Inorganic Chemistry

Article

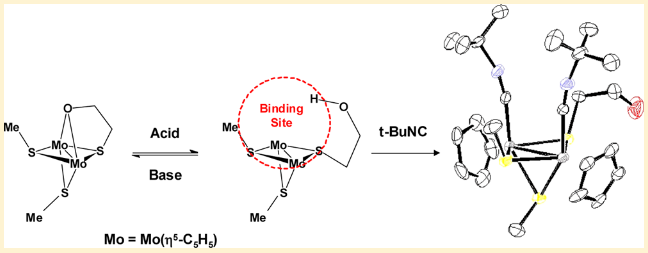
pubs.acs.org/IC

Acid-Base Control of Hemilabile Proton-Responsive Protecting Devices in Dimolybdenum, Thiolate-Bridged Complexes

Alan Le Goff,[†] David Vénec, Christine Le Roy, François Y. Pétillon,* Philippe Schollhammer,* and Jean Talarmin*

UMR CNRS 6521 ≪ Chimie, Electrochimie Moléculaires et Chimie Analytique ≫ Université de Bretagne Occidentale, UFR Sciences et Techniques, CS 93837, 29238 Brest-Cedex 3, France

S *Supporting Information*



ABSTRACT: Dimolybdenum thiolate-bridged complexes [$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2E)$] (E = O (**2**) or NH (**4**)) with a proton-dependent protecting device have been synthesized by reaction of [$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}Cl)_2$] (**1**) with SCH_2CH_2EH. The reactivity of the resultant quadruply bridged complexes with acid was investigated in the absence and in the presence of a potential ligand (N_2, MeCN, RNC). While the protonation of complexes **2** and **4** under N_2 in dichloromethane produced only the oxidized derivatives instead of the desired diazenido compound, ligand binding was observed in MeCN or in the presence of RNC (R = *t*-Bu, Xyl). Whereas acetonitrile loss from [$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2OH)(MeCN)_2$]$^+$ (**8**$^+$) prevented the isolation and characterization of this species, the *t*-BuNC analogue (**6**$^+$) could be characterized by an X-ray crystal structure. The electrochemistry of **2** and **2**$^+$ was investigated in CH_2Cl_2 and in MeCN, both in the absence and in the presence of acid. While the addition of $HBF_4{\cdot}Et_2O$ to a dichloromethane solution of **2** only produced **2**$^+$ (and presumably H_2), **8**$^+$ was the major product of the protonation in MeCN.

INTRODUCTION

Although the continuing efforts made for several decades resulted in a number of considerable advances,[1−17] chemical dinitrogen fixation under mild conditions remains a tremendous challenge for the scientific community. A process inspired by the biological N_2 fixation by the nitrogenase enzymes would be an ideal alternative to the highly energy-intensive and environmentally detrimental Haber process. However, the site where N_2 is bound and activated within the FeMo cofactor, the active site of the Mo-dependent enzyme, is not known with certainty.[18−23] Regardless, many synthetic complexes where dinitrogen is bound to, and activated by, Mo or Fe centers are known.[1−17,24−30]

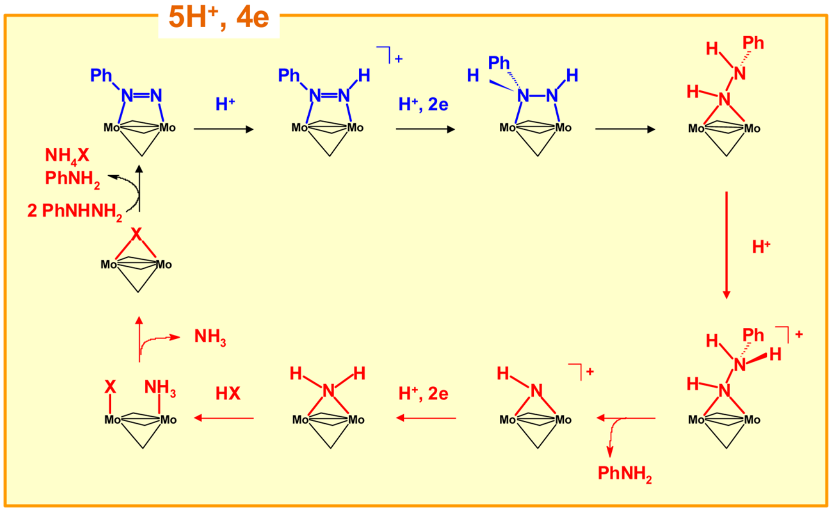
For many years, we have been interested in the activation of unsaturated substrates by metal−thiolate entities, and although it is known that the active site of the molybdenum nitrogenase contains a single Mo atom,[31,32] we have continued our exploration of the chemistry of dimolybdenum thiolate-bridged complexes since these compounds are able to activate substrates with C≡C,[33] C≡N,[34] or N═N bonds.[35] We have in particular shown the possibility of electrochemically converting alkynes to alkenes or alkyls[33f] at the conserved {$Cp_2Mo_2(\mu\text{-}SMe)_3$} site (Cp = $\eta^5\text{-}C_5H_5$) (see Schemes S1A and S1B, Supporting Information), and we found that a diazenido ligand (R−N═N$^-$, R = Me or Ph) coordinated to the same diMo platform in a $\mu-\eta^1$ or a $\mu-\eta^1{:}\eta^1$ mode can be reduced to ammonia and an amine by successive proton- and electron-transfer steps[35c−e] (Scheme 1). Theoretical calculations later showed that the reduction of N_2 at a di-iron site of FeMoco[36] or at a synthetic $Fe_2(SR)_2$ center[37] could follow the same pathway as that illustrated in Scheme 1.

The transformations in Scheme 1 and Supporting Information, Scheme S1A,B are relevant to several stages of the reduction of unsaturated substrates by the nitrogenases; however, the initial step of the reduction of dinitrogen, that is, N_2 binding at the {$Cp_2Mo_2(\mu\text{-}SMe)_3$} site, is missing. This limitation is not restricted to the {$Cp_2Mo_2(\mu\text{-}SMe)_3$} entity since most of the synthetic metal−sulfur sites (and even the isolated FeMo cofactor in NMF solution[38]) are unable to bind N_2. Only a few dinitrogen complexes are known where the metal center(s) is (are) in a thioether, thiolate, dithiocarbamate, or sulfide environment.[25c,29,30,39−47]

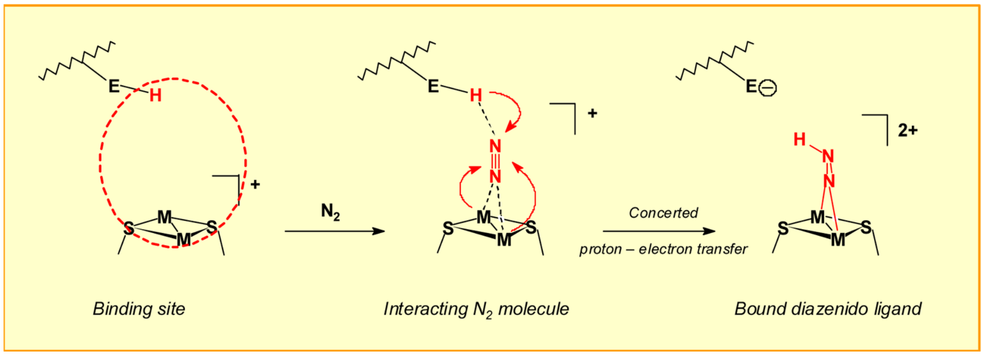
Theoretical calculations concerning the different steps shown in Scheme 1 showed that the cleavage of the π and σ components of the N═N bond arise from processes where the protonation triggers the transfer of electron(s) from the metal core to the {NN} ligand.[48] Thus, protonation at the remote nitrogen atom of the phenyl-hydrazido(1−) ligand caused the transfer of two electrons from the HOMO (δ orbital) to the ligand. This resulted in the cleavage of the N−N σ bond (with the release of aniline, Scheme 1) and in the oxidation of the metal centers to the $Mo^{IV}−Mo^{IV}$ state in the resulting imide cation.[48] The fact that dinitrogen does not bind at the

Received: November 20, 2013
Published: February 5, 2014

Scheme 1. Reduction of Nitrogenous Ligands at the $\{Cp_2Mo_2(\mu\text{-}SMe)_3\}$ Site[35]



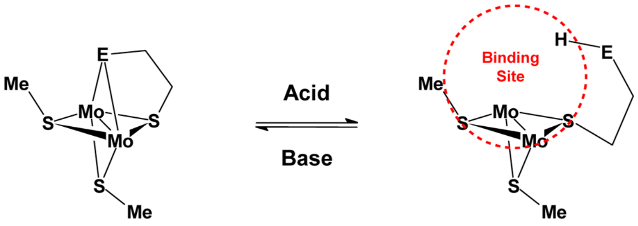
Scheme 2. M = Mo, Fe



$\{Cp_2Mo_2(\mu\text{-}SMe)_3\}$ site, which is otherwise able to accommodate various reduced forms of N_2, combined with the above observations, brought us to consider the possible implication of such a proton-coupled electron transfer[49] mechanism also in the cleavage of the first N−N bond of dinitrogen. At the same time, the formation of a hydrogen bond between a suitable proton donor and a weakly bound, labile N_2 could contribute to hold the substrate in the vicinity of the metal site[50] (Scheme 2). If the occurrence of such a hydrogen interaction is sufficient to cause an electron transfer from the metal core to the substrate, the net result would be the complete transfer of the proton from the pendant group to the N atom. This concerted process akin to a "dinitrogen trap" would give rise to the coordination of a diazenido ligand, and thus circumvent the difficulties associated with the binding of N_2 at a metal−sulfur site (Scheme 2).

To explore this possibility, we chose to anchor a protonatable functionality to a bridging sulfur atom, thus constituting a hemilabile protecting device that would expose a coordination site only under acidic conditions. To this end, as a first, simple model of the device shown in Scheme 2, we synthesized a new version of the $\{Cp_2Mo_2(\mu\text{-}SMe)_3\}$ core, where one equatorial thiolate bridge is replaced by a doubly bridging arm (Scheme 3). In this Paper, we describe the synthesis, the characterization, and some aspects of the chemical and electrochemical reactivity of the new compounds, $[Cp_2Mo_2(\mu\text{-}SMe)_2(\mu_2\text{-}SCH_2CH_2E)]$ (E = O (**2**) or NH (**4**)) in the presence of acid and of an unsaturated substrate.

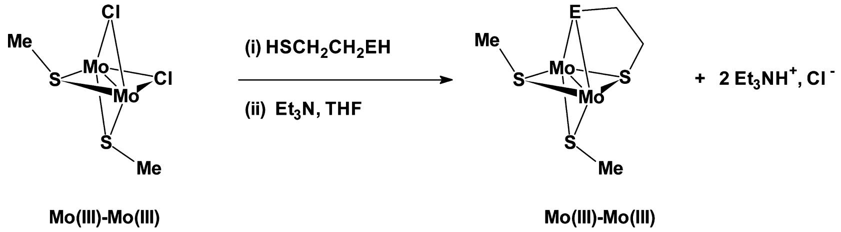
Scheme 3. Mo = Cp−Mo, E = O or NH



■ RESULTS AND DISCUSSION

Synthesis and Characterization of $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu_2\text{-}SCH_2CH_2E)]$ (E = O (2), NH (4)). Reactions of $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}Cl)_2]$ (**1**) with $HSCH_2CH_2EH$ (2-mercaptoethanol (E = O) or cysteamine (E = NH)) in refluxing tetrahydrofuran (THF) gave products **2** or **4** (Scheme 4) in high yields via a substitution process. These two complexes were characterized by elemental analyses and NMR (^1H and ^{13}C $\{^1H\}$) spectroscopy. The assignments of the ^{13}C NMR spectra for **2** and **4** (see Experimental Section) were based on standard ^{13}C NMR, two-dimensional heteronuclear multiple quantum correlation (HMQC) techniques. ^1H NMR spectroscopy clearly shows that in solution, complexes **2** and **4** are present in two isomeric forms, which differ only in the orientations (syn and anti) of the bridging SMe groups. These isomers, **2a**,**b** and **4a**,**b**, were inseparable by conventional chromatographic techniques and were observed in about 10:1

Scheme 4. Mo = Cp−Mo



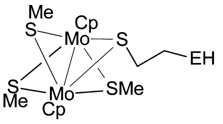
1

2 : E = O
4 : E = NH

and 2:1 ratios, respectively. The ^{1}H NMR spectrum of each isomer displays only one cyclopentadienyl resonance, typical for a symmetrical molecule. In the two complexes **2** and **4**, the entrant $HSCH_2CH_2EH$ molecule acts as a bridging bidentate ligand. Accordingly, ^{1}H and ^{13}C {^{1}H} NMR spectra of **2** and **4** show the presence of only two SMe groups in their molecule. The presence, in the ^{1}H NMR spectrum of **4**, of a broad singlet at 2.76 ppm, attributed to the N*H* group, and a doublet of triplets at 2.10 ppm (see Experimental Section), assigned to the $HNCH_2-$ group, confirm the presence of a μ-ethaneaminothiolato in **4**. In the ^{1}H NMR spectrum of the related derivative **2a**, the absence of splitting of the triplet at 3.47 ppm, attributed to the OCH_2 group, is in accordance with the presence of a μ-ethanedithiolato ligand in **2**. Complexes with a comparable structure, with four ligands bridging two MoCp′ entities (Cp′ = diversely substituted Cp rings) have previously been studied in great detail by Rakowski-DuBois.[51] However, **2** and **4** are, to the best of our knowledge, the only dimolybdenum cyclopentadienyl complexes with doubly bridging O,S and N,S ligands.

It is worth noting that variable amounts of minor side-products $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}SCH_2CH_2EH)]$ (E = O (**3a**,**b**), NH (**5**), see Chart 1), probably resulting from incomplete reactions, were occasionally detected by ^{1}H NMR spectroscopy (see Experimental Section) and confidently identified by comparison of their ^{1}H NMR spectra with those of already known similar derivatives $[Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}S(CH_2)_nSH)]$ (n = 1, 2), which have been characterized by X-ray diffraction analysis.[52] No effort was made to prepare **3** or **5** selectively. The formation of these two kinds of products, **2**−**4** and **3**−**5**, illustrates the two modes of coordination of such hemilabile protonatable bifunctionnal ligands acting as either bidentate in **2**−**4**, or monodentate in **3**−**5**.[53]

Chart 1



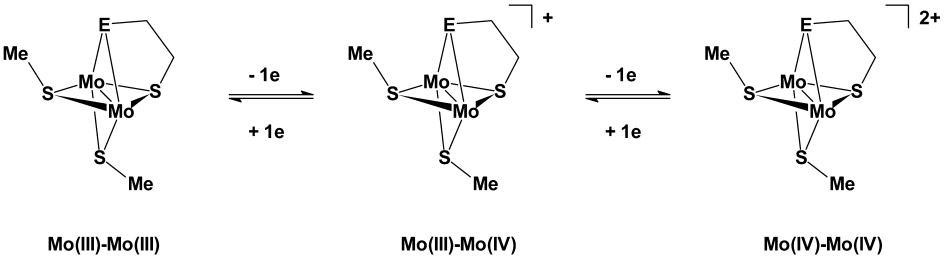
3 : E = O
5 : E = NH

Functioning of the Acid-Responsive Bridge in 2 and 4.

Electrochemical Behavior of 2 and 4 in CH_2Cl_2 and MeCN. To assess the functioning of their bidentate bridging ligand, we examined the electrochemical behavior of **2** and **4** under different conditions. From the usual cyclic voltammetric diagnostic criteria (ΔE_p, i_p^c/i_p^a, $i_p^a = f(v^{1/2})$),[54,55] the two successive oxidations of **2** and **4** are assigned as quasi-reversible,[56] diffusion-controlled one-electron processes (Scheme 5) in MeCN-$[NBu_4][PF_6]$ (Figure 1, black trace) or CH_2Cl_2-$[NBu_4][PF_6]$. As shown by the $E_{1/2}$ values in Table 1, the doubly bridging ligand where E = NH is a slightly better electron donor than the analogue with E = O.

Addition of increasing amounts of $HBF_4{\cdot}Et_2O$ to a solution of **2** in CH_2Cl_2-$[NBu_4][PF_6]$ leads to the progressive oxidation of the complex, as evidenced by linear scan voltammetry at a rotating disk electrode (RDE): after addition of 10 equiv of acid, a reduction wave is found at the same half-wave potential and with the same current intensity as the initial oxidation wave (Figure 2), which indicates the quantitative oxidation of **2** to $\mathbf{2}^+$. $HBF_4{\cdot}Et_2O$ was preferred to other acids such as HOTs (Ts = tosyl) or HCO_2CF_3 because it is a strong acid in MeCN[69] and because its conjugated base/anion are not likely to compete with weakly coordinating substrates (such as dinitrogen) for the exposed site because of the poor ligand ability of diethyl ether and BF_4^-. In contrast, the conjugated base of HOTs and trifluoroacetic acid are known to bind to the metal centers of the $\{Mo_2Cp_2(\mu\text{-}SMe)_3\}$ platform.[35d,61] Unfortunately, no reaction with N_2 could be detected upon acid addition under an atmosphere of dinitrogen since exactly the same voltammetric curves (cyclic voltammetry (CV) and RDE[55]) were obtained under N_2 and under Ar. The oxidation of **2** by HBF_4 in CH_2Cl_2 reported here is reminiscent of the reaction of

Scheme 5. Mo = Cp-Mo, E = O or NH



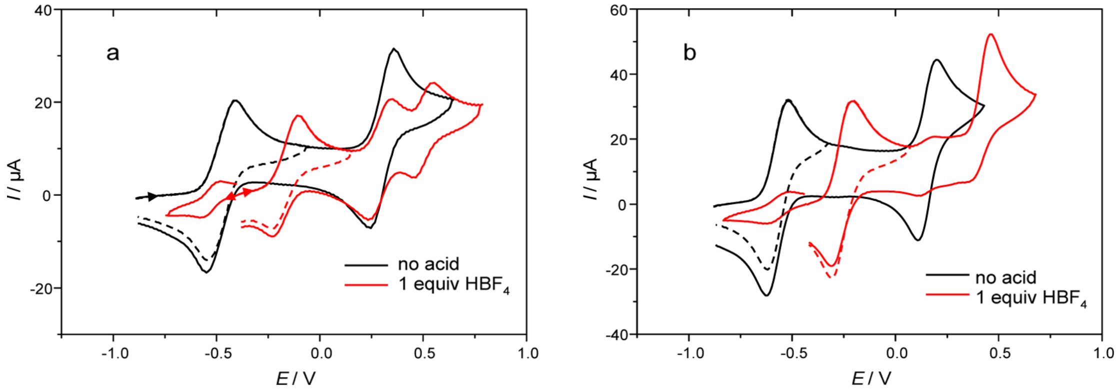


Figure 1. Cyclic voltammetry of (a) [$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu_2\text{-}SCH_2CH_2O)$], (**2** ; 1.1 mM) and (b) [$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu_2\text{-}SCH_2CH_2NH)$] (**4**, 1.4 mM) in the (black) absence and (red) presence of 1 equiv of $HBF_4{\cdot}Et_2O$ (MeCN-[NBu_4][PF_6], vitreous carbon electrode, ν = 0.2 V s^{-1}, E in V vs F_c^+/F_c; the scan directions in (b) are the same as in (a)).

Table 1. Oxidation Potentials of the Different Complexes

complex	solvent	$E_{1/2}^{ox1}$ (V) vs F_c^+/F_c	$E_{1/2}^{ox2}$ (V) vs F_c^+/F_c
[$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu_2\text{-}SCH_2CH_2O)$] (**2**)	MeCN	−0.50	0.22
	CH_2Cl_2	−0.49	0.28
[$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu_2\text{-}SCH_2CH_2NH)$] (**4**)	MeCN	−0.57	0.15
[$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2OH)(t\text{-}BuNC)_2$]$^+$ (**6**$^+$)	CH_2Cl_2	0.10	0.35
[$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2OH)(XylNC)_2$]$^+$ (**7**$^+$)	CH_2Cl_2	0.20	0.35
[$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2OH)(MeCN)_2$]$^+$ (**8**$^+$)	MeCN	−0.21	0.45
[$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2NH_2)(MeCN)_n$]$^+$ (**9**$^+$)[a]	MeCN	−0.27	0.43
[$Mo_2Cp_2(\mu\text{-}SMe)_3(MeCN)_2$]$^+$ (**10**$^+$)[b]	MeCN	−0.20	0.45
[$Mo_2Cp_2(\mu\text{-}SMe)_3(NH_3)(MeCN)$]$^+$ (**11**$^+$)[c]	MeCN	−0.35	0.39

[a] n = 1 or 2, see text. [b] See reference 57. [c] See reference 35b.

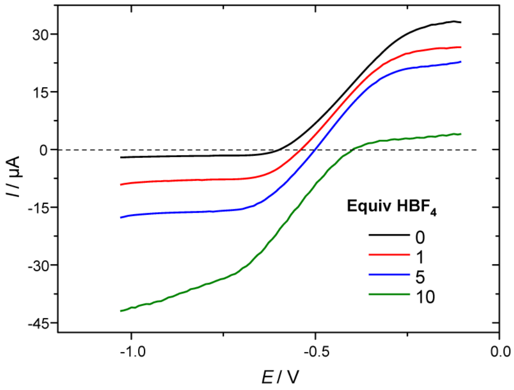


Figure 2. Voltammetry at a rotating vitreous carbon disk electrode of [$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu_2\text{-}SCH_2CH_2O)$], (**2** ; 0.9 mM) in the presence of increasing amounts of $HBF_4{\cdot}Et_2O$ in CH_2Cl_2-[NBu_4][PF_6] (ν = 0.01 V s^{-1}, potentials are in V vs F_c^+/F_c).

an analogous complex, [$Cp_2Mo_2(\mu\text{-}S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SR)$] (R = Me, *i*-Pr), with HSO_3CF_3 in CD_2Cl_2, which produced the oxidized derivative and H_2.[58]

Completely different results were obtained in acetonitrile. Thus, the CV change arising from the addition of $HBF_4{\cdot}Et_2O$ to a solution of **2** or **4** in MeCN-[NBu_4][PF_6] under Ar or N_2 (Figure 1, red trace) illustrates the formation of a new species (**8**$^+$ and **9**$^+$, respectively). The products **8**$^+$ and **9**$^+$ are characterized by two successive one-electron oxidation processes, with the first one quasi-reversible for both species (Figure 1). The comparison of the first oxidation peak current before and after addition of acid shows that **8**$^+$ and **9**$^+$ are obtained in >70% yield, assuming identical diffusion coefficients for **2** and **8**$^+$/**9**$^+$. Yet, CV and RDE voltammetry (Figure S1, Supporting Information) demonstrate that part of the initial complex is still oxidized to the corresponding cation **2**$^+$ and **4**$^+$, respectively.

Attempts to isolate the new complex **8**$^+$ formed upon addition of $HBF_4{\cdot}Et_2O$ to a MeCN solution of **2** failed; only the oxidized complex **2**$^+$ was recovered after evaporation of the solvent. This is very similar to the loss of the acetonitrile ligand previously observed when solutions of [$Mo_2Cp_2(\mu\text{-}SMe)_3(Cl)(MeCN)$]$^+$, prepared by oxidation of [$Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)$] in acetonitrile, were taken down to dryness. Indeed, only the oxidized complex [$Mo_2Cp_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)$]$^+$ was recovered after workup.[57]

*Reactivity of **2** toward RNC (R = t-Bu, Xyl) in the Presence of Acid.* With the aim of obtaining an isolable product, complex **2** was protonated in CH_2Cl_2 in the presence of an excess of isocyanide, which is a better ligand than acetonitrile for the dimolybdenum complexes.[57] Thus, the addition of *t*-BuNC to an acidic solution of **2** in CH_2Cl_2-[NBu_4][PF_6] produces a new species along with **2**$^+$, as evidenced by voltammetry at a rotating disk electrode (Figure 3).

To check the nature of the reaction product, a CH_2Cl_2 solution of **2** was treated with 1 equiv of tetrafluoroboric acid and an excess of isocyanide RNC (R = *t*-Bu, Xyl) under stirring at room temperature. This yielded a mixture of two products, [$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2OH)(RNC)_2$]$^+$ (R = *t*-Bu: **6**$^+$ or Xyl: **7**$^+$) and the oxidized form of **2**, [$Mo_2Cp_2(\mu\text{-}SMe)_2(\mu_2\text{-}SCH_2CH_2O)$]$^+$ (**2**$^+$) (Scheme 6).

2$^+$ has been independently prepared by reacting **2** with $NOBF_4$ (see the Experimental Section); it was undetectable by NMR spectroscopy and has been characterized by microanalysis and cyclic voltammetry. The samples of **6**$^+$ and **7**$^+$ were always contaminated by variable small (as shown by CV) amounts of **2**$^+$, which could not be satisfactorily separated from the isocyanide compounds, so that no reproducible elemental analysis is available for these two complexes. Despite the

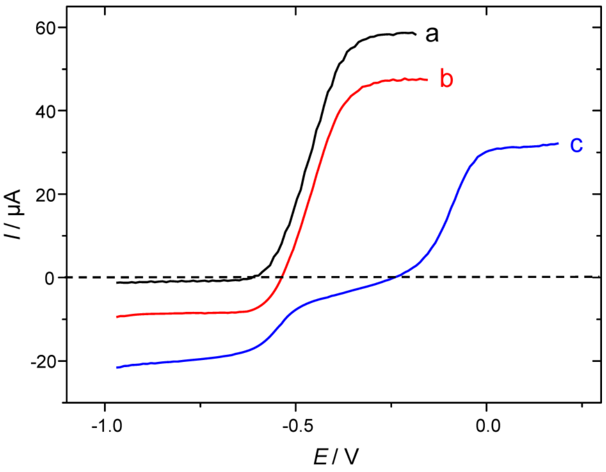


Figure 3. Voltammetry at a rotating vitreous carbon disk electrode of $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu_2\text{-}SCH_2CH_2O)]$, (**2** ; 1.2 mM) (a) in the absence of acid, (b) after addition of 1 equiv of $HBF_4.Et_2O$, and (c) after the addition of 1 equiv of *t*-BuNC in CH_2Cl_2-$[NBu_4][PF_6]$ (v = 0.01 V s^{-1}, potentials are in V vs F_c^+/F_c).

presence of 2^+, the formulation of 6^+ and 7^+ could be deduced from ^1H NMR data and is as depicted in Scheme 6.

^1H NMR spectroscopy showed that in solution (CD_2Cl_2 or $(CD_3)_2CO$ at 25 °C), complexes 6^+ and 7^+ are present in isomeric forms (**6a**–**c**$^+$ and **7a**,**b**$^+$) in variable ratios (see Experimental Section), depending on the solvent and the experimental conditions. These isomers may differ in the orientations (syn and anti) of the bridging SMe and SCH_2CH_2OH groups (Scheme S2 in Supporting Information). Similar ^1H NMR spectra are observed for each isomer of 6^+ and 7^+. They display a single cyclopentadienyl resonance, indicating symmetrical molecules. Interestingly, the ^1H NMR spectra of the three isomers of 6^+ in acetone-d_6 show a broad singlet between 4.35 and 3.90 ppm, typical for a hydroxyl group, which accords with the presence of a monodentate thioethanol-bridging ligand in these complexes. The resonance for the CH_2OH atoms in 6^+ and 7^+ is easily identified as the only one exhibiting a triplet between 4.33 and 3.71 ppm ($^3J \approx 7.0$ Hz), which was broadened upon *O*H coupling to give in some cases a multiplet. As noted above for **2** and as expected, only two resonances corresponding to the SMe groups are observed for each isomer **6a**–**c**$^+$ and **7a**,**b**$^+$. Other spectroscopic data of compounds 6^+ and 7^+ (^1H NMR, see the Experimental Section) are in agreement with the formulation depicted in Scheme 6 and deserve no particular comments. The structure of 6^+ was confirmed by the X-ray analysis of a single crystal of this compound. Crystals of $6[BF_4]$ are built from discrete $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2OH)(t\text{-}BuNC)_2]^+$ cations and BF_4^- anions (Figure 4). The cation is structurally closely analogous to that of the previously reported complexes $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2Cl)(CO)_2]Cl{\cdot}H_2O$[34c] and $[Mo_2Cp^*{}_2(\mu\text{-}SMe)_2(\mu\text{-}SI)(CO)_2]I_5$ (Cp* = C_5Me_5).[59] Thus, two nearly eclipsed CpMo(*t*-BuNC) units are linked by a Mo–Mo bond whose length (2.7941(4) Å) is typical of the values found in dimeric Mo^{III} or W^{III} complexes containing three bridging groups.[34c,59,60] The resulting metal coordination can be described as a distorted four-legged piano stool supplemented by a metal–metal bond. The molybdenum atoms are nearly coplanar with the methanethiolate and the thioethanol sulfur atoms (S1–Mo1–S3–Mo2 = −4.68(3)°); moreover, the two isocyanides, one methanethiolate, and the thioethanol groups lie on the same side of this plane, according

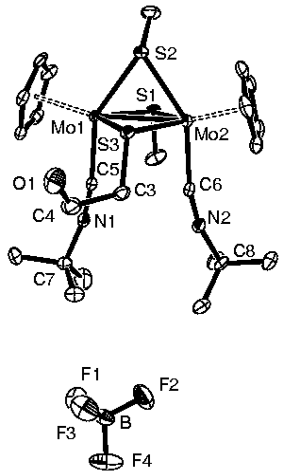
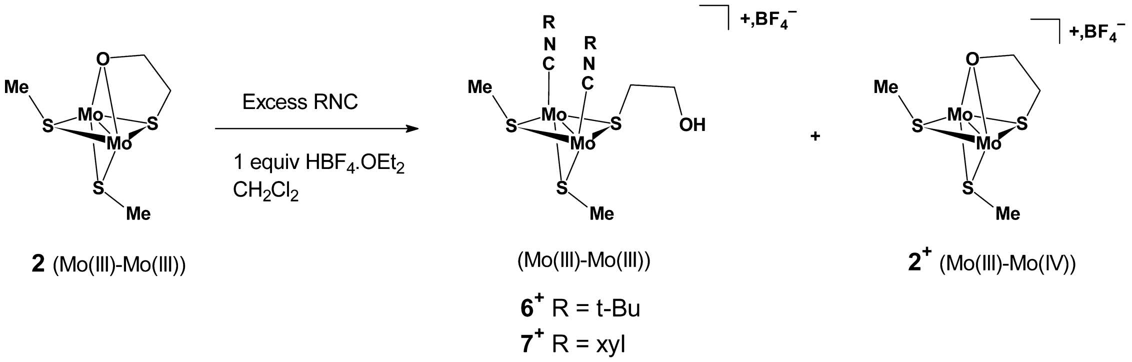
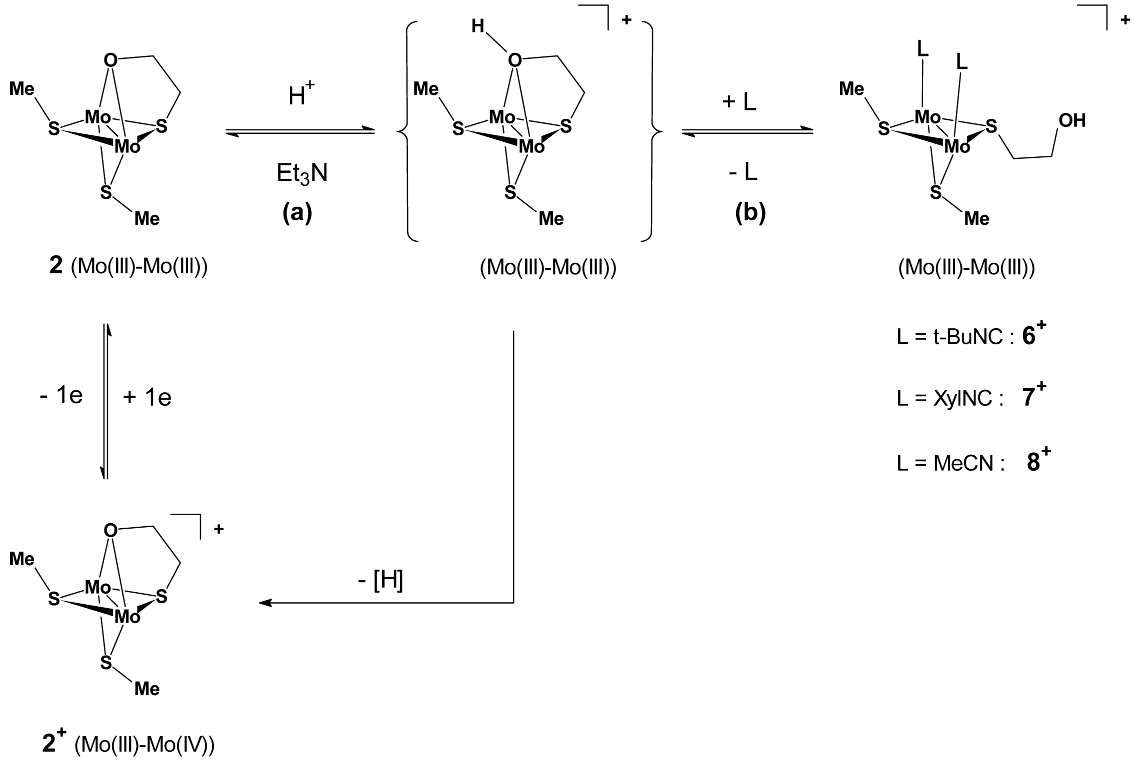


Figure 4. View of $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2OH)(t\text{-}BuNC)_2]$-$(BF_4)$ (**6**(BF_4)) showing 30% probability ellipsoids. Selected bond lengths (Å), angles (deg), torsion angles (deg), and dihedral angles (deg): Mo1–Mo2 = 2.7941(4), Mo1–S1 = 2.4383(9), Mo2–S1 = 2.4433(9), Mo1–S2 = 2.4456(9), Mo2–S2 = 2.4575(8), Mo1–S3 = 2.4575(9), Mo2–S3 = 2.4616(9), Mo1–S1–Mo2 = 69.83(2), Mo1–S2–Mo2 = 69.48(2), Mo1–S3–Mo2 = 69.22(2), C5–Mo1–S1 = 88.41(9), C5–Mo1–S3 =89.50(9), C5–Mo1–S2 = 147.36(8), C6–Mo2–S1 = 87.13(9), C6–Mo2–S3 = 92.42(9), C6–Mo2–S2 = 148.50(8), C5–Mo1–Mo2 = 92.04(8), C6–Mo2–Mo1 = 93.44(8), Mo1–C5–N1 = 170.6(3), Mo2–C6–N2 = 167.7(3), S1–Mo1–S3–Mo2 = −4.684(31), S1–S3–C3–C4 = −108.665(25), S1–S3–C3/Mo1–S2–Mo2 = 89.92(7).

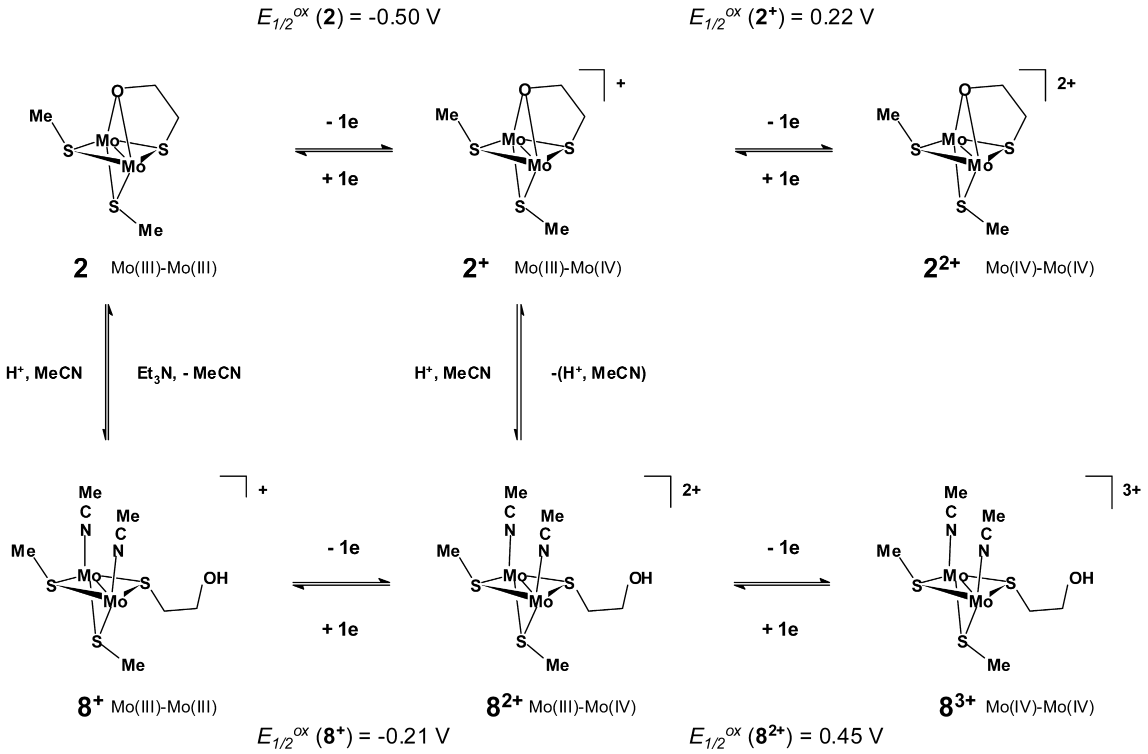
Scheme 6. Mo = Cp–Mo



Scheme 7. The Species between Brackets Is Postulated; Steps (a and b) are Observed only for L = MeCN; Mo = Cp−Mo



Scheme 8. The Orientation of the Thiolate Substituents Is Arbitrary[a]



[a]The postulated intermediates (see Scheme 7) have been omitted here; Mo = Cp−Mo.

to a syn form. Thus, the position of the thioethanol ligand in 6^+ differs from that observed for the methanethiolate chloride in $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2Cl)(CO)_2]Cl{\cdot}H_2O$; instead, the latter ligand and the two carbonyl groups are trans in this derivative.[34c] The CH_2OH group stands outside of the plane defined by the two sulfur and carbon (C3) atoms (S1−S3−C3−C4(OH) = −108.66(25)°), and the planes S1−S3−C3 and Mo1−S2−Mo2 are nearly perpendicular (dihedral angle = 89.92(7)°).

*Acid–Base and Redox Control of the Hemilabile Proton-Responsive Bridge in **2**.* The formation of the isocyanide derivatives $\mathbf{6}^+$ and $\mathbf{7}^+$ from **2** is proposed to arise as shown in Scheme 7. The occurrence of an undetected intermediate that would evolve toward the substrate-bound product or toward the oxidized complex, depending on the experimental conditions, is consistent with previously reported results concerning a hydroxo-bridged analogue of **2**, namely, $[Mo_2Cp_2(\mu\text{-SMe})_3(\mu\text{–OH})]$, the protonation of which was suggested to involve an intermediate with an aqua bridge.[61] Other examples of the stepwise conversion of an oxo bridge to hydroxo and aqua ligands are known. Facile dissociation of these ligands (hydroxyl or water) liberates a coordination site for substrate binding and activation.[62] Note that such a discrimination by the solvent is also observed for the reaction of $[Mo_2Cp_2(\mu\text{-SMe})_4]$ with HBF_4, which generates the bis-acetonitrile complex $[Mo_2Cp_2(\mu\text{-SMe})_3(MeCN)_2]^+$ $\mathbf{10}^+$ in MeCN, and the one-electron oxidized complex in tetrahydrofuran (THF) in the absence of substrate (see Supporting Information, Figures S2 and S3).

Although $\mathbf{8}^+$ could not be isolated and characterized, the resemblance of the reactions in the presence of *t*-BuNC (Figure 3c) and acetonitrile (Supporting Information, Figure S1) strongly suggests that, in MeCN, the opening of the protonated $\{SCH_2CH_2OH^+\}$ bridge, followed by solvent binding, produces the analogue of $\mathbf{6}^+$ and $\mathbf{7}^+$, that is $[Mo_2Cp_2(\mu\text{-SMe})_2(\mu\text{-}SCH_2CH_2OH)(MeCN)_2]^+$, $\mathbf{8}^+$. This assignment is further supported by the similarity of the redox potentials of the tris(methylthiolate)-bridged, bis(acetonitrile) complex $[Mo_2Cp_2(\mu\text{-SMe})_3(MeCN)_2]^+$ ($\mathbf{10}^+$)[57] with those of $\mathbf{8}^+$ (Table 1). The analogy of the conditions leading to the formation of $\mathbf{9}^+$ from **4** and HBF_4 in MeCN suggests that proton attack at the N-bridgehead leads to the opening of the amine bridge and to MeCN binding. However, whether $\mathbf{9}^+$ contains one or two solvent molecule(s) could not be determined by ^1H NMR spectroscopy due to the presence of the paramagnetic impurity $\mathbf{4}^+$, which alters the quality of the spectra. Furthermore, the oxidation potentials of $\mathbf{9}^+$ are rather close to those of the mixed ammine/acetonitile complex $[Mo_2Cp_2(\mu\text{-SMe})_3(NH_3)(MeCN)]^+$ ($\mathbf{11}^+$)[35b] (Table 1) so that the possibility that n = 1 in $[Mo_2Cp_2(\mu\text{-SMe})_2(\mu\text{-}SCH_2CH_2NH_2)(MeCN)_n]^+$ ($\mathbf{9}^+$) cannot be ruled out.

The acid–base and solvent-binding equilibria in Scheme 7 can be shifted in both directions when L = MeCN since **2** can be quantitatively regenerated from the bis-acetonitrile complex $\mathbf{8}^+$ upon neutralization of the acidified solution by addition of Et_3N (Figure S4, Supporting Information). Such a proton-dependent coordination of acetonitrile also exists for the one-electron oxidized derivatives. Indeed, the cyclic voltammogram in Figure 1a (red trace) shows that the current for the oxidation of $\mathbf{2}^+$ ($E^{ox}_{1/2}$ = 0.22 V) is larger than the current associated with its reduction ($E^{red}_{1/2}$ = −0.50 V), which indicates that the oxidation of $\mathbf{8}^+$ to $\mathbf{8}^{2+}$ at −0.21 V on the positive-going scan regenerates the precursor $\mathbf{2}^+$ via proton loss and MeCN elimination from $\mathbf{8}^{2+}$ (Scheme 8). This reversible reaction can be restrained upon addition of an excess of acid as revealed by the decrease of the oxidation peak of $\mathbf{2}^+$ under these conditions (see Figure S5b,c, Supporting Information). The shift of the protonation equilibrium at the one-electron oxidized level is also clearly shown by cyclic voltammetry (Figure S6, Supporting Information) or by voltammetry at a stationary electrode (Figure 5) of $\mathbf{2}^+$ in the presence of acid. The scan rate dependence of the ratio of the reduction peak current i_p of $\mathbf{8}^{2+}$ and $\mathbf{2}^+$ ($i_p^{red}(\mathbf{8}^{2+})/i_p^{red}(\mathbf{2}^+)$) decreases from 1.5 to 0.7 upon raising the scan rate from 0.02 to 0.5 V s^{-1} (Figure 5)) shows that, at the electrode surface, the lower the scan rate, the more the protonation equilibrium is shifted toward $\mathbf{8}^{2+}$ by the reduction of the bis(acetonitrile) complex at a potential less negative than that of $\mathbf{2}^+$.

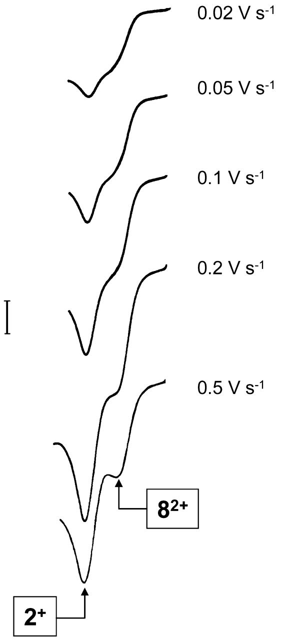


Figure 5. Stationary electrode voltammetry of $[Mo_2Cp_2(\mu\text{-SMe})_2(\mu_2\text{-}SCH_2CH_2O)]^+$ ($\mathbf{2}^+$) in MeCN-$[NBu_4][PF_6]$ in the presence of HBF_4; the current scale corresponds to 2 μA (v = 0.02–0.2 V s^{-1}) or 4 μA (v = 0.5 V s^{-1}).

The relationship between the redox state of the metal center(s) and the pK_a of a ligand is widely documented.[49,63] In the present case, the effect of the oxidation of the complex on the acidity of the OH proton is qualitatively shown by the fact that, at the Mo(III)–Mo(III) level, the recovery of the starting material from $\mathbf{8}^+$ requires the addition of Et_3N, while such a strong base is not required to deprotonate the OH function at the Mo(III)–Mo(IV) state. The chemical equilibria in Scheme 8 are a composite of acid–base and substrate-binding reactions, which are proposed to involve the transient $\{[Mo_2Cp_2(\mu\text{-SMe})_2(\mu_2\text{-}SCH_2CH_2OH)]^{n+}\}$ intermediates (see Scheme 7), so that the overall equilibrium constant is $K_{eq} = K_a \times K_{binding}$. The quantitative information accessible from the thermodynamic cycle in Scheme 8 thus concerns the effect of the oxidation on the overall equilibrium constants, not on the acidity constants, for example, $pK_{eq} - pK^+_{eq}$ = 4.9. Nevertheless, these results indicate that the functioning of the proton-dependent arm can be tuned by the redox state of the complex.

■ CONCLUSION

The results presented herein can be summarized as follows. The course of the reaction with protons, that is, metal oxidation or ligand binding, appears as a common characteristic of quadruply bridged complexes with O, NH, or S (in $[Mo_2Cp_2(\mu\text{-SMe})_4]$) bridgehead atom(s). The protonation of the complex with a mercaptoethanol or cysteamine bridge in the presence of a potential ligand (L) leads, as expected, to the opening of the bridge and to the binding of L (L = MeCN, RNC). The complexes where L = isocyanide could be isolated and characterized by an X-ray crystal structure for L = *t*-BuNC.

This Work thus contributes to validate the principle of the proton-responsive device anchored on a bridging sulfur atom. The flexibility of the linkage, which allows the protonated functionality to point far away from the binding site, does not favor the sought for and yet hypothetical {Mo ..N≡N..HO} interaction. The design of more rigid systems favoring such an interaction remains extremely challenging.

Despite the fact that no reaction with dinitrogen was observed, several interesting points must be noted. First, addition of acid results in oxidation of the complex (and presumably the release of H_2) when no suitable substrate is present. This prevents the degradation of the dinuclear core in acidic medium since, under reducing conditions in the absence of substrate, the observed reaction will be the reduction of protons while the dimetal core shuttles between the Mo(III)−Mo(III) and Mo(III)−Mo(IV) states (see Scheme 7). This is reminiscent of the fact that the nitrogenase enzyme works as a hydrogenase in the absence of N_2. When a ligand such as acetonitrile is weakly bound to the metal centers of the dimolybdenum complex, a change in the acidity conditions can lead to the loss of the MeCN ligand, still without degradation of the complex. This again shows that the switchable arm effectively protects the metal site from decomposition.

■ EXPERIMENTAL SECTION

General Procedures. All the experiments were carried out under an inert atmosphere, using Schlenk techniques for the syntheses. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. The starting compound $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}Cl)_2]$ (**1**) was prepared as described previously.[64] All other reagents were purchased commercially and used as received. Chemical analyses were performed by the Service de Microanalyse ICSN-CNRS, Gif sur Yvette, France. Yields of all products are relative to the starting dimolybdenum complexes. The NMR spectra (^1H; ^{13}C {^1H}) were recorded on a Bruker AMX3−400 or a Bruker DRX 500 spectrometers and were referenced to $SiMe_4$.

The preparation and the purification of the $[NBu_4][PF_6]$ supporting electrolyte were as described elsewhere.[65] The electrochemical equipment comprised either a GCU potentiostat (Tacussel/Radiometer) driven by a PAR 175 Universal Programmer (CVs were obtained using a SEFRAM TGM 164 X-Y recorder), or a PGSTAT 12 or a μ-AUTOLAB (Type III) driven by the GPES software. Coulometric charges were obtained using a IG5-N integrator (Tacussel/Radiometer). The cell and electrodes were as described previously.[65] All the potentials (text, table, figures) are quoted against the ferrocene-ferrocenium couple; ferrocene was added as an internal standard at the end of the experiments.

Synthesis of $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2O)]$ (2). Complex **1** (0.35 g, 0.72 mmol), 1.5 equiv of 2-mercaptoethanol (72 μL), and 5 equiv of Et_3N (495 μL) were stirred in THF (300 mL) at reflux for 12h. The solution color turned from green to brown. After evaporation of the solvent, compound **2** was extracted with diethylether (2 × 100 mL). Evaporation of the volatiles and washing of the residue with cold pentane (2 × 50 mL) afforded **2** as a brown powder (0.255 g, 84% yield). Complex **2** was obtained as a mixture of the two inseparable isomers **2a** and **2b** in about a 10:1 ratio.

The above experiment was repeated several times, and in a few cases a mixture of two products **2** (major) and **3** (minor) was obtained. These two complexes could not be separated by chromatography; according to ^1H NMR spectra, complex **3** could be formed in yields up to 30%.

Data for **2** are as follows: Anal. Calcd for $C_{14}H_{20}Mo_2OS_3$: C, 34.15; H, 4.09. Found: C, 33.96; H, 4.14%. ^1H NMR (C_6D_6, 25 °C): **2a**, δ 5.16 (s, 10H, C_5H_5), 3.47 (t, $^3J_{H-H}$ = 6.0 Hz, 2H, OCH_2-), 2.39 (t, $^3J_{H-H}$ = 6.0 Hz, 2H, SCH_2-), 1.87 and 1.41 (s, 3H, SCH_3); **2b**, δ 5.17 (s, 10H, C_5H_5), 3.27 (m, 2H, OCH_2-), 2.28 (m, 2H, SCH_2-), 1.92 and 1.64 (s, 3H, SCH_3). ^{13}C {^1H} (C_6D_6, 25 °C): **2**,δ 93.0 (C_5H_5), 78.0 (OCH_2), 36.2 and 30.2 (SCH_2-), 21.3 and 12.0 (SCH_3).

Data for **3** are as follows. ^1H NMR (C_6D_6, 25 °C): **3a**, δ 5.16 (s, 10H, C_5H_5), 2.72 (t, $^3J_{H-H}$ = 6.7 Hz, 2H, SCH_2-), 1.78, 1.61, and 1.37 (s,3H, SCH_3), 1.53 (dt, $^3J_{H-H}$ = 6.7 Hz, $^3J_{H-H}$ = 2.3 Hz, 2H, $HOCH_2-$); **3b**, δ 5.22 (s, 10H, C_5H_5), 2.62 (t, $^3J_{H-H}$ = 6.7 Hz, 2H, SCH_2-), 1.81, 1.70, and 1.35 (s, 3H, SCH_3), 1.59 (dt, $^3J_{H-H}$ = 6.5 Hz, $^3J_{H-H}$ = 2.3 Hz, 2H, $HOCH_2-$).

Synthesis of $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2NH)]$ (4). In a typical reaction, a mixture of **1** (350 mg, 0.72 mmol) and cysteamine ($HSCH_2CH_2NH.HCl$; 124 mg, 1.5 equiv), with 498 μL (5 equiv) of Et_3N was heated in THF (300 mL) at reflux for 12h, under stirring. After this time the solution turned from green to brown. The solvent was then removed, and the crude product was extracted with diethylether (2 × 100 mL). The solvent (Et_2O) was evaporated, and the resultant residue was washed with pentane (2 × 50 mL), affording a brown powder of **4** (297 mg, 84% yield). Complex **4** exists in solution (benzene-d_6) in two isomeric forms **4a** and **4b**. These isomers were obtained in a 2:1 ratio. After a night at room temperature in C_6D_6, the **4a**:**4b** ratio was 4:1.

In several reactions a mixture of two compounds **4** and **5** was formed. These two products could not properly be separated by chromatography. According to ^1H NMR data, **5** could be obtained in yields up to 13%, depending on experimental conditions.

Data for **4** are as follows: Anal. Calcd for $C_{14}H_{21}Mo_2NS_3$: C, 34.22; H, 4.31; N, 2.85. Found: C, 34.21; H, 4.47; N, 2.73%. ^1H NMR (C_6D_6): **4a**, δ 5.02 (s, 10H, C_5H_5), 2.76 (s-br, 1H, NH), 2.10 (dt, $^3J_{H-H}$ = 6.6 Hz, $^3J_{(N)H-H}$ = 2.0 Hz, 2H, NCH_2-), 1.83 and 1.70 (s, 3H, SCH_3), 1.51 (t, $^3J_{H-H}$ = 6.6 Hz, 2H, SCH_2-); **4b**, δ 5.03 (s, 10H, C_5H_5), 3.57 (s-br, 1H, NH), 2.16 (dt, $^3J_{H-H}$ = 6.7 Hz, $^3J_{(N)H-H}$ = 1.8 Hz, 2H, NCH_2-), 1.89 and 1.23 (s, 3H, SCH_3), 1.65 (t, $^3J_{H-H}$ = 6.7 Hz, 2H, SCH_2-). ^{13}C {^1H} NMR (C_6D_6): **4a**, δ 90.92 (C_5H_5), 57.33 (NCH_2-), 34.13 (SCH_2-), 17.33 and 10.40 (SCH_3); **4b**, δ 91.03 (C_5H_5), 57.07 (NCH_2-), 34.27 (SCH_2-), 17.67 and 13.80 (SCH_3).

Data for **5** are as follows: ^1H NMR (C_6D_6): δ 5.04 (s, 10H, C_5H_5), 2.05 (t-br, $^3J_{H-H}$ = 7.1 Hz, 2H, $-CH_2NH_2$), 1.77, 1.61, and 1.12 (s, 3H, SCH_3), 1.31 (m, 2H, SCH_2-); the proton resonances of the NH_2 group were not observed.

Synthesis of $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2O)](BF_4)$ (2^+). A solution of complex **2** (100 mg, 0.2 mmol) in THF (50 mL) was stirred in the presence of 1 equiv of $NOBF_4$ (27 mg) for 1 h at room temperature. The color of the solution turned from dark-brown to pink. The solvent was then removed under vacuum, and the residue was washed with diethylether (2 × 10 mL), giving complex $\mathbf{2}^+$ as a purple powder (103 mg, 88% yield). Anal. Calcd for $C_{14}H_{20}BF_4Mo_2OS_3$: C, 29.03; H, 3.48. Found: C, 29.14; H, 3.72%.

Reaction of 2 with Isocyanide RNC (R = *t*-Bu, Xyl) in the Presence of Tetrafluoroboric Acid. In a typical experiment, 40 equiv of RNC [R = *t*-Bu (1.85 mL), Xyl (1.36 g)] and 1 equiv of $HBF_4 \cdot OEt_2$ (54 μL) in CH_2Cl_2 (20 mL) were added with stirring (15 min) to a solution of $[Mo_2Cp_2(\mu\text{-}SMe)_2(\mu\text{-}SCH_2CH_2O)]$ (**2**) (0.20 g, 0.41 mmol) in dichloromethane (20 mL) at room temperature. After concentration, diethylether (80 mL) was added to the solution to precipitate a red powder that was collected by filtration. The analysis of the residue by electrochemical techniques (CV) indicated the formation of a mixture of the oxidized derivative $\mathbf{2}^+$ and the new products $\mathbf{6}^+$ (248 mg) or $\mathbf{7}^+$ (265 mg). Compound $\mathbf{6}^+$ or $\mathbf{7}^+$ was extracted from this mixture with THF (10 mL). Evaporation of the solvent gave mainly $\mathbf{6}^+$ or $\mathbf{7}^+$ as orange powders, which were analyzed in CD_2Cl_2 (and $(CD_3)_2CO$) by NMR spectroscopy. Similar results were obtained for $\mathbf{7}^+$. On the basis of NMR and electrochemical data, the yields of $\mathbf{6}^+$ and $\mathbf{7}^+$ were estimated to be about 45%. The above experiment was performed six times and was shown to be reproducible; compound $\mathbf{6}^+$ exists in solution as a mixture of three inseparable isomers $\mathbf{6a}^+$, $\mathbf{6b}^+$, and $\mathbf{6c}^+$ in the range of the ratios of 86−2:7−1:2−1, respectively, whereas $\mathbf{7}^+$ exists as a mixture of only two isomers $\mathbf{7a}^+$ and $\mathbf{7b}^+$ in the ratio of 2:1. No reliable elemental analysis is available for $\mathbf{6}^+$ and $\mathbf{7}^+$ because the samples are polluted by traces of $\mathbf{2}^+$, which is undetectable by NMR technics. Nevertheless, compound $\mathbf{6}^+$ has been fully characterized by X-ray analysis of orange crystals of

Table 2. Crystallographic Data for Complex $[Mo_2Cp_2(\mu\text{-SMe})_2(\mu\text{-SCH}_2CH_2OH)(t\text{-BuNC})_2][BF_4]$ (6^+)

empirical formula	$C_{24}H_{39}BF_4Mo_2N_2OS_3$
formula weight	746.44
temperature	170(2) K
wavelength	0.71073 Å
crystal system, space group	monoclinic, $P2_1c$
unit cell dimensions	a = 9.0236(3) Å, α = 90°
	b = 12.5884(3) Å, β = 97.331(2)°
	c = 26.6685(7) Å, γ = 90°
volume	3004.58(15) $Å^3$
Z, calculated density	4, 1.650 Mg/m^3
absorption coefficient	1.089 mm^{-1}
F(000)	1512
crystal size	0.30 × 0.13 × 0.09 mm
θ range for data collection	2.58 to 26.37°
limiting indices	$-11 \leq h \leq 10, -15 \leq k \leq 15, -33 \leq l \leq 33$
reflections collected/unique	25220/6150 [R(int) = 0.0385]
completeness to θ = 26.37	99.9%
absorption correction	multiscan
max. and min transmission	0.9083 and 0.7359
refinement method data/restraints/parameters	full-matrix least-squares on F^2 6150/0/343
goodness-of-fit on F^2	0.957
final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0315, w$R2$ = 0.0709
R indices (all data)	$R1$ = 0.0556, w$R2$ = 0.0756
largest diff. peak and hole	0.724 and −0.347 e.$Å^{-3}$

this complex, obtained from a CH_2Cl_2/pentane solution at low temperature.

Data for **6**$^+$ are as follows. ^{1}H NMR (CD_2Cl_2, 25 °C): **6a**$^+$, δ 5.29 (s,10H, C_5H_5), 3.76 (t-br, $^3J_{H-H}$ = 6.5 Hz, 2H, CH_2OH), 2.93 and 2.89 (t, $^3J_{H-H}$ = 6.5 Hz, 1H, SCH_2-), 1.53 (s, 18H, $C(CH_3)_3$), 1.41 and 1.39 (s, 3H, SCH_3); **6b**$^+$, δ 5.30 (s, 10H, C_5H_5), 3.86 (m, 2H, CH_2OH), 3.10 (m, 2H, SCH_2-), 2.43 and 2.38 (s, 3H, SCH_3), 1.51 (s, 18H, $C(CH_3)_3$); **6c**$^+$, δ 5.28 (s,10H, C_5H_5), 4.33 (t-br, $^3J_{H-H}$ = 7.7 Hz, 2H, CH_2OH), 2.74 (m, 2H, SCH_2-), 2.44 and 2.39 (s, 3H, SCH_3). ^{1}H NMR ($(CD_3)_2CO$, 25 °C): **6a**$^+$, δ 5.43 (s, 10H, C_5H_5), 3.90 (s-br, 1H, CH_2OH), 3.73 (m-br,2H, CH_2OH), 3.01 and 2.97 (t, $^3J_{H-H}$ = 6.8 Hz, 1H, SCH_2-), 1.61 (s, 18H, $C(CH_3)_3$), 1.57 and 1.51 (s, 3H, SCH_3); **6b**$^+$, δ 5.47 (s, 10H, C_5H_5), 4.23 (s-br, 1H, CH_2OH), 3.71 (m,-br, 2H,CH_2OH), 2.84 (m, $^3J_{H-H}$ = 7.5 Hz, 2H, SCH_2-), 2.49 and 2.46 (s, 3H, SCH_3), 1.44 (s, 18H, $C(CH_3)_3$); **6c**$^+$, δ 5.49 (s, 10H, C_5H_5), 4.35 (s-br, 1H, CH_2OH), 2.84 (m, $^3J_{H-H}$ = 7.5 Hz, 2H, SCH_2-), 2.50 and 2.47 (s, 3H, SCH_3), 1.43 (s, 18H, $C(CH_3)_3$). IR (KBr, cm^{-1}): ν(B−F) 1083 (s, br).

Data for **7**$^+$ are as follows. ^{1}H NMR ($(CD_3)_2CO$, 25 °C): **7a**$^+$, δ 6.84 (m, 6H, $C_6H_3Me_2$), 5.67 (s, 10H, C_5H_5), 3.77 (t-br, 2H, CH_2OH), 3.21 (t, $^3J_{H-H}$ = 6.6 Hz, 2H, SCH_2-), 2.25 (s, 12H, CH_3(Xyl)), 1.87 and 1.68 (s, 3H, SCH_3). **7b**$^+$, δ 6.96 (m, 6H, $C_6H_3Me_2$), 5.70 (s, 10H, C_5H_5), 3.98 (m, 2H, CH_2OH), 3.41 (t, 2H, SCH_2-), 2.67 (s, 3H, SCH_3), 2.23 (s, 12H, CH_3(Xyl)), 1.65 (s, 3H, SCH_3). IR (KBr, cm^{-1}): ν (B−F) 1076 (s, br).

X-ray Structural Determination. Measurements for compound **6**$^+$ were carried out on a Oxford Diffraction X-Calibur-2 CDD diffractometer equipped with a jet cooler device. Graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was used in this experiment. The structure was solved and refined by standard procedures.[66−68] Selected bond lengths and angles are collected in the caption to Figure 4. Crystal data collection and processing are given in Table 2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Schemes of the reduction of unsaturated CC ligands at the $\{Cp_2Mo_2(\mu\text{-SMe})_3\}$ site (Scheme S1); scheme of the possible isomers for **6**$^+$ and **7**$^+$ (Scheme S2); voltammetry at a rotating vitreous carbon disk electrode of **2** in MeCN$[NBu_4][PF_6]$ after the addition of acid (Figure S1); CV of $[Mo_2Cp_2(\mu\text{-SMe})_4]$ in the presence of acid in MeCN-$[NBu_4][PF_6]$ (Figure S2) and in THF-$[NBu_4][PF_6]$ (Figure S3); CV of complex **8**$^+$ in MeCN-$[NBu_4][PF_6]$ after the addition of Et_3N (Figure S4); CV of **2** (Figure S5) and of **2**$^+$ (Figure S6) in MeCN-$[NBu_4][PF_6]$ in the absence and in the presence of acid.

This material is available free of charge via the Internet at http://pubs.acs.org

■ AUTHOR INFORMATION

Corresponding Authors

*Email: francois.petillon@univ-brest.fr.
*Email: philippe.schollhammer@univ-brest.fr.
*Email: jean.talarmin@univ-brest.fr.

Present Address

[†]Université Joseph Fourier Grenoble I, CNRS/Département de Chimie Moléculaire (DCM), UMR-5250, 38401 Grenoble-Cedex 9 France

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to Dr. François Michaud for the X-ray crystal analysis and to Sandrine Gonzalès, DUT under instruction, for technical assistance. The Centre National de la Recherche Scientifique (CNRS) and Université de Bretagne Occidentale are acknowledged for financial support.

■ REFERENCES

(1) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589−625 and references therein.

(2) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197 and references therein.

(3) Pickett, C. J. *JBIC, J. Biol. Inorg. Chem.* **1996**, *1*, 601−606 and references therein.

(4) Sellmann, D.; Sutter, J. *JBIC, J. Biol. Inorg. Chem.* **1996**, *1*, 587–593 and references therein.

(5) Hidai, M.; Mizobe, Y. *Chem. Rev.* **1995**, *95*, 1115–1133 and references therein.

(6) Bazhenova, T. A.; Shilov, A. E. *Coord. Chem. Rev.* **1995**, *144*, 69–145 and references therein.

(7) *Nitrogen Fixation at the Millennium*; Leigh, G.J. Ed.; Elsevier Science B.V.: Amsterdam, The Netherlands, 2002.

(8) (a) Fryzuk, M. D. *Acc. Chem. Res.* **2009**, *42*, 127–133. MacLachlan, E. A.; Fryzuk, M. D. *Organometallics* **2006**, *25*, 1530–1543. (b) Fryzuk, M. D.; Johnson, S. A. *Coord. Chem. Rev.* **2000**, *200–202*, 379–409 and references therein.

(9) (a) Barrière, F.; Durrant, M. C.; Pickett, C. J. In Chapter 7: Catalysts for Nitrogen Fixation-Nitrogenases, Relevant Chemical Models and Commercial Processes; Smith, B. E.; Richards, R. L.; Newton, W. E., Eds.; *Nitrogen Fixation: Origins, Applications, and Research Progress* Vol. *1*; Kluwer Academic Publishers: The Netherlands, 2004, pp 161–199. (b) Barrière, F. *Coord. Chem. Rev.* **2003**, *236*, 71–89 and references therein.

(10) Crossland, J. L.; Tyler, D. R. *Coord. Chem. Rev.* **2010**, *254*, 1883–1894.

(11) Schrock, R. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 5512–5522.

(12) Hinrichsen, S.; Broda, H.; Gradert, C.; Söncksen, L.; Tuczek, F. *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **2012**, *108*, 17–47.

(13) Broda, H.; Hinrichsen, S.; Tuczek, F. *Coord. Chem. Rev.* **2013**, *257*, 587–598.

(14) (a) Nishibayashi, Y. *Dalton Trans.* **2012**, *41*, 7447–7453. (b) Tanabe, Y.; Nishibayashi, Y. *Coord. Chem. Rev.* **2013**, *257*, 2551–2564.

(15) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76–78.

(16) Weare, W. W.; Dai, X.; Byrnes, M. J.; Min Chin, J.; Schrock, R. R.; Müller, P. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 17099–17106.

(17) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. *Nature Chem.* **2011**, *3*, 120–125.

(18) Christiansen, J.; Dean, D. R.; Seefeldt, L. C. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **2001**, *52*, 269–295.

(19) Igarashi, R. Y.; Seefeldt, L. C. *Crit. Rev. Biochem. Mol. Biol.* **2003**, *38*, 351–384 and references therein.

(20) Seefeldt, L. C.; Dance, I. G.; Dean, D. R. *Biochemistry* **2004**, *43*, 1401–1409 and references therein.

(21) Dos Santos, P. C.; Igarashi, R. Y.; Lee, H.-I.; Hoffman, B. M.; Seefeldt, L. C.; Dean, D. R. *Acc. Chem. Res.* **2005**, *38*, 208–214.

(22) Sarma, R.; Barney, B. M.; Keable, S.; Dean, D. R.; Seefeldt, L. C.; Peters, J. W. *J. Inorg. Biochem.* **2010**, *104*, 385–389.

(23) Peters, J. W.; Szilagyi, R. K. *Curr. Opin. Chem. Biol.* **2006**, *10*, 101–108 and references therein.

(24) (a) Pickett, C. J.; Talarmin, J. *Nature* **1985**, *317*, 652–653. (b) Al-Salih, T. I.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1255–1264. (c) Pickett, C. J.; Ryder, K. S.; Talarmin, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1453–1457. (d) Mohammed, M. Y.; Pickett, C. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1119–1121. (e) Hussain, W.; Leigh, G. J.; Mohd. Ali, H.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1988**, 553–555. (f) Hughes, D. L.; Ibrahim, S. K.; Pickett, C. J.; Querné, G.; Laouénan, A.; Talarmin, J.; Queiros, A.; Fonseca, M. *Polyhedron* **1994**, *13*, 3341–3348. (g) Adachi, T.; Hughes, D. L.; Ibrahim, S. K.; Okamoto, S.; Pickett, C. J.; Yabanouchi, N.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1081–1083. (h) Alias, Y.; Ibrahim, S. K.; Queiros, A. M.; Fonseca, A.; Talarmin, J.; Volant, F.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1997**, 4807–4815.

(25) (a) Anderson, J. S.; Rittle, J.; Peters, J. C. *Nature* **2013**, *501*, 84–88. (b) Lee, Y.; Mankad, N. P.; Peters, J. C. *Nature Chem.* **2010**, *2*, 558–565. (c) Takaoka, A.; Mankad, N. P.; Peters, J. C. *J. Am. Chem. Soc.* **2011**, *133*, 8440–8443.

(26) Rodriguez, M. M.; Bill, E.; Brennessel, W. W.; Holland, P. L. *Science* **2011**, *334*, 780–783.

(27) Anderson, J. S.; Moret, M.-E.; Peters, J. C. *J. Am. Chem. Soc.* **2013**, *135*, 534–537.

(28) (a) Arashiba, K.; Sasaki, K.; Kuriyama, S.; Miyake, Y.; Nakanishi, H.; Nishibayashi, Y. *Organometallics* **2012**, *31*, 2035–2041. (b) Kinoshita, E.; Arashiba, K.; Kuriyama, S.; Miyake, Y.; Shimazaki, R.; Nakanishi, H.; Nishibayashi, Y. *Organometallics* **2012**, *31*, 8437–8443. (c) Tanaka, H.; Sasada, A.; Kouno, T.; Yuki, M.; Miyake, Y.; Nakanishi, H.; Nishibayashi, Y.; Yoshizawa, K. *J. Am. Chem. Soc.* **2011**, *133*, 3498–3506.

(29) Yoshida, T.; Adachi, T.; Kaminaka, M.; Ueda, T. *J. Am. Chem. Soc.* **1988**, *110*, 4872–4873.

(30) Morris, R. H.; Ressner, J. M.; Sawyer, J. F.; Shiralian, M. *J. Am. Chem. Soc.* **1984**, *106*, 3683–3684.

(31) Einsle, O.; Tezcan, F. A.; Andrade, S. L. A.; Schmid, B.; Yoshida, M.; Howard, J. B.; Rees, D. C. *Science* **2002**, *297*, 1696–1700.

(32) Spatzal, T.; Aksoyoglu, M.; Zhang, L. M.; Andrade, S. L. A.; Schleicher, E.; Weber, S.; Rees, D. C.; Einsle, O. *Science* **2011**, *334*, 940–940.

(33) (a) Schollhammer, P.; Cabon, N.; Capon, J.-F.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *Organometallics* **2001**, *20*, 1230–1242. (b) Cabon, N.; Schollhammer, P.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W. *Organometallics* **2002**, *21*, 448–450. (c) Cabon, N.; Le Goff, A.; Le Roy, C.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; McGrady, J. E.; Muir, K. W. *Organometallics* **2005**, *24*, 6268–6278. (d) Ojo, W.-S.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Organometallics* **2006**, *25*, 5503–5505. (e) Ojo, W.-S.; Capon, J.-F.; Le Goff, A.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *J. Organomet. Chem.* **2007**, *692*, 5351–5367. (f) Le Goff, A.; Le Roy, C.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J. *New J. Chem.* **2007**, *31*, 265–276.

(34) (a) Cabon, N.; Pétillon, F. Y.; Orain, P.-Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *J. Organomet. Chem.* **2005**, *690*, 4583–4601. (b) Ojo, W.-S.; Paugam, E.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Organometallics* **2006**, *25*, 4009–4018. (c) Ojo, W.-S.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J. *Organometallics* **2008**, *27*, 4207–4222.

(35) (a) Schollhammer, P.; Guénin, E.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W.; Yufit, D. S. *Organometallics* **1998**, *17*, 1922–1924. (b) Pétillon, F. Y.; Schollhammer, P.; Talarmin, J. *J. Chem. Soc., Dalton Trans.* **1997**, 4019–4024. (c) Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Inorg. Chem.* **1999**, *38*, 1954–1955. (d) Cabon, J.-Y.; Le Roy, C.; Muir, K. W.; Pétillon, F. Y.; Quentel, F.; Schollhammer, P.; Talarmin, J. *Chem.—Eur. J.* **2000**, *6*, 3033–3042. (e) Le Grand, N.; Muir, K. W.; Pétillon, F. Y.; Pickett, C. J.; Schollhammer, P.; Talarmin, J. *Chem.—Eur. J.* **2002**, *8*, 3115–3127. (f) Schollhammer, P.; Didier, B.; Le Grand, N.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W.; Teat, S. J. *Eur. J. Inorg. Chem.* **2002**, 658–663. (g) Le Goff, A.; Le Roy, C.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J. *New J. Chem.* **2006**, *30*, 929–938.

(36) Kästner, J.; Blöchl, P. E. *ChemPhysChem* **2005**, *6*, 1724–1726.

(37) Luo, Y.; Li, Y.; Yu, H.; Zhao, J.; Chen, Y.; Hou, Z.; Qu, J. *Organometallics* **2012**, *31*, 335–344.

(38) Pickett, C. J.; Vincent, K. A.; Ibrahim, S. K.; Gormal, C. A.; Smith, B. E.; Best, S. P. *Chem.—Eur. J.* **2003**, *9*, 76–87.

(39) Aresta, M.; Sacco, A. *Gazz. Chim. Ital.* **1972**, *102*, 755–759.

(40) Cruz-Garrits, D.; Gelover, S.; Torrens, H.; Leal, J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1988**, 2393–2396.

(41) Dilworth, J. R.; Hu, J.; Thompson, R. M.; Hughes, D. L. *J. Chem. Soc., Chem. Commun.* **1992**, 551–553.

(42) O'Regan, M. B.; Liu, A. H.; Finck, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331–4338.

(43) Schrock, R. R.; Wesolek, M.; Liu, A. H.; Wallace, K. C.; Dewan, J. C. *Inorg. Chem.* **1988**, *27*, 2050–2054.

(44) Sellmann, D.; Hautsch, B.; Rösler, A.; Heinemann, F. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 1505–1507.

(45) Chatt, J.; Crabtree, R. H.; Dilworth, J. R.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, 2358–2362.

(46) Dilworth, J. R.; Henderson, R. H.; Hills, A.; Hughes, D. L.; Macdonald, C.; Stephens, A. N.; Walton, D. R. M. *J. Chem. Soc., Dalton Trans.* **1990**, 1077–1085.

(47) Mori, H.; Seino, H.; Hidai, M.; Mizobe, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 5431–5434.

(48) Padden Metzker, J. K.; McGrady, J. E. *Chem.—Eur. J.* **2004**, *10*, 6447−6455.

(49) For recent reviews on PCET, see: (a) Savéant, J.-M. *Energy Environ. Sci.* **2012**, *5*, 7718−7731. (b) Weinberg, D. R.; Gagliardi, C. J.; Hull, J. F.; Fecenko Murphy, C.; Kent, C. A.; Westlake, B. C.; Paul, A.; Ess, D. H.; Granville McCafferty, D.; Meyer, T. J. *Chem. Rev.* **2012**, *12*, 4016−4093. (c) Gagliardi, C. J.; Vannucci, A. K.; Concepcion, J. J.; Chen, Z.; Meyer, T. J. *Energy Environ. Sci.* **2012**, *5*, 7704−7717, and a special issue of *Chemical Reviews*, including the following contributions. (d) Costentin, C.; Robert, M.; Savéant, J.-M. *Chem. Rev.* **2010**, *10*, PR1−PR40. (e) Hammes-Schiffer, S.; Stuchebrukhov, A. A. *Chem. Rev.* **2010**, *10*, 6939−6960. (f) Warren, J. J.; Tronic, T. A.; Mayer, J. M. *Chem. Rev.* **2010**, *10*, 6961−7001. (g) Dempsey, J. L.; Winkler, J. R.; Gray, H. B. *Chem. Rev.* **2010**, *10*, 7024−7039. (h) Siegbahn, P. E. M.; Blomberg, M. R. A. *Chem. Rev.* **2010**, *10*, 7040−7061.

(50) (a) Crabtree, R. H. *New J. Chem.* **2011**, *35*, 18−23. (b) Gruet, K.; Crabtree, R. H.; Lee, D.-H.; Liable-Sands, L.; Rheingold, A. L. *Organometallics* **2000**, *19*, 2228−2232. (c) Lee, D.-H.; Kwon, H. J.; Patel, B. P.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H. *Organometallics* **1999**, *18*, 1615−1621.

(51) (a) Rakowski DuBois, M. *Polyhedron* **1997**, *16*, 3089−3098 and references therein. (b) Rakowski DuBois, M. *J. Cluster Sci.* **1996**, *7*, 293−315 and references therein. (c) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1−9. (d) Rakowski DuBois, M.; VanDerveer, M. C.; DuBois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456−7461. (e) Rakowski DuBois, M.; Haltiwanger, R. C.; Miller, D. J.; Glatzmaier, G. *J. Am. Chem. Soc.* **1979**, *101*, 5245−5252.

(52) (a) Schollhammer, P.; Guénin, E.; Poder-Guillou, S.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W.; Baguley, P. *J. Organomet. Chem.* **1997**, *539*, 193−199. (b) Poder-Guillou, S. Ph.D. Thesis, University of Bretagne Occidentale: Brest, France; 1995, pp. 1−129.

(53) Camus, J.-M.; Morales, D.; Andrieu, J.; Richard, P.; Poli, R.; Braunstein, P.; Naud, F. *J. Chem. Soc., Dalton Trans.* **2000**, 2577−2585.

(54) (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications;* Wiley: New York, 1980, Chapter 11, pp 429−485. (b) Savéant, J.-M. *Elements of Molecular and Biomolecular Electrochemistry—An Electrochemical Approach to Electron Transfer Chemistry;* Wiley: New York, 2006, pp 78−181.

(55) 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, and RDE stands for rotating disk electrode; v (V s^{-1}) is the scan rate in CV experiments. An ECE process consists of a chemical reaction (C) comprised between two electron transfer steps (E).

(56) For both oxidations, $\Delta E_p > 60$ mV at a scan rate of 0.2 V s^{-1}, which is due in part to uncompensated solution resistance.

(57) Barrière, F.; Le Mest, Y.; Pétillon, F. Y.; Poder-Guillou, S.; Schollhammer, P.; Talarmin, J. *J. Chem. Soc., Dalton Trans.* **1996**, 3967−3976.

(58) Lopez, L. L.; Bernatis, P.; Birnbaum, J.; Haltiwanger, R. C.; Rakowski DuBois, M. *Organometallics* **1992**, *11*, 2424−2435.

(59) Schollhammer, P.; Pétillon, F. Y.; Talarmin, J.; Muir, K. W.; Fun, H. K.; Chinnakali, K. *Inorg.Chem.* **2000**, *39*, 5879−5882.

(60) (a) Gomes de Lima, M. B.; Guerchais, J. E.; Mercier, R.; Pétillon, F. Y. *Organometallics* **1986**, *5*, 1952−1964. (b) Schollhammer, P.; Pétillon, F. Y.; Pichon, R.; Poder-Guillou, S.; Talarmin, J.; Muir, K. W.; Manojlovíc-Muir, Lj. *Organometallics* **1995**, *14*, 2277−2287. (c) Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *Coord. Chem. Rev.* **1998**, *178−180*, 203−247. (d) García, M. E.; García-Vivo, D.; Ruiz, M. A.; Herson, P. *Organometallics* **2008**, *27*, 3879−3891.

(61) Le Hénanf, M.; Le Roy, C.; Muir, K. W.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J. *Eur. J. Inorg. Chem.* **2004**, 1687−1700.

(62) Poli, R. *Coord. Chem. Rev.* **2008**, *252*, 1592−1612.

(63) Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3601−3603.

(64) Cabon, N.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J.; Muir, K. W. *J .Chem. Soc., Dalton Trans.* **2004**, 2708−2719.

(65) Lounissi, S.; Zampella, G.; Capon, J.-F.; De Gioia, L.; Matoussi, F.; Mahfoudhi, S.; Pétillon, F. Y.; Schollhammer, P.; Talarmin, J. *Chem.—Eur. J.* **2012**, *18*, 11123−11138.

(66) Sheldrick, G. M. *Acta Crystallogr. Sec. A* **2008**, *64*, 112−1122.

(67) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343−350.

(68) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

(69) (a) The pK_a of $HBF_4{\cdot}Et_2O$ in MeCN is assumed to be the same as that of protonated diethyl ether,[69b] that is, $pK_a = 0.1$;[69c] the pK_a of $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 is not known. (b) Hu, X. L.; Brunschwig, B. S.; Peters, J. C. *J. Am. Chem. Soc.* **2007**, *129*, 8988−8998. (c) Izutzu, K. In *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents;* IUPAC Chemical Data Series No. 35, Blackwell Scientific Publications: Oxford, 1990.