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Deoxygenation of Mono-oxo Bis(dithiolene) Mo and W Complexes by Protonation

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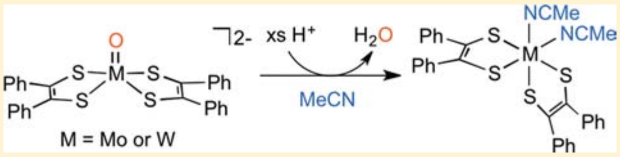
Supporting Information



ABSTRACT: Protonation-assisted deoxygenation of a mono-oxo molybdenum center has been observed in many oxotransferases when the enzyme removes an oxo group to regenerate a substrate binding site. Such a reaction is reported here with discrete synthetic mono-oxo bis(dithiolene) molybdenum and tungsten complexes, the chemistry of which had been rarely studied because of the instability of the resulting deoxygenated products. An addition of tosylic acid to an acetonitrile solution of $[Mo^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (**1**) and $[W^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (**2**) results in the loss of oxide with a concomitant formation of novel deoxygenated complexes, $[M(MeCN)_2(S_2C_2Ph_2)_2]$ (M = Mo (**3**), W (**4**)), that have been isolated and characterized. Whereas protonation of **1** exclusively produces **3**, two different reaction products can be generated from **2**; an oxidized product, $[WO(S_2C_2Ph_2)_2]^-$, is produced with 1 equiv of acid while a deoxygenated product, $[W(MeCN)_2(S_2C_2Ph_2)_2]$ (**4**), is generated with an excess amount of proton. Alternatively, complexes **3** and **4** can be obtained from photolysis of $[Mo(CO)_2(S_2C_2Ph_2)_2]$ (**5**) and $[W(CO)_2(S_2C_2Ph_2)_2]$ (**6**) in acetonitrile. A di- and a monosubstituted adducts of **3**, $[Mo(CO)_2(S_2C_2Ph_2)_2]$ (**5**) and $[Mo(PPh_3)(MeCN)(S_2C_2Ph_2)_2]$ (**7**) are also reported.

1. INTRODUCTION

Nature utilizes chemistry of high-valent metal oxo species to carry out a wide range of important catalytic reactions. Many heme and nonheme iron enzymes (e.g., cytochrome P450) use highly reactive $Fe^{IV}{=}O$ for their oxygenase and oxidase activity.[1−3] Photosynthesis relies on high-valent $Mn{=}O$ species to carry out water splitting.[4,5] In addition to Fe and Mn, nature also uses a metal-oxo motif with a second and a third row transition metal ion such as Mo and W which have considerably different chemical properties from those of Fe- and Mn-oxo species.[6−10] In contrast to the highly reactive Fe/Mn oxo counterparts, molybdenum and tungsten in high oxidation state (IV−VI) are stabilized by the oxo ligand. The high valent $Mo{=}O$ or $W{=}O$ species are often considered a thermodynamic sink in synthesis because they can be easily generated by a trace amount of O_2 or water contamination.[11−14] Nature, however, efficiently utilizes the $Mo{=}O$ or $W{=}O$ unit to achieve difficult multielectron redox catalysis of oxotransferases, in which the addition and removal of the oxo group of the Mo/W center is elegantly coordinated as involving water, protons, and electrons.[6−10]

One of the best studied oxotransferases is dimethylsulfoxide reductase (DMSOR) from *R. sphaeroides*.[15−24] DMSOR catalyzes the reduction of dimethylsulfoxide (DMSO) to dimethylsulfide (DMS). The X-ray structure reveals that the active site in the reduced state has a penta-coordinate Mo^{IV} ion ligated by two pterin-dithiolene cofactors and a serine side chain, while the oxidized state has an additional oxo group at the Mo^{VI} center (Scheme 1a).[15] The catalytic cycle begins with an oxygen atom transfer from DMSO to the Mo^{IV} center in the oxidative half-cycle ($DMSO + Mo^{IV} \rightarrow DMS + Mo^{VI}{=}O$). In the reductive half-cycle, the Mo^{IV} site is restored by removing the oxo group assisted by proton/electron transfer ($Mo^{VI}{=}O + 2\ e^- + 2\ H^+ \rightarrow Mo^{IV} + H_2O$), Scheme 1a. The EPR spectroscopic studies on DMSOR suggest that the reductive half reaction proceeds by two successive one-electron reduction/protonation via the formation of an EPR active $Mo^{V}{-}OH$ species.[18,24−27] Although naturally occurring DMSORs exclusively use molybdenum, a W-substituted isoenzyme (W-DMSOR) has been reported to have comparable enzyme activity.[28−30]

The O-atom transfer chemistry in the oxidative half-reaction has been extensively studied with synthetic bis(dithiolene) metal (Mo or W) complexes by a group of researchers (Scheme 1b).[13,14,31−36,41−43] The comparative studies between Mo and W complexes with various substrates by Holm and co-workers showed that the ligand electronic environment as well as the metal ion can affect the oxo-transfer reaction rate, $XO + M^{IV} \rightarrow X + M^{VI}{=}O$, where M = Mo, W; X = sulfides, amines, and others (Scheme 1b).[13,14,31,34,35]

In contrast to the oxidative half-reaction, synthetic studies on the deoxygenation chemistry in the reductive half-reaction that involve proton/electron transfer reactions are rather limited. A general challenge in the deoxygenation of the $M^{IV-VI}{=}O$ complexes (M = Mo, W) lies in the highly stable nature of metal-oxo group when the metal center has the oxidation state over 4+ and d orbital electrons less than 4.[44] With the exceptions of the enzyme active sites, such a protonation-dehydration process has been observed mostly in the polyoxo

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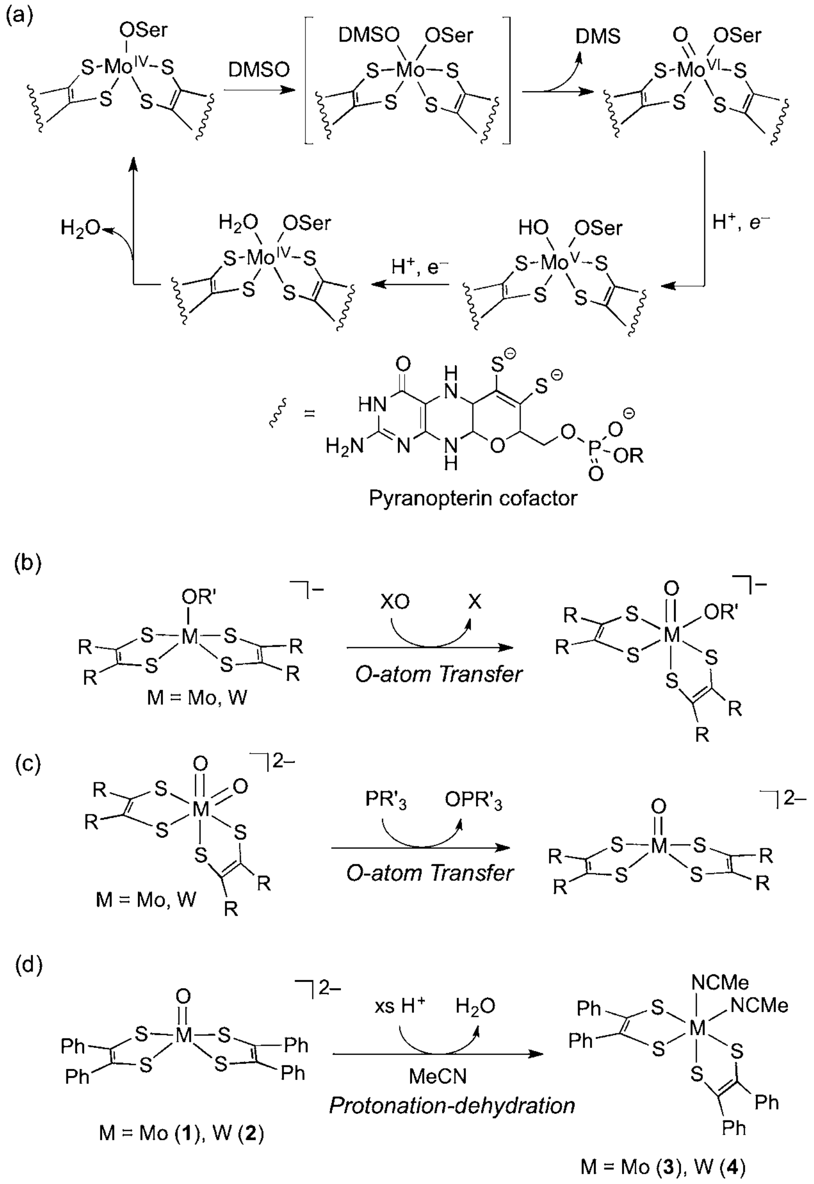
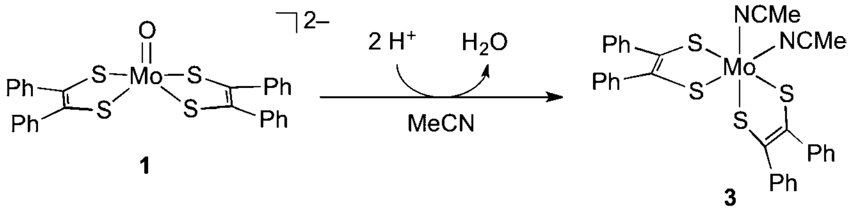
Scheme 1. (a) Proposed Catalytic Cycle for DMSOR;[15,20,24] (b) Known Synthetic Modeling Chemistry of O-Atom Transfer from the Substrate to the Metal Center;[13,14,31−37] (c) Known Synthetic Modeling Chemistry of O-Atom Transfer from Metal to Phosphine (e.g. PPh_3);[37−40] (d) Present Work Demonstrating Protonation-Assisted Deoxygenation Chemistry of $M^{IV}{=}O$ in Synthetic Models



metal complexes, in which the metal ion can be stabilized with the remaining oxo ligand(s) after the removal of one of the oxo ligands by protonation as shown with Re(V),[45] W(VI),[46−48] and Mo(VI)[47,49] polyoxo complexes. Elimination of the oxo group from mono-oxo Mo/W complexes by protonation appears to be much more difficult to achieve, for which Sarkar and co-workers have made considerable efforts.[48,50] They found that $[W^{IV}O(mnt)_2]^{2-}$, where mnt^{2-} = 1,2-dicyanoethylenedithiolate, is not stable in the acidic condition (<pH 4) and decomposes to $[W(mnt)_3]^{2-}$,[48] whereas the presence of thiols in the acidic medium converts $[W^{IV}O(mnt)_2]^{2-}$ to a thiolate-bridged dimerized compound, $[W^{IV}_2(SR)_2(mnt)_4]^{2-}$.[50] Although these results indicate that the oxo group must have been removed by protonation prior to the formation of the observed products, there has been no literature precedent that demonstrates that protonation itself can remove the oxide of the mono-oxo bis(dithiolene) Mo/W complexes without altering the core structure of bis(dithiolene) metal complexes. The only successful way of removing the oxo group from the bis(dithiolene) metal site appears to be the use of nonbiological oxygen abstractors like phosphines (e.g., PPh_3) by which the O-atom, as opposed to oxide (O^{2-}), can be removed from the metal site with a concomitant reduction of the metal ion (Scheme 1c).[33] Inspired by the biological process of converting a metal-bound oxo ligand to water, we have studied the protonation chemistry of discrete molybdenum and tungsten oxo complexes. Herein, we report for the first time that the oxo-group of mono-oxo bis(dithiolene) Mo^{IV}/W^{IV} complexes can be removed by simple protonation (Scheme 1d) to yield the unprecedented deoxygenated products $[M(MeCN)_2(S_2C_2Ph_2)_2]$.

Scheme 2



2. RESULTS AND DISCUSSION

Protonation of $[Mo^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (1) to Form $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (3). We examined the protonation of a bis(dithiolene) molybdenum complex, $[Mo^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (**1**), with *p*-toluenesulfonic acid (TsOH) as a proton source. We found that 2 equiv of acid was required to remove the oxo group of **1** producing deoxygenated bis(dithiolene)-molybdenum(IV) complex that can be stabilized by solvent without generating any intermediate (Scheme 2). Addition of 1 equiv of TsOH to an acetonitrile solution of **1** at room temperature led to an immediate UV−vis spectral change (red dashed, Figure 1) indicating a fast but incomplete conversion of **1** to $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (**3**), in which a new band at 446 nm from **3** arose as the 282, 320, and 365 nm absorptions from **1** decreased. The 446 nm band reached to a maximum with an additional 1 equiv of TsOH (purple solid, Figure 1), suggesting that the complete conversion of **1** to **3** requires at least 2 equiv of acid. Further addition of excess TsOH (a total of 4 equiv) did not affect the UV−vis features of **3** at λ_{max} (ε_M) = 265 (sh, 66000), 375 (16000), 446 (20000), 536 (sh, 9100) nm.

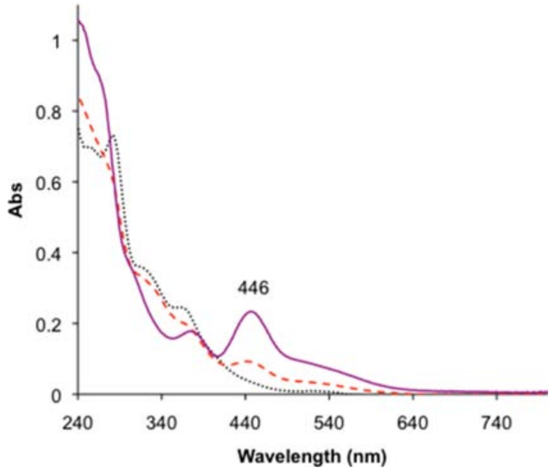


Figure 1. UV−vis spectral changes during titration of $(Et_4N)_2[MoO(S_2C_2Ph_2)_2]$ (**1**) (black dotted) with tosylic acid (TsOH) in acetonitrile at room temperature. An addition of 1 equiv of TsOH to **1** results in the incomplete conversion (red dashed) of **1** to $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (**3**). A further addition of extra 1 equiv of TsOH leads to the complete formation of **3** (purple solid).

The isolation of $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (**3**) was possible because of differential solubility of $[MoO(S_2C_2Ph_2)_2]^{2-}$ (**1**) and **3** in acetonitrile. Complex **3** as a dark violet precipitation was slowly developed from the reaction solution of **1** with TsOH. The IR spectrum of the isolated precipitate lacks the characteristic $Mo^{IV}{=}O$ stretch frequency of **1** at 881 cm^{-1}, which indicates the elimination of the molybdenum-oxo group by protonation (Supporting Information, Figure S1). In addition, the IR spectrum of the precipitate displays the ν(CN) stretch frequencies at 2317 and 2282 cm^{-1} (Supporting Information, Figure S2) which are in the expected range for the metal-bound acetonitriles[51−53] and are particularly very close to those found in $[MoCl_4(MeCN)_2]$ (2320, 2291 cm^{-1}).[54] On the basis of the data obtained from IR spectroscopy and elemental analysis, we formulate the reaction product as $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (**3**) and propose a six coordination geometry for the metal ion ligated by two MeCN molecules and bis(dithiolene). We were unable to obtain an X-ray structure of **3**. However, a six-coordinate geometry for **3** would be in line with all the known neutral bis(dithiolene) molybdenum complexes,[32,55−59] in addition to our own analogue with PPh_3, $[Mo(CH_3CN)(PPh_3)(S_2C_2Ph_2)_2]$ (**7**), that has been crystallographically characterized (see below).

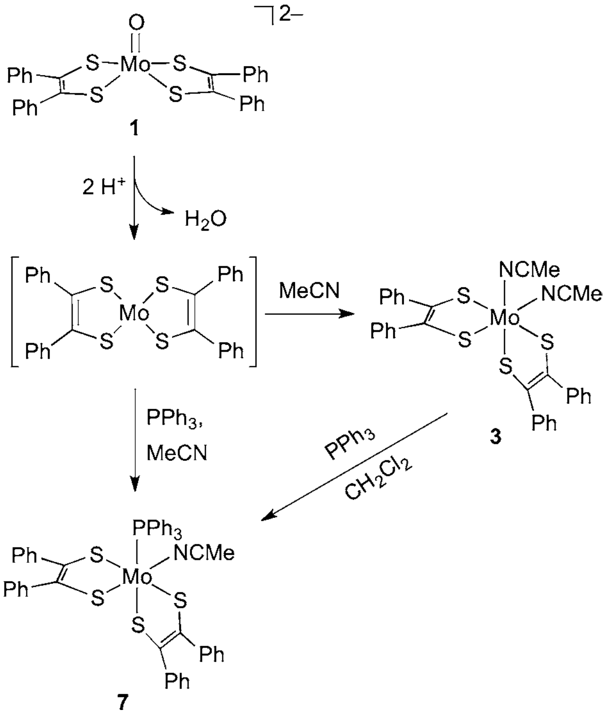
Reaction of $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (3) with CO and PPh_3. Compound **3** is stable as a solid, but its stability in solution is very much dependent on the solvent. In the absence of acetonitrile, **3** immediately decomposes to a known[60] tris(dithiolene) complex, $[Mo(S_2C_2Ph_2)_3]$; however, **3** is stable in a solvent mixture that contains at least 1% acetonitrile (e.g, 1% CH_3CN: 99% CH_2Cl_2). The coordinated MeCN ligands in **3** could be easily replaced by a stronger ligand such as CO or phosphine, which makes **3** a valuable precursor for many bis(dithiolene) Mo^{IV} complexes.

Substitution reactions of the MeCN ligand in **3** were first studied with CO because the spectroscopic characterizations of the expected reaction product, $[Mo(CO)_2(S_2C_2Ph_2)_2]$ (**5**), were well-known.[55,61] When CO was bubbled through an acetonitrile solution of **3** in dark for ~10 s, a characteristic electronic absorption in the visible region (λ_{max} = 555 nm) known for **5** started to develop, and the complete conversion of **3** to **5** was achieved in an hour (eq 1) (Supporting Information, Figure S3). The formation of **5** was further supported by IR spectroscopy, in which two characteristic ν(CO) frequencies of **5** were observed at 1996 and 2035 cm^{-1} (Nujol).

$$[Mo(MeCN)_2(S_2C_2Ph_2)_2](\mathbf{3}) \xrightarrow[MeCN]{2CO} [Mo(CO)_2(S_2C_2Ph_2)_2](\mathbf{5}) \qquad (1)$$

Synthesis of a monosubstituted analogue was achieved as we employed a bulky substituent (Scheme 3). Upon addition of solid **3** to a solution of PPh_3 in CH_2Cl_2, the reaction mixture instantly turned into a red brown solution of $[Mo(MeCN)(PPh_3)(S_2C_2Ph_2)_2]$ (**7**) with UV−vis absorptions at λ_{max} ($\varepsilon_{M,}$ CH_2Cl_2) = 251 (76000), 270 (sh, 63000), 375 (9500), 454 (20000), 543 (sh, 6000) nm (Supporting Information, Figure S4), which is similar to the UV−vis spectrum of **3** with a noticeable red-shift. The ^1H NMR spectrum of the isolated product from a CH_2Cl_2/pentane solution indicates the presence of coordinated MeCN (1.63 ppm in CD_2Cl_2) in addition to the PPh_3 ligand (Supporting Information, Figure S5). Consistent with this, the ν(CN) stretching frequency of

Scheme 3



the MeCN ligand appears at 2264 cm^{-1} in the IR spectrum (Supporting Information, Figure S2). Likewise, the molybdenum-bound PPh_3 is supported by a single peak at 62.5 ppm (in CD_2Cl_2) in the ^{31}P NMR spectrum (Supporting Information, Figure S6). All of these spectroscopic features are consistent with the X-ray structure of 7 (see below). Complex 7 can be alternatively prepared in a high yield (96%) from the way of one-pot reaction of $[Mo^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (1), PPh_3, and TsOH, Scheme 3.

The crystal structure of 7 (Figure 2) reveals a six-coordinate molybdenum ion ligated by bis(dithiolene), PPh_3, and MeCN in a trigonal prismatic geometry which is a common structure for six-coordinate bis(dithiolene) complexes such as $[Mo(CO)_2(S_2C_2Me_2)_2]$.[55,59] Similar to all the known structures of neutral six coordinate bis(dithiolene) Mo or W complexes,[32,55−59] the PPh_3 and MeCN ligands in 7 are *cis* to each other, which explains why only one of the MeCN ligands undergoes substitution by a bulky PPh_3 ligand. Conversely, a six-coordinate bis(dithiolene) W complex coordinated by two smaller phosphine ligands, $[W(PMe_3)_2(S_2C_2Me_2)_2]$, is known.[59]

Protonation of $[WO(S_2C_2Ph_2)_2]^{2-}$ (2) to form $[WO(S_2C_2Ph_2)_2]^{-}$ or $[W(MeCN)_2(S_2C_2Ph_2)_2]$ (4). In the case of a tungsten analogue, we found that the amount of acid played a critical role in determining the reaction products. This is quite different from the reactivity observed with $[MoO(S_2C_2Ph_2)_2]^{2-}$ (1) with acid from which the deoxygenated product, $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (3), was exclusively generated. Upon addition of 1 equiv of tosylic acid (TsOH) to an acetonirile solution of $[W^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (2), a clean formation of the known oxidized product, $[W^{V}O(S_2C_2Ph_2)_2]^{-}$, was observed by UV−vis spectroscopy with an absorption at 721 nm, Figure 3 and Scheme 4. In fact, this reaction is exactly analogous to the previously reported reaction of 2 with $HBF_4\cdot Et_2O$ that yields $[W^{V}O(S_2C_2Ph_2)_2]^{-}$ and H_2.[63] With additional TsOH (over 2 equiv), the oxidized compound, $[W^{V}O(S_2C_2Ph_2)_2]^{-}$, was decomposed to become another known complex, $[W(S_2C_2Ph_2)_3]$, (λ_{max} = 657 nm),[60] Figure 3 and Scheme 4. A similar decomposition reaction to a tris(dithiolene) tungsten complex in the acidic medium has been reported with $[W^{IV}O(mnt)_2]^{2-}$.[48]

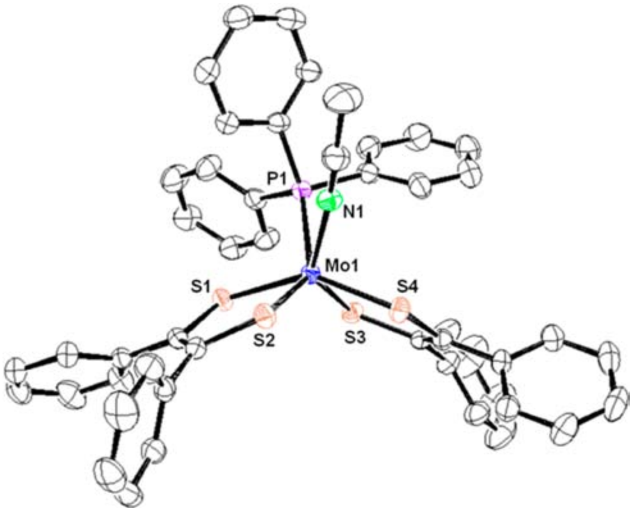


Figure 2. Structure (ORTEP view) of $Mo(PPh_3)(MeCN)(S_2C_2Ph_2)_2$ (7) with 50% probability thermal ellipsoids.[62] Hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: Mo(1)−N(1) 2.155, Mo(1)−P(1) 2.547, Mo(1)−S(1) 2.333, Mo(1)−S(2) 2.357, Mo(1)−S(3) 2.330, Mo(1)−S(4) 2.350, N(1)−Mo(1)−P(1) 79.5, N(1)−Mo(1)−S(2) 82.7, N(1)−Mo(1)−S(4) 81.0, S(2)−Mo(1)−S(4) 84.1, P(1)−Mo(1)−S(1) 82.7, P(1)−Mo(1)−S(3) 80.2, S(1)−Mo(1)−S(3) 87.1.

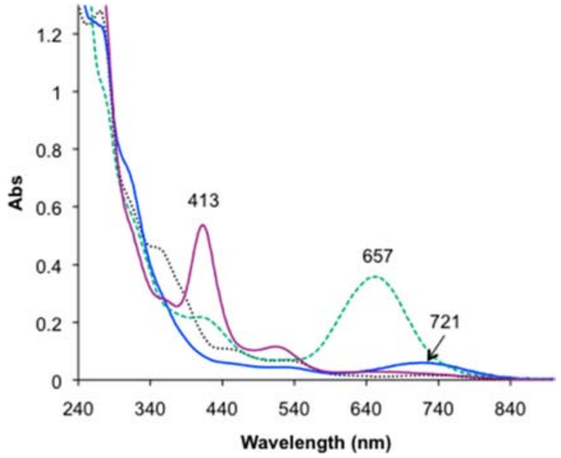
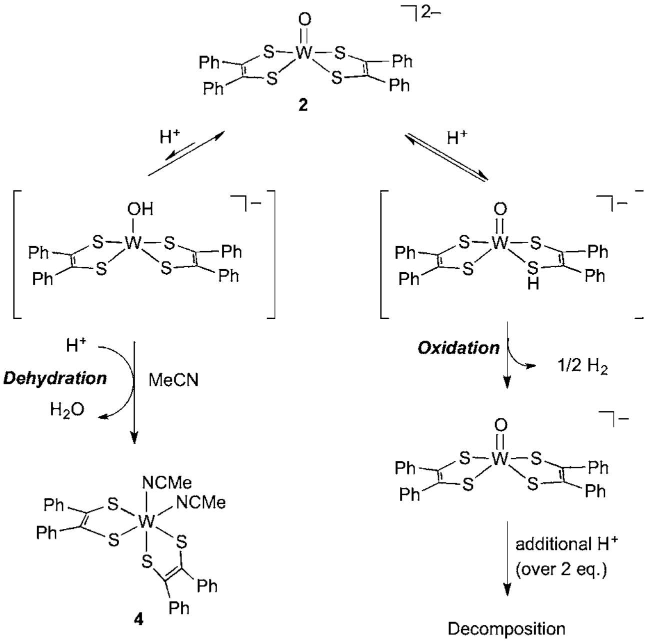


Figure 3. UV−vis spectra displaying three different products from reaction between $[WO(S_2C_2Ph_2)_2]^{2-}$ (2) (black dotted) with TsOH in acetonitrile. UV−vis spectra of the reaction of 2 with 1 equiv of TsOH generating $[WO(S_2C_2Ph_2)_2]^{-}$ (blue solid), the reaction of in situ generated $[WO(S_2C_2Ph_2)_2]^{-}$ with additional 2 equiv of TsOH forming $[W(S_2C_2Ph_2)_3]$ (green dashed), and the reaction of 2 with 4 equiv of TsOH generating $[W(MeCN)_2(S_2C_2Ph_2)_2]$ (4) (purple solid).

To our surprise, an addition of excess (4−10 equiv) amount of TsOH to $[W^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (2), as opposed to a sequential addition, led to the formation the deoxygenated product, $[W(MeCN)_2(S_2C_2Ph_2)_2]$ (4). Complex 4 has similar UV−vis features to those of its molybdenum analogue, $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (3), at λ_{max} (ε_M) = 257 (54000), 360 (8000) 413 (16000), 512 (3000) nm (Figure 3). As with 3,

Scheme 4



two ν(CN) frequencies at 2275 and 2258 cm^{-1} were observed for **4** in the IR spectrum (Supporting Information, Figure S2), and the formulation was further supported by elemental analysis.

The observed two different protonation reaction products, $[W(MeCN)_2(S_2C_2Ph_2)_2]$ (**4**) and $[W^{V}O(S_2C_2Ph_2)_2]^-$, might be explained by the presence of two different protonation sites (i.e., O- vs S-atom) in the complex, Scheme 4. To remove the oxo ligand of $[W^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (**2**) with acid, generation of a hydroxo species, $[W^{IV}(OH)(S_2C_2Ph_2)_2]^-$, through protonation of the O atom is expected as an intermediate. However, such a hydroxo species is known to be easily deprotonated to become $[W^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (**2**),[13,63] implying the equilibrium of the protonation reaction, $\{W{-}OH\} \rightleftharpoons \{W{=}O\} + H^+$, must lie to the right. Consistent with this, we were able to obtain $[W(MeCN)_2(S_2C_2Ph_2)_2]$ (**4**) only with an excess amount of acid. Once the {W−OH} species is generated, however, the dehydration step in the presence of acid appears to be an efficient and preferred pathway as judged by the high yield of **4** (~88% as isolated). On the contrary, the oxidized complex, $[W^{V}O(S_2C_2Ph_2)_2]^-$, is generated (~95%) with an 1 equiv of acid, which indicates the existence of a different protonation reaction pathway, Scheme 4. Reduction of protons to dihydrogen (H_2) has been observed with many bis(dithiolene) complexes possessing Ni,[64] Fe,[64] or Co[65,66] ions. Although the mechanism of the proton reduction to H_2 is not yet fully understood with these complexes, protonation of the S-atom of bis(dithiolene) cobalt complexes has been suggested to be a critical step to achieve the catalytic activity.[67] In the case of $[W^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (**2**), the S-atom of the dithiolne ligand is known to be susceptible to alkylating agents (e.g., MeI, $PhCH_2Br$) to produce mono-S-alkylated complexes such as $[WO(MeS_2C_2Ph_2)(S_2C_2Ph_2)_2]^-$.[12] Therefore, it is reasonable to consider the S-atom of **2** as a potent protonation site along with the O-atom of **2**. We cautiously conjecture that protonation at the different sites (S vs O) may lead to the formation of different reaction products. The efficient conversion from **2** to $[W^{V}O(S_2C_2Ph_2)_2]^-$ by 1 equiv of acid may imply that the S-atom is the preferred site for protonation, which is associated with the reduction of protons to H_2 with a concomitant oxidation of **2**, Scheme 4.

Generation of $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (3) and $[W(MeCN)_2(S_2C_2Ph_2)_2]$ (4) by Photolysis. The deoxygenated compound, $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (**3**) and $[W(MeCN)_2(S_2C_2Ph_2)_2]$ (**4**), can be alternatively generated from the appropriate dicarbonyl precursors by photolysis (eq 2). Upon irradiation of an acetonitrile solution of the known

$$[M(CO)_2(S_2C_2Ph_2)_2](\mathbf{5},\ \mathbf{6}) \xrightarrow[\text{MeCN}]{\text{UV}} [M(MeCN)_2(S_2C_2Ph_2)_2](\mathbf{3},\ \mathbf{4}) \tag{2}$$

dicarbonyl complexes $[Mo(CO)_2(S_2C_2Ph_2)_2]$ (**5**) or $[W(CO)_2(S_2C_2Ph_2)_2]$ (**6**) with a laboratory UV lamp (254−365 nm) for ~5 min at room temperature, the clean formation of **3** or **4** were observed in the UV−vis spectra (Figure 4 and Supporting Information, Figure S7). The generation of **3** or **4** from this method is noteworthy considering that photolysis of a related monocarbonyl compound, $[Mo(CO)(SPh)(S_2C_2Me_2)_2]^-$, is known to decompose to a tris(dithiolene) complex, $[Mo(S_2C_2Me_2)_3]^-$.[55]

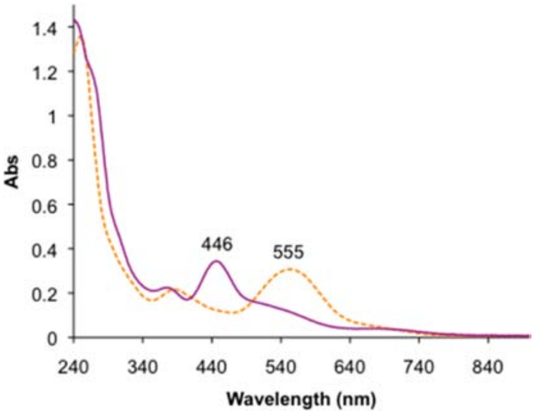


Figure 4. UV−vis spectra of $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (**3**) (purple solid) generated by photolysis of $[Mo(CO)_2(S_2C_2Ph_2)_2\ ]$ (**5**) (orange dashed) in acetonitrile at room temperature.

3. CONCLUSION

We have reported a novel deoxygenation chemistry of mono-oxo bis(dithiolene) Mo and W complexes by protonation. It had been a challenge to achieve deoxygenation chemistry with this group of complexes because the removal of the oxo ligand often causes a complex decomposition to tris(dithiolene) Mo/W species. Our study presented here demonstrates that simple protonation can efficiently remove the oxo group from the mono-oxo bis(dithiolene) Mo or W complexes, and the resulting deoxygenated products can be stabilized by the solvent. Protonation of $[Mo^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (**1**) and $[W^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (**2**) in acetonitrile efficiently generates novel deoxygenated complexes, $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (**3**) and $[W(MeCN)_2(S_2C_2Ph_2)_2]$ (**4**), in which the coordinated MeCN ligands can be easily substituted by a stronger ligand such as CO and PPh_3. While CO replaces both MeCN ligands to yield dicarbonyl products, $[M(CO)_2(S_2C_2Ph_2)_2]$, a sterically demanding incoming ligand like PPh_3 results in a monosubstitution, $[Mo(MeCN)(PPh_3)(S_2C_2Ph_2)_2]$ (**7**). Differential reactivity between $[Mo^{IV}O(S_2C_2Ph_2)_2]^{2-}$ (**1**) and $[W^{IV}O-$

$(S_2C_2Ph_2)_2]^{2-}$ (**2**) with protons has been observed. Whereas **3** is the sole product from the reaction between **1** and acid, two different reaction products, $[WO(S_2C_2Ph_2)_2]^-$ and $[W(MeCN)_2(S_2C_2Ph_2)_2]$ (**4**), can be generated from **2** depending on the amount of acid added. The former is predominantly generated with 1 equiv of acid while the latter is the main product with an excess amount of acid.

4. EXPERIMENTAL SECTION

Materials and Methods. Solvents were purified by passing through alumina columns under an argon atmosphere (MBraun solvent purification system) and stored over 4 Å molecular sieves. Carbon monoxide (99.0+%), triphenylphosphine, Bu_4NPF_6, and *p*-toluenesulfonic acid ($TsOH{\cdot}H_2O$) were purchased from Aldrich and used as received. Complexes of $(Et_4N)_2[MoO(S_2C_2Ph_2)_2]$ (**1**),[14] $(Et_4N)_2[WO(S_2C_2Ph_2)_2]$ (**2**),[12] $[Mo(CO)_2(S_2C_2Ph_2)_2]$ (**5**),[55] and $[W(CO)_2(S_2C_2Ph_2)_2]$ (**6**)[12] were synthesized following literature procedures. All syntheses and manipulations were performed under an inert atmosphere using an MBraun glovebox (<0.1 ppm O_2, <0.1 ppm H_2O) or standard Schlenk techniques. Elemental analyses were carried out by Columbia Analytical Services (Tucson, AZ). UV−vis spectra were recorded on a Varian Cary 50 Bio spectrometer. Infrared spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. X-ray crystallographic data were collected on a Bruker Smart Apex I diffractometer. A single crystal was mounted on glass capillary fibers in grease and cooled in a stream of dinitrogen. The structure was solved and refined using the Bruker SHELXTL Software Package. Electrochemical data were collected with a CV-50W, Version 2.3, from Bioanalytical Systems, Inc. A 3-electrode system composed of a glassy carbon working electrode (circular, 3 mm diameter), a Ag/Ag^+ reference electrode, and a platinum wire auxiliary electrode was employed. All experiments were conducted with 0.10 M Bu_4NPF_6 as supporting electrolyte at room temperature under N_2 atmosphere, and the data were referred to ferrocene/ferrocenium couple at 0.00 V.

Synthesis of $[Mo(MeCN)_2(S_2C_2Ph_2)_2]{\cdot}H_2O$ (3·H_2O). To a solution of $TsOH{\cdot}H_2O$ (54 mg, 0.284 mmol) dissolved in 4 mL of acetonitrile was added a solution of $(Et_4N)_2[MoO(S_2C_2Ph_2)_2]$ (**1**) (60 mg, 0.07 mmol) in 4 mL of MeCN. The solution color changed immediately from orange brown to dark yellow brown. The reaction mixture was allowed to stir vigorously for an hour during which time a dark violet solid precipitated. The supernatant fluid was removed by decanting. The excess TsOH and $[Et_4N][OTs]$ were removed by washing the solid with MeCN (5 × 2 mL). The resulting solid was dried in vacuo to yield 32 mg (69%) of $[Mo(MeCN)_2(S_2C_2Ph_2)]{\cdot}H_2O$ (**3**·H_2O). UV−vis (MeCN): λ_{max} (ε_M) 265 (sh, 66000), 375 (16000), 446 (20000), 536 (sh, 9100) nm. IR (Nujol): 2317, 2282 cm^{-1} (w, ν_{CN}). Redox couples (CH_2Cl_2/toluene =1:1 v/v): $E_{1/2} = -0.56$ and −1.04 V vs $FeCp_2/FeCp_2^+$. Anal. Calcd for $C_{32}H_{28}N_2OS_4Mo$: C, 56.45; H, 4.15; N, 4.11. Found: C, 55.99; H, 3.81; N, 4.11.

Synthesis of $[W(MeCN)_2(S_2C_2Ph_2)_2]$ (4). To a solution of $TsOH{\cdot}H_2O$ (40 mg, 0.21 mmol) dissolved in 4 mL of acetonitrile was added a solution of $(Et_4N)_2[MoO(S_2C_2Ph_2)_2]$ (**1**) (60 mg, 0.07 mmol) in 4 mL of MeCN. The solution color changed immediately from red brown to dark yellow. The reaction mixture was allowed to stir vigorously for an hour during which time a brown solid precipitated. The supernatant fluid was removed by decanting. The excess TsOH and $[Et_4N][OTs]$ were removed by washing the solid with MeCN (5 × 2 mL). The resulting solid was dried in vacuo to yield 35 mg (88%) of $[W(MeCN)_2(S_2C_2Ph_2)]$ (**4**). UV−vis (MeCN): λ_{max} (ε_M) 257 (54000), 360 (8000) 413 (16000), 512 (3000) nm. IR (Nujol): 2275, 2258 cm^{-1} (w, ν_{CN}). Redox couples (CH_2Cl_2/toluene =1:1 v/v): $E_{1/2} = -0.61$ and −1.10 V vs $FeCp_2/FeCp_2^+$. Anal. Calcd for $C_{32}H_{26}N_2S_4W$: C, 51.20; H, 3.49; N, 3.73. Found: C, 51.13; H, 3.30; N, 3.48.

Photolysis of $[Mo(CO)_2(S_2C_2Ph_2)_2]$ (5) and $[W(CO)_2(S_2C_2Ph_2)_2]$ (6). The formation of $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (**3**) or $[W(MeCN)_2(S_2C_2Ph_2)_2]$ (**4**) via photolysis was studied by in situ UV−vis spectroscopy. An acetonitrile solution of $[Mo(CO)_2(S_2C_2Ph_2)_2]$ (**5**) or $[W(CO)_2(S_2C_2Ph_2)_2]$ (**6**) was prepared in a Schlenk cuvette (0.01−0.03 mM) which was then irradiated with UV light (254/365 nm, 4 W) for 5 min. Upon irradiation, the color of the sample solution changed from purple to yellow. The conversion yield was estimated as 70−75% based on the molar concentrations deduced from the absorbance with known extinction coefficients of **3**−**6**.

Reaction of $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (3) with CO. A dilute solution (23 μM) of $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (**3**) was prepared in a Schlenk cuvette. (***Caution!*** *complex 3 has poor solubility in acetonitrile and this experiment is possible only with a dilute sample*) Gaseous CO was bubbled through the solution of **3** for 10 s in the dark. The solution was allowed to sit in the dark for 1 h to complete the conversion from **3** to $[Mo(CO)_2(S_2C_2Ph_2)_2]$ (**5**), which was monitored by UV−vis spectroscopy. After the UV−vis monitoring, the final sample was saved, and the solvent was removed by vacuum. The IR spectrum (Nujol) of the final reaction product showed two strong ν(CO) peaks at 1996, 2035 cm^{-1} suggesting the formation of **5**.

Synthesis of $[Mo(MeCN)(PPh_3)(S_2C_2Ph_2)_2]{\cdot}2H_2O$ (7·2H_2O). *Method 1.* To a mixture of $(Et_4N)_2[Mo^{IV}O(S_2C_2Ph_2)_2]$ (**1**) (20 mg, 0.023 mmol) and PPh_3 (20 mg, 0.069 mmol) in 4 mL of MeCN was added a solution of $TsOH{\cdot}H_2O$ (16 mg, 0.092 mmol) in 4 mL of MeCN with stirring. The color of the reaction mixture changed instantly from orange brown to red brown upon addition of TsOH. The resulting mixture was allowed to stir for 1 h, during which a red brown precipitate was slowly developed. The red brown solid was isolated, washed with MeCN (3 × 2 mL), and dried under vacuum. The solid was redissolved in 1 mL of CH_2Cl_2, and the solution was layered with 10 mL of pentane. The red brown crystals were obtained overnight to yield 18 mg (96%) of $[Mo(MeCN)(PPh_3)(S_2C_2Ph_2)_2]{\cdot}2H_2O$ (**7**). Absorption spectrum (DCM): λ_{max} (ε_M) 251 (76000), 270 (sh, 63000), 375 (9500), 454 (20000), 543 (sh, 6000) nm. IR (KBr): 2264 cm^{-1} (w, ν_{CN}). ^1H NMR (CD_2Cl_2): δ 1.63 (s, 3), 7.43−7.24 (m, 35) ppm. ^{31}P NMR (CD_2Cl_2): δ 62.5 ppm (referenced by H_3PO_4). Anal. Calcd for $C_{48}H_{42}NO_2PS_4Mo$: C, 62.66; H, 4.60; N, 1.52. Found: C, 63.27; H, 4.41; N, 1.32.

Method 2. To a solution of PPh_3 (12 mg, 0.045 mmol) in 3 mL of CH_2Cl_2 was added powder $[Mo(MeCN)_2(S_2C_2Ph_2)_2]$ (**3**) (10 mg, 0.015 mmol). The reaction mixture instantly became a red brown color. After stirring the reaction mixture for 1 h, the solvent was removed in vacuo to a half of the original volume. An addition of pentane to the concentrated reaction solution led to the formation of a red brown precipitate that was isolated and was washed with pentane (3 × 2 mL). The obtained precipitate was spectroscopically identical to the product of method 1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

IR spectra of **1** and **3**, UV−vis spectra of **3**−**7**, IR ν(CN) comparisons of **3**, **4**, **7**, and free acetonitrile, ^1H- and ^{31}P- NMR spectra of **7**, and X-ray crystallographic data of **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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