (and **2**) was obtained instead. Therefore, it appears that the reactivity (the lability) of the acetonitrile bound to one Mo atom is affected by the nature of the ligand present at the adjacent metal centre of the $\{Mo_2(Cp)_2(\mu\text{-}SMe)_3\}$ site.

Electrochemistry of $[Mo_2(Cp)_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1,\eta^1\text{-}OC(Me)NH\}]^{0/+}$ ($\mathbf{2}^{0/+}$)

Several compounds containing an amidato ligand are known,[17,18,25] although no electrochemical study of such a complex has been reported so far, to the best of our knowledge. We now report the electrochemistry of $\mathbf{2}^{0/+}$ in THF and MeCN containing $[NBu_4][PF_6]$. We paid special attention to the reduction of $\mathbf{2}^+$ in the presence of acid in order to investigate the mechanism of the release of the amidato ligand as acetamide.[11]

Complex $\mathbf{2}^+$ undergoes diffusion-controlled, one-electron reduction and oxidation steps in both solvents (Scheme 3). Controlled-potential electrolysis at –1.0 V afforded the neutral compound **2** essentially quantitatively[26] after transfer of 1 F per mol of $\mathbf{2}^+$.

The CV of $\mathbf{2}^+$ in MeCN/$[NBu_4][PF_6]$ (Figure 4, a) is strongly affected by the presence of protons, although the changes only concern the reduction step, which becomes irreversible and shifts by about 100 mV towards positive potentials (Figure 4, b). This is indicative of the occurrence of a follow-up reaction (EC process)[13,27,28] under these conditions.

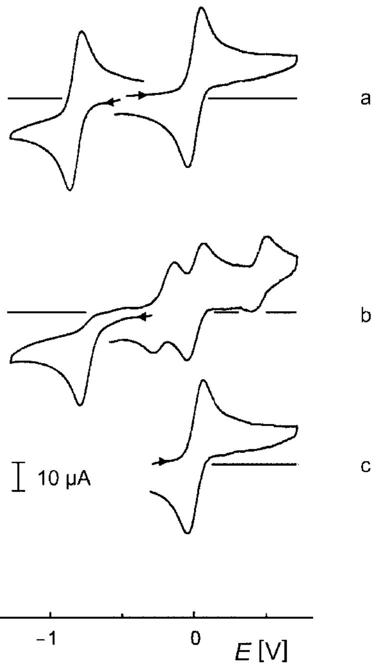
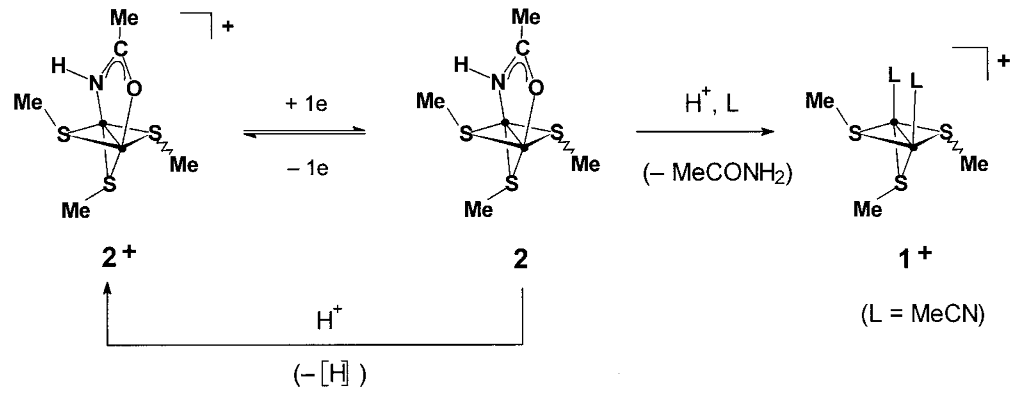


Figure 4. Cyclic voltammetry of $[Mo_2(Cp)_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1,\eta^1\text{-}OC(Me)NH\}]^+$ ($\mathbf{2}^+$; 1 mM) in MeCN/$[NBu_4][PF_6]$ a) before, and b) and c) after addition of an excess of HBF_4/H_2O (vitreous carbon electrode, v = 0.2 V s^{-1}; potentials are against ferrocene/ferrocenium).

The reduction of $\mathbf{2}^+$ in the presence of acid in MeCN/$[NBu_4][PF_6]$ affords a product that was identified as $\mathbf{1}^+$ from its redox systems detected on the return scan (Figure 4, b). Controlled-potential electrolysis at –0.9 V effectively produces $\mathbf{1}^+$. However, the CV recorded after the passage of 1 F per mol of $\mathbf{2}^+$ demonstrates that $\mathbf{2}^+$ is still present in solution; conversion of $\mathbf{2}^+$ to $\mathbf{1}^+$ is almost complete (>90%) [26] only after the transfer of about 1.5 F per mol of $\mathbf{2}^+$. While these experiments are entirely consistent with previous ones showing that protonation of **2** in MeCN produces $\mathbf{1}^+$ and acetamide,[11] they also suggest that part of the charge consumed during electrolysis is used to reduce protons. This can be described as shown in Scheme 4.

In contrast to what is observed in MeCN/$[NBu_4][PF_6]$, addition of two equivalents of HBF_4/H_2O to a THF/$[NBu_4][PF_6]$ solution of $\mathbf{2}^+$ did not lead to a significant change of the cyclic voltammogram. However, in the pres-



Scheme 4. ● = MoCp.

ence of larger amounts of acid (10–20 equiv. HBF_4/H_2O or HBF_4/Et_2O), the reduction of $\mathbf{2}^+$ in this solvent occurs according to an EC process, as shown by the decrease of the anodic-to-cathodic peak current ratio $[(i_p^a)/(i_p^c)^{red}]$, and by the presence of a product (**3**) detected by its redox steps on the return scan at $E_{1/2}$ = –0.43 V and 0.21 V (Figure 5, b; note that the presence of acid has no effect on the oxidation, cf. Figure 5, c).

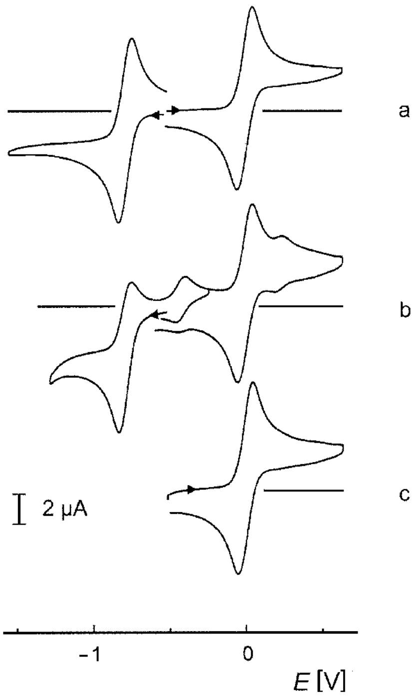


Figure 5. Cyclic voltammetry of $[Mo_2(Cp)_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1,\eta^1\text{-}OC(Me)NH\}]^+$ ($\mathbf{2}^+$; 1 mM) in THF/$[NBu_4][PF_6]$ a) before, and b) and c) after addition of a large excess (17 equiv.) of HBF_4/Et_2O (vitreous carbon electrode, v = 0.05 V s^{-1}; potentials are against ferrocene/ferrocenium).

Cyclic voltammetry after controlled-potential reduction of $\mathbf{2}^+$ in the presence of acid (10 equiv. HBF_4/Et_2O) in THF shows that a substantial amount of the starting material $\mathbf{2}^+$ is still present along with product **3** after the passage of 2 and 3 F per mol of $\mathbf{2}^+$ (ca. 60% and 50% $\mathbf{2}^+$ present, respectively).[26] This clearly shows that the charge diverted to reduce protons (see Scheme 4) is larger in THF than in MeCN. Consistent with this, addition of H^+ to an electrogenerated solution of **2** in THF leads to the formation of $\mathbf{2}^+$ along with product **3** (Figure S1c in the Supporting Information). Complex **3** decomposed upon work-up. However, its reaction with acetonitrile affords $\mathbf{1}^+$.[29] This indicates that **3** retains the $\{Mo_2(Cp)_2(\mu\text{-}SMe)_3\}$ core and possesses labile ligand(s) bound to the metal centres. Species such as $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(L)(L')]^+$ (L, L′ = THF and/or H_2O), or a derivative retaining the acetamide ligand, $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(NH_2COMe)(L)]^+$ (L = THF or H_2O), are possible. It should be noted that protonation of $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(\mu\text{-}NH_2)]$ with HBF_4/H_2O in MeCN affords $\mathbf{1}^+$, while a product tentatively assigned as $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(NH_3)(THF)]^+$ [$E_{1/2}^{ox}$ = –0.39 V and 0.31 V] was obtained by protonation with HBF_4/Et_2O in THF.[30]

As mentioned above, a major difference between the CV experiments carried out in THF and in MeCN lies with the detection of **2** in the former solvent, even in the presence of a large excess of acid. The addition of MeCN to an acidic THF solution of $\mathbf{2}^+$ leads to the CV detection of $\mathbf{1}^+$ instead of **3** on the reverse scan (see Figures 6a and b), without a change in the characteristics of the reduction process $[(i_p^c)^{red}, (i_p^a/i_p^c)^{red}]$, that is, without a change in the overall kinetics of the following chemical reaction(s). Therefore, the solvent-dependence of the kinetics of the reduction of $\mathbf{2}^+$ in the presence of acid does not originate in the solvent-binding step itself. This would be consistent with the fact that $\mathbf{1}^+$ is formed from **3**.

Monitoring the course of the reaction of **2** with a large excess of acid by amperometry at a rotating disc electrode (E = –0.6 V, on the plateau of the first oxidation of **2**) indicates[31] the existence of an equilibrium between **2** and a protonated intermediate, which would be shifted by the slower conversion of the intermediate into products [$\mathbf{2}^+$ (with loss of an H atom) and **3** or $\mathbf{1}^+$ (with the release of the amidato bridge upon L binding) in THF or MeCN respectively] (Scheme 5).[32]

The possibility of releasing the amidato bridge upon electrochemical reduction of $\mathbf{2}^+$ in the presence of 10–20 equiv. of acid in THF was confirmed by controlled-potential electrolyses performed in the presence of an excess of substrate

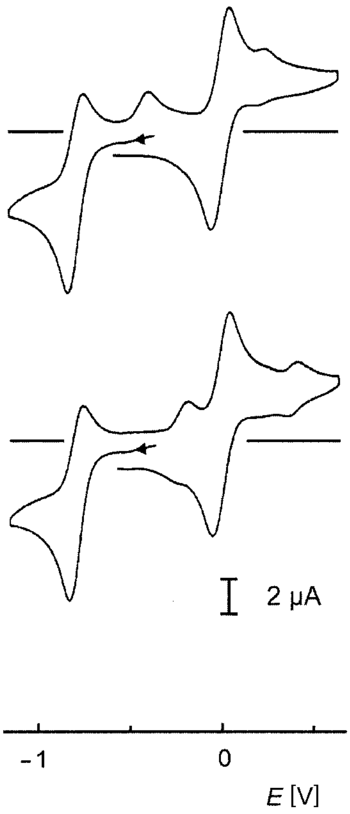


Figure 6. Cyclic voltammetry of $[Mo_2(Cp)_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1,\eta^1\text{-}OC(Me)NH\}]^+$ ($\mathbf{2^+}$; 1 mM) in THF/$[NBu_4][PF_6]$ in the presence of a large excess (17 equiv.) of HBF_4/Et_2O a) before, and b) after addition of MeCN (vitreous carbon electrode, v = 0.05 V s^{-1}; potentials are against ferrocene/ferrocenium).

(10 equiv. *t*BuNC). Under these conditions, the bis(isocyanide) analogue of $\mathbf{1^+}$ was obtained in about 80% yield[26] along with $\mathbf{2^+}$, after the transfer of more than 2 F per mol of $\mathbf{2^+}$. The nature of the product was confirmed by comparison of its redox potentials with those of an authentic sample of $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(t\text{BuNC})_2]^+$.[34]

Conclusions

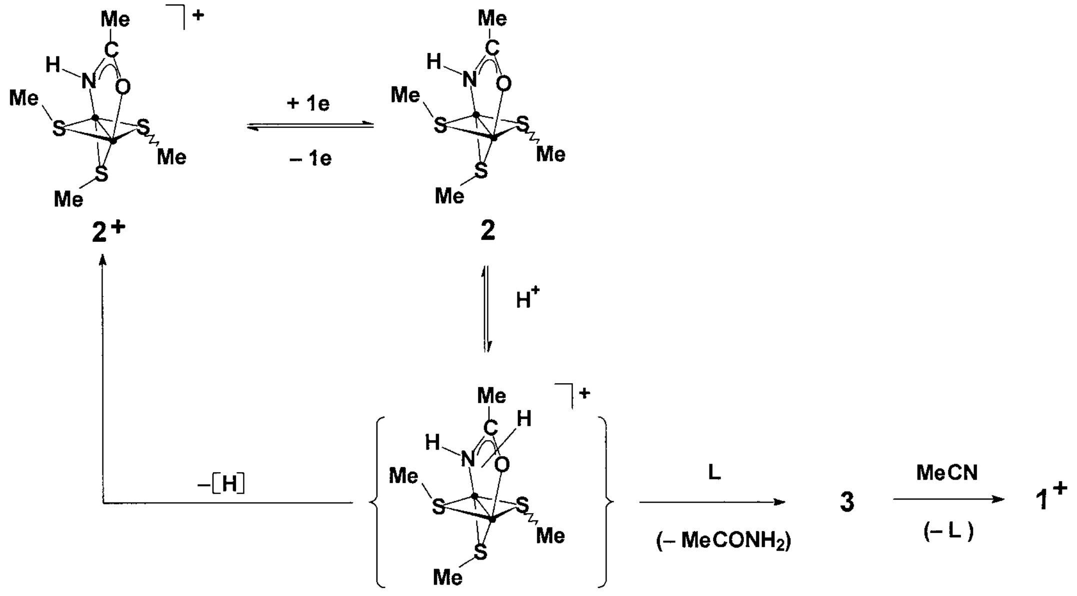
The results reported in this paper illustrate an original oxyfunctionalization of an acetonitrile bound to a bimetallic sulfur core $\{Mo_2(Cp)_2(\mu\text{-}SMe)_3\}$ by oxygen-containing anions, XO^- (X = NO, NO_2, ClO_3), which initially arises from substitution (or less likely direct attack) of MeCN by XO^-, and produces the amidate complex $\mathbf{2^{0/+}}$.

The electrochemical reduction of $\mathbf{2^+}$ in the presence of acid demonstrates that the amidate bridge can be released, since $\mathbf{1^+}$, the precursor of $\mathbf{2^+}$, is regenerated when the reactions are carried out in MeCN. Because $\mathbf{2^+}$ is also formed from $\mathbf{1^+}$ in a wet atmosphere,[11] the present results exemplify the possibility of a cyclic conversion of acetonitrile into acetamide.

Experimental Section

Methods and Materials: All experiments were carried out under an inert atmosphere using Schlenk techniques. THF was purified as described previously.[33] Acetonitrile (Merck, HPLC grade) was used as received. The fluoroboric acid [diethyl ether complex and aqueous solution (Aldrich)], was used as received. The preparation and the purification of the supporting electrolyte $[NBu_4][PF_6]$ and the electrochemical equipment were as described previously.[33] All the potentials quoted in the text and figures are relative to the ferrocene-ferrocenium couple; ferrocene was added as an internal standard at the end of the experiments. ^{1}H NMR spectra were recorded on a Bruker AC300 spectrometer. Shifts are relative to tetramethylsilane as an internal reference. Complexes $[Mo_2(Cp)_2(\mu\text{-}SMe)_3(L)_2]^+$ (L = MeCN, *t*BuNC) were synthesised as described previously.[10,34]

Preparation of $[Mo_2(Cp)_2(\mu\text{-}SMe)_3\{\mu\text{-}\eta^1,\eta^1\text{-}OC(Me)NH\}]$ (2) by treatment of $\mathbf{1^+}$ with NO_x^- (x = 2, 3): In a typical experiment, a



Scheme 5. ● = MoCp; the species in brackets was not detected.

mixture of 1^+ (0.0565 g, 8.9×10^{-5} mol) and [NBu$_4$][NO$_3$] (0.1445 g, 4.7×10^{-4} mol, 5.3 equiv.) in 15 mL of THF was stirred under dinitrogen for 3 h. After filtration, the solution was taken to dryness. The solid was dissolved in MeCN and NaBH$_4$ was added in excess (0.017 g, 4.5×10^{-4} mol, 5 equiv.). The solution was stirred for 30 min and then filtered to remove a brown precipitate. The volume of the solution was reduced to 2 mL under reduced pressure, and addition of Et$_2$O (15 mL) led to the formation of a white precipitate. The latter was removed by filtration, and the solution was taken to dryness. The solid residue was dried under vacuum. The ^{1}H NMR spectrum of the solid demonstrated that the amidate complex **2** had formed. CV of the NMR sample showed the presence of **2**, with a small amount of $\mathbf{2}^+$ resulting from the oxidation of the neutral complex ($E_{1/2}{}^{\mathrm{ox}} = -0.8$ V).

A similar procedure was followed for the reaction of 1^+ with nitrite. [NBu$_4$][NO$_2$] (0.0182 g, 6.3×10^{-5} mol) and 1^+ (0.0418 g, 6.6×10^{-5} mol) were dissolved in THF (15 mL). The solution was stirred for about 1 h, after which time it was taken to dryness. The solid was dissolved in MeCN (10 mL) and an excess of NaBH$_4$ (0.0164 g, 4.3×10^{-4} mol, 6.6 equiv.) was added. After a few minutes stirring, the solvent was evaporated under reduced pressure. Et$_2$O (10 mL) was added to the residue, and after 10 min stirring the solution was filtered and taken to dryness. The solid was stirred for 10 min in pentane (5 mL), and, after evaporation of the solvent, the solid was dried under vacuum. As above, the ^{1}H NMR spectrum of the solid demonstrated that the amidate complex **2** had formed.

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[1] a) F. Y. Pétillon, P. Schollhammer, J. Talarmin, K. W. Muir, *Coord. Chem. Rev.* **1998**, *178–180*, 203–247; b) P. Schollhammer, N. Cabon, J. F. Capon, F. Y. Pétillon, J. Talarmin, K. W. Muir, *Organometallics* **2001**, *20*, 1230–1242; c) N. Cabon, P. Schollhammer, F. Y. Pétillon, J. Talarmin, K. W. Muir, *Organometallics* **2002**, *21*, 448–450; d) P. Schollhammer, B. Didier, N. Le Grand, F. Y. Pétillon, J. Talarmin, K. W. Muir, S. J. Teat, *Eur. J. Inorg. Chem.* **2002**, 658–663.

[2] a) F. Y. Pétillon, P. Schollhammer, J. Talarmin, K. W. Muir, *Inorg. Chem.* **1999**, *38*, 1954–1955; b) N. Le Grand, K. W. Muir, F. Y. Pétillon, C. J. Pickett, P. Schollhammer, J. Talarmin, *Chem. Eur. J.* **2002**, *8*, 3115–3127.

[3] A. Le Goff, N. Cabon, C. Le Roy, F. Y. Pétillon, P. Schollhammer, J. Talarmin, unpublished results.

[4] J. K. Padden Metzker, J. E. McGrady, *Chem. Eur. J.* **2004**, *10*, 6447–6455.

[5] K. B. Shiu, L.-T. Tang, S.-W. Jean, C.-H. Li, R.-R. Wu, J.-C. Wang, L.-S. Liou, M. Y. Chiang, *Inorg. Chem.* **1996**, *35*, 7845–7849.

[6] a) B. K. Hui, W.-T. Wong, *J. Chem. Soc., Dalton Trans.* **1996**, 2177–2178; b) B. K. Hui, W.-T. Wong, *J. Chem. Soc., Dalton Trans.* **1998**, 3977–3985.

[7] a) W. S. Han, S. W. Lee, *Inorg. Chim. Acta* **2003**, *348*, 15–24; b) W. S. Han, S. W. Lee, *J. Organomet. Chem.* **2003**, *678*, 102–107.

[8] a) C. Kimblin, V. J. Murphy, T. Hascall, B. M. Bridgewater, J. B. Bonanno, G. Parkin, *Inorg. Chem.* **2000**, *39*, 967–974; b) S. Ogo, H. Nakai, Y. Watanabe, *J. Am. Chem. Soc.* **2002**, *124*, 597–601; c) P. J. Arnold, S. C. Davies, M. C. Durrant, D. V. Griffiths, D. L. Hughes, P. C. Sharpe, *Inorg. Chim. Acta* **2003**, *248*, 143–149.

[9] F. V. Kudrik, S. V. Makarov, A. Zahl, R. Van Eldik, *Inorg. Chem.* **2003**, *42*, 618–624.

[10] F. Barrière, Y. Le Mest, F. Y. Pétillon, S. Poder-Guillou, P. Schollhammer, J. Talarmin, *J. Chem. Soc., Dalton Trans.* **1996**, 3967–3976.

[11] P. Schollhammer, M. Le Hénanf, C. Le Roy-Le Floch, F. Y. Pétillon, J. Talarmin, K. W. Muir, *J. Chem. Soc., Dalton Trans.* **2001**, 1573–1577.

[12] R. A. Holwerda, *Inorg. Chim. Acta* **1999**, *288*, 211–214.

[13] The parameters i_p and E_p are the peak current and the peak potential of a redox process, respectively; $E_{1/2} = (E_p{}^a + E_p{}^c)/2$; $E_p{}^a$, $i_p{}^a$ 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; $\Delta E_p = E_p{}^a - E_p{}^c$; an EC process comprises an electron transfer step (E) followed by a chemical reaction (C). CV stands for cyclic voltammetry; v (V s^{-1}) is the scan rate in CV experiments.

[14] a) J. Jiang, R. H. Holm, *Inorg. Chem.* **2005**, *44*, 1068–1072; b) B. A. Moyer, T. J. Meyer, *J. Am. Chem. Soc.* **1979**, *101*, 1326–1328; c) K. Tanaka, M. Honjo, T. Tanaka, *Inorg. Chem.* **1985**, *24*, 2662–2665, and references cited therein.

[15] D. A. Muccigrosso, F. Mares, S. E. Diamond, J. P. Solar, *Inorg. Chem.* **1983**, *22*, 960–965.

[16] I. M. Kolthoff, S. Bruckenstein, M. K. Chantooni Jr., *J. Am. Chem. Soc.* **1961**, *83*, 3927–3935.

[17] a) F. Meyer, E. Kaifer, P. Kircher, K. Heinze, H. Pritzkow, *Chem. Eur. J.* **1999**, *5*, 1617–1630; b) C. D. Bauer, T. E. Concolino, J. L. Eglin, R. D. Rodgers, R. J. Staples, *J. Chem. Soc., Dalton Trans.* **1998**, 2813–2817; c) S. T. Frey, N. N. Murthy, S. T. Weintraub, L. K. Thompson, K. D. Karlin, *Inorg. Chem.* **1997**, *36*, 956–957; d) N. J. Curtis, K. S. Hagen, A. M. Sargeson, *J. Chem. Soc., Chem. Commun.* **1984**, 1571–1573.

[18] E. C. Wilkinson, Y. Dong, L. Que Jr., *J. Am. Chem. Soc.* **1994**, *116*, 8394–8395.

[19] L. Siegfried, A. Comparone, M. Neuburger, T. A. Kaden, *Dalton Trans.* **2005**, 30–36.

[20] E. J. Moore, J. M. Sullivan, J. R. Norton, *J. Am. Chem. Soc.* **1986**, *108*, 2257–2263 and references cited therein.

[21] T. Fujinaga, I. Sakamoto, *J. Electroanal. Chem.* **1977**, *85*, 185–201.

[22] a) M. Hoogenraad, K. Rampkisoensing, W. L. Driessen, H. Kooijman, A. L. Spek, E. Bouwman, J. G. Haasnoot, J. Reedijk, *Inorg. Chim. Acta* **2001**, *320*, 117–126; b) S. C. Chaffee, J. C. Sutton, C. S. Babitt, J. T. Mayer, K. A. Guy, R. D. Pike, G. B. Carpenter, *Organometallics* **1998**, *17*, 5586–5590; c) A. S. Kanmani, S. Vancheesan, *J. Mol. Catal. A: Chem.* **1999**, *150*, 95–104; d) J.-L. Pascal, J. Potier, D. J. Jones, J. Rozière, A. Michalowicz, *Inorg. Chem.* **1985**, *24*, 238–241; e) J.-L. Pascal, J. Potier, D. J. Jones, J. Rozière, A. Michalowicz, *Inorg. Chem.* **1984**, *23*, 2068–2073; f) P. L. Johnson, J. H. Enemark, R. D. Feltham, K. Bizot Swedo, *Inorg. Chem.* **1976**, *15*, 2989–2993.

[23] a) I. I. Creaser, J. MacB. Harrowfield, F. R. Keene, A. M. Sargeson, *J. Am. Chem. Soc.* **1981**, *103*, 3359–3364; b) A. W. Zanella, P. C. Ford, *Inorg. Chem.* **1975**, *14*, 42–47.

[24] a) S. Thomas, P. J. Lim, R. W. Gable, C. G. Young, *Inorg. Chem.* **1998**, *37*, 590–593; b) M. N. Kopylovich, V. Y. Kukushkin, M. Haukka, J. J. R. Frausto da Silva, A. J. L. Pombeiro, *Inorg. Chem.* **2002**, *41*, 4798–4804; c) N. A. Bokach, V. Y. Kukushkin, M. L. Kuznetsov, D. A. Garnovskii, G. Natile, A. J. L. Pombeiro, *Inorg. Chem.* **2002**, *41*, 2041–2053; d) K. V. Luzyanin, V. Y. Kukushkin, M. L. Kuznetsov, D. A. Garnovskii, M. Haukka, A. J. L. Pombeiro, *Inorg. Chem.* **2002**, *41*, 2981–2986; e) N. A. Bokach, A. V. Khripoun, V. Y. Kukushkin, M. Haukka, A. J. L. Pombeiro, *Inorg. Chem.* **2003**, *42*, 896–903.

[25] a) R. A. Michelin, M. Mozzon, R. Bertani, *Coord. Chem. Rev.* **1996**, *147*, 299–338; b) J. L. Eglin, *Comments Inorg. Chem.* **2002**, *23*, 23–43; c) V. Y. Kukushkin, A. J. L. Pombeiro, *Inorg. Chim. Acta* **2005**, *358*, 1–21; d) V. Y. Kukushkin, A. J. L. Pombeiro, *Chem. Rev.* **2002**, *102*, 1771–1802; e) C. S. Chin, D. Chong, B. Lee, H. Jeong, G. Won, Y. Do, Y. J. Park, *Organome-*

tallics **2000**, *19*, 638–648; f) T. E. Concolino, J. L. Eglin, R. J. Staples, *Polyhedron* **1999**, *18*, 915–921; g) F. A. Cotton, L. M. Daniels, C. A. Murillo, X. Wang, *Polyhedron* **1998**, *17*, 2781–2793; h) A. Erxleben, B. Lippert, *J. Chem. Soc., Dalton Trans.* **1996**, 2329–2333; i) M. B. Hursthouse, M. A. Mazid, S. D. Robinson, A. Sahajpal, *J. Chem. Soc., Dalton Trans.* **1993**, 2835–2839; j) W.-Y. Yeh, S.-M. Peng, L.-K. Liu, *Inorg. Chem.* **1993**, *32*, 2965–2967.

[26] The yield of the reduction of $\mathbf{2}^+$ was calculated by comparing the peak current of the reactant to that of the product, assuming identical diffusion coefficients.

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

[28] The variations of the current function $[i_p^{red}(H^+)/v^{1/2}]$ associated with the reduction peak of $\mathbf{2}^+$ in the presence of acid $[i_p^{red}(H^+)]$ against scan rate, and the peak current ratio of the reduction in the presence and in the absence of protons $[i_p^{red}(H^+)/i_p^{red} \approx 1.1]$ are consistent with the transfer of a single electron in the reduction in the presence of acid. Also, the fact that the oxidation of $\mathbf{2}^+$ is not affected by the presence of H^+ (Figure 4, c) indicates that $\mathbf{2}^+$ is not protonated, and that the change in the reduction step arises from the protonation of electrogenerated **2** (EC process).

[29] Addition of MeCN to the solution in Figure S1c (see Supporting Information) results in the conversion of product **3** into $\mathbf{1}^+$. This indicates (see part b in Figure 6) that $\mathbf{1}^+$ is most probably formed from **3**, with no change in the reduction mechanism due to the presence of MeCN.

[30] F. Y. Pétillon, P. Schollhammer, J. Talarmin, *J. Chem. Soc., Dalton Trans.* **1997**, 4019–4024.

[31] The oxidation current measured at the rotating disc electrode drops to the background level on addition of H^+ to **2** in MeCN, which shows that **2** is removed very rapidly from the solution. In contrast, after an initial abrupt fall of about 30% on adding H^+ to a THF solution of **2**, the oxidation current decreases more slowly.

[32] The mechanism in Scheme 5 was used for CV simulations (VirtualCV 1.0, written by A. Laouénan, is available on the web). The main characteristics of the CVs in Figures 6a and 6b $\{[(i_p^a/i_p^c)^{red}\ \mathbf{2}^+], [i_p^a(\mathbf{3})\text{ or }(\mathbf{1}^+)/i_p^c(\mathbf{2}^+)]\}$ were reproduced assuming that $\mathbf{1}^+$ is formed from **3**.[29] The solvent-dependence of the overall kinetics (see Figures 4b and 5b) was simulated by an increase of the forward rate constant for protonation, and of the second-order rate constant for the solvent-binding step, on going from THF to MeCN. This is entirely consistent with the fact that HBF_4/H_2O (i.e. H_3O^+) and HBF_4/Et_2O should be stronger acids in MeCN than in THF, and with the properties of MeCN compared to THF as a ligand for the metal sites in this type of complexes. The fact that the amount of $\mathbf{2}^+$ formed on reacting **2** with H^+, and that the charge used to reduce protons upon electrolysis of acidic solutions of $\mathbf{2}^+$, are larger in THF than in MeCN is assigned to the smaller rate constant of the substrate-binding step (Scheme 5) in the former. This is consistent with the fact that protonation of **2** in MeCN produces $\mathbf{1}^+$ with little $\mathbf{2}^+$.

[33] M. Le Hénanf, C. Le Roy, K. W. Muir, F. Y. Pétillon, P. Schollhammer, J. Talarmin, *Eur. J. Inorg. Chem.* **2004**, 1687–1700.

[34] N. Cabon, E. Paugam, F. Y. Pétillon, P. Schollhammer, J. Talarmin, K. W. Muir, *Organometallics* **2003**, *22*, 4178–4180.

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