

Electrochemistry

Hydrogen Bond-Assisted PCET and Formation of W^{III} –OH in Bis(Dithiolene) Complex

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Abstract: The redox non-innocent nature of dithiolene ligands is well known for stabilizing high-valent metal ions and facilitating proton-coupled electron transfer (PCET) processes. Until now, proton reactivity at the dithiolene site has been primarily associated with low-valent metal centers, as high-valent metal-dithiolene complexes were not considered viable for such reactivity. This study introduces high-valent bis(dithiolene) tungsten (W)-oxo complexes featuring hydrogen-bonding interactions, unveiling a novel proton reduction mechanism mediated by the dithiolene moiety. The process begins with a nucleophilic W-oxo, forming a hydrogen bond, followed by a second hydrogen bond at the dithiolene-sulfur (S) site. These hydrogen-bonding interactions significantly modulate the molecular orbital energy levels, enabling the $W^{IV} \rightarrow III$ reduction at -1.75 V (E_{exp}) and allowing, for the first time, the acquisition of an EPR spectrum of a W^{III} –OH intermediate species. In contrast, direct electron transfer into the $W^{IV}=\text{O}$ state would populate the dithiolene π^* orbital, demanding substantially larger energy ($E_{\text{cal}} = -3.45$ V). For catalytic proton reduction, the proton transfer through the dithiolene-S site was identified as the energetically most favorable pathway for generating the W^V –H catalytic species.

Introduction

Electrocatalytic hydrogen gas evolution is a key reaction in advancing sustainable energy systems. Designing effective catalysts and understanding their reaction mechanisms have become major focuses of recent research.^[1] One promising approach involves transition metal complexes, with particular emphasis on ligand design to enhance catalytic center activity. While the redox potential and hydricity of the metal center are critical determinants of catalytic efficiency,^[2] redox non-innocent ligands provide additional avenues for modifying reaction pathways.^[3] Ligands, such as porphyrins,^[4–6] polypyridines,^[7–9] iminopyridines,^[10–12] thiosemicarbazones,^[13–15] and dithiolenes,^[16–18] have been shown to influence the redox behaviors of these com-

plexes. In several cases, ligand-based catalysis has also been observed.^[13,18]

Among these, dithiolenes are notable due to their longstanding importance in chemistry^[19] and versatility in biomimetic reactions.^[20–22] Dithiolene complexes have been widely studied for their electrocatalytic or photocatalytic proton reduction activity, especially with nickel (Ni), cobalt (Co), and W centers.^[23] They can undergo protonation either directly at the metal center or via an axial chalcogen or dithiolene ligands. In low-valent transition metals such as Co^{II} , Zn^{II} , and Ni^{II} , the electron-rich dithiolene-S sites are potential protonation points.^[17,24,25] For instance, Letko et al. demonstrated that Co-dithiolene complexes favor H_2 formation via heterolytic coupling of a Co–H with a protonated dithiolene-SH (Figure 1a).^[17] Certainly, the nucleophilic reactivity of

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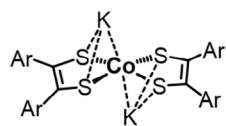
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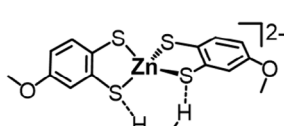
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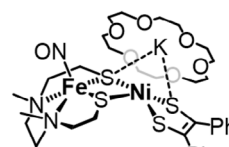
a) Nucleophilicity of sulfur in bis(dithiolene) complexes



Head-Gordon and Tilley, 2014

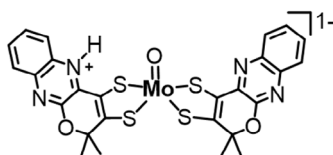


Dekura and Mori, 2015

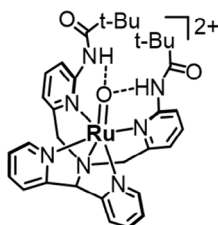


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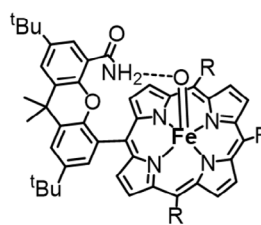
b) Proton reactivity in mono-oxo complexes



Fontecave, 2015



Kojima, 2023



Nam and Guo, 2024

c) This work

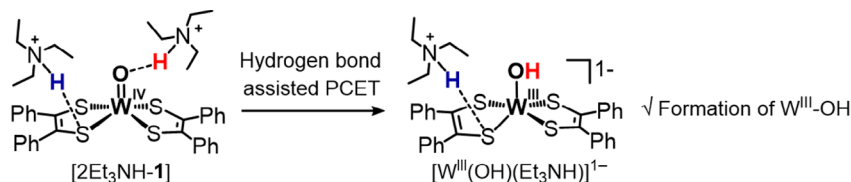


Figure 1. The effects of hydrogen bonding interactions on proton-coupled electron transfer (PCET) reaction pathways. a) Reactivity of nucleophilic dithiolene-S in M-bis(dithiolene) complexes (M = Co^{II}, Zn^{II}, and Ni^{II}), (b) nucleophilic reactivity of M=O complexes (M = Mo^{IV}, Ru^{IV}, and Fe^{IV}), and (c) hydrogen bonding interactions on both the nucleophilic sites of W^{IV}=O and dithiolene-S, and ET-driven formation of W^{III}-OH.

M=O (M = Mo^{IV}, Ru^{IV}, and Fe^{IV}) species is well established in various complexes (Figure 1b).^[26–28] Additionally, protonation of a quinoxaline-pyran-fused dithiolene has been shown to shift the reduction potential positively.^[26,29,30] This observation aligns with findings by Hammes-Schiffer and Solis, who suggested that ligand protonation induces an inductive effect that positively shifts the catalytic reaction potential.^[31] Also, proton reactivity of pyranopterin structure is known to induce structural distortions in dithiolene complexes, thereby modulating electron transfer process.^[32] Rothery et al. reported that tetrahydro-pyranopterin enhances electron transfer to the Mo/W center in DMSO reductase, likely due to strong hydrogen-bonding interactions.^[33] Further, Bourrez et al.^[34] and Huang et al.^[35] have outlined the formation of low-valent W–H species in cyclopentadienyl-bound W complexes, highlighting the stepwise electron–proton transfer (ET–PT) process and the significant reorganization energies associated with PCET. Overall, the ligand's redox non-innocence is highly interesting, as it expands their application potential, especially in molecular-surface hybrid systems.^[36–38] This reactivity largely arises from the strong orbital interactions between the central metal and the dithiolene ligands, making the investigation of both the metal center and the dithiolene-S sites of particular interest.

While W–H formation is acknowledged as a critical step in H₂ production, the specific role of dithiolene in high-valent W-oxo complexes, particularly in electrochemical proton reduction pathways, remains underexplored. The axial oxo ligand indeed tends to be more susceptible to

protonation in high-valent metal-oxo complexes. Metal-oxo's interactions with HA (proton sources) have been discussed in the literature for various transition metals.^[27,28,39] For instance, IR spectroscopy has indicated the formation of a hydrogen bond in [W^V=O–H–OC₆H₅].^[40] Strong acids, such as *p*-toluenesulfonic acid (TsOH, pK_a 8.5 in CH₃CN) and anilinium tetrafluoroborate (PhNH₂·HBF₄, pK_a 10.64),^[41] have been shown to induce dehydration through double protonation of W=O, yielding W(CH₃CN)₂(S₂C₂(C₆H₅)₂)₂.^[42,43] Gomez-Mingot et al. previously also identified the W^{IV}=O bond as the main protonation site.^[44] They showed that in a W-oxo dithiolene complex, a concerted PCET at the oxo site forms a W–H intermediate, suggesting that H₂ evolution proceeds via intramolecular coupling of W(H)(OH). The protonation of W^{IV}=O to form W^{IV}–OH should lower the highest occupied molecular orbital (HOMO) energy level, thereby altering the electronic properties of the complex.^[21] However, in theory, additional protonation at the dithiolene-S site can strengthen the inductive effect, further facilitating electron transfer to the W^{IV} center. Computational results also showed that such sequential protonation lowers the free energy of the electron transfer reaction to the W^{IV} center (Figure 2), leading to a more positive shift in the W^{IV}→^{III} reduction potential.

After electron transfer, in turn, the increased nucleophilicity of the W^{III} center can enhance the propensity for W^V–H species formation. Despite the recognized role of W–H species as a key intermediate in the catalytic cycle, the precise pathway by which proton transfer occurs

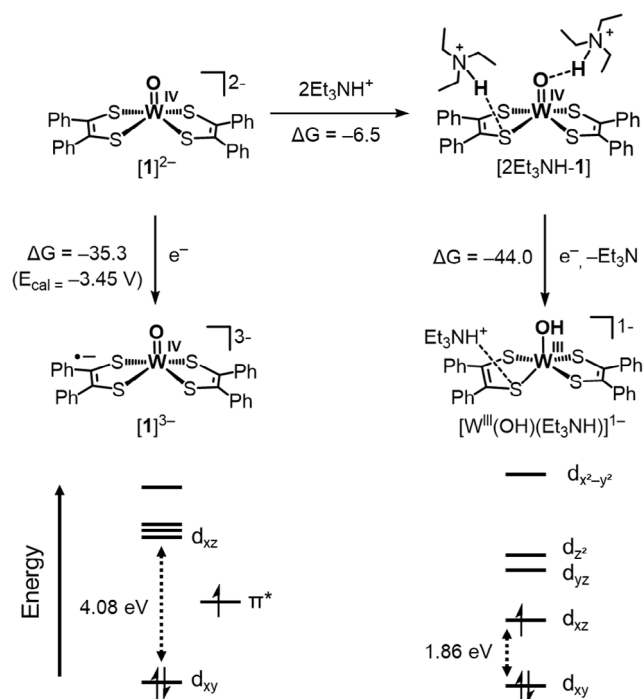


Figure 2. Relative free energy changes due to the [dithiolene-S-H·NEt₃] hydrogen-bonding interaction and proton transfer into W=O site.

within the system remains experimentally unresolved. Furthermore, the substantial energy gap between the HOMO and the lowest unoccupied molecular orbital (LUMO) in the bis(dithiolene) W^{IV}=O complex (Figures 2 and S1) has thus far prevented the observation of any W^{III}-oxo species, leaving the proton-coupled electron transfer (PCET) mechanism in W-oxo complexes unclear. To our knowledge, no prior studies have examined whether the dithiolene-S site directly influences proton reactivity of high-valent W-oxo complexes. We present for the first time evidence that in high-valent W-oxo bis(dithiolene) complexes, the dithiolene-S site can participate in hydrogen bonding with a proton source, acting as a proton relay (Figure 1c). This hydrogen-bonding interaction significantly impacted the efficiency of electrochemical proton reduction. Formation of a hydrogen bond induces a distortion in the molecular orbital (MO) structure of the complex, notably lowering the energy level of the LUMO. This decrease in the LUMO energy level facilitates electron transfer into the W d orbital, thereby enhancing the catalytic reactivity.

Results and Discussion

Our investigation starts with density functional theory (DFT) calculations, which were conducted on a [W(O)(S₂C₂(C₆H₅)₂)₂]²⁻ complex ([1]²⁻, Figure 2).^[45] The geometry was optimized with unrestricted B3LYP functional, def2-SVP basis set, effective core potentials, and C-PCM solvation model (ε = 35.688 for acetonitrile).^[26,44] Single-point energy was calculated at the B3LYP/def2-TZVPPD

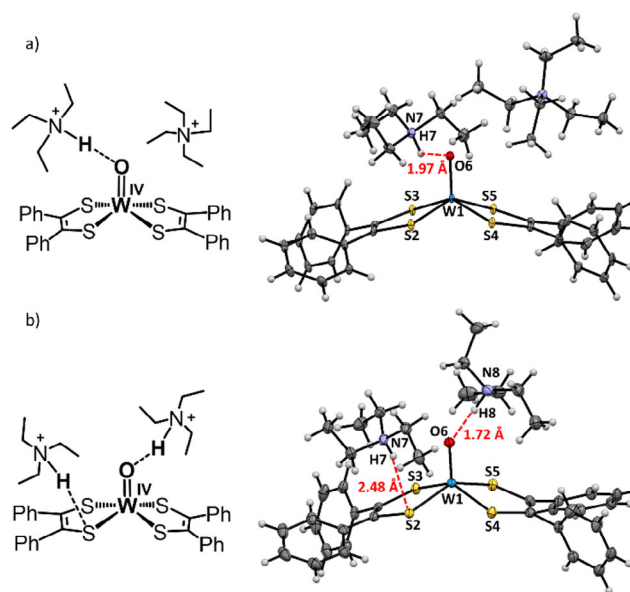


Figure 3. Single crystal X-ray structures of a) (Et₄N)[Et₃NH-1] and b) [2Et₃NH-1] with 50% probability ellipsoids.

Table 1: Structure information of (Et₄N)[Et₃NH-1] and [2Et₃NH-1].^{a)}

Complex	W-O (Å)	O-H (Å)	S-H (Å)	ν(W ^{IV} =O) (cm ⁻¹)	δ(OH) (ppm)
(Et ₄ N)[Et ₃ NH-1]	1.733	1.972	—	878	9.51
[2Et ₃ NH-1]	1.748	1.717	2.480	866, 857	8.99

^{a)} ¹H NMR chemical shift of δ(OH) in (Et₄N)[Et₃NH-1] and [2Et₃NH-1] were obtained using CD₃CN or CD₂Cl₂, respectively.

level (see the Supporting Information). The computational results showed that 21% of the HOMO is localized on the S₄ core (Figure S2), as well as 10% of the LUMO. Therefore, the electron density distribution in [1]²⁻ suggests that the dithiolene-S site might also participate in proton reactions, depending on the pK_a of proton source or the complex's electronic configuration.

Upon reaction of (Et₄N)₂[1] with 1 equivalent of the weak acid triethylammonium tetrafluoroborate (Et₃N·HBF₄, pK_a 18.83) in CH₃CN, dark red star-shaped crystals were obtained (detailed crystallographic data are provided in Tables S1 and S6). Single-crystal X-ray analysis revealed the displacement of one Et₄N⁺ counter ion, replaced by Et₃NH⁺, which forms a hydrogen bond with the W=O site at a distance of 1.972 Å (Figure 3a and Table 1). The ν(W^{IV}=O) stretching frequency shifted from 887 to 878 cm⁻¹ (Figure 4a, black and red, respectively), indicative of hydrogen bonding at the W=O site, which reduced electron density on the bond. The ¹H NMR signal for [W=O-H·NEt₃] appeared at 9.51 ppm in CD₃CN, and the ²H NMR signal for [W=O-D·NEt₃] was detected at 9.67 ppm in CH₃CN (Figure S3). In the complex, the C=C bond was slightly elongated, while the W-S and C-S bonds showed slight contraction compared to (Et₄N)₂[1].^[45] This elongation of the C=C bond was attributed to reduced electron density resulting from the increased cationic character. Thus, it is very clear that a

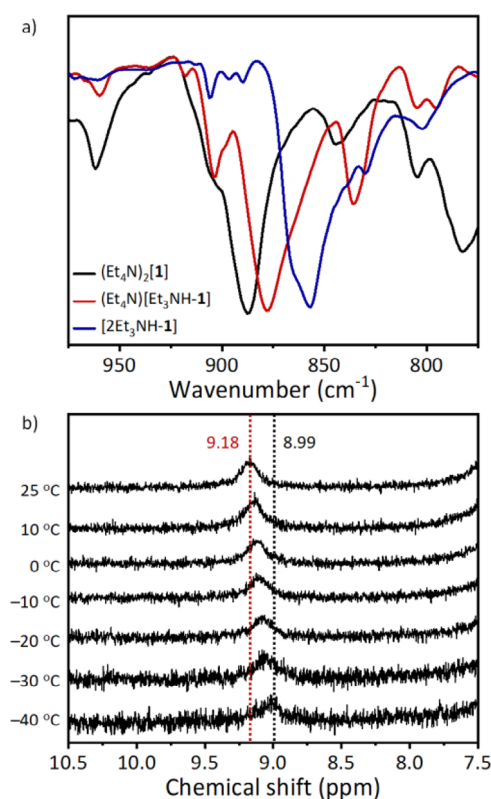


Figure 4. a) Compared IR spectra of $(\text{Et}_4\text{N})_2[\mathbf{1}]$, $(\text{Et}_4\text{N})[\text{Et}_3\text{NH}-\mathbf{1}]$, and $[\text{2Et}_3\text{NH}-\mathbf{1}]$. b) variable-temperature (VT) ^1H NMR spectra of $[\text{2Et}_3\text{NH}-\mathbf{1}]$.

hydrogen bond has formed to the $\text{W}=\text{O}$ moiety, and the obtained structure is characterized as $(\text{Et}_4\text{N})[\text{Et}_3\text{NH}-\mathbf{1}]$.

When $(\text{Et}_4\text{N})_2[\mathbf{1}]$ was treated with 2 equivalents of $\text{Et}_3\text{N}\cdot\text{HBF}_4$ in CH_3CN , a red-brown precipitate formed. Due to its neutral state, the product showed better solubility in nonpolar solvents like CH_2Cl_2 , and orange needle-shaped crystals were obtained by vapor diffusion of diethyl ether. X-ray crystallography revealed two hydrogen-bonding interactions: one at the dithiolene-S site ([dithiolene-S–H– NEt_3], S2–H7 ~ 2.48 Å) and another one at the $\text{W}=\text{O}$ site ($[\text{W}=\text{O}-\text{H}\cdot\text{NEt}_3]$, H8–O6 ~ 1.72 Å) (Figure 3b and Table 1). The S2–N7 bond length was approximately 3.33 Å, with $\angle\text{S2}-\text{H7}-\text{N7}$ angle of 162° (Figure S4), consistent with established hydrogen-bonding geometries.^[46–48] The W1–O6 bond length was 1.748(3) Å, while the W1–S2 bond was 2.368(1) Å. Further redshifted $\nu(\text{W}^{\text{IV}}=\text{O})$ stretching frequencies were observed at 866 and 857 cm^{-1} (Figure 4a, blue), with two vibrational modes present (Figure S5). Variable-temperature (VT) ^1H NMR spectra of $[\text{2Et}_3\text{NH}-\mathbf{1}]$ were recorded in CD_2Cl_2 from -40 to 25°C to evaluate hydrogen-bond strength (Figures 4b and S6). The $[\text{W}=\text{O}-\text{H}\cdot\text{NEt}_3]$ peak appeared at 8.99 ppm at -40°C and shifted downfield to 9.18 ppm as temperature increased (Figure 4b). In $[\text{2Et}_3\text{NH}-\mathbf{1}]$, the peak corresponding to hydrogen bonding was observed to shift slightly upfield compared to $(\text{Et}_4\text{N})[\text{Et}_3\text{NH}-\mathbf{1}]$, but two distinct peaks were not observed, likely due to an overlap of NMR signals caused by nearly identical hydrogen-bonding strengths.

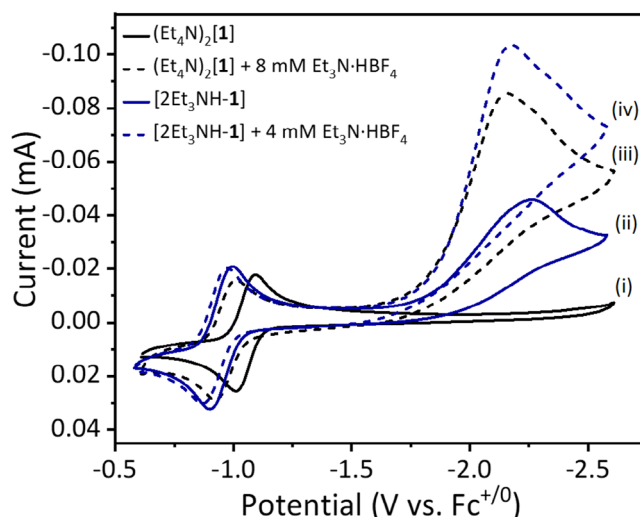


Figure 5. Cyclic voltammograms (CVs) of i) $(\text{Et}_4\text{N})_2[\mathbf{1}]$ (black solid, 2 mM), ii) $[\text{2Et}_3\text{NH}-\mathbf{1}]$ (blue solid, 2 mM), iii) $(\text{Et}_4\text{N})_2[\mathbf{1}]$ in the presence of 8 mM of $\text{Et}_3\text{N}\cdot\text{HBF}_4$ (black dashed), iv) $[\text{2Et}_3\text{NH}-\mathbf{1}]$ in the presence of 4 mM of $\text{Et}_3\text{N}\cdot\text{HBF}_4$ (blue dashed). Conditions: 0.1 M $n\text{Bu}_4\text{NPF}_6$ electrolyte under N_2 , scan rate 100 mV/s.

Investigating the redox potentials, cyclic voltammogram (CV) studies of the complex $(\text{Et}_4\text{N})_2[\mathbf{1}]$ displayed a reversible $\text{W}^{\text{V-IV}}$ redox couple with a half-wave potential ($E_{1/2}$) of -1.05 V (all potentials are versus ferrocenium/ferrocene ($\text{Fc}^{+/0}$)), and a peak separation (ΔE_p) of 80 mV at a scan rate of 100 mV/s (Figure 5, black solid). The linear relationship between the anodic-to-cathodic peak current ratio ($i_{\text{pa}}/i_{\text{pc}}$) and the square root of the scan rate ($v^{1/2}$) indicated homogeneous electrochemical behavior of the complex (Figure S7), with a diffusion coefficient (D) measured at 4.83×10^{-6} . No additional reductive current appeared in the cathodic scan extending to -2.58 V, likely due to the strong $\text{W}^{\text{IV}}=\text{O}$ bond, which results in a substantial ligand field splitting and positions the LUMO at a relatively high energy level.^[49] However, hydrogen bonding interactions can modify the molecular orbital energy levels, potentially shifting the complex's redox potential to more positive values. This effect was observed in the CV of $[\text{2Et}_3\text{NH}-\mathbf{1}]$, where the $\text{W}^{\text{V-IV}}$ redox couple shifted from -1.05 V to -0.95 V, and an irreversible reduction peak appeared at -2.26 V (Figure 5, blue solid). The reversible nature of the $\text{W}^{\text{V-IV}}$ redox peak indicates that the hydrogen bond is stable under electrochemical conditions. Upon addition of 4 mM $\text{Et}_3\text{N}\cdot\text{HBF}_4$ to $[\text{2Et}_3\text{NH}-\mathbf{1}]$ solution, an irreversible reduction current increased at -1.75 V (Figure 5, blue dashed). This catalytic reaction of $[\text{2Et}_3\text{NH}-\mathbf{1}]$ exhibited the same onset potential in the CV of $(\text{Et}_4\text{N})_2[\mathbf{1}]$ in the presence of 8 mM $\text{Et}_3\text{N}\cdot\text{HBF}_4$ (Figure 5, black dashed), indicating that $[\text{2Et}_3\text{NH}-\mathbf{1}]$ is indeed the reaction intermediate in the catalytic cycle. The increase in reductive current, which correlated with the proton source concentration, suggested the occurrence of an electrocatalytic reaction (Figure S8). This catalytic activity showed a half-wave potential of -2.28 V with 100 mM of $\text{Et}_3\text{N}\cdot\text{HBF}_4$, yielding a catalytic current-to-peak current ratio (i_{cat}/i_p at 100 mV/s) of 76.17. The turnover frequency (TOF)

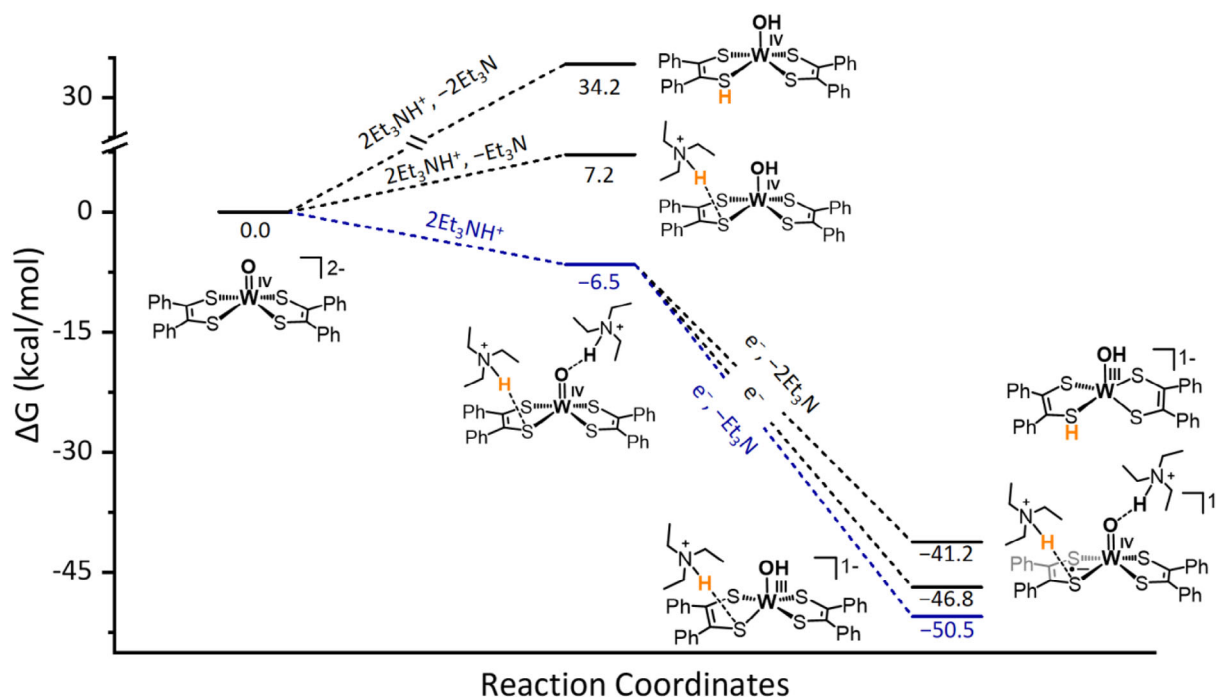


Figure 6. Calculated relative energies for protonated and hydrogen-bonded state of the complex.

determined using the foot-of-the-wave analysis (FOWA) was $122,277\text{ s}^{-1}$ (Figure S9), with details provided in the Supporting Information.^[50] Chronoamperometry confirmed that the reductive current was associated with catalytic H_2 evolution, achieving a Faradaic efficiency (FE) of 99%.

Gomez-Mingot et al. previously proposed a concerted PCET pathway in which acetic acid acts as a proton donor to $(\text{Et}_4\text{N})_2[\text{W}(\text{O})(\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2)_2]$ to generate a $[\text{W}(\text{H})(\text{OH})]$ intermediate.^[44] This mechanism appeared feasible due to the favorable free energy associated with W–H bond formation. In our investigation, we initially considered a similar PCET process, especially given our experimental detection of a hydrogen bond in the $(\text{Et}_4\text{N})[\text{Et}_3\text{NH-1}]$ structure. However, the presence of an additional hydrogen bond at the [dithiolene-S–H· NEt_3] site suggested that an alternative route via the dithiolene-S site might be more likely. To evaluate this possibility, we compared the relative energies of various protonated and hydrogen-bonded states of the complex theoretically (Figure 6 and Table S2). Our analysis revealed that protonation of both the W-oxo and dithiolene-S sites was highly endergonic, requiring $34.2\text{ kcal mol}^{-1}$ with Et_3NH^+ as the proton source. Protonation of the W-oxo site alone, with hydrogen bonding at the dithiolene-S site, was also endergonic but less so, at 7.2 kcal mol^{-1} . In contrast, the formation of two hydrogen bonds—one at the W-oxo site and another at the dithiolene-S site—was exergonic, with a free energy change of $-6.5\text{ kcal mol}^{-1}$, favoring the formation of the $[\text{2Et}_3\text{NH-1}]$ complex. This finding was consistent with the X-ray crystallographic data. The hydrogen bond to S in $[\text{2Et}_3\text{NH-1}]$ lowers the energy by 4.4 kcal mol^{-1} compared to $[\text{Et}_3\text{NH-1}]^{1-}$, which lacks the Et_3NH^+ hydrogen bond to S. The calculated reduction potential for the $[\text{2Et}_3\text{NH-1}]^{0/1-}$ redox couple was $E_{\text{cal}} = -3.23\text{ V}$ ($\Delta G = -40.3\text{ kcal mol}^{-1}$),

suggesting a ligand-based reduction process. Analysis of the LUMO of $[\text{2Et}_3\text{NH-1}]$ indicated that the W atom contributed only 7%, with 84% of the LUMO localized on the dithiolene $(\text{S}_2\text{C}_2\text{Ph}_2)_2$ moiety (Figure S10). Similarly, Löwdin spin density and HOMO analysis of the $[\text{2Et}_3\text{NH-1}]^{1-}$ species showed a 3% contribution from the W atom and 90% from the dithiolene moiety (Figure S11). These results imply that a process involving only electron transfer to W would be challenging. PCET, on the other hand, would involve an intramolecular proton transfer to form $[\text{W}^{\text{III}}(\text{OH})(\text{Et}_3\text{NH})]^{1-}$, with a free energy change of $\Delta G = -44.0\text{ kcal mol}^{-1}$ (relative to $[\text{2Et}_3\text{NH-1}]$). The HOMO of this intermediate showed a 53% contribution from the W center and 22% from the S atoms of the dithiolene moiety, indicating delocalized electron density across the W–S₄ core (Figure S12).

Electron paramagnetic resonance (EPR) spectroscopy was employed to investigate the potential formation of $\text{W}^{\text{III}}\text{—OH}$ species following the reduction of $[\text{2Et}_3\text{NH-1}]$. The EPR sample was prepared by reacting $[\text{2Et}_3\text{NH-1}]$ with potassium-anthracene ($\text{C}_{14}\text{H}_{10}\text{K}$) as a chemical reductant in dichloromethane at -40°C , and the reaction mixture was quickly frozen in liquid N_2 . The EPR spectrum of the reduced $[\text{2Et}_3\text{NH-1}]$ sample exhibited a rhombic signal with $g = [2.04, 1.94, 1.91]$ (Figure 7a, blue solid) accompanied by an almost isotropic signal centered at $g = 1.99$ (Figure 7a, black solid). First, the isotropic signal centered at $g \sim 1.99$ in Figure 7a is a characteristic EPR signal for a $\text{W}^{\text{V}}\text{=O}$ species.^[51,52] The presence of the $\text{W}^{\text{V}}\text{=O}$ species is likely attributable to partial protonation of $\text{W}^{\text{III}}\text{—OH}$ species by residual proton donors during the isolation process. For comparison, we separately prepared an $(\text{Et}_4\text{N})[\text{W}^{\text{V}}(\text{O})(\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2)_2]$ species through one-electron oxidation of $(\text{Et}_4\text{N})_2[\text{1}]$ using I_2 .^[45] The EPR spectrum of this species displayed an isotropic signal centered

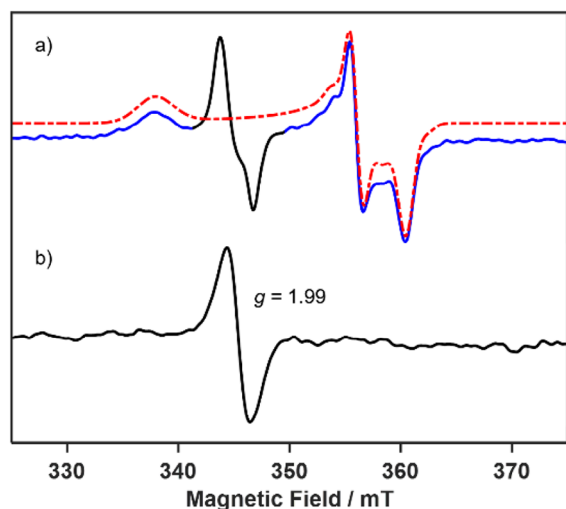


Figure 7. X-band EPR spectra of a) a W^{III} (blue) and W^V (black) species generated by addition of $C_{14}H_{10}K$ to $[2Et_3NH-1]$ with simulation (red) and b) $(Et_4N)[W^V(O)(S_2C_2(C_6H_5)_2)_2]$ (black), measured at 50 K.

at $g = 1.99$ (Figure 7b), which is almost identical to the one shown in Figure 7a (black solid). Next, we tentatively assigned the rhombic EPR signal as W^{III} . Only a few studies have described the EPR spectrum of low-spin ($S = 1/2$) W^{III} species.^[53–55] We simulated the rhombic signal with a g -tensor of $g = [2.040, 1.936, 1.912]$ and an isotropic hyperfine coupling constant of $A_{iso}(^{183}W) = 100$ MHz. The simulation shows good agreement with the experimental data (Figure 7a, red dashed). Interestingly, a hyperfine coupling with ^{183}W was necessary to simulate the weak and broad features around $g = 1.95$ and 1.92 in the EPR spectrum, although the hyperfine interaction of the ^{183}W nucleus ($I = 1/2$, 14.3%) is almost unresolvable due to line broadening.

In addition, in order to gain electron density information of the W^{III} species, we utilized a “magic pentagon” that represents the effect of spin-orbit coupling on the deviation of g -values^[56,57] by considering the orbital reduction factor. If the singly occupied molecular orbital (SOMO) is d_{xz} , the g -tensor can be expressed as follows:

$$g_{xx} = 2.040 = g_e \pm \frac{2\xi k^2}{E_{xz} - E_{xy}} \quad (1)$$

$$g_{yy} = 1.936 = g_e \pm \left(\frac{2\xi k^2}{E_{x^2-y^2} - E_{xz}} + \frac{6\xi k^2}{E_{z^2} - E_{xz}} \right) \quad (2)$$

$$g_{zz} = 1.912 = g_e \pm \frac{2\xi k^2}{E_{yz} - E_{xz}} \quad (3)$$

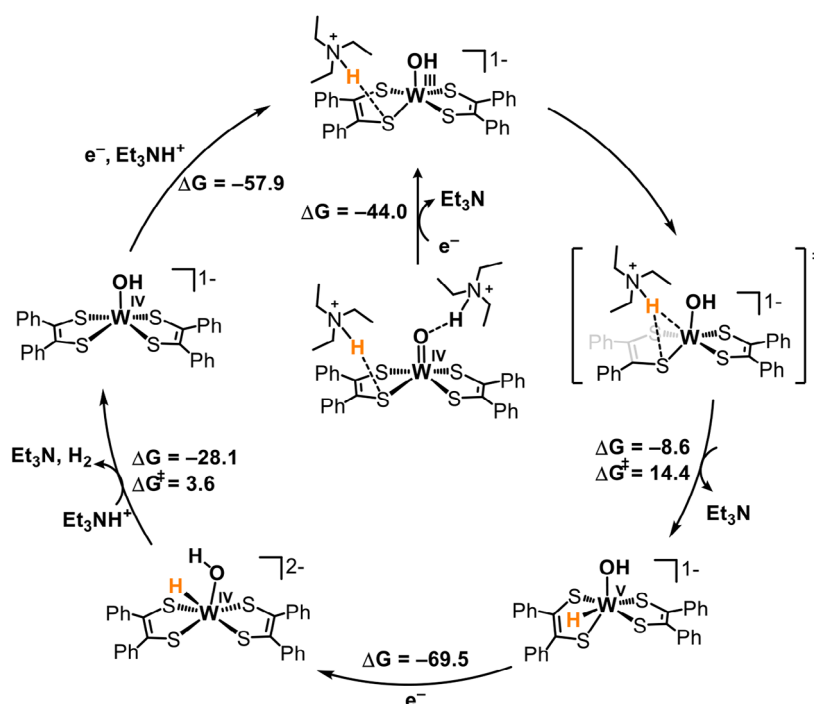
where g_e is the g -value of the free electron (2.0023), E_n is the energy of the d orbital, ξ is the spin-orbit coupling constant, and k is the orbital reduction factor. In general, positive and negative g -value shifts are caused by transitions from the doubly occupied molecular orbital (DOMO) to the SOMO and from the SOMO to the virtual molecular orbital (VMO), respectively.^[58] According to DFT calculations, the energy gap between the HOMO (d_{xz}) and HOMO-1 (d_{xy}) of $[W^{III}(OH)(Et_3NH)]^{1-}$ is 1.86 eV ($\sim 15,000$ cm $^{-1}$, Figure

S13). Adopting ξ of 2,654 cm $^{-1}$ for W^{III} ion^[59] and the $d_{xy} \rightarrow d_{xz}$ transition energy, the k value is estimated to be 0.33, with further details provided in the Supporting Information (Equation 3). This k value suggests that approximately 42% of the d -electron spin is delocalized to the ligand p orbitals, indicating the strong covalency between W and the dithiolene ligand. Thus, we assigned the rhombic EPR signal with $g = [2.04, 1.94, 1.91]$ to be a W^{III} species with the electron spin of the metal ion delocalized into dithiolene ligands (Figure 7a).

It is known that hydrogen bonding in a complex can facilitate proton shift during PCET processes.^[60,61] From the CV of the $[2Et_3NH-1]$ complex, we observed an irreversible reduction peak at -2.26 V corresponding to the conversion of $[2Et_3NH-1]$ to $[W^{III}(OH)(Et_3NH)]^{1-}$ (Figure 5). Subsequently, a proton involved in hydrogen bonding with the dithiolene-S site migrates to the W^{III} center, forming $[W^V(H)(OH)]^{1-}$. The calculated activation barrier for this step is $\Delta G^\ddagger = 14.4$ kcal mol $^{-1}$ ($\Delta G = -8.6$ kcal mol $^{-1}$), which is higher than that of other transition states, indicating that the formation of the W^V-H species is the rate-determining step (RDS). (Scheme 1 and Figure S14). An experimental activation energy of $\Delta G^\ddagger_{298K} = 11.0$ kcal mol $^{-1}$ obtained from the Eyring plot (Figure S15) is in good agreement with our computational results.^[62] Furthermore, to determine the kinetic isotope effect (KIE(H/D)),^[63] we performed analogous experiments using the deuterated complex $[2Et_3ND-1]$. From this, we obtained a KIE(H/D) value of 1.62 for the intramolecular proton shift step (Figure S16).^[64,65] Once the $[W^V(H)(OH)]^{1-}$ intermediate is formed, electron transfer proceeds at a reasonable potential of $E_{cal} = -1.96$ V, corresponding to $\Delta G = -69.5$ kcal mol $^{-1}$. The final step involves H_2 release from $[W^{IV}(H)(OH)]^{2-}$ through intramolecular coupling between the $W-OH$ and $W-H$ sites.^[44] This coupling is an exergonic process with $\Delta G = -35.5$ kcal mol $^{-1}$ and $\Delta G^\ddagger = 15.6$ kcal mol $^{-1}$ (Figure S17). Alternatively, a heterolytic coupling between $W^{IV}-H$ and an external Et_3NH^+ is feasible, with $\Delta G = -28.1$ kcal mol $^{-1}$ and a significantly low activation energy of $\Delta G^\ddagger = 3.6$ kcal mol $^{-1}$ (Figure S18). Although the intramolecular coupling pathway is thermodynamically more favorable by -7.4 kcal mol $^{-1}$, the higher kinetic barrier suggests that intermolecular coupling is more probable. Another possible pathway involves further protonation of the $W-OH$ moiety to form $W-OH_2$ rather than $H-H$ coupling in $[W^{IV}(H)(OH)]^{2-}$. However, this step is highly endergonic, with $\Delta G = 115.6$ kcal mol $^{-1}$ (Figure S19), making it unlikely. The pK_a of the proton source is too high to allow for double protonation at the W -oxo site. To complete the catalytic cycle, one-electron reduction process coupled with Et_3NH^+ hydrogen bonding ($\Delta G = -57.9$ kcal mol $^{-1}$) would regenerate $[W^{III}(OH)(Et_3NH)]^{1-}$. Relative energies of all reaction intermediates are represented in Figure S20 and Table S3, and detailed spin populations and geometric parameters from these simulations are available in Tables S4 and S5.

Conclusion

This study provides the first experimental evidence that in high-valent W -oxo bis(dithiolene) complexes, the



Scheme 1. Plausible HER pathways of [2Et₃NH-1].

dithiolene-S site can engage in hydrogen bonding with a proton source, acting as a proton relay. The presence of these hydrogen bonds significantly influences the molecular orbital structure, particularly lowering the LUMO energy level, thereby enhancing electron transfer and catalytic efficiency. Through a combination of crystallographic, spectroscopic, and electrochemical analyses, we have demonstrated that hydrogen bonding at both the W^{IV}=O and dithiolene-S sites induces structural distortions that facilitate proton-coupled electron transfer (PCET), ultimately promoting electrocatalytic hydrogen evolution. Furthermore, our study successfully characterizes the W^{III}–OH species for the first time, providing insights into its electronic structure via EPR spectroscopy. Computational investigations further confirm that protonation at the dithiolene-S site contributes to a reduction in the W^{IV}→W^{III} redox potential, enhancing catalytic activity by modulating the electronic properties of the complex. The identification of a dithiolene-based proton relay mechanism in a high-valent metal-oxo system deepens our understanding of the critical role of dithiolene in facilitating proton transfer and tuning electronic properties. The broader implications of these findings extend beyond W-dithiolene chemistry, as they suggest that ligand-based protonation and hydrogen bonding interactions can play a pivotal role in regulating catalytic activity in transition metal complexes.

Supporting Information

Details about characterization, materials and synthetic procedures, experimental procedures, computational details, and

mechanistic studies are provided in the Supporting Information. Deposition Numbers [2381980](#) (for (Et₄N)[Et₃NH-1]) and [2381760](#) (for [2Et₃NH-1]) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Dithiolene • Hydrogen bond • PCET • W^{III}–OH • W-oxo

- [1] J. R. McKone, S. C. Marinescu, B. S. Brunschwig, J. R. Winkler, H. B. Gray, *Chem. Sci.* **2014**, 5, 865–878.
- [2] A. L. Ostericher, K. M. Waldie, C. P. Kubiak, *ACS Catal.* **2018**, 8, 9596–9603.
- [3] Z. Thammavongsy, I. P. Mercer, J. Y. Yang, *Chem. Commun.* **2019**, 55, 10342–10358.
- [4] B. H. Solis, A. G. Maher, D. K. Dogutan, D. G. Nocera, S. Hammes-Schiffer, *Proc. Natl. Acad. Sci. USA* **2016**, 113, 485–492.
- [5] H. M. Castro-Cruz, N. A. Macías-Ruvalcaba, *Coord. Chem. Rev.* **2022**, 458, 214430.
- [6] X. Peng, M. Zhang, H. Qin, J. Han, Y. Xu, W. Li, X. P. Zhang, W. Zhang, U. P. Apfel, R. Cao, *Angew. Chem. Int. Ed.* **2024**, 63, 202401074.
- [7] J. W. Jurss, R. S. Khnayzer, J. A. Panetier, K. A. El Roz, E. M. Nichols, M. Head-Gordon, J. R. Long, F. N. Castellano, C. J. Chang, *Chem. Sci.* **2015**, 6, 4954–4972.
- [8] L. Tong, R. Zong, R. P. Thummel, *J. Am. Chem. Soc.* **2014**, 136, 4881–4884.
- [9] N. Queyriaux, R. T. Jane, J. Massin, V. Artero, M. Chavarot-Kerlidou, *Coord. Chem. Rev.* **2015**, 304–305, 3–19.
- [10] A. C. Bowman, C. Milsman, C. C. Hojilla Atienza, E. Lobkovsky, K. Wieghardt, P. J. Chirik, *J. Am. Chem. Soc.* **2010**, 132, 1676–1684.
- [11] B. Butschke, K. L. Fillman, T. Bendikov, L. J. Shimon, Y. Diskin-Posner, G. Leitun, S. I. Gorelsky, M. L. Neidig, D. Milstein, *Inorg. Chem.* **2015**, 54, 4909–4926.
- [12] B. Jiang, M. Gil-Sepulcre, P. Garrido-Barros, C. Gimbert-Suriñach, J.-W. Wang, J. Garcia-Anton, P. Nolis, J. Benet-Buchholz, N. Romero, X. Sala, A. Llobet, *Angew. Chem. Int. Ed.* **2022**, 61, 202209075.
- [13] A. Z. Haddad, B. D. Garabato, P. M. Kozłowski, R. M. Buchanan, C. A. Grapperhaus, *J. Am. Chem. Soc.* **2016**, 138, 7844–7847.
- [14] T. Straistari, J. Fize, S. Shova, M. Réglie, V. Artero, M. Orio, *ChemCatChem* **2017**, 9, 2262–2268.
- [15] A. Z. Haddad, S. P. Cronin, M. S. Mashuta, R. M. Buchanan, C. A. Grapperhaus, *Inorg. Chem.* **2017**, 56, 11254–11265.
- [16] H. Jabosen, J. P. Donahue, *Inorg. Chem.* **2008**, 47, 10037–10045.
- [17] C. S. Letko, J. A. Panetier, M. Head-Gordon, T. D. Tilley, *J. Am. Chem. Soc.* **2014**, 136, 9364–9376.
- [18] A. Zarkadoulas, M. J. Field, V. Artero, C. A. Mitsopoulou, *ChemCatChem* **2017**, 9, 2308–2317.
- [19] R. Eisenberg, H. B. Gray, *Inorg. Chem.* **2011**, 50, 9741–9751.
- [20] F. J. Hine, A. J. Taylor, C. D. Garner, *Coord. Chem. Rev.* **2010**, 254, 1570–1579.
- [21] A. L. Tenderholt, J.-J. Wang, R. K. Szilagy, R. H. Holm, K. O. Hodgson, B. Hedman, E. I. Solomon, *J. Am. Chem. Soc.* **2010**, 132, 8359–8371.
- [22] Y. Li, M. Gomez-Mingot, T. Fogeron, M. Fontecave, *Acc. Chem. Res.* **2021**, 54, 4250–4261.
- [23] M. Drosou, F. Kamatsos, C. A. Mitsopoulou, *Inorg. Chem. Front.* **2020**, 7, 37–71.
- [24] S. Yokomori, S. Dekura, T. Fujino, M. Kawamura, T. Ozaki, H. Mori, *J. Mater. Chem. C* **2020**, 8, 14939–14947.
- [25] M. Quiroz, M. M. Lockart, M. R. Saber, S. W. Vali, L. C. Elrod, B. S. Pierce, M. B. Hall, M. Y. Darensbourg, *Proc. Natl. Acad. Sci. USA* **2022**, 119, 2201240119.
- [26] J.-P. Porcher, T. Fogeron, M. Gomez-Mingot, E. Derat, L.-M. Chamoreau, Y. Li, M. Fontecave, *Angew. Chem. Int. Ed.* **2015**, 127, 14296–14299.
- [27] T. Ishizuka, T. Kogawa, C. Ogawa, H. Kotani, Y. Shiota, K. Yoshizawa, T. Kojima, *JACS Au* **2023**, 3, 2813–2825.
- [28] Z. Gong, L. Wang, Y. Xu, D. Xie, X. Qi, W. Nam, M. Guo, *Adv. Sci.* **2024**, 11, 2310333.
- [29] T. Fogeron, J. P. Porcher, M. Gomez-Mingot, T. K. Todorova, L. M. Chamoreau, C. Mellot-Draznieks, Y. Li, M. Fontecave, *Dalton Trans.* **2016**, 45, 14754–14763.
- [30] J. P. Dicks, M. Zubair, E. S. Davies, C. D. Garner, C. Schulzke, C. Wilson, J. McMaster, *Eur. J. Inorg. Chem.* **2015**, 2015, 3550–3561.
- [31] B. H. Solis, S. Hammes-Schiffer, *J. Am. Chem. Soc.* **2012**, 134, 15253–15256.
- [32] P. Basu, S. J. Burgmayer, *Coord. Chem. Rev.* **2011**, 255, 1016–1038.
- [33] R. A. Rothery, B. Stein, M. Solomonson, M. L. Kirk, J. H. Weiner, *Proc. Natl. Acad. Sci. USA* **2012**, 109, 14773–14778.
- [34] M. Bourrez, R. Steinmetz, S. Ott, F. Gloaguen, L. Hammarström, *Nat. Chem.* **2015**, 7, 140–145.
- [35] T. Huang, E. S. Rountree, A. P. Traywick, M. Bayoumi, J. L. Dempsey, *J. Am. Chem. Soc.* **2018**, 140, 14655–14669.
- [36] S. W. Ke, Y. Wang, J. Su, K. Liao, S. Lv, X. Song, T. Ma, S. Yuan, Z. Jin, J. L. Zuo, *J. Am. Chem. Soc.* **2022**, 144, 8267–8277.
- [37] Y. Wang, S. W. Ke, G. Qiao, J. Liang, X. Zhou, X. Song, Z. Tie, S. Yuan, J. L. Zuo, Z. Jin, *Adv. Energy Mater.* **2024**, 14, 2303051.
- [38] S. W. Ke, W. Li, Y. Gu, J. Su, Y. Liu, S. Yuan, J. L. Zuo, J. Ma, P. He, *Sci. Adv.* **2023**, 9, eadf2398.
- [39] R. Bakker, A. Bairagi, M. Rodríguez, G. L. Tripodi, A. Y. Pereverzev, J. Roithová, *Inorg. Chem.* **2023**, 62, 1728–1734.
- [40] J. Seo, E. Kim, *Inorg. Chem.* **2012**, 51, 7951–7953.
- [41] S. Tshepelevitsh, A. Kütt, M. Lök, I. Kaljurand, J. Saame, A. Heering, P. G. Plieger, R. Vianello, I. Leito, *Eur. J. Org. Chem.* **2019**, 2019, 6735–6748.
- [42] J. Seo, P. G. Williard, E. Kim, *Inorg. Chem.* **2013**, 52, 8706–8712.
- [43] W. T. Eckenhoff, W. W. Brennessel, R. Eisenberg, *Inorg. Chem.* **2014**, 53, 9860–9869.
- [44] M. Gomez-Mingot, J. P. Porcher, T. K. Todorova, T. Fogeron, C. Mellot-Draznieks, Y. Li, M. Fontecave, *J. Phys. Chem. B* **2015**, 119, 13524–13533.
- [45] C. A. Goddard, R. H. Holm, *Inorg. Chem.* **1999**, 38, 5389–5398.
- [46] P. Zhou, F. Tian, F. Lv, Z. Shang, *Proteins* **2009**, 76, 151–163.
- [47] V. R. Mundlapati, S. Gautam, D. K. Sahoo, A. Ghosh, H. S. Biswal, *J. Phys. Chem. Lett.* **2017**, 8, 4573–4579.
- [48] A. Chand, D. K. Sahoo, A. Rana, S. Jena, H. S. Biswal, *Acc. Chem. Res.* **2020**, 53, 1580–1592.
- [49] M. L. Kirk, R. L. McNaughton, M. E. Helton in *Dithiolene Chemistry: Synthesis, Properties, and Applications*, Vol. 52 (Eds.: E. I. Stiefel, K. D. Karlin), John Wiley & Sons, Inc., New York **2004**, pp. 112–198.
- [50] C. Costentin, S. Drouet, M. Robert, J. M. Savéant, *J. Am. Chem. Soc.* **2012**, 134, 11235–11242.
- [51] J. Mitra, S. Sarkar, *Inorg. Chem.* **2013**, 52, 3032–3042.
- [52] S. Sproules, P. Banerjee, T. Weyhermüller, Y. Yan, J. P. Donahue, K. Wieghardt, *Inorg. Chem.* **2011**, 50, 7106–7122.
- [53] E. Ceausescu, A. Cornilescu, E. Nicolescu, M. Popescu, S. Coca, C. Belloiu, C. Oprea, M. Dimonie, Gh. Hubca, V. Dragutan, M. Chipara, *J. Mol. Catal.* **1985**, 28, 351–357.
- [54] C. J. Adams, K. M. Anderson, N. G. Connelly, D. J. Harding, O. D. Hayward, A. G. Orpen, E. Patrón, P. H. Rieger, *Dalton Trans.* **2009**, 530–543.
- [55] U. Jayarathne, P. Chandrasekaran, A. F. Greene, J. T. Mague, S. DeBeer, K. M. Lancaster, S. Sproules, J. P. Donahue, *Inorg. Chem.* **2014**, 53, 8230–8241.
- [56] M. Ju, J. Kim, J. Shin, *Bull. Korean Chem. Soc.* **2024**, 45, 835–862.
- [57] R. S. Drago in *Physical Methods for Chemists*, Surfside Scientific Publishers, Gainesville **1992**, pp.564–571.
- [58] H. C. Chang, B. Mondal, H. Fang, F. Neese, E. Bill, S. Ye, *J. Am. Chem. Soc.* **2019**, 141, 2421–2434.
- [59] J. Bendix, M. Brorson, C. E. Schaffer, *Inorg. Chem.* **1993**, 32, 2838–2849.

- [60] A. Pannwitz, O. S. Wenger, *Dalton Trans.* **2019**, 48, 5861–5868.
- [61] Y. Deng, J. A. Roberts, S. M. Peng, C. K. Chang, D. G. Nocera, *Angew. Chem. Int. Ed.* **1997**, 36, 2124–2127.
- [62] K. F. Morris, L. E. Erickson, *J. Chem. Educ.* **1996**, 73, 471.
- [63] S. Dey, T. K. Todorova, M. Fontecave, V. Mougél, *Angew. Chem. Int. Ed.* **2020**, 59, 15726–15733.
- [64] C. Costentin, M. Robert, J. M. Savéant, *Acc. Chem. Res.* **2010**, 43, 1019–1029.
- [65] T. F. Markle, M. T. Zhang, M. P. Santoni, L. O. Johannissen, L. Hammarström, *J. Phys. Chem. B* **2016**, 120, 9308–9321.

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Research Article

Electrochemistry

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Hydrogen Bond-Assisted PCET and
Formation of W^{III} —OH in Bis(Dithiolene)
Complex

The single crystal structure of complex $[2Et_3NH^+][1^-]$ reveals hydrogen bonding at both W-oxo and dithiolene-S sites within the bis(dithiolene) W^{IV} -oxo complex. This finding provides critical evidence for dithiolene's involvement in proton reactions in high-valent W-oxo complexes. Hydrogen-bonding interactions promote the electrochemical formation of W^{III} —OH, characterized here for the first time using EPR spectroscopy.

