Influence of the initial bonding mode of the hydrocarbyl bridge on the mechanisms and products of the electrochemical reduction of alkyne- and vinylidene dimolybdenum tris(μ-thiolate) complexes†

Alan Le Goff, Christine Le Roy, François Y. Pétillon, Philippe Schollhammer and Jean Talarmin*

Received (in Durham, UK) 13th October 2006, Accepted 28th November 2006
First published as an Advance Article on the web 2nd January 2007
DOI: 10.1039/b614948k

The electrochemical reduction of isomeric complexes, $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}HCCPh)]^+$ ($\mathbf{1}^+$) and $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}CHPh)]^+$ ($\mathbf{3}^+$), where the hydrocarbyl bridges in a η^1:η^1- or a η^1:η^2 mode, has been studied by cyclic voltammetry and controlled-potential electrolysis in thf–$[NBu_4][PF_6]$ and CH_2Cl_2–$[NBu_4][PF_6]$, in the absence and in the presence of acid. The binding mode of the CC fragment induces different electrochemical behaviour of the complexes in acid-free solutions since $\mathbf{1}^+$ reduces in two diffusion-controlled one-electron steps while the first reduction of $\mathbf{3}^+$ is characterized by slow electron transfer kinetics. Controlled-potential reduction of both $\mathbf{1}^+$ and $\mathbf{3}^+$ produces a mixture of the acetylide $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CCPh)]$ (**2**) and alkylidyne complexes $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CCH_2Ph)]$ (**4**). In the presence of acid, the electrochemical reduction of $\mathbf{1}^+$ and of $\mathbf{3}^+$ occurs according to ECE processes. The nature of the products formed by controlled-potential reduction of $\mathbf{1}^+$ depends on the nature of the acid and of the solvent. The transient formation of a complex with a μ-alkenyl ligand, either $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH{=}CHPh)]$ (**7**) or an isomer, is suggested by the oxidative electrochemistry of **7** and by its reaction with acids. In thf–$[NBu_4][PF_6]$ in the presence of an excess of acid (HBF_4/Et_2O) and of phenylacetylene, electrolysis of $\mathbf{1}^+$ gives rise to catalytic reduction of phenylacetylene to styrene. However, unidentified reactions limit the efficiency of this process. The reduction of $\mathbf{3}^+$ in acidic medium produces the alkyl complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CH_2CH_2Ph)]$ (**6**) through alkylidyne $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CCH_2Ph)]$ (**4**) and alkylidene $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CHCH_2Ph)]^+$ ($\mathbf{5}^+$) intermediates. Some ethylbenzene was formed after reduction of $\mathbf{5}^+$ in the presence of acid. These results show an effect of the binding mode of the hydrocarbyl bridge on the mechanism and products of the reduction of the corresponding complexes.

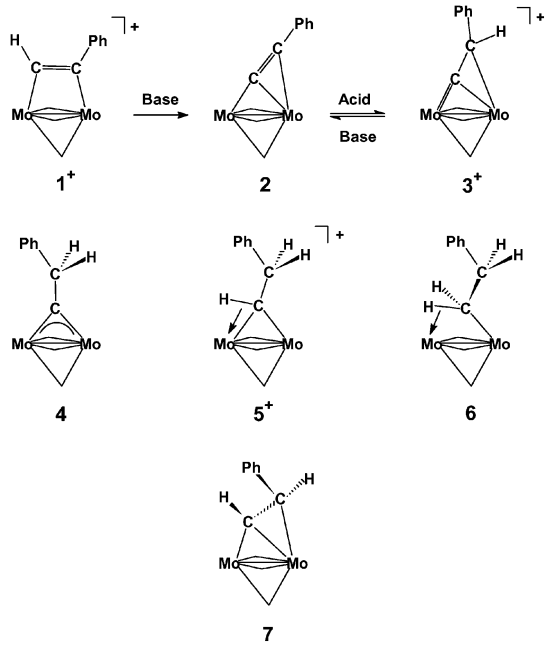
Introduction

Di- or polynuclear complexes where the metal centres are situated in a sulfur-rich environment are attractive models to study the way unsaturated substrates are activated and reduced by nitrogenase enzymes.[1] However, the presence of S ligands in the coordination sphere of the metal centres of model compounds still remains a major difficulty as far as binding the dinitrogen molecule itself is concerned.[1–3] This has led to the "rocket fuel approach"[3] of chemical nitrogen fixation where an {NN} moiety is introduced in the compounds by using hydrazines. Although it does not solve the central problem of N_2 binding at a metal-sulfur centres, this indirect approach is helpful in that it may provide information as to how a {NN} ligand is progressively reduced by successive $\{H^+/e\}$ transfers at such sites. Using this approach for the synthesis of {NN}-containing complexes, we demonstrated previously that the HN=NPh ligand bound in a $\mu\text{-}\eta^1\text{:}\eta^1$ fashion to the $\{[Mo_2Cp_2(\mu\text{-}SMe)_3]^+\}$ core could be cleaved to aniline and ammonia by controlled-potential reduction of the phenyldiazene complex in acidic medium.[4]

Another indirect approach consists in investigating the reduction of nitrogenase co-substrates by sulfur-containing model complexes. Although the nitrogenases have not yet disclosed all their secrets as to how the substrates are coordinated and reduced at the active site,[5] the FeMo cofactor,[6] it recently became possible to obtain information on the site where the C≡C bond is reduced[7] within FeMo-co. On our side of chemical modelling, several complexes bearing {CC} bridging units at the $\{[Mo_2Cp_2(\mu\text{-}SMe)_3]^+\}$ site are now available.[8] In particular, the synthesis of compounds where isomeric alkyne and vinylidene bridging ligands are bound to $\{[Mo_2Cp_2(\mu\text{-}SMe)_3]^+\}$[8a] in a respectively $\mu\text{-}\eta^1\text{:}\eta^1$ and $\mu\text{-}\eta^1\text{:}\eta^2$ fashion (Scheme 1) provides the opportunity to examine whether the initial bonding mode of the substrate effects the course of the electrochemical reduction at a single bimetallic

UMR CNRS 6521 "Chimie, Electrochimie Moléculaires et Chimie Analytique" UFR Sciences et Techniques, Université de Bretagne Occidentale, CS 93837, 29238 Brest-Cedex 3, France. E-mail: Jean.Talarmin@univ-brest.fr; Fax: + 332 98 01 70 01; Tel: + 332 98 01 79 10

† Electronic supplementary information (ESI) available: Scheme S1. See DOI: 10.1039/b614948k



Scheme 1 In this and the following schemes, the SMe groups of the bridges and the Cp rings were omitted for clarity.

site. It is interesting to note that the μ-η^1:η^2 coordination of the vinylidene ligand is similar to the binding of the isoelectronic N_2 molecule discovered by Fryzuk *et al.* in ([NPN]Ta)$_2$(μ-H)$_2$(μ-η^1:η^2-N_2) [NPN = PhP(SiMe$_2$CH$_2$NPh)$_2$].[1c,9]

All the complexes in Scheme 1 were fully characterized previously, and different aspects of their reactivity were reported.[8] While the coordination mode of the μ-vinylidene ligand in $\mathbf{3}^+$ was established by a crystal structure determination, the assignment of the bonding mode of the alkyne in $\mathbf{1}^+$ was based upon NMR spectroscopy,[8a] and on the crystal structures of an analogue of $\mathbf{1}^+$,[10] and of a complex similar to $\mathbf{1}^+$, namely [Mo_2Cp_2(μ-SPr^i)$_2$(μ-S)(μ-η^1:η^1-PhCCPh)].[11] The formation of the μ-alkylidyne derivative [Mo_2Cp_2(μ-SMe)$_3$(μ-η^1-CCH$_2$Ph)] (**4**) by treatment of $\mathbf{3}^+$ with hydride, and the protonation of **4** to the μ-alkylidene complex [Mo_2Cp_2(μ-SMe)$_3$(μ-η^1-CHCH$_2$Ph)]$^+$ ($\mathbf{5}^+$) were also reported,[8b] as well as the chemical and electrochemical conversion of $\mathbf{5}^+$ to the μ-alkyl [Mo_2Cp_2(μ-SMe)$_3$(μ-CH$_2$CH$_2$Ph)] (**6**).[8c] The kinetic analysis of the protonation of the μ-alkylidyne to μ-alkylidene ligand will be the object of a forthcoming paper.[12]

In this paper, we report on the electrochemical reduction of [Mo_2Cp_2(μ-SMe)$_3$(μ-η^1:η^1-HCCPh)]$^+$, $\mathbf{1}^+$, and [Mo_2Cp_2(μ-SMe)$_3$(μ-η^1:η^2-C=CHPh)]$^+$,$\mathbf{3}^+$, both in the absence and in the presence of acid.

Results and discussion

1 Electrochemical reduction of complexes $\mathbf{1}^+$ and $\mathbf{3}^+$ in the absence of acid

The first part of this study focuses on the primary reduction of $\mathbf{1}^+$ and $\mathbf{3}^+$. The nature of the follow-up chemical step(s) that is (are) revealed by the scan rate dependence of the peak current ratio [$(i_p^a/i_p^c)^{red1}$][13] will be examined in Section 1.2. No electron-transfer induced alkyne to vinylidene interconversion[14] was observable in the present case.

1.1 The primary reduction of $\mathbf{1}^+$ and $\mathbf{3}^+$. The cyclic voltammetry (CV) of $\mathbf{1}^+$ and $\mathbf{3}^+$ in CH_2Cl_2–[NBu_4][PF_6] (Fig. 1) shows that both complexes undergo two one-electron reduction steps (Table 1, Scheme 2) and irreversible or partially reversible oxidation(s). Similar results are obtained in thf–[NBu_4][PF_6].

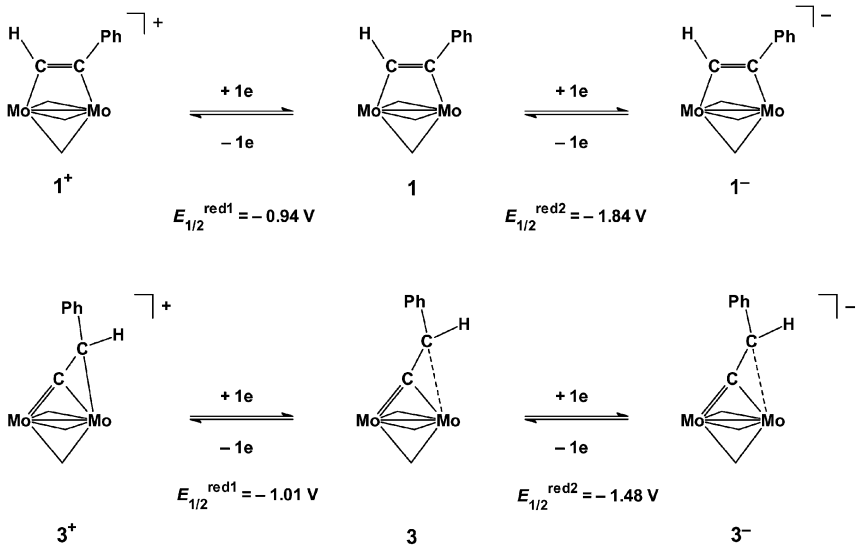
The reduction processes of the μ-alkyne and μ-vinylidene species present similarities, both showing two one-electron steps the first of which is observed at very close potentials for $\mathbf{1}^+$ and $\mathbf{3}^+$ (Table 1, Scheme 2). However, there is also a major difference between these processes. Indeed, both reductions of $\mathbf{1}^+$ are electrochemically reversible ($\Delta E_p^{red} \sim 60$ mV, Table 1)[13,15] which suggests that the initial geometry of the complex is essentially retained[16,17] in its one- and two-electron reduced forms (Scheme 2). This is consistent with the substantial metal (δ) character of the LUMO of [Mo_2Cp_2(μ-SPr^i)$_2$(μ-S)(μ-η^1:η^1-PhCCPh)],[11] a compound that is similar to $\mathbf{1}^+$.

In contrast, the first reduction of $\mathbf{3}^+$ is characterized by slower electron transfer kinetics, as evidenced by the large peak to peak separation[18] (Table 1), and by the scan rate- and temperature dependence of ΔE_p^{red1} [at 18 °C, ΔE_p^{red1}($\mathbf{3}^+$) increases from 90 mV for $v = 0.02$ V s^{-1} to 350 mV for $v = 2$ V s^{-1}; for a common scan rate of 0.2 V s^{-1}, ΔE_p^{red1} increases from 170 mV to 770 mV upon lowering the temperature from 18 to −38 °C]. The shift of E_p^{red1} to more negative potentials as the temperature is lowered (Fig. 2) makes the first reduction of $\mathbf{3}^+$ overlap with the second one at −38 °C. It can also be seen from Fig. 2 that ΔE_p^{red2} is little affected by the temperature changes, what indicates that the second reduction step of $\mathbf{3}^+$ is electrochemically more reversible than the first one.

Table 1 Redox data[a] of the complexes as measured by cyclic voltammetry in CH_2Cl_2–[NBu_4][PF_6] ($v = 0.2$ V s^{-1}, vitreous carbon electrode; potentials are in V/Fc)

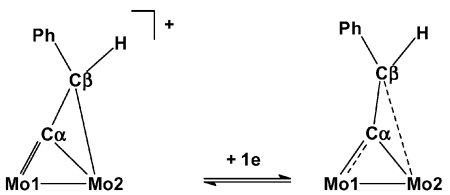
Complex	$E_{1/2}^{red1}$	$E_{1/2}^{red2}$	$E_{1/2}^{ox1}$	$E_{1/2}^{ox2}$
[Mo_2Cp_2(μ-SMe)$_3$(μ-η^1:η^2-C=CHPh)]$^+$ ($\mathbf{1}^+$)	−0.94 (60)	−1.84 (60)	0.4 (irr)	0.7 (irr)
[Mo_2Cp_2(μ-SMe)$_3$(μ-η^1:η^2-C=CHPh)]$^+$ ($\mathbf{3}^+$)	−1.01 (170)	−1.48 (90)	0.44	—
[Mo_2Cp_2(μ-SMe)$_3$(μ-η^1-CHCH$_2$Ph)]$^+$ ($\mathbf{5}^+$)[b]	−0.95	−1.72	0.56 (irr)	0.81 (irr)
[Mo_2Cp_2(μ-SMe)$_3$(μ-η^1:η^2-C≡CPh)] (**2**)	—	—	−0.62	0.17
[Mo_2Cp_2(μ-SMe)$_3$(μ-η^1-CCH$_2$Ph)] (**4**)	—	—	−0.54	0.9 (irr)
[Mo_2Cp_2(μ-SMe)$_3$(μ-CH$_2$CH$_2$Ph)] (**6**)[b]	—	—	−0.68	0.5 (irr)
[Mo_2Cp_2(μ-SMe)$_3$(μ-η^1:η^2-CH=CHPh)] (**7**)	—	—	−0.68	0.43

[a] The figures in parentheses are the peak separation (ΔE_p) in mV; irr: irreversible. [b] Ref. 8*c*.



Scheme 2

Slow electron transfer kinetics may be caused by concurrent structure changes if the modifications in bond lengths and bond angles that accompany electron transfer create a large activation barrier to the electrode reaction.[16,17] In the present case, EHMO calculations on a model of $\mathbf{3}^+$ (SMe replaced by SH bridges) indicate that the LUMO possesses Mo2–Cβ and Mo1–Cα antibonding characters (Scheme 3). Therefore, the first one-electron reduction of $\mathbf{3}^+$ might induce a reorientation of the hydrocarbyl bridge, with an opening of the Mo2–Cα–Cβ angle and a lengthening of the Mo1–Cα and Mo2–Cβ bonds, that would result in an intermediate geometry between those of $\mathbf{3}^+$ and of the μ-alkylidyne ligand in **4** that were both characterized structurally.[8]



Scheme 3

The fact that the reduction of **3** to $\mathbf{3}^-$ is electrochemically reversible suggests[16] that the structure change occurs essentially during the first reduction step.

From these results, it appears that the initial bonding mode of the unsaturated hydrocarbyl bridge has an effect on the primary electrochemical reduction of the complexes.

1.2 The follow-up chemical steps. The scan rate dependence of the peak current ratio $[(i_p^a/i_p^c)^{red1}$ approaches 1 with increasing v] indicates that the primary reduction of both $\mathbf{1}^+$ and $\mathbf{3}^+$ is followed by chemical steps (EC process).[13,15] The products of the follow-up reaction(s) are detected by the presence of oxidation peaks around −0.6 V on the return CV scan (Fig. 1). Controlled-potential electrolyses of the complexes at the potential of their first reduction ($E_{applied}$ = −1.2 V) were complete after the passage of *ca.* 1 F mol^{-1} starting material. CV of the catholyte shows the formation of products with redox potentials consistent with those of the μ-acetylide complex **2** ($E_{1/2}^{ox1}$ = −0.62 V; $E_{1/2}^{ox2}$ = 0.17 V) and of the μ-alkylidyne derivative $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CCH_2Ph)]$ (**4**) ($E_{1/2}^{ox1}$ = −0.54 V; E_p^{ox2} = 0.9 V). The nature of the electrolysis products was confirmed by comparison of the ^{1}H NMR spectrum of the solid isolated from the catholyte (after removal of the supporting electrolyte) with those of authentic samples of **2** and **4**.[8] The ^{1}H NMR spectrum showed that the solid residue extracted from the catholyte consisted in a mixture of **2** and **4** in a *ca.* 1 : 1 ratio in the case of $\mathbf{1}^+$, and in a 70 : 30 ratio in the case of $\mathbf{3}^+$.

Two possibilities may be considered to rationalize these results.

An H-atom transfer between two one-electron reduced species (**1** or **3**) might produce $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CCPh)]$ (**2**) and $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CCH_2Ph)]$ (**4**) after the passage of 1 F mol^{-1} of the cationic starting material. H-atom transfer has been reported in the case of the one-electron reduction of a μ_2-ethylidyne cation to μ_2-vinylidene and μ_2-ethylidene neutral compounds[19] and this was also considered as a possible follow-up step in the electrochemical reduction of the alkylidene complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CHCH_2Ph)]^+$ ($\mathbf{5}^+$).[8c] For complex $\mathbf{3}^+$, the loss of a H atom from **3** might also contribute to the formation of the acetylide complex **2** in more than 50% yield, while an isomerization (1,2-H shift) would be required in the case of the μ-alkyne derivative in order to generate $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CCH_2Ph)]$ (**4**).

On the other hand, it has been shown that **2** is formed upon treatment of $\mathbf{1}^+$ or $\mathbf{3}^+$ with a base[8a] (Scheme 1, top) while **4** resulted from the reaction of $\mathbf{3}^+$ with H^-.[8b] Therefore, the formation of both **2** and **4** upon electrochemical reduction of $\mathbf{3}^+$ could derive from a proton transfer between $\mathbf{3}^+$ and **3**. Such a "father–son" acid–base reaction[8c,20] (Scheme 4, eqn. (1)) would occur if the increased electron density resulting from the one-electron reduction of $\mathbf{3}^+$ to **3** makes the latter

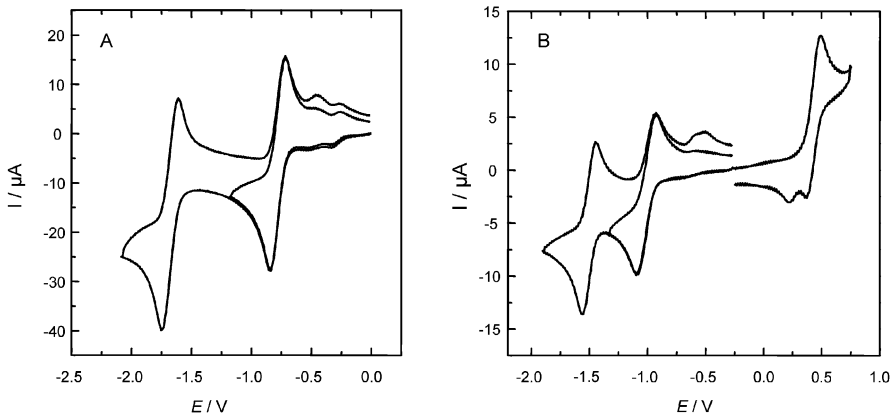


Fig. 1 Cyclic voltammetry of (A) $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}HCCPh)]^+$ $\mathbf{1}^+$ (1.3 mM), and (B) $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}CHPh)]^+$ $\mathbf{3}^+$ (0.9 mM) in CH_2Cl_2–$[NBu_4][PF_6]$ (vitreous carbon electrode, $v = 0.2$ V s^{-1}).

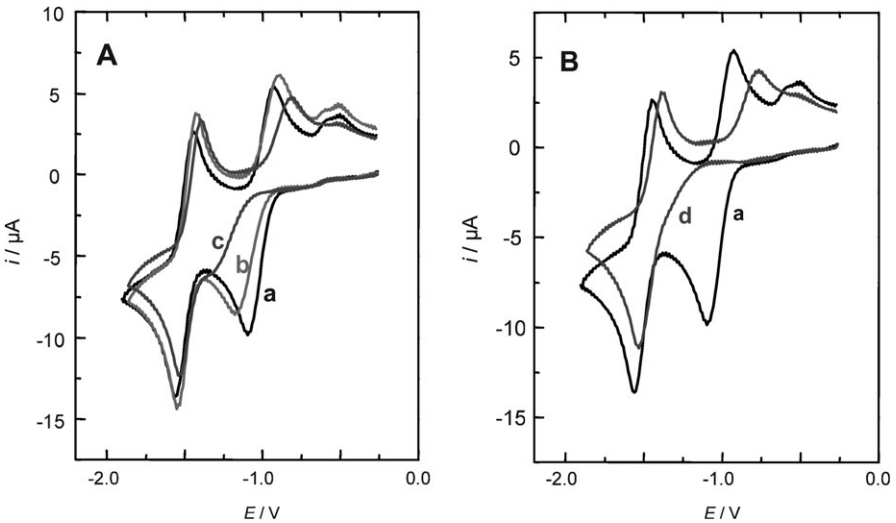
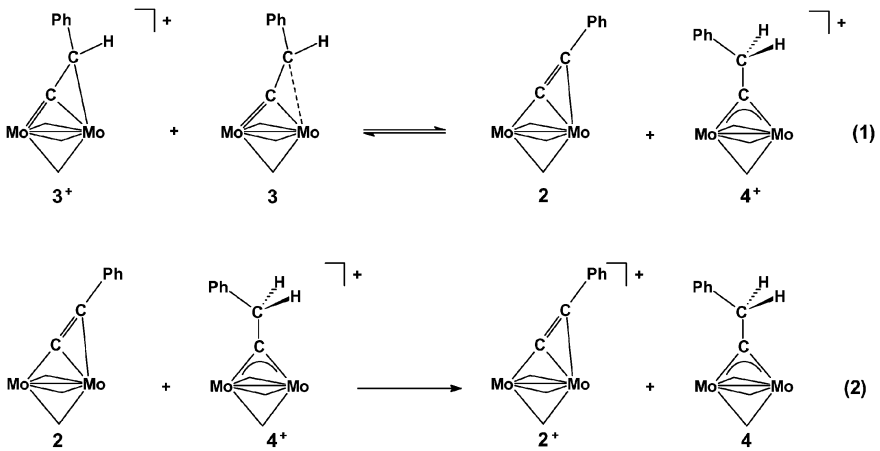


Fig. 2 Temperature dependence of the cyclic voltammetry of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}C{=}CHPh)]^+$ $\mathbf{3}^+$ (0.9 mM, CH_2Cl_2–$[NBu_4][PF_6]$; vitreous carbon electrode; $v = 0.2$ V s^{-1}). (A) (a) 18 °C, (b) −18 °C and (c) −25 °C; (B) (a) 18 °C, (d) −38 °C



Scheme 4 Possible reactions contributing to the formation of **2** and **4** upon reduction of $\mathbf{3}^+$.

sufficiently basic to deprotonate the former.[21] The intervening acid–base reaction would be followed by the reduction of $\mathbf{4}^+$ at the electrode ($E_{applied} = -1.2$ V) or by complex **2** ($E_{1/2}^{ox1}(\mathbf{2}) = -0.62$ V; $E_{1/2}^{red}(\mathbf{4}^+) = -0.54$ V, Scheme 4, eqn. (2)). In the latter case, the overall process in Scheme 4 would be equivalent to a H-atom transfer between $\mathbf{3}^+$ and **3**, and the ECE-type mechanism would be completed by the one-electron reduction of $\mathbf{2}^+$ at the electrode. However, the scan rate dependence of

the current function $(i_p^c)^{red1}/v^{1/2}$ does not provide conclusive evidence for an ECE mechanism [$(i_p^c)^{red1}/v^{1/2}$ was found essentially independent of scan rate]. At this point it should be underlined that the increase in the current function at slow scan rates that would typify an ECE process[15] might be obscured by the fact that the steps (the "father–son" reaction and the electrochemical reduction of either $\mathbf{4}^+$ or $\mathbf{2}^+$) involved in the overall process have opposite effects on $(i_p^c)^{red1}$.[8c]

In the case of the μ-alkyne complex $\mathbf{1}^+$, the acid–base reaction corresponding to eqn. (1) in Scheme 4 would produce **2** and the protonated alkyne complex, that is not $\mathbf{4}^+$ but most probably a μ-vinyl cation.[22] Whether the formation of **4** results from an isomerization or from a sequence of acid–base and electron transfer reactions is not known. It has been shown[8a] that $\mathbf{1}^+$ isomerizes to $\mathbf{3}^+$ (that is a precursor of **4**) but in CH_2Cl_2 this was observed on a much longer time scale (days) than that of controlled-potential electrolysis (hour(s)). A $\mathbf{1}^+ \rightarrow \mathbf{3}^+$ isomerization catalyzed by **1** could be envisaged, but the reactions in Scheme SI-1 (ESI†) are not likely to take place when acid is present, while **4** is also formed by electrolysis of $\mathbf{1}^+$ under acidic conditions.

2 Electrochemical reduction of $\mathbf{1}^+$ and $\mathbf{3}^+$ in acidic medium

2.1 Reduction of $\mathbf{1}^+$ in the presence of acid and electrochemical oxidation of 7. The cyclic voltammetry of $\mathbf{1}^+$ in CH_2Cl_2–$[NBu_4][PF_6]$ in the presence of acid ($HBF_4 \cdot Et_2O$ or CF_3CO_2H, Fig. 3(A), curve (b)) is consistent with the occurrence of an ECE process, characterized by an increase in the first reduction peak current and suppression of the second reduction. This is confirmed by the profile of the plot [$(i_p^c)^{red1}/v^{1/2}$] against v that deviates from linearity at slow scan rates. The occurrence of an ECE mechanism in acidic medium demonstrates that protonation of the one-electron reduced complex (**1**) generates a species that is easier to reduce than $\mathbf{1}^+$. There is ample precedent showing that protonation of alkyne ligands produce alkenyl derivatives.[22] Because the protonation of **1** might afford the μ-vinyl cation [Mo_2Cp_2(μ-SMe)$_3$(μ-η^1:η^2-CH=CHPh)]$^+$ ($\mathbf{7}^+$), we first looked at the CV of complex **7**, and examined its reaction with acids.

2.1.1 The electrochemical oxidation of **7**. The μ-vinyl complex $\mathbf{7}$[8c] undergoes two one- electron oxidation steps (Table 1) that are more reversible in CH_2Cl_2–$[NBu_4][PF_6]$ than in thf. Controlled-potential oxidation of **7** in thf affords $\mathbf{7}^+$ as the major product along with a species reducible around −0.9 V, after consumption of 1.3 F mol^{-1} **7**. Upon addition of a base (2 equiv. Et_3N) to the electrolyzed solution, the reduction peak of $\mathbf{7}^+$ decreases while the reduction at −0.9 V increases, suggesting that the latter might be due to a product arising from the deprotonation of $\mathbf{7}^+$. In thf in the presence of a base (Et_3N or $[NBu_4]OH$), a slight increase of the current function $(i_p^a)^{ox1}/v^{1/2}$ [where $(i_p^a)^{ox1}$ is the first oxidation peak current of **7**] at low v (Fig. 4) suggests the occurrence of an ECE process where the intervening chemical step would consist in either a slow reaction or an equilibrium that is little shifted away from $\mathbf{7}^+$. The scan rate dependence of the current function and the detection potential of the product are consistent with the formation of the μ-alkyne complex $\mathbf{1}^+$ ($E_{1/2}^{red1} = -0.91$ V in thf) upon oxidation of **7** (Scheme 5). The assignment of the intervening chemical step as an acid–base equilibrium is also in agreement with the formation of alkenyl species upon protonation of alkyne ligands.[22]

2.1.2 Reaction of **7** *with acids*. Treatment of **7** with acid generated an intermediate that was detected by CV but could not be isolated nor identified. The final product was shown to depend on the nature of the acid and of the solvent used for the reaction.

When a MeCN–$[NBu_4][PF_6]$ solution of **7** was treated with $HBF_4 \cdot Et_2O$, an intermediate that oxidizes at $E_p^{ox} = -0.22$ V was formed. It eventually afforded [Mo_2Cp_2(μ-SMe)$_3$(MeCN)$_2$]$^+$ ($\mathbf{8}^+$) that was identified by its two characteristic oxidation processes.[23] The fact that styrene was a co-product of the reaction was evidenced by NMR spectroscopy. ^{1}H NMR study of the protonation of **7** by DCl in CD_3CN showed

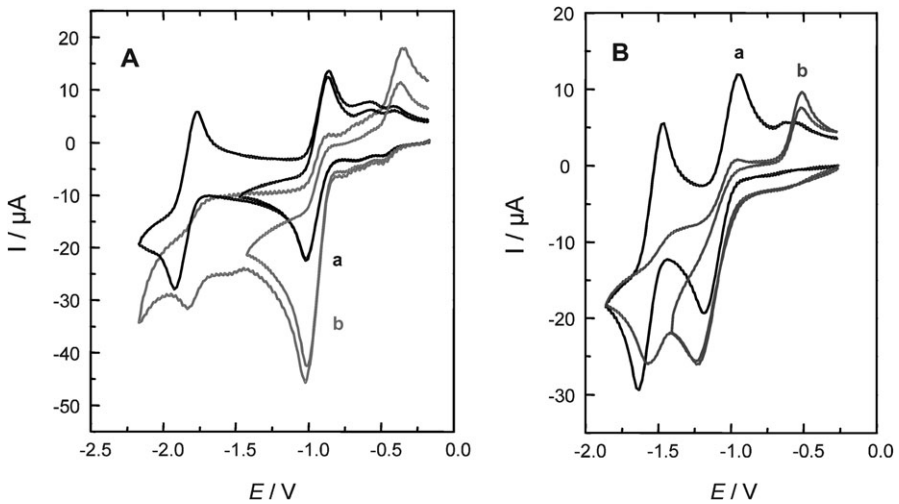


Fig. 3 Cyclic voltammetry of (A) [Mo_2Cp_2(μ-SMe)$_3$(μ-η^1:η^1-HCCPh)]$^+$ $\mathbf{1}^+$ (0.6 mM) (a) before and (b) after addition of 2 equiv. CF_3CO_2H, and (B) [Mo_2Cp_2(μ-SMe)$_3$(μ-η^1:η^2-C=CHPh)]$^+$ $\mathbf{3}^+$ (1.2 mM) (a) before and (b) after addition of 1 equiv. $HBF_4 \cdot Et_2O$ (CH_2Cl_2–$[NBu_4][PF_6]$, vitreous carbon electrode, $v = 0.2$ V s^{-1}).

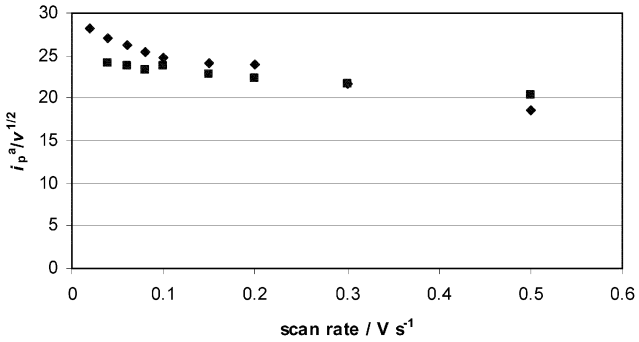
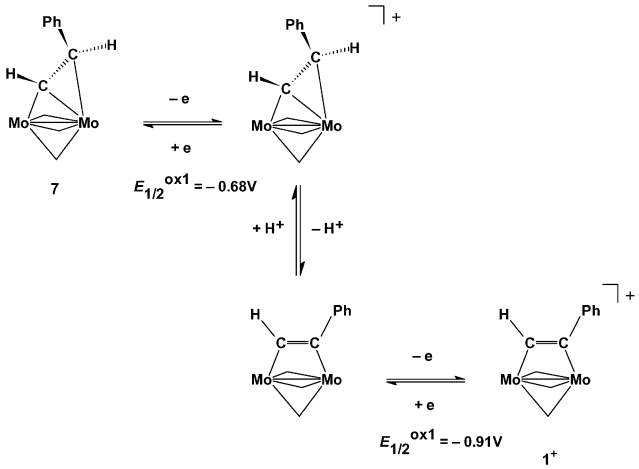


Fig. 4 Scan rate dependence of the current function for the first oxidation of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}HC{=}CHPh)]$ **7** (0.6 mM) in the absence (■) and in the presence (◆) of $[NBu_4]OH$ in thf–$[NBu_4][PF_6]$.



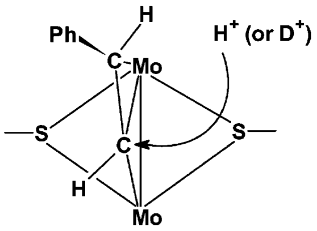
Scheme 5

the formation of only the (*E*)-PhCHCHD isomer, which shows that H^+ (or D^+) attack is stereospecific and occurs on the opposite side of the phenyl group, probably for steric reasons (Scheme 6).

Treatment of **7** with $HBF_4 \cdot Et_2O$ in CH_2Cl_2 produced $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ (**9**)[23] both in its neutral and cationic forms as shown by rotating disc electrode (RDE) voltammetry, while the reaction with CF_3CO_2H in CH_2Cl_2 afforded $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}OCOCF_3)]$ (**10**)[24] essentially quantitatively.[25] CV of a thf–$[NBu_4][PF_6]$ solution of **7** in the presence of 1 equiv. $HBF_4 \cdot Et_2O$ showed that most of the starting material was still present after *ca.* 20 min stirring. Partial oxidation to $\mathbf{7}^+$ and the formation of an intermediate with $E_p^{ox} = -0.3$ V were also noted. Addition of phenylacetylene (5 equiv.) to this solution resulted in the replacement of the oxidation peaks of **7** and of the intermediate by the redox processes of the μ-alkyne complex $\mathbf{1}^+$. These reactions are summarized in Scheme 7, where $[\mathbf{7}\text{-H}]^+$ represents the detected but uncharacterized intermediate.

The release of an alkene molecule upon protonation of an alkenyl complex had already been reported.[26,27]

2.1.3 The electrochemical reduction of $\mathbf{1}^+$ *in acidic medium.* As mentioned above, the reduction of $\mathbf{1}^+$ in the presence of acid follows an ECE process, consistent with the mechanism in



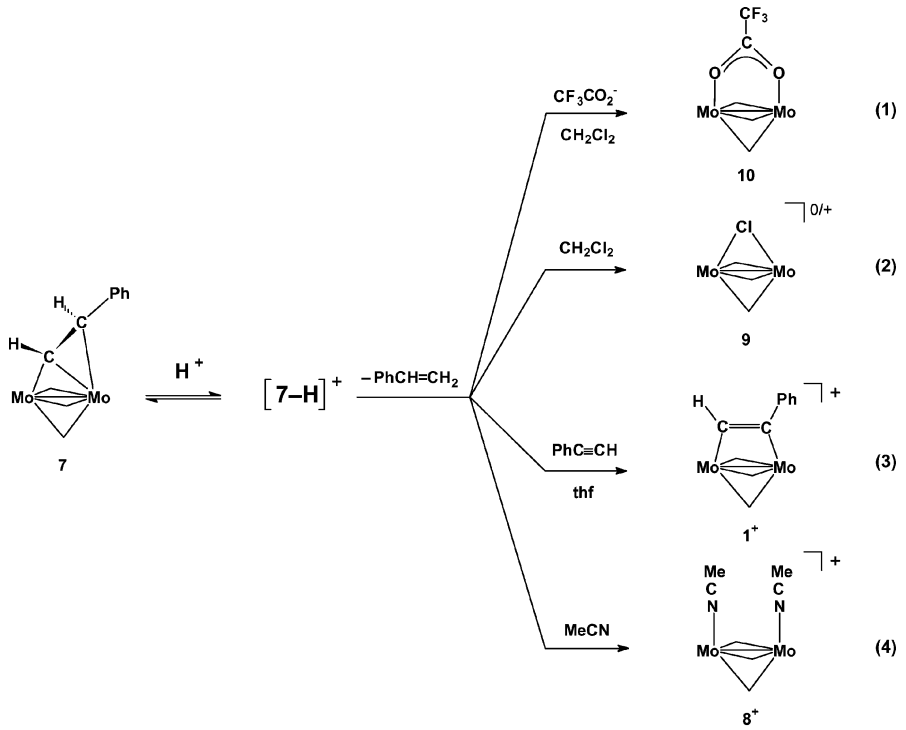
Scheme 6

Scheme 5 (starting from $\mathbf{1}^+$ in this case). Controlled-potential electrolyses of $\mathbf{1}^+$ in the presence of ~2 equiv. of acid under the same conditions as those in Scheme 7 (nature of the acid and of the solvent) produced the complexes also obtained by protonation of **7** (that is $\mathbf{8}^+$, **9** or **10**). Although it does not prove that $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}CH{=}CHPh)]$ (**7**) is an intermediate of the ECE reduction of $\mathbf{1}^+$ in acidic medium, this appears as a reasonable possibility.

However, the reactions in Scheme 5 and Scheme 7 are not sufficient to represent the entire reduction process. Indeed, the μ-alkylidyne complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CCH_2Ph)]$ (**4**) is always a co-product of the electrolyses (~30–50%). While it is expected[28] that **4** be obtained by reduction of $\mathbf{3}^+$ under acidic conditions (see below), there is no straightforward explanation for its formation from $\mathbf{1}^+$ both in the absence and in the presence of acid. Monitoring of a solution of $\mathbf{1}^+$ by RDE voltammetry in acid-free thf–$[NBu_4][PF_6]$ shows that substantial (*ca.* 50%) isomerization to $\mathbf{3}^+$ takes place within 2 h.[29] Therefore, the formation of **4** might result, at least in thf, from partial isomerization of $\mathbf{1}^+$ to $\mathbf{3}^+$ during the electrolysis. Although interconversion of μ-alkylidyne and μ-alkenyl species has been reported,[30] the possibility of an equilibrium between **7** and **4** can be ruled out in the present case on the basis of (i) the formation of **7** (and no **4**) as one of the products obtained by electrolysis of $\mathbf{5}^+$ (no acid, 0 °C),[8c] and (ii) the formation of **4** (no **7**) as one of the products of the reduction of $\mathbf{1}^+$ in the absence of acid.

The transient formation of a μ-alkenyl species upon electrochemical reduction of $\mathbf{1}^+$ in acidic medium is a reasonable possibility, but the intermediate might be different from $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^2\text{-}CH{=}CHPh)]$ (**7**) since **7** was prepared by deprotonation of the alkylidene complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CHCH_2Ph)]^+$ ($\mathbf{5}^+$) at the β carbon atom,[8c] while the intermediate results from the protonation of the reduced alkyne complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}CHCPh)]$ (**1**). Conceivably, **1** may possess different sites for protonation. These reactions might afford distinct μ-alkenyl complexes [for example with hydrogen atoms either in a *cis* (**7′**) or *trans* (**7**) disposition] that show different reactivity as far as isomerization to the alkylidyne $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CCH_2Ph)]$ (**4**) is concerned.

Taken together, the reactions in Scheme 5 and Scheme 7 (eqn. (3)) suggest the possibility to achieve the catalytic reduction of phenylacetylene to styrene by reducing $\mathbf{1}^+$ in thf, in the presence of an excess of acid and of PhC≡CH. Controlled-potential electrolysis of $\mathbf{1}^+$ was thus performed at −1.2 V in the presence of 10 equiv. $HBF_4 \cdot Et_2O$ and of a large excess of PhC≡CH (15–40 equiv.). The electrolysis was complete after consumption of *ca.* 8 F mol^{-1} $\mathbf{1}^+$ while only



Scheme 7 Protonation of **7** by CF_3CO_2H [reaction (1)] or $HBF_4 \cdot Et_2O$ [reactions (2)–(4)].

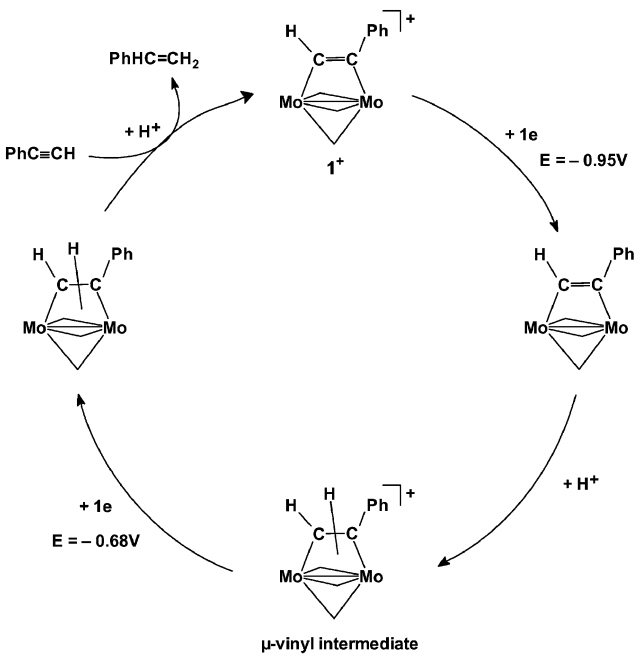
2 F mol^{-1} $\mathbf{1}^+$ were used in the absence of the unsaturated substrate. Although the charge (11 F mol^{-1} $\mathbf{1}^+$) that was expected under the present (acid limiting) conditions was not reached, the difference with respect to the charge used when no PhC≡CH is present can be assigned to the reduction of this substrate (Scheme 8).

GC/MS analysis of the electrolyzed solution confirmed the formation of about 3 mole of styrene per mole of $\mathbf{1}^+$ (that is a 60% yield, since the maximum amount of styrene expected under these acid-limiting conditions was 5 mol/mol $\mathbf{1}^+$), corresponding to a charge consumption of *ca.* 6 F mol^{-1} $\mathbf{1}^+$. The cumulated amount of styrene and phenylacetylene found after electrolysis accounts for only *ca.* 50% of the phenylacetylene initially present. The presence of **4** in the catholyte once more underlines that uncontrolled reactions perturbed the course of the reduction of $\mathbf{1}^+$.

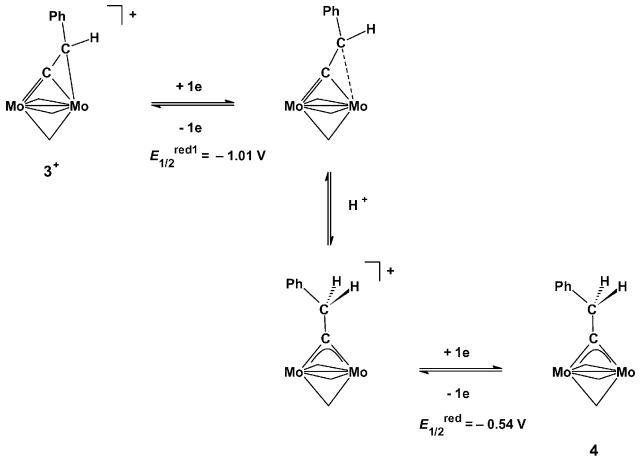
Despite the side reactions producing **4**, the formation of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}OCOCF_3)]$, $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)]$ or $[Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)_2]^+$ upon electrochemical reduction of $\mathbf{1}^+$ in acidic medium demonstrates that the initial alkyne bridge was converted to a labile ligand and eventually released, as confirmed by the detection of styrene after controlled-potential electrolysis.

2.2 Electrochemical reduction of $\mathbf{3}^+$ in the presence of acid.

The electrochemical reduction of the μ-vinylidene complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}CHPh)]^+$ $\mathbf{3}^+$ in the presence of acid ($HBF_4 \cdot Et_2O$) occurs according to an ECE mechanism, like that of the μ-alkyne isomer. This is evidenced by the increase of the first reduction peak current (Fig. 3(B)) and by the scan rate dependence of the associated current function which deviates markedly from linearity at low *v*. Consistent with the reactivity of vinylidene compounds with acid,[28] the reduction of $\mathbf{3}^+$ in the presence of protons produced the μ-alkylidyne complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CCH_2Ph)]$ (**4**) that was detected by its first oxidation at $E_{1/2}^{ox1} = -0.54$ V (Fig. 3(B), Scheme 9). Controlled-potential electrolysis ($E_{applied} = -1.2$ V, 1 equiv. $HBF_4 \cdot Et_2O$ in CH_2Cl_2–$[NBu_4][PF_6]$) afforded the μ-acetylide complex $[Mo_2Cp_2$



Scheme 8 The identity of the μ-vinyl intermediate (**7** or **7′**) is not known.



Scheme 9

(μ-SMe)$_3$(μ-η^1:η^2-CCPh)] (**2**) and the μ-alkylidyne **4** in a 1 : 4 ratio after the transfer of 1.8 F mol^{-1} **3**$^+$. Since **2** is known to protonate readily to **3**$^+$,[8a] its presence (20%) after completion of the electrolysis indicates that there has been a shortage of H$^+$ during the reduction process. This is assigned to a futile proton reduction loop due to oxidation of **4** by H$^+$,[12] followed by reduction of **4**$^+$ at the electrode. Controlled-potential electrolysis in the presence of 2 equiv. acid produced **4** in almost quantitative yield[25] as expected, after the transfer of 2.1 F mol^{-1} **3**$^+$. The identity of the products of the electrolyses was ascertained by comparison of the ^{1}H NMR spectrum of the solid extracted from the catholyte with those of authentic samples of **2** and **4**.

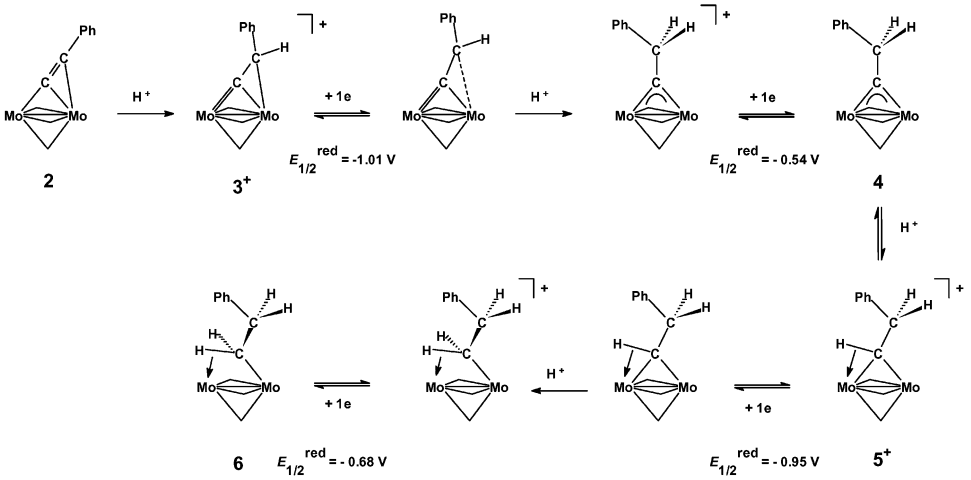
It has been shown that protonation of **4** by HBF$_4$ · Et$_2$O produces the μ-alkylidene complex [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-η^1-CHCH$_2$Ph)]$^+$ (**5**$^+$)[8b] (along with **4**$^+$ as a by-product[12]), and that the electrochemical reduction of **5**$^+$ in acidic medium affords the μ-alkyl complex [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-CH$_2$CH$_2$Ph)] (**6**) along with [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-Cl)] (**9**).[8c] The latter was previously shown to arise from the reaction of **6** and/or **7** with HBF$_4$ · Et$_2$O in CH$_2$Cl$_2$.[8c]

Therefore, by setting the electrolysis potential at −1.2 V, it should be possible to generate **6** directly from the μ-acetylide complex **2** along the {4H$^+$/4e} process in Scheme 10 since the redox steps involved in this sequence all occur at less negative potentials than the initial one ($E_{1/2}^{red}$ = −1.01 V).

Controlled-potential electrolysis of a CH$_2$Cl$_2$–[NBu$_4$][PF$_6$] solution of **2** in the presence of 4 equiv. HBF$_4$ · Et$_2$O ($E_{applied}$ = −1.2 V) leads to the formation of the alkylidyne complex **4** essentially quantitatively[25] after consumption of 4.6 F mol^{-1} **3**$^+$. The excess charge passed with respect to that needed to produce **4** is assigned to proton reduction (see above), but no attempt was made to detect H$_2$. A supplement of 3 equiv. acid was added at this stage, and the electrolysis was resumed at −1.2 V. Cyclic voltammetry of the catholyte obtained after the passage of a further 2.5 F mol^{-1} **3**$^+$ showed the presence of the alkyl compound [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-CH$_2$CH$_2$Ph)] (**6**) (∼60%) along with the chloro-bridged species [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-Cl)] (**9**) in *ca.* 40% yield.[25]

A controlled-potential electrolysis of a CH$_2$Cl$_2$–[NBu$_4$][PF$_6$] solution of **2** was performed in the presence of a larger excess of acid (about 10 equiv. HBF$_4$ · Et$_2$O) in an attempt to overcome the limiting step of the process, that is the protonation of the alkylidyne complex **4**. Under these conditions ($E_{applied}$ = −1.2 V; 5.4 F mol^{-1} **3**$^+$), [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-CH$_2$CH$_2$Ph)] (**6**) was effectively obtained (*ca.* 40%[25]), but **4** (*ca.* 45%[25]) and the chloro-bridged derivative **9** (*ca.* 15%[25]) were also detected by CV of the catholyte.

Although the process in Scheme 10 is rendered non-quantitative by the limiting protonation of [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-η^1-CCH$_2$Ph)] (**4**) that is also responsible for a {H$^+$/e} waste, the electrochemical reduction of the C≡C triple bond of a μ-alkynyl species (**2**) straight to the C–C single bond of a μ-alkyl complex (**6**) is unprecedented as far as we know. Treatment of **6** with acid resulted in the oxidation to **6**$^+$ and in the formation of [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-Cl)] (**9**). GC/MS analysis of the solution obtained by controlled-potential electrolysis of the μ-alkylidene complex [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-η^1-CHCH$_2$Ph)]$^+$ (**5**$^+$) in the presence of an excess of HBF$_4$ · Et$_2$O (3 equiv, 3 F mol^{-1} **5**$^+$) revealed the presence of both styrene (0.24 mol per mol **5**$^+$) and ethylbenzene (0.28 mol per mol **5**$^+$), along with a mixture of **6** and **6**$^+$ in a combined 45% yield, [Mo$_2$Cp$_2$(μ-SMe)$_3$(μ-Cl)] (*ca.* 25%) and unidentified products.[25] While the formation of styrene might arise from the protonation of the μ-vinyl complex [Mo$_2$Cp$_2$(μ-SMe)$_3$



Scheme 10

(μ-η^1:η^2-CH=CHPh)] (**7**) that was previously shown to be produced upon reduction of $\mathbf{5}^+$,[8c] the formation of some $PhCH_2CH_3$ suggests that the μ-alkyl complex **6** may undergo protonation at the α-carbon and release the hydrocarbyl group as an alkane.

3 Concluding comments

3.1 On the effect of the initial {μ-CC} binding mode upon the reduction processes. The results presented above show that the electrochemical reductions of the μ-alkyne and μ-vinylidene complexes in the presence of acid result in successive transformations of the hydrocarbyl bridge along two main routes that depend, to some extent, upon the initial {μ-CC} binding mode (Scheme 11).

The reduction of the vinylidene isomer $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-C=CHPh})]^+$ $\mathbf{3}^+$ consists in two consecutive ECE processes separated by a difficult protonation. These {H^+/e} transfer steps afford an alkyl derivative *via* alkylidyne and alkylidene intermediates. While protonation of vinylidene to alkenyl is known,[31] we obtained no evidence for protonation of **3** at the α carbon atom, that would have generated $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-CH=CHPh})]^+$, a μ-alkenyl complex such as $\mathbf{7}^+$.

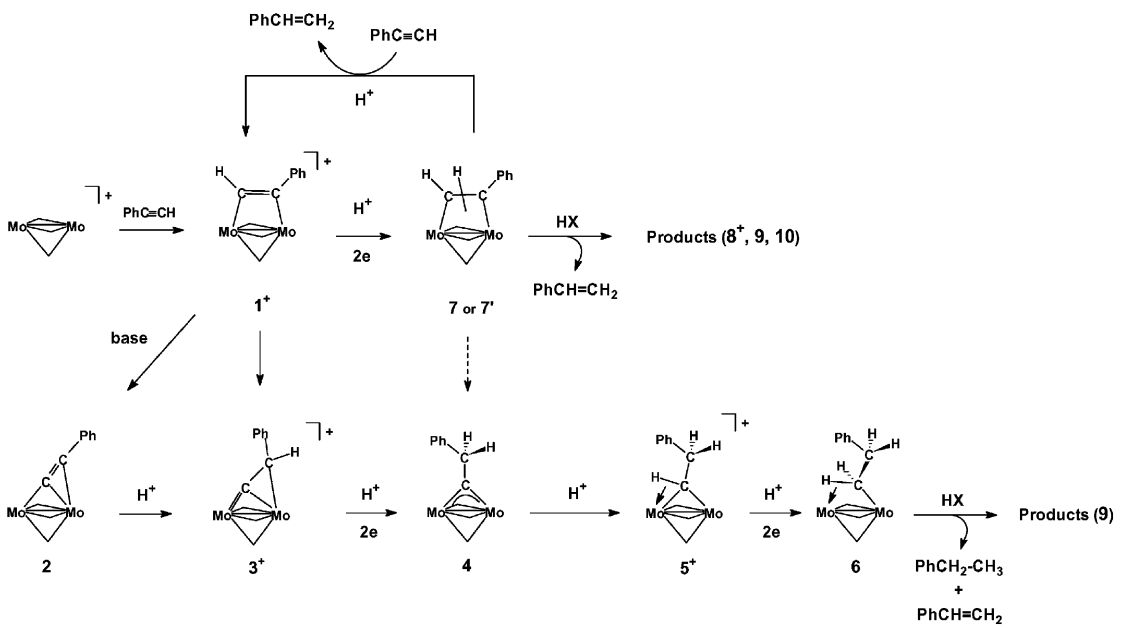
In the case of the alkyne complex $\mathbf{1}^+$, the initial ECE process probably produces a μ-alkenyl complex (**7** or an isomer, **7′**) that releases the hydrocarbyl unit as styrene upon protonation. This is in keeping with the known reactivity of alkyne and alkenyl compounds with acid.[22,26,27] Under appropriate conditions (thf, PhC≡CH), the starting material $\mathbf{1}^+$ can be regenerated, so the conditions are met for a catalytic reduction of phenylacetylene to styrene. Nevertheless, this process suffers from severe restrictions due to unidentified side reactions that generate $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CCH_2Ph)]$ **4**.

Therefore, while the initial binding mode of the hydrocarbyl ligand appears to privilege one route over the other, there exist ways through that connect both pathways.

A parallel can be made between the results of the present work and those of previous studies focused on the reduction of {N=N} ligands bound at the same $\{[Mo_2Cp_2(\mu\text{-}SMe)_3]^+\}$ site. The electrochemical reduction of the organodiazene complex $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-HN=NR})]^+$ in acidic medium resulted in the cleavage of the N=N bond (and the release of ammonia plus an amine) when R = Ph, but not when R = Me.[4d] This was assigned to the rearrangement of the {NN} ligand from a μ-η^1:η^1 to a μ-η^1 coordination mode at the hydrazido(1−) stage that was possible only for R = Ph. When R = Me, the electrochemical reduction in acidic medium of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-N=NHMe})]^+$, that is the hydrazido(2−) isomer of the methyldiazene complex, afforded NH_3 and NH_2Me,[4d] showing that the initial bonding mode of the {NN} ligand affected the course of the reduction process.

3.2 Relevance to the reduction of the C≡C bond by nitrogenases? Recent studies provided unique information on the bonding mode and the geometry of an intermediate trapped by rapid freezing of the α-70^{Ala} mutant Mo nitrogenase turning over in the presence of propargyl alcohol ($HC{\equiv}CCH_2OH$) as the substrate.[7] The EPR-detection of the substrate-derived intermediate identified as the {$2H^+$/2e}-reduced form of propargyl alcohol (that is allyl alcohol, $H_2C{=}CHCH_2OH$) bound in a η^2 fashion to a single iron atom of a [4Fe–4S] face of FeMo-co[7b] was dependent upon its stabilization by hydrogen bonding with α-195^{His}.[7c] Although this gives unprecedented data on the ultimate intermediate of the reduction of a C≡C bond by α-70^{Ala}-modified Mo nitrogenase, this does not preclude that the initial binding mode of the alkyne substrate may be different.

The reactions occurring at the bimetallic-sulfur site (Scheme 11) are reminiscent to those proposed to illustrate the reduction of C_2H_2 by nitrogenase, on the bases of kinetic studies of the enzyme and of the chemistry of mononuclear model compounds.[1b,32] Keeping in mind the limitations underlined



Scheme 11

above, the {$2H^+/2e$} reduction of an alkyne ligand bound in a μ-η^1:η^1 fashion to a bimetallic-sulfur site to a free alkene, and the {$4H^+/4e$} reduction of an isomeric μ-η^1:η^2 vinylidene ligand bound at the same site to an alkyl complex (and some alkane) raise the question of whether the substrate specificity shown by Mo-, V- and Fe-dependent nitrogenases might result from a different coordination mode of the C≡C substrate to FeMo-co, FeV-co and FeFe-co.

Experimental

Methods and materials

All the experiments were carried out under an inert atmosphere, using Schlenk techniques for the syntheses. Tetrahydrofuran (thf) and dichloromethane were purified as described previously.[4c] Acetonitrile (Merck) was used as received. Fluoroboric acid (diethyl ether complex), phenylacetylene and trifluoroacetic acid (Aldrich) were used as received. The complexes $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}HCCPh)]^+$ (**1**$^+$), $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CCPh)]$ (**2**), $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{=}CHPh)]^+$ (**3**$^+$), $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CCH_2Ph)]$ (**4**), $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{-}CHCH_2Ph)]^+$ (**5**$^+$), $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}CH_2CH_2Ph)]$ (**6**) and $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH{=}CHPh)]$ (**7**) were prepared according to reported procedures.[8]

The preparation and the purification of the $[NBu_4][PF_6]$ supporting electrolyte were as described previously.[4c] Cyclic voltammetric experiments were performed with a PGSTAT 12 driven by an AUTOLAB software. Controlled-potential electrolyses were performed using Tacussel/Radiometer GCU potentiostat and IG5-N integrator. The cell and electrodes were as described previously.[4c] All the potentials (text, tables, figures) are quoted against the ferrocene-ferrocenium couple; ferrocene was added as an internal standard at the end of the experiments.

The ^{1}H NMR spectra ($CDCl_3$ or C_6D_6) were recorded with a Bruker AC 300 or AMX 400 spectrometer and were referenced to $SiMe_4$. GC-MS analysis was performed on a GC/MS VARIAN 2100T Technology Ion Trap, equiped with a Chrompack CpSil 8 CB capillary column (30 m × 0.25 mm internal diameter).

Controlled-potential electrolyses of 1$^+$ and 3$^+$

In the absence of acid. In a typical experiment 10 mg (1.5×10^{-5} mol) of complex were dissolved in 15 mL of CH_2Cl_2–$[NBu_4][PF_6]$ under N_2, and the potential of the Pt cathode was set at −1.2 V. The electrolysis was complete after the transfer of about 1 F mol^{-1} complex. The catholyte was cannulated in a Schlenk flask under N_2, and the solvent was removed under reduced pressure. 10 mL pentane were then added to the solid residue and the mixture was stirred for 10 min before being filtrated. The filtrate was taken down to dryness, and the solid dried under vacuum. The solid residue was dissolved in C_6D_6 or $CDCl_3$ and the products formed by electrolysis were characterized by ^{1}H NMR spectroscopy.

In the presence of $HBF_4 \cdot Et_2O$. The same conditions as above were used except for the addition of 1 or 2 equiv. $HBF_4 \cdot Et_2O$ before the electrolysis ($E_{applied}$ = −1.2 V) is started. The catholyte was treated as above.

Controlled-potentiel reduction of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}HCCPh)]^+$ (1$^+$) in the presence of acid and phenylacetylene. 1$^+$ (0.0084 g, 1.29×10^{-5} mol) was dissolved in 30 mL thf–$[NBu_4][PF_6]$ in the electrochemical cell wrapped in an aluminium foil. After addition of 10 equivalents $HBF_4 \cdot Et_2O$ and 15 equiv. (657 mg L^{-1}) phenylacetylene, the solution was electrolysed (graphite electrode) at −1.2 V *vs.* Fc/Fc^+. The electrolysis was complete after the passage of *ca.* 8 F mol^{-1} 1$^+$ (*ca.* 0.8 F mol^{-1} H^+). The catholyte was filtered through a SPE (DSC-18 500 mg) cartridge in order to remove the metal products and the supporting electrolyte. The filtrate was subjected to GC/MS analysis for phenylacetylene and styrene that confirmed the presence of styrene (140 mg L^{-1}) and of phenylacetylene (215 mg L^{-1}) after electrolysis. The amount of styrene detected after electrolysis following the above procedure accounted for about 60% of the maximum amount that could form under these acid-limiting conditions.

Controlled-potentiel reduction of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CHCH_2Ph)]^+$ (5$^+$) in the presence of acid, and ethylbenzene analysis. A solution of 5$^+$ (14 mg, $2.15\ 10^{-5}$ mol) in 20 mL CH_2Cl_2 in the presence of 3 equiv. $HBF_4 \cdot Et_2O$ was electrolyzed at −1.2 V. After the passage of *ca.* 3 F mol^{-1} 5$^+$, the electrolysis was stopped, and 1 equiv. of acid was added to the catholyte. After filtration through a SPE (DSC-18 500 mg) cartridge a sample of the filtrate was subjected to GC-MS for detection of styrene and of ethylbenzene. The amounts of styrene (*ca.* 24.5 mg L^{-1}) and ethylbenzene (*ca.* 32.80 mg L^{-1}) were quantified using calibrations plots.

EH calculations

Extended Hückel calculations were performed with the CACAO package developed by Mealli and Proserpio.[33] Standard atomic parameters were taken for H and C.[34] The exponents (ζ) and the valence shell ionization potential (H_{ii} in eV) used for Mo are the standard CACAO parameters,[33] that is, respectively, 1.956 and −8.34 for 5s, 1.921 and −5.24 for 5 p. The H_{ii} value for 4d was −10.50; a linear combination of two Slater-type orbitals (ζ_1 = 4.54, c_1 = 0.5899; ζ_2Å = 1.900, c_2 = 0.5899) was used to represent the atomic 4d orbitals.

The model used in the calculations for 3$^+$ was built from the crystallographically determined bond lengths and bond angles of this complex[8] (except C–H = 1.09 Å) with the Me substituents of the equatorial S atoms replaced by H.

Acknowledgements

The authors thank the CNRS (Centre National de la Recherche Scientifique) and UBO (Université de Bretagne Occidentale) for financial support.

References

1 (*a*) F. Barrière, M. C. Durrant and C. J. Pickett, in *Catalysts for Nitrogen Fixation: Nitrogenases, Relevant Chemical Models, and Commercial Processes*, ed. B. E. Smith, R. L. Richards and W. E. Newton, Kluwer Academic Publishers, The Netherlands, 2004, ch. 7, pp. 161; (*b*) D. J. Evans, R. A. Henderson and B. E. Smith,

in *Bioinorganic Catalysis*, ed. J. Reedijk and E. Bouwman, Marcel Dekker, New York, 2nd edn, 1999, ch. 7, pp. 153; (*c*) B. A. McKay and M. D. Fryzuk, *Chem. Rev.*, 2004, **104**, 385; (*d*) F. Barrière, *Coord. Chem. Rev.*, 2003, **236**, 71; (*e*) D. Sellmann and J. Sutter, *J. Biol. Inorg. Chem.*, 1996, **1**, 587; (*f*) D. Coucouvanis, *J. Biol. Inorg. Chem.*, 1996, **1**, 594; (*g*) M. Hidai and Y. Mizobe, *Chem. Rev.*, 1995, **95**, 1115; (*h*) E. A. MacLachlan and M. D. Fryzuk, *Organometallics*, 2006, **25**, 1530, and references therein.

2 (*a*) D. Sellmann, B. Hautsch, A. Rösler and F. W. Heinemann, *Angew. Chem., Int. Ed.*, 2001, **40**, 1505; (*b*) D. Sellmann, B. Hautsch, A. Rösler and F. W. Heinemann, *Angew. Chem.*, 2001, **113**, 1553, and references therein; (*c*) D. Sellmann, A. Hille, A. Rössler, F. W. Heinemann, M. Moll, G. Brehm, S. Schneider, M. Reiher, B. A. Hess and W. Bauer, *Chem.–Eur. J.*, 2004, **10**, 819; (*d*) D. Sellmann, A. Hille, F. W. Heinemann, M. Moll, A. Rössler, J. Sutter, G. Brehm, M. Reiher, B. A. Hess and S. Schneider, *Inorg. Chim. Acta*, 2003, **348**, 194; (*e*) M. Reiher, O. Salomon, D. Sellmann and B. A. Hess, *Chem.–Eur. J.*, 2001, **7**, 5195, and references therein.

3 C. J. Pickett, *J. Biol. Inorg. Chem.*, 1996, **1**, 601.

4 (*a*) P. Schollhammer, E. Guénin, F. Y. Pétillon, J. Talarmin, K. W. Muir and D. S. Yufit, *Organometallics*, 1998, **17**, 1922; (*b*) F. Y. Pétillon, P. Schollhammer, J. Talarmin and K. W. Muir, *Inorg. Chem.*, 1999, **38**, 1954; (*c*) J.-Y. Cabon, C. Le Roy, K. W. Muir, F. Y. Pétillon, F. Quentel, P. Schollhammer and J. Talarmin, *Chem.–Eur. J.*, 2000, **6**, 3033; (*d*) N. Le Grand, K. W. Muir, F. Y. Pétillon, C. J. Pickett, P. Schollhammer and J. Talarmin, *Chem.–Eur. J.*, 2002, **8**, 3115.

5 (*a*) L. C. Seefeldt, I. G. Dance and D. R. Dean, *Biochemistry*, 2004, **43**, 1401; (*b*) D. C. Rees, *Annu. Rev. Biochem.*, 2002, **71**, 221; (*c*) J. Christiansen, D. R. Dean and L. C. Seefeldt, *Annu. Rev. Plant Physiol. Plant Mol. Biol.*, 2001, **52**, 269; (*d*) J. B. Howard and D. C. Rees, *Chem. Rev.*, 1996, **96**, 2965; (*e*) B. K. Burgess and D. J. Lowe, *Chem. Rev.*, 1996, **96**, 2983; (*f*) J. Kim and D. C. Rees, *Biochemistry*, 1994, **33**, 389; (*g*) B. K. Burgess, *Chem. Rev.*, 1990, **90**, 1377, and references therein.

6 (*a*) J. Kim and D. C. Rees, *Science*, 1992, **257**, 1677; (*b*) J. Kim and D. C. Rees, *Science*, 1993, **260**, 792; (*c*) S. M. Mayer, B. M. Lawson, C. A. Gormal, M. Roe and B. E. Smith, *J. Mol. Biol.*, 1999, **292**, 871; (*d*) O. Einsle, F. A. Tezcan, S. L. Andrade, B. Schmid, M. Yoshida, J. B. Howard and D. C. Rees, *Science*, 2002, **297**, 1696.

7 (*a*) P. M. C. Benton, M. Laryukhin, S. M. Mayer, B. M. Hoffman, D. R. Dean and L. C. Seefeldt, *Biochemistry*, 2003, **42**, 9102; (*b*) H.-I. Lee, R. Y. Igarashi, M. Laryukhin, P. E. Doan, P. C. Dos Santos, D. R. Dean, L. C. Seefeldt and B. M. Hoffman, *J. Am. Chem. Soc.*, 2004, **126**, 9563; (*c*) R. Y. Igarashi, P. C. Dos Santos, W. G. Niehaus, I. G. Dance, D. R. Dean and L. C. Seefeldt, *J. Biol. Chem.*, 2004, **279**, 34770; (*d*) B. M. Barney, R. Y. Igarashi, P. C. Dos Santos, D. R. Dean and L. C. Seefeldt, *J. Biol. Chem.*, 2004, **279**, 53621; (*e*) H.-I. Lee, M. Sorlie, J. Christiansen, T.-C. Yang, J. Chao, D. R. Dean, B. J. Hales and B. M. Hoffman, *J. Am. Chem. Soc.*, 2005, **127**, 15880.

8 (*a*) P. Schollhammer, N. Cabon, J.-F. Capon, F. Y. Pétillon, J. Talarmin and K. W. Muir, *Organometallics*, 2001, **20**, 1230; (*b*) N. Cabon, P. Schollhammer, F. Y. Pétillon, J. Talarmin and K. W. Muir, *Organometallics*, 2002, **21**, 448; (*c*) N. Cabon, A. Le Goff, C. Le Roy, F. Y. Pétillon, P. Schollhammer, J. Talarmin, J. E. McGrady and K. W. Muir, *Organometallics*, 2005, **24**, 6268.

9 (*a*) M. D. Fryzuk, S. A. Johnson, B. O. Patrick, A. Albinati, S. A. Mason and T. F. Koetzle, *J. Am. Chem. Soc.*, 2001, **123**, 3960; (*b*) M. D. Fryzuk, *Chem. Rec.*, 2003, **3**, 2.

10 The crystal structure of $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}\eta^1{:}\eta^1\text{-}HCCCO_2Me)]^+$ shows that the coordination of the alkyne is as illustrated in Scheme 1 for complex $\mathbf{1}^+$; P. Schollhammer and W. Solo-Ojo, unpublished results.

11 H. Adams, M. J. Morris, P. Mountford, R. Patel and S. E. Spey, *J. Chem. Soc., Dalton Trans.*, 2001, 2601.

12 A. Le Goff, C. Le Roy, F. Y. Pétillon, P. Schollhammer, J. Talarmin and R. A. Henderson, to be published.

13 The parameters i_p and E_p are respectively the peak current and the peak potential of a redox process; $E_{1/2} = (E_p^a + E_p^c)/2$; E_p^a, i_p^a and E_p^c, i_p^c are respectively the potential and the current of the anodic and of the cathodic peak of a reversible process; $\Delta E_p = E_p^a - E_p^c$. CV stands for cyclic voltammetry; v (V s^{-1}) is the scan rate in CV experiments.

14 N. G. Connelly, W. E. Geiger, M. C. Lagunas, B. Metz, A. L. Rieger, P. H. Rieger and M. J. Shaw, *J. Am. Chem. Soc.*, 1995, **117**, 12202.

15 (*a*) A. J. Bard and L. R. Faulkner, *Electrochemical Methods. Fundamentals and Applications*, Wiley, New York, 1980, ch. 11, pp. 429; (*b*) E. R. Brown and R. F. Large, in *Techniques of Chemistry Volume I-Physical Methods of Chemistry*, Part IIA, ed. A. Weissberger, Wiley, 1971, ch. 6, pp. 423.

16 Although Nernstian electron transfers are usually associated with preservation of the structural integrity of the redox partners, and slow electron transfers are taken as indicative of accompanying structure change, this is not necessarily true, see: (*a*) ref. 17; (*b*) A. M. Bond and K. B. Oldham, *J. Phys. Chem.*, 1983, **87**, 2492; (*c*) T. Gennett, W. E. Geiger, B. Willett and F. C. Anson, *J. Electroanal. Chem.*, 1987, **222**, 151; (*d*) A. Miedaner, R. C. Haltiwanger and D. L. DuBois, *Inorg. Chem.*, 1991, **30**, 417; (*e*) A. J. Downard, L. R. Hanton, D. A. McMorran and R. L. Paul, *Inorg. Chem.*, 1993, **32**, 6028, and references therein.

17 For leading references on structural changes accompanying electron transfer steps, see: (*a*) W. E. Geiger, *Prog. Inorg. Chem.*, 1985, **33**, 275, and references therein; (*b*) D. H. Evans, K. M. O'Connell, *Electroanalytical Chemistry*, ed. A. J. Bard, Marcel Dekker, New York, 1986, vol. 14, pp. 113, and references therein.

18 Comparison of ΔE_p for the first reduction of $\mathbf{1}^+$ to that of $\mathbf{3}^+$, and for the first and second reductions of $\mathbf{3}^+$ provides an estimate for the contribution of slow electron transfer kinetics (*vs.* uncompensated solution resistance) in ΔE_p, since all were measured under the same experimental conditions.

19 T. Aase, M. Tilset and V. D. Parker, *Organometallics*, 1989, **8**, 1558.

20 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.

21 Considering the fact that $\mathbf{3}^+$ is likely to be a much stronger base than **3**, an electrolysis carried out at the potential of the second reduction of $\mathbf{3}^+$ should involve a proton transfer reaction between $\mathbf{3}^+$ and $\mathbf{3}^-$ that would lead to the formation of **2** and **4** in 1 : 1 ratio. That this is effectively the case was shown by a differential pulse polarogram of the catholyte obtained after completion of the electrolysis at –1.8 V (n = 1 F mol^{-1} $\mathbf{3}^+$).

22 For examples of the protonation of alkyne to alkenyl ligands, see: (*a*) M. Etienne, C. Carfagna, P. Lorente, R. Mathieu and D. de Montauzon, *Organometallics*, 1999, **18**, 3075; (*b*) C. P. Casey, J. T. Brady, T. M. Boller, F. Weinhold and R. K. Hayashi, *J. Am. Chem. Soc.*, 1998, **120**, 12500; (*c*) G. A. Acum, M. J. Mays, P. R. Raithby and G. A. Solan, *J. Organomet. Chem.*, 1995, **492**, 65; (*d*) L.-S. Wang and M. Cowie, *Can. J. Chem.*, 1995, **73**, 1058; (*e*) R. A. Henderson, K. E. Oglieve and P. Salisbury, *J. Chem. Soc., Dalton Trans.*, 1995, 2479; (*f*) M. J. Chetcuti, J. C. Gordon, K. A. Green, P. E. Fanwick and D. Morgenstern, *Organometallics*, 1989, **8**, 1790; (*g*) R. F. Gerlach, D. N. Duffy and M. D. Curtis, *Organometallics*, 1983, **2**, 1172.

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

24 M. Le Hénanf, C. Le Roy, K. W. Muir, F. Y. Pétillon, P. Schollhammer and J. Talarmin, *Eur. J. Inorg. Chem.*, 2004, 1687.

25 The yields of the products formed upon controlled-potential electrolyses were obtained by comparison of the CV peak current of the products with that of the starting material before controlled-potential electrolysis, assuming identical diffusion coefficients.

26 D. Glushove, G. Hogarth and M. H. Lavender, *J. Organomet. Chem.*, 1997, **528**, 3.

27 D. S. Frohnapfel and J. L. Templeton, *Coord. Chem. Rev.*, 2000, **206–207**, 199, and references therein.

28 For examples of protonation of vinylidene to alkylidyne, see: (*a*) G. M. Dawkins, M. Green, J. C. Jefferey, C. Sambale and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1983, 499; (*b*) R. A. Colborn, D. L. Davies, A. F. Dyke, A. Endesfelder, S. A. R. Knox, A. G. Orpen and D. Plaas, *J. Chem. Soc., Dalton Trans.*, 1983, 2661; (*c*) K. R. Birdwhistell, T. L. Tonker and J. L. Templeton, *J. Am. Chem. Soc.*, 1985, **107**, 4474; (*d*) A. Hills, D.

L. Hughes, N. Kashef, N. A. N. D. A. Lemos, A. J. L. Pombeiro and R. L. Richards, *J. Chem. Soc., Dalton Trans*., 1992, 1775; (*e*) M. F. N. N. Carvalho, S. S. P. R. Almeida, A. J. L. Pombeiro and R. A. Henderson, *Organometallics*, 1997, **16**, 5441; (*f*) T. B. Wen, Y. K. Cheung, J. Yao, W.-T. Wong, Z. Y. Zhou and G. Jia, *Organometallics*, 2000, **19**, 3803; (*g*) P. Gonzalez-Herrero, B. Weberndörfer, K. Ilg, J. Wolf and H. Werner, *Organometallics*, 2001, **20**, 3672; (*h*) N. J. Beach, H. A. Jenkins and G. J. Spivak, *Organometallics*, 2003, **22**, 5179.

29 The isomerization process is much slower in CH_2Cl_2[8b].

30 (*a*) C. P. Casey, S. R. Marder and P. J. Fagan, *J. Am. Chem. Soc*., 1983, **105**, 7197; (*b*) C. P. Casey, S. R. Marder and B. R. Adams, *J. Am. Chem. Soc*., 1985, **107**, 7700.

31 For examples of protonation of a vinylidene to an alkenyl ligand, see: (*a*) H. Werner, R. Weinand, W. Knaup, K. Peters and H. G. von Schnering, *Organometallics*, 1991, **10**, 3967; (*b*) M. Bamber, G. C. Conole, R. J. Deeth, F. T. Froom and M. Green, *J. Chem. Soc., Dalton Trans*., 1994, 3569.

32 (*a*) D. J. Lowe, K. Fisher and R. N. F. Thorneley, *Biochem. J*., 1990, **272**, 621; (*b*) G. A. Ashby, M. J. Dilworth and R. N. F. Thorneley, *Biochem. J*., 1987, **247**, 547.

33 C. Mealli and D. M. Proserpio, *J. Chem. Educ*., 1990, **67**, 399.

34 (*a*) R. Hoffmann, *J. Chem. Phys*., 1963, **39**, 1397; (*b*) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys*., 1962, **36**, 2179.

