Electrochemical Reduction of Nitrogenous Ligands at a Conserved Dinuclear Metal−Sulfur Site: Cleavage of the N=N Bond of Phenyldiazene and Reduction of an Imide to NH_3

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Received November 18, 1998

The crystal structure of the MoFe cluster of Mo nitrogenase (FeMoco)[1,2] has raised the question of whether the N_2 binding and reduction site on FeMoco[1,3,4] is mononuclear (Mo, Fe) or polynuclear. Reduction of nitrogenous substrates, including N_2 itself, at synthetic mono- or polymetallic sulfur sites may give insight into the biological process catalyzed by the enzyme.[4−8] While the possibility that Mo is the active site is substantiated by extensive work on mononuclear $M(P_4)$ complexes (M = Mo, W; P = phosphine donor),[9,10] statements that a second metal center is not *essential*[11] or constitutes a disadvantage[12] for the stepwise conversion of N_2 to NH_3, are based essentially on the chemistry of M(μ-L)M′ assemblies where the metal centers are bridged *only* by the substrate L.[11−13,14c] Substrate transformations (protonation, reduction) lead to the disruption of these complexes into mononuclear fragments at some stage of the reduction process; *in these models* the utility of the second metal center is clearly questionable, even though they include one example wherein easy cleavage of the dinitrogen triple bond has been demonstrated.[14] Our approach is conceptually quite different and is not open to the same objection, even though it involves two metal centers. It is focused on complexes with a $\{M_2(\mu\text{-SR})_n\}$ core.[15] These models are robust, they have vacant or readily accessible coordination sites on each metal center, and the electronic and steric properties of the metal atoms and bridging ligands preclude linear M(μ-L)M arrangements.[15] As an illustration of our approach we present here a study of the reactivity of {N−N} fragments at a dinuclear $\{M_2(\mu\text{-SR})_n\}$ site and of the role played by the metal centers in the transformation of the nitrogenous ligands. This follows our recent description of the synthesis of the phenyldiazenido complex $[Mo_2(cp)_2(\mu\text{-SMe})_3(\mu\text{-}\eta^1\text{-NNPh})]$, **1**, and of its protonation to give the phenyldiazene derivative $[Mo_2(cp)_2(\mu\text{-SMe})_3(\mu\text{-}\eta^2\text{-HNNPh})]^+$, **2**.[16] Here we present a preliminary report on the electrochemical reduction of **2** and of the cationic imido complex $[Mo_2(cp)_2(\mu\text{-SMe})_3(\mu\text{-NH})]^+$, **3**.[17,18]

The electrochemical reduction of **2** ($E_{applied} = -1.8$ V vs fc^+/fc, graphite cathode, thf-$[NBu_4][PF_6]$) in the presence of acid (3 equiv of HTsO) under Ar produces the known[19] amido complex $[Mo_2(cp)_2(\mu\text{-SMe})_3(\mu\text{-NH}_2)]$, **4**, as the major product (75%[20]) after consumption of nearly 4 (3.7 ± 0.2) F per mole of **2**. Complex **4** was characterized by comparison of its redox potentials with those of an authentic sample[18] and by ^{1}H NMR spectroscopy of the solid isolated from the catholyte. Monitoring by cyclic voltammetry of controlled-potential reduction of **2** performed in the presence of 4−6 equiv of CF_3CO_2H demonstrated that the ammine complex $[Mo_2(cp)_2(\mu\text{-SMe})_3(NH_3)(CF_3CO_2)]$ was formed steadily. Cyclic voltammetry of the catholyte after completion of the electrolyses showed the presence of this complex in ca. 70−75% yield[20,21]; aniline was detected in the catholyte by GC analysis. The ammine complex was characterized by its redox potentials[18] and by its reactions with a base and with chloride which produce **4** and $[Mo_2(cp)_2(\mu\text{-SMe})_3(\mu\text{-Cl})]$, respectively. The

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(17) $[Mo_2(cp)_2(\mu\text{-SMe})_3(\mu\text{-NH})][BF_4]$: calcd for $C_{13}H_{20}BF_4Mo_2NS_3$, C, 27.6; H, 3.5; N, 2.5%. Found, C, 27.6; H, 3.6; N, 3.1. Spectroscopic data (^{1}H NMR and IR) of **3** have been reported previously.[18]
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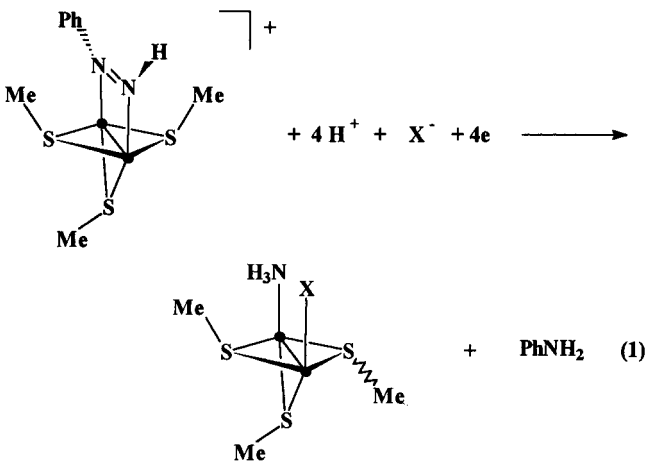
(20) The yields of controlled-potential electrolyses were obtained by cyclic voltammetry by comparing the oxidation peak currents of the products to the peak current of the starting material, and assuming identical diffusion coefficients.
(21) A second product, $[Mo_2(cp)_2(\mu\text{-SMe})_3(\mu\text{-OCOCF}_3)]$,[22] was also observed (ca. 20%). The charge consumed during electrolyses in the presence of 4−6 equiv of acid was dependent on the excess acid and exceeded the theoretical charge in eq 1, so that dihydrogen might also be produced; the design of the electrochemical cell used throughout did not allow H_2 detection because a dinitrogen or argon stream was continuously circulating over the solution during the experiments (cv or controlled-potential electrolyses).

10.1021/ic9813359 CCC: $18.00
Published on Web 04/17/1999

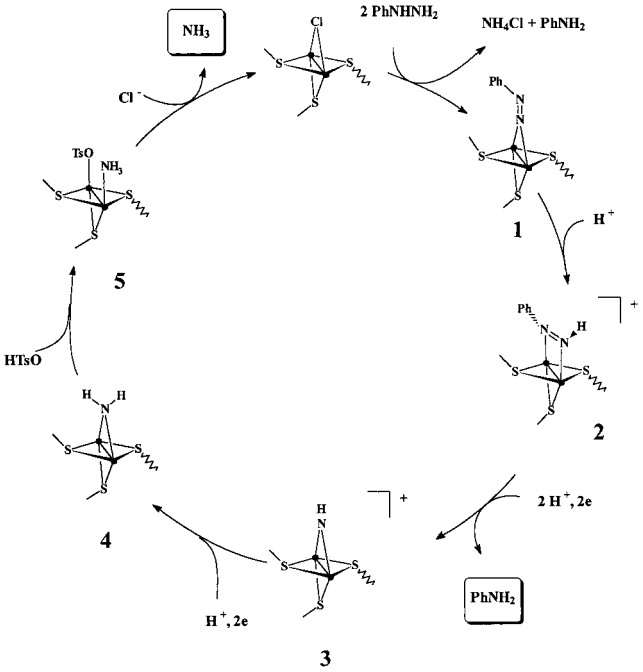
nature of the reduction products demonstrates unambiguously that the N═N bond of the diazo bridge was cleaved (eq 1).



This reduction may involve the formation of an imido intermediate. The imide complex **3** reduces at a potential less negative than **2** (E_p^{red} **3** = −1.25 V vs fc^+/fc; $E_{1/2}^{red}$ **2** = −1.63 V vs fc^+/fc) so that, if it is formed during the reduction of **2**, it will be immediately reduced at the electrolysis potential of −1.8 V. Controlled-potential electrolysis of **3** ($E_{applied}$ = −1.4 V vs fc^+/fc, Pt cathode, thf-[NBu_4][PF_6]) in the presence of 1 equiv of acid produces **4** (yield ca. 87%[20]) after consumption of 1.8 F per mole of **3**. In the presence of 2 equiv of acid, the ammine complex [$Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(X)$] (X = CF_3CO_2, TsO) was the final metal product. Electrolyses of **3** were also performed in the presence of acid and chloride since treatment of [$Mo_2(cp)_2(\mu\text{-}SMe)_3(NH_3)(X)$] with Cl^- is known[18] to induce the release of ammonia and to afford [$Mo_2(cp)_2(\mu\text{-}SMe)_3(\mu\text{-}Cl)$]. Controlled-potential reduction of **3** under these conditions (3 equiv of H^+, ≥2 equiv of Cl^-) produced the (μ-Cl) complex (≥95%[20]) and ammonium chloride (65−72%[23]).

These results convincingly demonstrate that the μ-η^1 diazenido species **1** can be converted by successive proton and electron-transfer steps *which conserve the dinuclear* {$Mo_2(cp)_2(\mu\text{-}SMe)_3^+$} *metal-sulfur site* (Scheme 1) into an ammine complex from which ammonia can be released.[18] Complexes **1**−**5** (Scheme 1) have all been fully characterized[16,18,19]; the X-ray crystal structures of

Scheme 1[a]



[a] Key: ● = Mo(cp); the methyl substituents of the bridging sulfur were omitted.

1, **2**, and **4** have been reported previously.[16,19] They are dinuclear analogues of intermediates invoked by the Chatt cycle for [$M(P)_4$][8,10,11] and by the Schrock cycle for [$M(cp^*)Me_3$][24] complexes (M = Mo, W).

Our results and those reported by Hidai's group[6] demonstrate that N−N multiple bond can be cleaved at dinuclear metal-sulfur sites, under mild conditions. Together with the new mode of coordination of N_2 to two metal centers recently discovered by Fryzuk,[25] these results suggest that several steps of the biological N_2 reduction could also take place at a di- or polymetallic site.

Acknowledgment. We thank CNRS (Centre National de la Recherche Scientifique), UBO (Université de Bretagne Occidentale), Conseil Régional de Bretagne (Opération No. 98CCO9), and Glasgow University for financial support.

IC9813359

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