Published in final edited form as:

Inorg Chem. 2019 February 04; 58(3): 2054–2068. doi:10.1021/acs.inorgchem.8b03093.

REMOTE CHARGE EFFECTS ON OXYGEN-ATOM TRANSFER REACTIVITY AND THE RELATIONSHIP TO MOLYBDENUM ENZYMES

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Abstract

We report the syntheses, crystal structures, and characterization of the novel *cis*-dioxo molybdenum(VI) complexes [Tpm*Mo^{VI}O₂Cl](MoO₂Cl₃) (**1**) and [Tpm*Mo^{VI}O₂Cl](ClO₄) (**2**), which are supported by the charge-neutral Tpm* ligand (Tpm* = tris(3,5-dimethyl-1-pyrazolyl)methane). A comparison between isostructural [Tpm*Mo^{VI}O₂Cl]⁺ and Tp*Mo^{VI}O₂Cl (Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) reveals the effects of one unit of overall charge difference on their spectroscopic and electrochemical properties, geometric and electronic structures, and OAT reactivities, providing new insight into pyranopterin molybdoenzyme OAT reactivity.

Computational studies of these molecules indicate that the delocalized positive charge lowers the LUMO energy of cationic [Tpm*MoO₂Cl]⁺ relative to Tp*MoO₂Cl. Despite their virtually identical geometric structures revealed by crystal structures, the Mo^{VI}/Mo^V redox potential of **2** is increased by 350 mV relative to Tp*Mo^{VI}O₂Cl. This LUMO stabilization also contributes to an increased effective electrophilicity of [Tpm*MoO₂Cl]⁺ relative to Tp*MoO₂Cl, resulting in a more favorable resonant interaction between the Mo complex LUMO and the HOMO of the PPh₃ substrate. This leads to a greater thermodynamic driving force, an earlier transition state, and a lowered activation barrier for the orbitally controlled first step of the OAT reaction in the Tpm* system relative to the Tp* system. An Eyring plot analysis shows that this initial step yields an O≡Mo^{IV}–OPPh₃ intermediate via an associative TS, and the reaction is ~500-fold faster for **2** than for Tp*MoO₂Cl. The second step of the OAT reaction entails the solvolysis of the O≡Mo^{IV}–OPPh₃ intermediate to afford the solvent-substituted Mo^{IV} product, and is 750-fold faster for the Tpm* system at –15 °C compared to the Tp* system. The observed rate enhancement for the second step is ascribed to a switch of reaction mechanism from a *dissociative* pathway for the Tp* system, to an alternative *associative* pathway for the Tpm* system. This is due to a more Lewis acidic Mo(IV) center in the Tpm* system.

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Supporting Information:

The Supporting Information is available free of charge on the ACS Publications website. Eyring plots and kinetic data of the reaction of [Tp*MoO₂Cl] and PPh₃, Cartesian coordinates of DFT geometry-optimized structures, computed thermochemical data for OAT reactions, and computed bond distances, HOMO and LUMO, and Löwdin atomic charges of important species of OAT reactions.

TOC Graphic:

TOC Synopsis:

Novel *cis*-dioxo molybdenum(VI) complexes supported by a charge-neutral N_3 ligand were synthesized and characterized. Relative to a structurally analogous but anionic ligand, the use of a charge-neutral ligand enhances rates of oxygen atom transfer reactions mediated such complexes by 500-fold, without perturbing their geometric structures. The rate acceleration is due primarily to LUMO stabilization of the Mo(VI) complex, facilitating the nucleophilic attack of substrate in an earlier transition state.

1. Introduction

The electronic charge of a catalyst is expected to influence the nature of the reaction coordinate for catalytic transformations, and this should be observed as a measureable effect on the reaction rate. Metalloenzyme active sites are excellent exemplars of how electronic charge affects reactivity and rate. For example, the atypical coordination environment of the 3-His metal binding motif found in some thiol dioxygenases, including cysteine dioxygenase, supports these mononuclear nonheme iron enzymes with distinct reactivity.^{1,2} The active site structure and physiological role of these thiol dioxygenases deviate from canonical nonheme iron enzymes (including monooxygenases, dioxygenases, oxidases, and halogenases) that possess a remarkably conserved 2-His, 1-carboxylate facial triad metal binding motif.^{3,4} As a second example, DFT studies of heme enzymes have been used to support charge effects leading to the stronger oxidizing capacity of Compound I compared with Compound II.^{5,6} Another example is found in the mononuclear molybdenum enzyme sulfite oxidase (SO),⁷ which possesses an overall -1 charge for the Mo ion and its first coordination sphere ligand set.^{8–12} This active site oxidizes a negatively charged sulfite substrate, which is correctly positioned in the substrate binding pocket due to the presence of three positively charged arginine residues.¹³ Examples of how electronic charge can affect reactivity are also observed in synthetic metal complexes and homogeneous catalysts. In a seminal study of charge effects on reactivity, Seymore and Brown reported the reaction of a cationic $\{Re^VO\}$ complex with triarylphosphines to form an $\{Re^{III}(OPR_3)\}$ adduct was 1000-fold faster than that of a charge neutral $\{Re^VO\}$ complex.¹⁴ Later, Gunnoe and

Cundari *et al.* were able to show that cationic $[\text{Tpm}^{5\text{-Me}}\text{Ru}^{\text{II}}(\text{BPhos})(\text{NCCH}_3)(\text{Ph})]$ is a much more stable catalyst for ethylene hydrophenylation, with turnover numbers observed to be 28-fold higher than its charge neutral $[\text{TpRu}^{\text{II}}(\text{BPhos})(\text{NCCH}_3)(\text{Ph})]$ counterpart (Tp = hydrotris(pyrazolyl)borate; BPhos = $\text{P}(\text{OCH}_2)_3\text{CEt}$; $\text{Tpm}^{5\text{-Me}}$ = tris(5-methylpyrazolyl)methane.¹⁵ Recently, it was demonstrated that oxygen atom transfer (OAT) reactivities can be significantly accelerated by appending (photoinduced) electron-transfer units like ferrocene¹⁶ or Ru-based photosensitizer¹⁷ to *cis*-dioxo Mo(VI) complexes.

While the effects of different ligand donor sets,^{18–23} and second coordination sphere hydrogen-bonding interactions^{24–31} have been well studied, systematic studies of charge effects remote from the catalytically active metal site are rare. This is primarily due to the difficulty in directly probing charge contributions to reactivity in the absence of complicating steric and electronic effects. For the few cases where charge effects were shown to affect reactivities or catalysis,^{14–17} there was a lack of systematic studies to substantiate whether and to what extent thermodynamic driving force, kinetic reaction barriers, and/or electronic structure effects were altered by the difference in charge. Here, we explore OAT reactivity as a test case for understanding charge effects on reactivity. The work is relevant for understanding charge effects on OAT and other reactions in general, but also important for obtaining additional insight into the reaction mechanisms of molybdenum oxotransferase enzymes. These enzymes contain a mononuclear molybdenum center at their active site and catalyze a wide range of oxidative transformations that are of key importance to human health and global S, C, and N cycles.^{32–36} We focus on developing an understanding of the molecular-level mechanistic details for OAT reactions mediated by molybdenum(VI)-dioxo centers. In studies of molybdoenzyme model complexes, some of us³⁷ and others^{25–27,30,31,38} have recently noted that specific interactions with Brønsted and/or Lewis acids are capable of accelerating OAT reaction rates. In the current work, we probe how a single unit of charge difference resulting from a single atom substitution remote from the molybdenum ion influences OAT reaction rates.

Here, we report the preparation, crystal structure, spectroscopy, electrochemistry, OAT reactivities, and a computational investigation of cationic $[\text{Tpm}^*\text{Mo}^{\text{VI}}\text{O}_2\text{Cl}]^+$, which employs a charge neutral Tpm^* scorpionate ligand in lieu of the anionic Tp^* ligand used in previously reported *cis*- $\text{Mo}^{\text{VI}}\text{O}_2$ complexes³⁹ [Tpm^* = tris(3,5-dimethyl-1-pyrazolyl)methane; Tp^* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate; See Scheme 1]. At structural parity, a single unit of charge change (+1) on the *cis*- $\text{Mo}^{\text{VI}}\text{O}_2$ moiety decreases the LUMO energy, leads to an early transition state (TS) while lowering the TS barrier, and contributes to a 500-fold rate enhancement for the key OAT step. This charge-mediated change in electronic structure also shifts the $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{V}}$ redox potential by +350 mV, and gives rise to a greater thermodynamic driving force for the reaction. These results point to an effective, yet previously overlooked, strategy to modulate reactivities of molybdenum oxotransferases.

2. Experimental Section

2.1 Materials and Synthesis.

All reagents, including 3,5-dimethylpyrazole, molybdenum(VI) dichloride dioxide, and anhydrous solvents (e.g. acetonitrile, dichloromethane (DCM), diethyl ether, and tetrahydrofuran (THF)), were purchased from commercial vendors (e.g. Sigma-Aldrich) and used as received unless stated otherwise. Proton NMR data were collected using a 300 MHz Varian NMR spectrometer at room temperature with tetramethylsilane as an internal standard for calibrating chemical shifts. FT-IR spectra were measured in a Thermo Scientific Nicolet iS 10 spectrometer equipped with a Smart iTR sampling accessory operated by the OMNIC software (v.8.1). All syntheses of molybdenum complexes were carried out in a high-purity nitrogen-filled glovebox, unless otherwise indicated. X-ray crystallographic data collection and refinement were carried out on a PLATFORM three circle diffractometer equipped with an APEX II CCD detector using the APEX 3 software suite. Elemental Analyses were performed by Atlanta Micro Lab. The potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligand (KTP*)⁴⁰ and the Tp*MoO₂Cl complex³⁹ were synthesized according to published procedures. EtCN (150 mL) was dried over activated molecular sieves 3 Å (4–8 mesh) for 48 hours, refluxed with 1.5 g CaH₂ for 7–8 hours under nitrogen, distilled under nitrogen, and then degassed. *Although no problems were encountered during the syntheses of complexes in small quantities in our laboratory, perchlorate salts are potentially explosive and should be handled with care.*

The Tpm* ligand was synthesized using a previously published procedure (Scheme 2).⁴¹ 1.17 g (3.63 mmol) tetra-*n*-butyl ammonium bromide was added to an aqueous solution of 7.00 g (72.8 mmol) 3,5-dimethylpyrazole in 70 ml distilled water. The solution was vigorously stirred, and 45.83 g (432.4 mmol) Na₂CO₃ was added gradually. 38 ml chloroform was subsequently added to the solution which was then refluxed for 80 hours. The resulting dark orange-brown emulsion was filtered. 2 ml water and 5 ml chloroform was added to extract the precipitate, and the aqueous layer was separated from the organic layer. The unreacted 3,5-dimethylpyrazole was removed from the organic layer by extraction with potassium carbonate solution in distilled water (30 ml) 3–4 times. The final organic layer was dried with Na₂SO₄ and rotary evaporated. The crude product was then dissolved in dichloromethane, and flushed through a plug of silica. The final product was collected after removing the dichloromethane solvent by rotary evaporation. Yield: 3.6 g (50%). NMR (¹H, δ, ppm) in CDCl₃: 8.07 (s, 1H, CH), 5.87 (s, 3H, Pz 4-H), 2.18 (s, 9H, CH₃), 2.01 (s, 9H, CH₃).

[Tp*Mo^{VI}O₂Cl](MoO₂Cl₃) (1).—0.40 g MoO₂Cl₂ (2.0 mmol) dissolved in cold THF was allowed to react with 0.30 g Tpm* (1.0 mmol) for an hour (Scheme 2). A light yellow precipitate was collected by filtration, washed twice with 3 mL diethyl ether and dried in vacuum. Yield: 0.63 g (91%). NMR (¹H, δ, ppm) in CD₃CN: 7.90 (s, 1H, CH), 6.35 (s, 1H, Pz 4-H), 6.31 (s, 2H Pz 4-H), 2.71 (s, 6H, CH₃), 2.69 (s, 3H, CH₃), 2.59 (s, 6H, CH₃), 2.58 (s, 3H, CH₃). Anal. Calcd. For C₁₆H₂₂O₄Cl₄N₆Mo₂ (MW: 696.1 g/mol): C 27.61; H, 3.19; N, 12.07. Found: C, 27.97; H, 3.18; N, 12.10. IR: ν_{as}(Mo=O) 944 cm⁻¹ (sh), ν_s(Mo=O) 905 cm⁻¹ (vsh). Mpt: 235°C. To obtain crystals of suitable quality for x-ray diffraction, diethyl

ether was allowed to diffuse into a concentrated solution of **1** in anhydrous dichloromethane. Colorless needle-shaped crystals of **1** formed within two days.

[Tpm*Mo^{VI}O₂Cl](ClO₄) (2**).—**0.87 g complex **1** (1.25 mmol) was stirred with 1.80 g NaClO₄ (14.7 mmol) in 15 ml dry acetonitrile for 30 minutes (Scheme 2). The solution became cloudy and was filtered. The filtrate was collected and reduced in volume to 4 ml followed by addition of 20 ml dry diethyl ether. The supernatant was decanted, and the off-white solid was collected, and washed with diethyl ether. The precipitate was then extracted using dichloromethane and the resulting solution was filtered. The colorless filtrate was reduced in volume to 4 ml, followed by addition of diethyl ether to precipitate the complex. The resulting precipitate was collected and washed with diethyl ether and dried in vacuum. Yield: 0.58 g (82%). NMR (¹H, δ, ppm) in CD₃CN: 7.89 (s, 1H, CH), 6.35 (s, 1H, Pz 4-H), 6.31 (s, 2H Pz 4-H), 2.70 (s, 6H, CH₃), 2.68 (s, 3H, CH₃), 2.59 (s, 6H, CH₃), 2.57 (s, 3H, CH₃). Anal. Calcd. For C₁₆H₂₂O₆Cl₂N₆Mo (MW: 561.2): C, 34.24; H, 3.95; N, 14.97. Found: C, 34.22; H, 3.88; N, 14.77. IR: ν_{as}(Mo=O) 951 cm⁻¹ (sh), ν_s(Mo=O) 912 cm⁻¹ (vsh). Mpt: 194 °C. Slow diffusion of diethyl ether into an acetonitrile solution of **2** produced colorless plate-like crystals for single-crystal X-ray crystallography.

2.2 X-ray crystallography.

General Data Collection.—Data were collected on a Bruker PLATFORM three circle diffractometer equipped with an APEX II CCD detector and operated at 1500 W (50kV, 30 mA) to generate (graphite monochromated) Mo Kα radiation (λ = 0.71073 Å). Crystals were transferred from the vial and placed on a glass slide in polyisobutylene. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The crystal and a small amount of the oil were collected on a M̄TiGen cryoloop and transferred to the instrument where it was placed under a cold nitrogen stream (Oxford) maintained at 100 K throughout the duration of the experiment. The sample was optically centered with the aid of a video camera to ensure that no translations were observed as the crystal was rotated through all positions.

A unit cell collection was then carried out. After it was determined that the unit cell was not present in the CCDC database a sphere of data was collected. Omega scans were carried out with a 10 sec/frame exposure time and a rotation of 0.50° per frame. After data collection, the crystal was measured for size, morphology, and color. These values are reported in Table 2.

Refinement Details.—After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects using the Bruker program APEX 3. A semi-empirical correction for adsorption was applied using the program *SADABS*.⁴² The *SHELXL-2014*,⁴³ series of programs was used for the solution and refinement of the crystal structure. Hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

For complex **1**, there was a significant amount of disorder about the Mo–O and Mo–Cl bonds, both for the Tpm* ligand-bound Mo atom and the MoO₂Cl₃⁻ anion. The final

solution consists of the Tpm*-ligated Mo1 site being occupied by either a Mo(VI) or Mo(V) atom with a ratio of 0.80:0.20, respectively. These site occupancies are inferred from the occupancies of the O1 and Cl7 atoms. Attempts to split the Cl1 and O2 sites to account for slightly different bond lengths that would be present with different oxidation states of the Mo atom did not produce a convergent model and were left as single sites. As for the $\text{MoO}_2\text{Cl}_3^-$ anion, three different orientations were determined, two about the Mo2A site and one about the Mo2B site. The first orientation about the Mo2A consists of atoms O3A, O4A, Cl2A, Cl3A, and Cl6 bound to Mo2A. This orientation is present 40% of the time. The second orientation about the Mo2A site consists of bound atoms O3A, O5, Cl2A, Cl3A, and Cl4. This orientation is also present 40% of the time. The final orientation about the Mo2B site consists of bonds to O3B, O4B, Cl2B, Cl3B, and Cl5. This orientation is present 20% of the time. To help model these disordered sites, all bonds between Mo and O and Cl atoms of the $\text{MoO}_2\text{Cl}_3^-$ anion were constrained with DFIX commands. The resulting Mo-O and Mo-Cl bonds were 1.691(16) and 2.382(13) Å, respectively. During the final refinement the RIGU restraint was used globally, and reflections 0 2 0 and 2 2 0 were omitted due to interference with the beamstop.

For complex **2**, once the majority of the structure was refined, it became apparent that there was some positional disorder about the MoO_2Cl portion of the molecule. To help model the three distinct orientations (A, B, and C) of the MoO_2Cl portion of the molecule, SUMP, SIMU, DELU, and free variable DFIX restraints were used. The site occupancies of the three sites were allowed to freely refine with a total occupancy constrained to 1. The occupancies of the three sites A, B, and C were 0.765, 0.126, and 0.109, respectively. The rigid-bond restraint RIGU was also applied globally to the structure during the final refinements.

2.3 Physical Methods and Kinetic Studies.

UV-visible Kinetic Studies.—UV-visible spectra were collected on a HP8453 diode-array spectrometer using Agilent Chemstation software (B.05.02) and equipped with a cryostat from Unisoku Scientific Instruments (Osaka, Japan) for controlling temperatures of kinetic studies. At -40°C , 0.2 mM or 0.5 mM solution of **2** was allowed to react with 5, 10, 15, 20 and 25 equivalents of PPh_3 solution in anhydrous acetonitrile. Progress of the conversion from **2** to $[\text{Tpm}^*\text{Mo}^{\text{IV}}\text{OCl}(\text{OPPh}_3)](\text{ClO}_4)$ (**3**) and then to $[\text{Tpm}^*\text{Mo}^{\text{IV}}\text{OCl}(\text{NCCH}_3)](\text{ClO}_4)$ (**4**) in CH_3CN was followed by monitoring the changes in absorbance at 795 nm for the initial formation and subsequent decay of **3**, and absorbance at 692 nm for the formation of **4**. The conversion of **3** to **4** is characterized by an isosbestic point at 720 nm. Fitting plots of reaction progress $[A(692)-A(720)]$ and $[A(795)-A(720)]$ against time using double exponential equations provided good fits that allowed the determination of observed rate constants k_{form} and k_{decay} , respectively. Errors associated with reaction rates came from at least three independent trials. Second order rate constants, $k_{2_{\text{form}}}$, were determined from the slope of the linear regression plots of k_{form} vs. $[\text{PPh}_3]$ (Origin 2017 b9.4.0220). To compare reaction rates, 0.2 mM of the $[\text{Tp}^*\text{MoO}_2\text{Cl}]$ complex in anhydrous acetonitrile was allowed to react with PPh_3 under the same reaction conditions.

Electrochemistry.—Cyclic Voltammograms (CVs) were collected at $100 \text{ mV} \cdot \text{S}^{-1}$ in anhydrous CH_3CN using 0.1 M potassium hexafluorophosphate as the supporting electrolyte. Measurements were performed using a CH Instrument (Model 600E). A standard three electrode system consisted of a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/Ag^+ reference electrode (in acetonitrile). The potentials were internally calibrated with reference to the ferrocenium/ferrocene couple.

2.4 Computational Methods.

All geometry optimizations and electronic structure calculations used the computational facilities at the Center for Advanced Research and Computing at The University of New Mexico. Computations were performed at the DFT level of theory using the Gaussian 09 (vC.01) software package.⁴⁴ All Gaussian 09 calculations used the B3LYP hybrid exchange-correlation functional^{45–48} in conjunction with the def2-TZVP basis set⁴⁹ for all atoms. All geometry optimizations and thermochemical data were calculated at 233.15 K using the Polarizable Continuum Model (PCM) with acetonitrile as the solvent.^{50,51} To facilitate computational performance, $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ and $\text{Tp}^*\text{MoO}_2\text{Cl}$ were truncated to $[\text{TpmMoO}_2\text{Cl}]^+$ and TpMoO_2Cl , with methyl groups at the 3- and 5-positions of Tpm^* and Tp^* replaced with hydrogen atoms ($\text{Tpm} = \text{tris}(\text{pyrazolyl})\text{methane}$). Truncated models possess computed structures that are virtually identical to structurally characterized $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ and $\text{Tp}^*\text{MoO}_2\text{Cl}$, respectively. Mulliken⁵² and Löwdin population^{53,54} analyses were performed as implemented in Gaussian 09. Molecular orbital compositions were further analyzed using the AOMix (v 6.51) software package.^{55,56} Fragment Molecular Orbital (FMO) compositions were obtained from single point energy calculations using AOMix. All transition states were found using a linear transit approach along the O-P reaction coordinate. Vibrational frequencies were calculated for each TS, and a single imaginary frequency was found that corresponds to a vibration along the Mo-O-P coordinate.

3. Results and Discussion.

3.1 Synthesis.

As part of a larger program to investigate the effects of electronic charge on the structure, spectroscopy and reactivity of oxomolybdenum complexes that mimic the active sites and/or functions of molybdoenzymes, we are developing strategies to synthesize new oxomolybdenum complexes that are supported by *charge-neutral* scorpionate and related ligands. Complex **1** was synthesized in THF by a stoichiometric combination (ratio 1:2) of Tpm^* ligand and $\text{MoO}_2\text{Cl}_2(\text{THF})_2$ that is formed *in situ* by dissolving solid MoO_2Cl_2 in cold THF. This reaction used to prepare **1** is nearly quantitative. Combining the Tpm^* ligand and $\text{MoO}_2\text{Cl}_2(\text{THF})_2$ in a 1:1 molar ratio yielded complex **1** as well, albeit in slightly lower yield ($\sim 80\%$ based on the amount of the limiting reactant MoO_2Cl_2). As complex **1** contains the $[\text{MoO}_2\text{Cl}_3]^-$ anion that might interfere with electrochemical characterizations and OAT reactivities of the cationic $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ moiety, we then attempted to replace this anion with a different anion. Complex **2** can now be successfully prepared in $>80\%$ yield by a double metathesis reaction of **1** with a large excess of NaClO_4 salt to replace the $[\text{MoO}_2\text{Cl}_3]^-$ anion with ClO_4^- . The $\text{NaMoO}_2\text{Cl}_3$ side product and unreacted NaClO_4 are

separated from the desired product complex **2** by extracting complex **2** from the precipitate using dichloromethane. Complex **1** is soluble in acetonitrile, dichloromethane, chloroform, and DMSO, slightly soluble in THF, and insoluble in diethyl ether. Complex **2** is soluble in acetonitrile, dichloromethane, and DMSO, slightly soluble in THF, and insoluble in chloroform and diethyl ether.

The infrared spectra of compound **2** exhibits $\nu_{\text{as}}(\text{Mo}=\text{O})$ and $\nu_{\text{s}}(\text{Mo}=\text{O})$ at 951 cm^{-1} and 912 cm^{-1} , respectively, reflecting contributions from the $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ cation. For complex **1**, the $\nu_{\text{as}}(\text{Mo}=\text{O})$ and $\nu_{\text{s}}(\text{Mo}=\text{O})$ stretches appear at 944 and 905 cm^{-1} , respectively, with contributions from both $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ cation and $[\text{MoO}_2\text{Cl}_3]^-$ anion.^{57,58} Notably, $\nu(\text{Mo}=\text{O})$ for the $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ cation in complexes **1** and **2** are only ~2% greater than those for neutral $\text{Tp}^*\text{MoO}_2\text{Cl}$ and fall into the typical range of asymmetric and symmetric Mo=O stretching frequencies that have been previously reported (Table 1). For complex **2**, a very strong peak at 1071 cm^{-1} is assigned to vibrational mode with Cl–O stretching character. As expected, this vibration was not observed in the FT-IR spectrum of complex **1**.

3.2 Crystallographic Data.

While several binuclear Mo(VI) complexes have been synthesized and recrystallized,^{61,66} there are no crystal structures reported for any *mononuclear cis*-dioxo Mo(VI) complex supported by the neutral Tpm^* ligand. In the current work, the crystal structures of **1** and **2** were determined by single crystal X-ray crystallography, and the crystal information and structural refinement data are shown in Table 2. Cationic **1** and **2** feature a distorted octahedral geometry with the molybdenum center coordinated facially by the three nitrogen atoms of the neutral, tridentate Tpm^* ligand (Figure 1; Table 2). The remaining coordination sites of the cation are occupied by two terminal oxo ligands and one chloride ligand. For complex **2**, there is a noticeable disorder between the chlorine atom and two oxygen atoms. This is explicitly modeled as three orientations (A, B, and C) with occupancies of 76.5%, 12.6%, and 10.9%, respectively. Further details are listed in the experimental section. The $\text{Mo1A}=\text{O1A}$ and $\text{Mo1A}=\text{O2A}$ bond distances in the primary orientation A are $1.672(7)$ and $1.681(7)\text{ \AA}$ (Table 3), respectively, and are comparable to Mo=O distances (ranging from 1.68 to $1.75\text{ \AA}$) reported for other *cis*- $\text{Mo}^{\text{VI}}\text{O}_2$ complexes (Table 4). The disorder between the chlorine and two oxygen atoms was less pronounced in the electron density map of complex **1**. It would require excessively heavy restraints to adopt the same disorder model used for complex **2** and therefore this was not pursued. As a result, the structure of **1** has slightly longer Mo=O bond distances and shorter Mo–Cl distance than those reported for **2** (Table 3). The Mo–N bond distances for **2** are $2.176(6)$ (*trans* to Cl1A), $2.329(4)$ (*trans* to O1A), and $2.324(4)\text{ \AA}$ (*trans* to O2A), respectively, which fall into the range of $r(\text{Mo}–\text{N})$ observed in $\text{Tp}^*\text{Mo}^{\text{VI}}\text{O}_2\text{X}$ complexes (2.16 – $2.41\text{ \AA}$ as tabulated in Table 4). Bond angles $\angle\text{O1A}–\text{Mo1A}–\text{N3} = 162.8(4)^\circ$, $\angle\text{O2A}–\text{Mo1A}–\text{N5} = 162.5(5)^\circ$, and $\angle\text{Cl1}–\text{Mo1}–\text{N1} = 158.10(17)^\circ$ of complex **2** quantitate the geometric distortions from a perfect octahedral geometry. The Mo(VI) atom is found $0.180\text{ \AA}$ and $0.176\text{ \AA}$ above the plane formed by O1(A), O2(A), N3, and N5 in complexes **1** and **2**, respectively. $\text{MoO}_2\text{Cl}_3^-$ or ClO_4^- anions are also present in crystal structures of **1** and **2** to balance the charge, respectively.

To further compare the geometric structures of *cis*-dioxo Mo(VI) complexes supported by Tpm* and Tp* ligands, the Tpm* carbon- and Tp* boron-based cone angles (θ) and molybdenum-based cone angles (β) were computed according to Scheme 3. These results are compared with those measured for crystal structures of previously reported Mo(VI)-dioxo complexes supported by similar ligand donor sets (Table 4). The θ angle for complexes **1** and **2** were determined to be 143.54° and 143.35°, respectively. These values are very similar to θ angles measured for three published crystal structures containing a Tpm*-bound Mo^{VI}O₂ core in binuclear Mo complexes (143.27 – 144.97° as tabulated in Table 4). By comparison, θ angles measured for available crystal structures of Tp*Mo^{VI}O₂X complexes were noticeably smaller, ranging from 135.06° to 140.22°. The very slight increase in θ angle for *cis*-dioxo Mo(VI) complexes supported by the Tpm* ligand, relative to those by supported by the negatively charged Tp* ligand, can be attributed to the increased electronegativity of carbon compared to boron, leading to increased bonding pair – bonding pair repulsions near the central C atom of Tpm* ligand, relative to the B atom of Tp* ligand. Similar trends in bond angle variations due to electronegativity differences of the central atom have been reported for other systems.⁶⁷ Conversely, Tpm*-bound *cis*-Mo^{VI}O₂ complexes similar to **1** and **2** exhibit β angles that range from 89.17 to 90.77°; β angles for the corresponding Tp* analogs vary from 93.67 to 95.16°. Given the slight variations in θ and β angles (2–3%) for *cis*-dioxo Mo(VI) complexes supported by a neutral Tpm* ligand (e.g. **1** and **2**) relative to those with anionic Tp* ligands, we conclude that our mononuclear *cis*-dioxo Mo(VI) complexes supported by Tpm* possess a nearly identical degree of steric bulk around the Mo ion as do their Tp* counterparts.

3.3 Electrochemistry.

The cyclic voltammogram (CV) of complex **2** is shown in Figure 2 and the results are tabulated in Table 5. Complex **2** exhibits a well-defined one-electron Mo^{VI}/Mo^V redox couple with $E_{1/2}$ value for the Mo^{VI}/Mo^V redox couple of –660 mV with respect to the ferrocenium/ferrocene (Fc⁺/Fc) couple. This $E_{1/2}$ value is 350 mV more positive than that reported for Tp*MoO₂Cl supported by the anionic Tp* ligand (Table 5).⁷¹ The peak potential separation E_{pp} ($E_{pc} - E_{pa}$) of complex **2** is 182 mV and the peak current ratio i_{pa}/i_{pc} is 0.71. These values are comparable to those reported for Tp*MoO₂Cl (E_{pp} of 230 mV and i_{pa}/i_{pc} of 0.5; see Table 5).⁷¹ The sizable peak separation, together with the i_{pa}/i_{pc} value deviating from unity, suggests that there is some degree of decomposition on the CV time scale for both systems. The large positive shift for the Mo^{VI}/Mo^V couple of **2** suggests that this complex will display an enhanced ability to oxidize substrates relative to [Tp*MoO₂X] complexes. A similar positive redox potential shift of 280 mV for the Ru^{III}/Ru^{II} couple has been observed when replacing the anionic Tp ligand in TpRu(BPhos)(NCCH₃)(Ph) with the neutral Tpm^{5-Me} ligand.¹⁵ A markedly smaller positive redox potential shift of 100 mV was reported for the replacement of the anionic Tp^{Ph2} ligand in Fe(Tp^{Ph2})(BIHQ) with a neutral TIP^{Ph2} ligand,⁷² and this is likely due to the presence of the non-innocent BIHQ ligand as a redox buffer (Tp^{Ph2} = hydrotris(3,5-diphenyl-1-pyrazolyl)borate); BIHQ = the mono-anion of 2-(1-methyl-1H-benzimidazol-2-yl)hydroquinone; TIP^{Ph2} = tris(4,5-diphenyl-1-methylimidazol-2-yl)phosphine).

3.4 Oxygen atom transfer reactivity of **2**.

3.4.1 Kinetic Studies by UV-visible Spectroscopy—For *cis*-dioxomolybdenum(VI) complexes supported by Tp* or Tp^{Pr} ligands, their OAT reactions with tertiary phosphine substrates (PR₃) have been well-established to proceed via a two-step process in CH₃CN.^{39,60,65,73–80} The first step involves nucleophilic attack by PR₃ on an oxo ligand of the {Mo^{VI}O₂} reactant to afford the corresponding mono-oxo {(O)Mo^{IV}–OPR₃} intermediate. These intermediates have been successfully trapped, isolated, and in some cases crystallized.^{65,74,75} In the second step, this {(O)Mo^{IV}–OPR₃} intermediate undergoes a solvolysis reaction in CH₃CN to produce the {(O)Mo^{IV}–NCCH₃} product. We examined the OAT reactivity of **2** towards PPh₃ to confirm if cationic [Tp*MoO₂Cl]⁺ also mediates OAT reactions *and* to investigate whether the reaction mechanism is similar to those of charge-neutral Mo(VI)-dioxo complexes supported by Tp*.

Complex **2** exhibited UV-visible spectral features that are very similar to those observed for Tp*MoO₂Cl in CH₃CN (Table 6). At –40° C, compound **2** quickly reacted with PPh₃ to afford a new intermediate (**3**) within 30 s (Figure 3 top panel). Intermediate **3** exhibits a strong UV-visible band with a λ_{max} at 371 nm (2330 M^{–1} cm^{–1}), a shoulder feature at 444 nm (400 M^{–1} cm^{–1}), and a weak absorbance at 795 nm (140 M^{–1} cm^{–1}). The yellow intermediate **3** underwent a subsequent decay over the course of 1000 s to produce a light green product (**4**). Clear isosbestic points are observed at 350 nm, 525 nm, and 720 nm for the conversion of **3** to **4**. Product **4** exhibited a strong absorbance band at 341 nm (2400 M^{–1} cm^{–1}), and weak spectral features at 692 nm (105 M^{–1} cm^{–1}) and 820 nm (70 M^{–1} cm^{–1}). The UV-vis features observed for **3**, **4**, and representative examples of Tp*Mo^{IV}O(OPR₃)(X) and Tp*Mo^{IV}O(NCCH₃)(X) (X = Cl or SPh) are compared in Table 6. Notably, **3** exhibits spectral features very analogous to those of Tp*Mo^{IV}O(OPR₃)(X), while the electronic absorption spectra of **4** and Tp*Mo^{IV}O(NCCH₃)(X) are also highly similar. Based on the extinction coefficients and UV-visible spectral assignments of Tp*Mo^{IV}O(OPR₃)(Cl) and Tp*Mo^{IV}O(NCCH₃)(Cl),⁶⁵ we attribute the 795 and 444 nm bands of **3**, as well as 810 and 690 nm transitions of **4**, to ligand field transitions. The extinction coefficients for the higher energy 371 nm band of **3** and the 340 nm band of **4** clearly indicate that these are charge transfer transitions.

Both the formation and subsequent decay of **3** (monitored at 795 nm), and the biphasic formation of **4** (monitored at 692 nm) vs. time can be well fit using a double exponential function, and this is shown in the bottom panel of Figure 3. This analysis yields observed formation and decay rate constants, *k*_{form} and *k*_{decay}, for the two-step process. Reaction rates obtained from fitting A(692) and A(795) data are essentially identical within experimental error (Figure 4). We carried out this reaction using different concentrations of PPh₃ (2.5 – 12 mM). *k*_{form} was found to be linearly correlated with [PPh₃], while *k*_{decay} is insensitive to [PPh₃]. The second-order formation rate of **3** (*k*_{2-form}) was determined to be 7.1(8) × 10¹ s^{–1} M^{–1}. These kinetic data are consistent with description of **2** reacting with PPh₃ to produce **3**, followed by the subsequent decay of **3** to afford **4** in CH₃CN. Therefore, the OAT reaction of **2** also follows a two-step process similar to the OAT reactions of previously reported Tp*Mo^{VI}O₂X systems. The spectroscopic similarity of **3** vs. Tp*Mo^{IV}O(OPR₃)(X) and **4** vs. Tp*Mo^{IV}O(NCCH₃)(X), *and* the observation of a similar two-step OAT mechanism of

Tpm* vs. Tp* systems, allow us to confidently assign complexes **3** and **4** as [Tpm*Mo^{IV}O(OPPh₃)(Cl)](ClO₄) and [Tpm*Mo^{IV}O(NCCH₃)(Cl)](ClO₄), respectively (Scheme 4).

3.4.2 Eyring Plots—OAT reactions of complex **2** with PPh₃ were carried out in EtCN between –30 to –60 °C. For the first-step of the two-step OAT process characterized with k_{form} , $H^\ddagger$ and $S^\ddagger$ are determined to be +22(2) kJ/mol and –158(8) J/(mol•T), respectively (Figure 5 and Table 7). A control Eyring plot analysis for the formation of Tp*MoO(OPPh₃)Cl from reaction Tp*MoO₂Cl and PPh₃ in EtCN yields $H^\ddagger$ and $S^\ddagger$ values of +32(1) kJ/mol and –170(4) J/(mol•T), respectively (Figure S2). Literature values for $H^\ddagger$ and $S^\ddagger$ range from +34 to +83 kJ/mol and –36 to –184 J/(mol•T), respectively (Table 7), for the first OAT step of *cis*-dioxo Mo(VI) complexes supported by Tp* and Tp^{Pr} ligands with a variety tertiary phosphine substrates in CH₃CN.^{60,75,79,80} Notably, the large negative activation entropy for converting **2** and PPh₃ into **3** is the same, within experimental error, as that for the transformation of Tp*MoO₂Cl and PPh₃ to produce Tp*MoO(OPPh₃)Cl. These results are consistent with an associative TS for the first-step in the OAT reaction for both the Tpm* and Tp* systems. $G^\ddagger$ is calculated to be –13 kJ/mol at –40 °C, consistent with the experimentally observed ~500-fold rate enhancement for the Tpm* system relative to its Tp* counterpart (see Section 3.4.3).

For the second OAT step characterized by k_{decay} , $H^\ddagger$ and $S^\ddagger$ values for our Tpm* system were determined to be +51(2) kJ/mol and –69(6) J/(mol•T), respectively (Figure 5, Table 7). Our control experiments for the conversion of Tp*MoO(OPPh₃)Cl and EtCN to produce Tp*MoO(NCEt)Cl provided $H^\ddagger$ and $S^\ddagger$ values to be +90(2) kJ/mol and +23(6) J/(mol•T), respectively (Figure S2). For the second-step in the OAT reaction, the sign change of $S^\ddagger$ suggests a switch of the energetically preferred reaction pathway from a dissociative TS in the Tp* system, to an associative TS in the Tpm* system with Mo–NCCH₂CH₃ bond formation being more important than Mo–OPMe₃ bond scission.

3.4.3 Comparison of OAT Reaction Rates as a Function of Charge—A similar two-step OAT reaction mechanism is observed for the new Tpm* system (Scheme 4) and the previously published Tp* system. Therefore, reaction rates of individual steps can be directly compared to quantitatively highlight how a single unit of charge influences OAT reactivities. Under identical reaction conditions, the second-order rate for the first step, k_{2_form} of our Tpm* system, is ~500-fold faster than the corresponding step in the Tp* system (Table 8). Notably, a similar magnitude of reaction rate enhancement as a function of charge has previously been observed in a similar OAT reaction of [(Tp)Re^VOC₂H₅]⁺ vs. [(Tp)Re^VOC₂H₅] by Seymore and Brown.¹⁴ Besides a much faster first step, the following solvolysis step characterized by the k_{decay} value for our Tpm* system was also significantly faster than that of the Tp* system (e.g., 750-fold rate enhancement at –15 °C as shown in Table 8 footnote).

3.5 Computations that Probe the First Oxygen Atom Transfer Step.

Geometry optimizations were computed for [(Tp)MoO₂Cl]⁺ and (Tp)MoO₂Cl, where the methyl groups of Tpm* and Tp* have been replaced with hydrogen atoms at the 3- and 5-

positions on the pyrazolyl rings (Tables 9, S1, S2). The computed metrical parameters are in excellent agreement with the corresponding crystallographic data. These calculations have been augmented by a combination of charge, electrostatic potential energy, electronic structure, and reaction coordinate computations to provide detailed insight into charge effects on OAT reactivity. A comparison of the computed Löwdin atomic charges for $[(\text{Tpm})\text{MoO}_2\text{Cl}]^+$ and TpMoO_2Cl indicate that the Tp B atom and the Tpm C atom bear ~50% of the difference in molecular charge between these two complexes (Table S5). The remainder of the charge difference between $[(\text{Tpm})\text{MoO}_2\text{Cl}]^+$ and $(\text{Tp})\text{MoO}_2\text{Cl}$ is highly delocalized over the other constituent atoms in these compounds. Computed electrostatic potential energy surfaces for $(\text{Tp})\text{MoO}_2\text{Cl}$, $[(\text{Tpm})\text{MoO}_2\text{Cl}]^+$, and the PPh_3 substrate are presented in Figure 6. The initial step along the reaction coordinate for oxygen atom transfer to PPh_3 involves nucleophilic attack of the P atom on one of the symmetry equivalent oxo oxygen atoms of $[(\text{Tpm})\text{MoO}_2\text{Cl}]^+$ or $(\text{Tp})\text{MoO}_2\text{Cl}$. Clearly, the electrostatic interaction between the oxo ligands in cationic $[(\text{Tpm})\text{MoO}_2\text{Cl}]^+$ and the PPh_3 lone pair at the geometry of the encounter complex is more favorable than that associated with charge neutral $(\text{Tp})\text{MoO}_2\text{Cl}$. Thus, at the early stages of the reaction sequence prior to significant charge transfer, charge contributions to catalysis will favor cationic $[(\text{Tpm})\text{MoO}_2\text{Cl}]^+$. As the system approaches the TS, significant charge transfer takes place and the $\text{Mo}=\text{O}_{\text{ap}}$ (ap = apical or spectator oxo) bond length decreases, indicative of the eventual $\text{Mo}\equiv\text{O}_{\text{ap}}$ triple bond formation in the Mo(VI) product state. Conversely, the $\text{Mo}=\text{O}_{\text{eq}}$ (eq = equatorial) bond lengthens with a concomitant decrease in the $\text{O}_{\text{eq}}-\text{P}$ distance, which is consistent with $\text{Mo}=\text{O}_{\text{eq}}$ bond weakening and nascent $\text{O}-\text{P}$ bond formation. The $\text{O}_{\text{eq}}-\text{P}$ bond length at the TS is greater for the Tpm system (2.27 Å) compared with the Tp system (2.08 Å), consistent with an early TS in the former (Figure 7). Combined with the negative values computed for $S^\ddagger$ (*vide infra*) our computational data support an associative TS for the formation of both $[(\text{Tpm})\text{MoOCl}(\text{OPPh}_3)]^+$ and $(\text{Tp})\text{MoOCl}(\text{OPPh}_3)$ intermediates. Despite the difference in $\text{O}_{\text{eq}}-\text{P}$ bond distances, the computed TS geometries for the two systems possess very similar $\text{O}\equiv\text{Mo}-\text{O}-\text{P}$ dihedral and $\text{O}-\text{P}-\text{C}$ bond angles (Table 9), both of which are comparable to those previously reported for similar transition states computed for OAT reactivity involving dioxomolybdenum systems.⁷⁶

The first OAT step for both $[(\text{Tpm})\text{MoO}_2\text{Cl}]^+$ and $(\text{Tp})\text{MoO}_2\text{Cl}$ was found to proceed smoothly through the TS to form the stable intermediates $[(\text{Tpm})\text{MoOCl}(\text{OPPh}_3)]^+$ and $\text{TpMoOCl}(\text{OPPh}_3)$. The computed Gibbs free energy of activation, $G^\ddagger$, for the reaction between $[(\text{Tpm})\text{MoO}_2\text{Cl}]^+$ and PPh_3 was found to be 63.4 kJ/mol, and this derives primarily from the negative activation entropy ($H^\ddagger = 23.6 \text{ kJ}\cdot\text{mol}^{-1}$, $S^\ddagger = -170.7 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) resulting from the associative nature of the TS. The calculated activation parameters of the Tpm system are in very good agreement with those determined experimentally (see Figure 7 for computed values and Table 7 for experimental values). By comparison, computed $G^\ddagger$ for the first OAT step between $(\text{Tp})\text{MoO}_2\text{Cl}$ and PPh_3 is markedly larger ($G^\ddagger = 100.0 \text{ kJ/mol}$), with $G^\ddagger$ attributed almost entirely to an increase in the enthalpic contribution ($H^\ddagger = 60.9 \text{ kJ}\cdot\text{mol}^{-1}$, $S^\ddagger = -167.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$). A lower activation barrier for oxygen atom transfer in $[(\text{Tpm})\text{MoO}_2\text{Cl}]^+$ is consistent with an earlier TS in this system relative to the Tp analog, since electronic repulsions are minimized between the phosphine lone pair and $\text{Mo}=\text{O}_{\text{eq}}$. Clearly this is a manifestation of the cationic character of $[(\text{Tpm})\text{MoO}_2\text{Cl}]^+$,

making it a better Lewis acid than (Tp)MoO₂Cl. In addition to the more favorable energy of activation, the driving force ($-G^0$) for the reaction [(Tpm)MoO₂Cl]⁺ → [(Tpm)MoOCl(OPPh₃)]⁺ was computed to be -87.6 kJ•mol⁻¹ (Figure 7). In contrast, stabilization of (Tp)MoO₂Cl(OPPh₃) relative to (Tp)MoO₂Cl was found to be markedly smaller ($-G^0 = -64.3$ kJ•mol⁻¹).

We have performed a fragment molecular orbital analysis (FMO) to probe the orbital nature of the reactivity in the first OAT step (Figure 8) as a function of the unit charge difference. The charge and orbital dependence of the total perturbation energy on the initial slope of the OAT reaction pathway toward the TS is defined in Eqn. 1:⁸¹

$$\Delta E = \frac{-q_a q_b}{R_{ab} \epsilon} + 2 \sum_i \sum_j \frac{(c_a^i c_b^j \beta_{ab}^{ij})^2}{E_i^a - E_j^b} \quad (1)$$

In the first term, q_a is the charge on the terminal oxo ligand acting as the electron acceptor and q_b is the charge on the phosphorus atom of PPh₃. The distance between these two atoms is R_{ab} , and ϵ is the local dielectric constant. The molecular orbital coefficients for the oxo ligand in the catalyst LUMO (c_a^i), and the P atom in the substrate HOMO (c_b^j), along with the resonance integral, β_{ab} , are found in the numerator of the second term in Eqn. 1, where the energy difference between the HOMO and LUMO is given by $E_i^a - E_j^b$. When the energy difference between the HOMO and LUMO is markedly greater than $2c_a^i c_b^j \beta_{ab}$, the first term in Eqn 1 dominates and the reaction is charge controlled. When the HOMO – LUMO energy difference is small, the second term dominates and the reaction is orbitally controlled. The close proximity of the {Mo^{VI}O₂} acceptor LUMO and PPh₃ donor HOMO energies (1.4 eV for the Tpm system and 2.2 eV for the Tp system) suggests that the first OAT step in both systems is under orbital control (Figure 8). An increased degree of mixing between the catalyst LUMO and the substrate HOMO occurs in the Tpm system at earlier stages along the reaction coordinate, and this ultimately leads to a more stabilized TS and faster reaction rates for this orbitally controlled reaction.

We observe that the HOMO and LUMO wavefunctions at the TS are similar for both the Tpm and Tp systems, with expected dominant contributions from the {Mo^{VI}O₂} LUMO and the PPh₃ HOMO (*vide infra*). However, the degree of PPh₃ HOMO character in the TS HOMO is markedly different for both systems. For the Tpm system, the PPh₃ HOMO character in the TS HOMO is 60.0%, while for the Tp system this is reduced to 48.5% (Figure 8). This result is fully consistent with the Tpm system possessing an earlier TS than the Tp system. Essentially, more electron density must be removed from the PPh₃ HOMO in the OAT reaction catalyzed by (Tp)MoO₂Cl in order to attain the TS. This requires a closer encounter between an oxo oxygen atom of (Tp)MoO₂Cl and the PPh₃ lone pair, leading to a greater electron-electron repulsion at the TS geometry. This increase in electron-electron repulsion also contributes to the concomitant increase in activation energy for the OAT reaction of the Tp system. The electron-electron repulsion at the TS may also be understood in terms of the greater Mo character in the respective TS HOMO of (Tp)MoO₂Cl (58.2%) compared with [(Tpm)MoO₂Cl]⁺ (31%).

4. Discussion

4.1 Charge Effects on Redox Potential and Oxygen Atom Transfer.

Our experimental and computational results on the conversion of $\{\text{Mo}^{\text{VI}}\text{O}_2\}$ to $\{\text{Mo}^{\text{IV}}\text{O}(\text{OPPh}_3)\}$, the first step of OAT reactions, indicate that the activation energy is considerably smaller for the $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ cation than for the neutral $\text{Tp}^*\text{MoO}_2\text{Cl}$ complex, consistent with the faster OAT reaction rate for the $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ complex. From a generalized frontier molecular orbital perspective, the more positively charged catalyst will possess lower energy acceptor orbitals due to the attractive potential induced by the additional charge. This has the effect of reducing the energy gap between the donor (substrate) and catalyst (acceptor) generalized frontier orbitals, leading to a reduction in the TS barrier for reactions that are predominantly under orbital control.⁸² In the context of Eqn. 1, these energy gap differences translate to an ~6-fold greater perturbation energy for the encounter complex between PPh_3 and $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ relative to that with charge neutral $\text{Tp}^*\text{MoO}_2\text{Cl}$. Thus, the larger resonance interaction between PPh_3 and $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ contributes to an earlier TS and lower activation energy for the first step in the OAT reaction. The effect of LUMO energy lowering on OAT rates has also been shown by Solomon and coworkers by varying the ancillary ligands ($\text{X} = \text{Cl} > \text{SR} > \text{OR}$) in a series of $\text{Tp}^*\text{Mo}^{\text{VI}}\text{O}_2\text{X}$ complexes.⁸¹ An additional contribution to lowering the TS energy for the reaction catalyzed by $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ derives from a reduction in electron-electron repulsion, since the O-P bond length is ~0.2 Å longer at the TS for the Tpm^* system compared with the Tp^* system. In addition to the lower kinetic barrier for the Tpm^* system, the Gibbs free energy, G^0 , of the reaction mediated by $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ is computed to be more exergonic than the neutral Tp^* analog by 23.3 kJ•mol⁻¹ (-87.6 kJ•mol⁻¹ vs. -64.3 kJ•mol⁻¹), defining the degree to which the first OAT step is thermodynamically more favorable for the $[\text{Tpm}^*\text{Mo}^{\text{VI}}\text{O}_2\text{Cl}]^+$ cation. The lower activation energy and larger thermodynamic driving force for $[\text{Tpm}^*\text{Mo}^{\text{VI}}\text{O}_2\text{Cl}]^+$ are therefore in accord with the Bell–Evans–Polanyi principle^{83–85} (Figure 9). Namely, the activation energy decreases as the thermodynamic driving force increases (red → blue in Figure 9). The larger thermodynamic driving force is partly attributed to the coordination of the neutral Tpm^* ligand, which increases the overall positive charge of the product complex.

Along the reaction coordinate, the two lone pair electrons that reside in the PPh_3 HOMO are used to reduce the Mo center. The smaller HOMO-LUMO gap at the encounter complex stage for $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+ + \text{PPh}_3$ relative to $\text{Tp}^*\text{MoO}_2\text{Cl} + \text{PPh}_3$ results in enhanced orbital mixing between one of the electrophilic oxo ligands and the phosphine lone pair. Thus, we emphasize that the first step of the OAT reaction for the Tpm^* and Tp^* systems *is primarily under orbital control*. Charge is still anticipated to contribute to an overall reduction in the TS barrier and an enhanced reaction rate for OAT. This derives from the fact that, at the encounter complex stage, the electrostatic interactions between reactants are favorable for $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+ + \text{PPh}_3$, but are repulsive for $\text{Tp}^*\text{MoO}_2\text{Cl} + \text{PPh}_3$ (Figure 6).

Carrano *et al.* have previously demonstrated that an empirical, semi-linear relationship exists between the $\text{Mo}(\text{VI})/\text{Mo}(\text{V})$ redox potential and the logarithm of the OAT reaction rates⁸⁶ in a series of *cis*-dioxo $\text{Mo}(\text{VI})$ complexes supported by a family of anionic heteroscorpionate

ligands differing in the identity of only one donor atom.¹⁸ For example, the most reactive complex of this family, $\text{Tp}^*\text{Mo}^{\text{VI}}\text{O}_2\text{Cl}$, mediated OAT to PPh_3 in pyridine to afford $\text{Tp}^*\text{Mo}^{\text{IV}}\text{OCl}(\text{py})$ at a reaction rate that is 10^3 -fold faster than the least reactive complex, $L5\text{OMo}^{\text{VI}}\text{O}_2\text{Cl}$, and also exhibited a 530 mV more positive $\text{Mo}(\text{VI})/\text{Mo}(\text{V})$ redox potential compared to $L5\text{OMo}^{\text{VI}}\text{O}_2\text{Cl}$ ($L5\text{O} = 2,2$ -bis(3,5-dimethylpyrazolyl)methane)ethoxide). The positive correlation of redox potential with OAT rates was also observed in a group of $\text{Tp}^*\text{Mo}^{\text{VI}}\text{O}_2\text{X}$ complexes with varying ancillary ligands ($\text{X} = \text{Cl} > \text{SR} > \text{OR}$).³⁹ In our system, $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ possesses a 350 mV more positive $\text{Mo}(\text{VI})/\text{Mo}(\text{V})$ redox potential and a ~ 500 -fold increase in OAT rate compared to $\text{Tp}^*\text{Mo}^{\text{VI}}\text{O}_2\text{Cl}$. Importantly, this result agrees well with the $E_{1/2}$ vs. $\log(k_{\text{OAT}})$ relationship developed by Carrano *et al.*¹⁸ There are several factors that affect the redox potential of transition metal catalysts, including the effective nuclear charge of the metal ion (Z'_{eff}), the relative energies of redox-active orbitals, ligand field effects, and electronic relaxation.^{81,87} The coordination of charge neutral Tpm^* to the $[\text{MoO}_2]^{2+}$ core dramatically lowers the LUMO orbital energy of $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$ relative to $\text{Tp}^*\text{Mo}^{\text{VI}}\text{O}_2\text{Cl}$, and this appears to be a dominant contributor to the increased reduction potential for $[\text{Tpm}^*\text{MoO}_2\text{Cl}]^+$. Since the LUMO stabilization of the catalyst also directly contributes to a lowered kinetic barrier for the first step in the OAT reaction, this is the likely reason behind the observed correlation between redox potential and $\log(k_{\text{OAT}})$ in the prior work.⁸¹

In addition to the observed rate enhancement for the first OAT step, substitution of the Mo-bound OPPh_3 ligand in cationic complex **3** by a solvent molecule (CH_3CN or EtCN) in the second OAT step is $\sim 10^3$ -fold faster than that of neutral $\text{Tp}^*\text{Mo}^{\text{VI}}\text{O}(\text{OPPh}_3)\text{Cl}$. This is a very interesting observation given the larger thermodynamic driving force for the formation $[\text{Tpm}^*\text{Mo}^{\text{VI}}\text{O}(\text{OPPh}_3)\text{Cl}]^+$ and the greater thermodynamic stability compared to $\text{Tp}^*\text{Mo}^{\text{VI}}\text{O}(\text{OPPh}_3)\text{Cl}$ as demonstrated by our computational results. In contrast, Brown *et al.* reported that the substitution of OPPh_3 in cationic $[(\text{Tpm})\text{Re}^{\text{III}}(\text{OPPh}_3)\text{Cl}_2]^+$ with pyridine in chlorinated solvents was ~ 50 times slower than that of the neutral compound $(\text{Tp})\text{Re}^{\text{III}}(\text{OPPh}_3)\text{Cl}_2$.¹⁴ We attribute the opposite trends observed in Mo^{VI} systems and the Re^{III} systems to different reaction mechanisms for the ligand exchange step. In Brown's $\text{Re}^{\text{III}}-\text{OPPh}_3$ complexes, the ligand substitution reactions were *dissociative* for both the cationic and neutral $\text{Re}^{\text{III}}-\text{OPPh}_3$ complexes, as evidenced by the positive $\Delta S^\ddagger$ values.¹⁴ The cationic $[(\text{Tpm})\text{Re}^{\text{III}}(\text{OPPh}_3)\text{Cl}_2]^+$ complex possesses a more electrophilic rhenium center than the charge neutral $(\text{Tp})\text{Re}^{\text{III}}(\text{OPPh}_3)\text{Cl}_2$ complex, and this will slow the rate of $\text{Re}^{\text{III}}-\text{OPPh}_3$ bond cleavage. In contrast, while the ligand substitution reaction of $[\text{Tp}^*\text{Mo}^{\text{VI}}\text{O}(\text{OPPh}_3)\text{Cl}]$ in CH_3CN has a *dissociative* TS (positive $\Delta S^\ddagger$), cationic $[\text{Tpm}^*\text{Mo}^{\text{VI}}\text{O}(\text{OPPh}_3)\text{Cl}]^+$ possesses an alternative associative pathway with a much lower activation barrier as evidenced by a negative $\Delta S^\ddagger$ value for the ligand substitution step. The alternative associative pathway is made possible by a more Lewis acidic $\text{Mo}(\text{IV})$ center of the Tpm^* system surrounded by solvent CH_3CN molecules abundantly present as the nucleophile.

4.2 Relevance to Molybdoenzymes and Other Systems.

The oxidized active sites of mononuclear molybdoenzymes possess a molybdenum center coordinated by one or two pyranopterin dithiolene ligands.^{32–36} The rest of the Mo

coordination sphere is occupied by oxo or sulfido ligands and other oxygen/sulfur donors from amino acid side chains,^{32–36} or metal activated water. The charges around the active site must be carefully modulated to fulfill the functions of each enzyme. Crystallographic data and studies of sulfite oxidase variants have identified three conserved arginine residues in the substrate access channel gating the Mo active sites.¹³ These arginine residues contribute to a positively charged binding pocket conducive to the binding of the anionic sulfite substrate.¹¹ Interestingly, the human SO Y343N/R472M variant diminished this sulfite oxidation activity,⁸⁸ while enabling the enzymes to reduce nitrate. However, other than charge stabilization of substrate binding, other charge control aspects are more difficult to directly probe in molybdoenzymes. In the current work, we illustrate the fundamental chemistry behind the effects of a single unit charge difference on reaction kinetics and thermodynamic parameters. The charge differential initiated by a single atom change located remotely from the Mo center can markedly accelerate OAT reaction rates by several orders of magnitude. In addition to rate acceleration, a greater thermodynamic driving force for these reactions is also driven by more favorable charge effects. In light of the insights obtained here regarding charge effects on reactivity, we suggest that similar kinetic and thermodynamic advantages result from active site charge modulations in the enzymes. These effects conspire to facilitate very fast OAT kinetics in the enzymes and may also affect the relative stabilization of key intermediates and products.

Interestingly, Mo(VI)/Mo(V) and Mo(V)/Mo(IV) redox potentials have been correlated with *E. coli* nitrate reductase A (NarGHI) activity and *E. coli* anaerobic respiratory growth on nitrate.⁸⁹ Weiner and coworkers have proposed that the changes in redox potential for different variants relative to wild type enzyme are likely due to an equilibrium between a protonated (higher Mo potential) vs. deprotonated (lower Mo potential) form of the bicyclic pyranopterin.⁸⁹ Our study is in agreement with this proposal, suggesting that molybdenum redox potential changes of up to a few hundred millivolts could be achieved by imparting more positive or less negative charges remotely located from the molybdenum center. Notably, such charge effects in molybdoenzymes would have easily eluded the scrutiny of protein X-ray crystallography when active site geometric structures and ligand conformations remain minimally perturbed, as exemplified by the very similar coordination environments and metrical parameters observed in X-ray crystal structures of [Tp⁺MoO₂Cl]⁺ and [Tp⁺MoO₂Cl].

5. Conclusions.

We have quantitatively illustrated a rare example of how one unit difference in overall complex charge influences geometric structure, electronic structure, redox potential, and OAT reactivity of *cis*-dioxo Mo(VI) complexes. Charge neutral Tp⁺Mo^{VI}O₂Cl and cationic [Tp⁺Mo^{VI}O₂Cl]⁺ exhibit almost identical geometric structures exemplified by their similar N₃O₂Cl donor set, C_s symmetry, metrical parameters, and steric accessibility to substrates. The ν(Mo=O) stretches are also very similar for these two systems. Thus, the observed charge effects on OAT reactivity do not derive from geometric changes and dominantly reflect critical electronic structure differences between the two systems. Using PPh₃ as substrate, OAT reactions mediated by [Tp⁺Mo^{VI}O₂Cl]⁺ proceed significantly faster than those mediated by Tp⁺MoO₂Cl. The first step of the OAT reaction produces the (O)Mo^{IV}–

OPPh₃ intermediate via an associative TS for both Tpm* and Tp* systems, and this is characterized by negative $S^\ddagger$ values of similar magnitude for both systems. Interestingly this step in the Tpm* system is ~500-fold faster than that determined for the Tp* system. Our computational studies reveal a greater electrophilicity and a decreased LUMO energy of the *cis*-dioxo Mo(VI) complex supported by the charge neutral Tpm* ligand, giving rise to a lower activation energy, earlier TS, and a greater thermodynamic driving force for the first OAT step. The second step of the OAT reaction entails the solvolysis of the OPPh₃-bound Mo^{IV} intermediate to afford the acetonitrile-bound Mo^{IV} product. Remarkably, the rate of the second step for the Tpm* system is ~750-fold faster at -15 °C than that observed for the Tp* system. This is ascribed to a switch in the mechanism from a dissociative pathway for the Tp* system to an associative pathway with a lower activation energy in the Tpm* system. Coupled to the observed enhancement of OAT reactivity, we note that the Mo^{VI}/Mo^V redox potential of [Tpm*Mo^{VI}O₂Cl]⁺ relative to Tp*MoO₂Cl is increased by 350 mV, which is also attributed to [Tpm*Mo^{VI}O₂Cl]⁺ LUMO stabilization. Overall, the fundamental knowledge gained through this work may contribute to a greater understanding of rate acceleration in molybdoenzymes and offers a new strategy to facilitate OAT reactions in small molecule catalysts, impacting the design of more efficient transition metal catalysts for oxidative transformations.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

F.L. and M.L.K. gratefully acknowledge the National Institutes of Health (project number: 1SC2GM121183 to F.L. and GM05378 to M. L. K.) for generous support of this work. All single crystal diffraction data were collected at the Texas Tech University X-ray Diffraction Facility. We thank Dr. Daniel K. Unruh for data collection and structure refinement of all single crystal data.

References

- (1). Buongiorno D; Straganz GD Structure and Function of Atypically Coordinated Enzymatic Mononuclear Non-Heme-Fe(II) Centers. *Coord. Chem. Rev.* 2013, 257 (2), 541–563. [PubMed: 24850951]
- (2). Leitgeb S; Nidetzky B Structural and Functional Comparison of 2-His-1-Carboxylate and 3-His Metallocentres in Non-Haem Iron(II)-Dependent Enzymes. *Biochem. Soc. Trans.* 2008, 36 (6), 1180–1186. [PubMed: 19021520]
- (3). Kal S; Que L Dioxygen Activation by Nonheme Iron Enzymes with the 2-His-1-Carboxylate Facial Triad That Generate High-Valent Oxoiron Oxidants. *J. Biol. Inorg. Chem.* 2017, 22 (2–3), 339–365. [PubMed: 28074299]
- (4). Costas M; Mehn MP; Jensen MP; Que L Dioxygen Activation at Mononuclear Nonheme Iron Active Sites: Enzymes, Models, and Intermediates. *Chem. Rev.* 2004, 104 (2), 939–986. [PubMed: 14871146]
- (5). Bell SR; Groves JT A Highly Reactive P450 Model Compound I. *J. Am. Chem. Soc.* 2009, 131 (28), 9640–9641. [PubMed: 19552441]
- (6). Ricciardi G; Baerends EJ; Rosa A Charge Effects on the Reactivity of Oxoiron(IV) Porphyrin Species: A DFT Analysis of Methane Hydroxylation by Polycationic Compound I and Compound II Mimics. *ACS Catal.* 2016, 6 (2), 568–579.
- (7). Hemann C; Hood BL; Fulton M; Hänsch R; Schwarz G; Mendel RR; Kirk ML; Hille R Spectroscopic and Kinetic Studies of Arabidopsis Thaliana Sulfite Oxidase: Nature of the Redox-

- Active Orbital and Electronic Structure Contributions to Catalysis. *J. Am. Chem. Soc.* 2005, 127 (47), 16567–16577. [PubMed: 16305246]
- (8). Helton ME; Kirk ML A Model for Ferricyanide-Inhibited Sulfite Oxidase. *Inorg. Chem.* 1999, 38 (20), 4384–4385. [PubMed: 11671145]
- (9). Kirk ML Spectroscopic and Electronic Structure Studies of Mo Model Compounds and Enzymes In Molybdenum and Tungsten Enzymes: Spectroscopic and Theoretical Investigations; Royal Society of Chemistry: Cambridge, UK, 2016; pp 1–12.
- (10). Schwarz G The Sulfite Oxidase Family of Molybdenum Enzymes In Molybdenum and Tungsten Enzymes: Biochemistry; Hille R, Schulzke C, Kirk ML, Eds.; The Royal Society of Chemistry: Cambridge, UK, 2016; pp 240–273.
- (11). Kappler U; Enemark JH Sulfite-Oxidizing Enzymes. *J. Biol. Inorg. Chem.* 2015, 20 (2), 253–264. [PubMed: 25261289]
- (12). Kirk ML The Molybdenum Enzymes In Comprehensive Inorganic Chemistry II; Jan R, Kenneth P, Eds.; Elsevier: Amsterdam, 2013; pp 263–293.
- (13). Kisker C; Schindelin H; Pacheco A; Wehbi WA; Garrett RM; Rajagopalan KV; Enemark JH; Rees DC Molecular Basis of Sulfite Oxidase Deficiency from the Structure of Sulfite Oxidase. *Cell* 1997, 91 (7), 973–983. [PubMed: 9428520]
- (14). Seymore SB; Brown SN Charge Effects on Oxygen Atom Transfer. *Inorg. Chem.* 2000, 39 (2), 325–332. [PubMed: 11272542]
- (15). Burgess SA; Joslin EE; Gunnoe TB; Cundari TR; Sabat M; Myers WH Hydrophenylation of Ethylene Using a Cationic Ru(II) Catalyst: Comparison to a Neutral Ru(II) Catalyst. *Chem. Sci.* 2014, 5 (11), 4355–4366.
- (16). Hüttinger K; Förster C; Heinze K Intramolecular Electron Transfer between Molybdenum and Iron Mimicking Bacterial Sulphite Dehydrogenase. *Chem. Commun.* 2014, 50 (33), 4285–4288.
- (17). Ducrot AB; Coulson BA; Perutz RN; Duhme-Klair A-K Light-Induced Activation of a Molybdenum Oxotransferase Model within a Ru(II)–Mo(VI) Dyad. *Inorg. Chem.* 2016, 55 (24), 12583–12594. [PubMed: 27690401]
- (18). Hammes BS; Chohan BS; Hoffman JT; Einwächter S; Carrano CJ A Family of Dioxo-molybdenum(VI) Complexes of N2X Heteroscorpionate Ligands of Relevance to Molybdoenzymes. *Inorg. Chem.* 2004, 43 (24), 7800–7806. [PubMed: 15554645]
- (19). Schulzke C Molybdenum and Tungsten Oxidoreductase Models. *Eur. J. Inorg. Chem.* 2011, No. 8, 1189–1199.
- (20). Majumdar A Structural and Functional Models in Molybdenum and Tungsten Bioinorganic Chemistry: Description of Selected Model Complexes, Present Scenario and Possible Future Scopes. *Dalton Trans.* 2014, 43 (24), 8990–9003. [PubMed: 24798698]
- (21). Heinze K Bioinspired Functional Analogs of the Active Site of Molybdenum Enzymes: Intermediates and Mechanisms. *Coord. Chem. Rev.* 2015, 300, 121–141.
- (22). Basu P; Burgmayer SJN Recent Developments in the Study of Molybdoenzyme Models. *J. Biol. Inorg. Chem.* 2015, 20 (2), 373–383. [PubMed: 25578808]
- (23). Molybdenum and Tungsten Enzymes: Bioinorganic Chemistry, 1st ed.; Hille R, Schulzke C, Kirk ML, Eds.; The Royal Society of Chemistry: Cambridge, UK, 2016.
- (24). Ueyama N; Okamura TA; Nakamura A Structure and Properties of Molybdenum(IV,V) Arenethiolates with a Neighboring Amide Group. Significant Contribution of NH•••S Hydrogen Bond to the Positive Shift of Redox Potential of Mo(V)/Mo(IV). *J. Am. Chem. Soc.* 1992, 114 (21), 8129–8137.
- (25). Oku H; Ueyama N; Nakamura A Association of Oxo-Molybdenum Dithiolene Complexes with a Multiamide Additive and Its Influence on the Ease of O-Atom Transfer. *Inorg. Chem.* 1997, 36 (7), 1504–1516. [PubMed: 11669732]
- (26). Maiti R; Nagarajan K; Sarkar S Synthesis and Structure of [L][MoIVO(mnt)2] {L = [(C2H5)4N]⁺, [C5H5NH]⁺, [(C2H5)3NH]⁺, [lysinium]²⁺ and (mnt²⁻ = 1,2-diacynoethylenedithiolate)} in relevance to molybdenum cofactor of diverse class of molybdoenzymes. *J. Mol. Struct.* 2003, 656 (1–3), 169–176.
- (27). Baba K; Okamura T; Suzuki C; Yamamoto H; Yamamoto T; Ohama M; Ueyama N O-Atom-Transfer Oxidation of [Molybdenum(IV) Oxo{3,6-(acylamino)2–1,2-benzenedithiolato}2]2-

Promoted by Intramolecular NH...S Hydrogen Bonds. *Inorg. Chem.* 2006, 45 (2), 894–901. [PubMed: 16411728]

- (28). Ng VWL; Taylor MK; Hill LMR; White JM; Young CG Novel O,O'-donor Oxo-MoIV hydrotris(3-Isopropylpyrazolyl)borate Complexes Formed by Chelation of Potentially Hydrogen-Bonding Phenolate Ligands on Reduction of Dioxo-Mo^{VI} Complexes. *Eur. J. Inorg. Chem.* 2010, 2 (21), 3261–3269.
- (29). Ng VWL; Taylor MK; White JM; Young CG Cis-Dioxo-and Cis-(Hydroxo)oxo-Mo(V) Complexes Stabilized by Intramolecular Hydrogen-Bonding. *Inorg. Chem.* 2010, 49 (20), 9460–9469. [PubMed: 20843068]
- (30). Okamura TA; Tatsumi M; Omi Y; Yamamoto H; Onitsuka K Selective and Effective Stabilization of Mo^{VI}=O Bonds by NH...S Hydrogen Bonds via Trans Influence. *Inorg. Chem.* 2012, 51 (21), 11688–11697. [PubMed: 23075211]
- (31). Okamura T; Yamada T; Hasenaka Y; Yamashita S; Onitsuka K Unexpected Reaction Promoted by NH⁺...O=Mo Hydrogen Bonds in Nonpolar Solvents. *Eur. J. Inorg. Chem.* 2016, 18, 2952–2961.
- (32). Hille R; Hall J; Basu P The Mononuclear Molybdenum Enzymes. *Chem. Rev.* 2004, 114, 3963–4038.
- (33). Hille R The Molybdenum Oxotransferases and Related Enzymes. *Dalt. Trans.* 2013, 42, 3029–3042.
- (34). Pushie MJ; Cotelesage JJ; George GN Molybdenum and Tungsten Oxygen Transferases - Structural and Functional Diversity within a Common Active Site Motif. *Metallomics* 2014, 6 (1), 15–24. [PubMed: 24068390]
- (35). Maia LB; Moura I; Moura JGG Molybdenum and Tungsten-Containing Enzymes In Molybdenum and Tungsten Enzymes: Biochemistry; Hille R, Schulzke C, Kirk ML, Eds.; The Royal Society of Chemistry: Cambridge, UK, 2016; pp 1–80.
- (36). Schwarz G Molybdenum Cofactor and Human Disease. *Curr. Opin. Chem. Biol.* 2016, 31, 179–187. [PubMed: 27055119]
- (37). Li F; Talipov MR; Dong C; Bali S; Ding K Acid-Facilitated Product Release from a Mo(IV) Center: Relevance to Oxygen Atom Transfer Reactivity of Molybdenum Oxotransferases. *J. Biol. Inorg. Chem.* 2018, 23 (2), 193–207. [PubMed: 29177705]
- (38). Elrod LT; Kim E Lewis Acid Assisted Nitrate Reduction with Biomimetic Molybdenum Oxotransferase Complex. *Inorg. Chem.* 2018, 57 (5), 2594–2602. [PubMed: 29443517]
- (39). Roberts SA; Young CG; Kipke CA; Cleland WE Jr.; Yamanouchi K; Carducci MD; Enemark JH Dioxomolybdenum(VI) Complexes of the Hydrotris(3,5-Dimethyl-1-Pyrazolyl)borate Ligand. Synthesis and Oxygen Atom Transfer Reactions. *Inorg. Chem.* 1990, 29 (13), 3650–3656.
- (40). Trofimenko S Boron-Pyrazole Chemistry. IV. Carbon- and Boron-Substituted Poly(1-Pyrazolyl)borate. *J. Am. Chem. Soc.* 1967, 89 (24), 6288–6294.
- (41). Reger DL; Grattan TC; Brown KJ; Little CA; Lamba JJS; Rheingold AL; Sommer RD Syntheses of Tris(pyrazolyl)methane Ligands and {[tris(pyrazolyl)methane}Mn(CO)₃}SO₃CF₃: Comparison of Ligand Donor Properties. *J. Organomet. Chem.* 2000, 607, 120–128.
- (42). Krause L; Herbst-Irmer R; Sheldrick GM; Stalke D Comparison of Silver and Molybdenum Microfocus X-Ray Sources for Single-Crystal Structure Determination. *J. Appl. Crystallogr.* 2015, 48 (1), 3–10. [PubMed: 26089746]
- (43). Sheldrick GM A Short History of SHELX. *Acta Crystallogr.* 2008, A64 (1), 112–122.
- (44). Frisch MJ; Trucks GW; Schlegel HB; Scuseria GE; Robb MA; Cheeseman JR; Scalmani G; Barone V; Mennucci B; Petersson GA; et al. Gaussian 09, Revision C.01. Gaussian, Inc: Wallingford CT 2009.
- (45). Becke AD Density-Functional Thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys.* 1993, 98 (7), 5648–5652.
- (46). Stephens PJ; Devlin FJ; Chabalowski CF; Frisch MJ Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* 1994, 98 (45), 11623–11627.
- (47). Lee C; Yang W; Parr RC Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* 1988, 37 (2), 785–789.

- (48). Vosko SH; Wilk L; Nusair M Accurate Spin-Dependent Electron Liquid Correlation Energies for Local Spin Density Calculations: A Critical Analysis. *Can. J. Phys.* 1980, 58 (8), 1200–1211.
- (49). Weigend F; Ahlrichs R Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys. Chem. Chem. Phys.* 2005, 7 (18), 3297–3305. [PubMed: 16240044]
- (50). Barone V; Cossi M; Tomasi J Geometry Optimization of Molecular Structures in Solution by the Polarizable Continuum Model. *J. Comput. Chem.* 1998, 19 (4), 404–417.
- (51). Tomasi J; Mennucci B; Cammi R Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* 2005, 105 (8), 2999–3094. [PubMed: 16092826]
- (52). Mulliken RS Electronic Population Analysis on LCAO-MO Molecular Wave Functions. I. *J. Chem. Phys.* 1955, 23 (10), 1833–1840.
- (53). Löwdin P-O On the Nonorthogonality Problem. In *Advances in Quantum Chemistry*; 1970; Vol. 5, pp 185–199.
- (54). Löwdin P On the Non-Orthogonality Problem Connected with the Use of Atomic Wave Functions in the Theory of Molecules and Crystals. *J. Chem. Phys.* 1950, 18 (3), 365–375.
- (55). Gorelsky SI AOMix: Program for Molecular Orbital Analysis - Version 6.5. <http://www.sg-chem.net/>, University of Ottawa, Ottawa, Canada 2011.
- (56). Gorelsky SI; Lever ABP Electronic Structure and Spectra of Ruthenium Diimine Complexes by Density Functional Theory and INDO/S. Comparison of the Two Methods. *J. Organomet. Chem.* 2001, 635 (1–2), 187–196.
- (57). Maghami M; Farzaneh F; Simpson J; Azarkish M Synthesis, Crystal Structure and Characterization a New Ionic Complex $\text{MoO}_2\text{Cl}_3(\text{MeOH})\cdot\text{H}_3\text{tpzt}\cdot\text{Cl}_2$ (tpzt=2,4,6-tris-(2-Pyridyl)-1,3,5-Triazine) as Epoxidation Catalyst. *Inorg. Chim. Acta* 2016, 445, 28–36.
- (58). Li J; Wang G; Shi Z; Yang M; Luck RL Two Hydrogen-Bond-Cross-Linked Molybdenum(VI) Network Polymers: Synthesis, Crystal Structures and Cyclooctene Epoxidation with H_2O_2 . *Struct. Chem.* 2009, 20 (5), 869–876.
- (59). Doonan CJ; Millar AJ; Nielsen DJ; Young CG Cis-Dioxomolybdenum(VI) and Oxo(phosphine oxide)molybdenum(IV) Complexes: Steric and Electronic Fine-Tuning of $\text{Cis-}[\text{MoOS}]^{2+}$ Precursors. *Inorg. Chem.* 2005, 44 (13), 4506–4514. [PubMed: 15962957]
- (60). Basu P; Nemykin VN; Sengar RS Substituent Effect on Oxygen Atom Transfer Reactivity from Oxomolybdenum Centers: Synthesis, Structure, Electrochemistry, and Mechanism. *Inorg. Chem.* 2009, 48 (13), 6303–6313. [PubMed: 19485389]
- (61). Neves P; Gago S; Balula SS; Lopes AD; Valente AA; Cunha-Silva L; Almeida Paz F. A.; Pillinger M; Rocha J; Silva CM; et al. Synthesis and Catalytic Properties of Molybdenum(VI) Complexes with Tris(3,5-Dimethyl-1-Pyrazolyl)Methane. *Inorg. Chem.* 2011, 50 (8), 3490–3500. [PubMed: 21438538]
- (62). Santos AM; Kühn FE; Bruus-Jensen K; Lucas I; Romão CC; Herdtweck E Molybdenum(VI) Cis-Dioxo Complexes Bearing (Poly)pyrazolyl-Methane and -Borate Ligands: Syntheses, Characterization and Catalytic Applications. *J. Chem. Soc. Dalt. Trans.* 2001, 8, 1332–1337.
- (63). Doonan CJ; Nielsen DJ; Smith PD; White JM; George GN; Young CG Models for the Molybdenum Hydroxylases: Synthesis, Characterization and Reactivity of Cis-Oxosulfido-Mo(VI) Complexes. *J. Am. Chem. Soc.* 2006, 128 (1), 305–316. [PubMed: 16390160]
- (64). Lincoln SE; Loehrt TM Chemistry and Electronic and Vibrational Spectroscopy of Mononuclear and Dinuclear (Tris(1-Pyrazolyl)borato)- and Chloromolybdenum(V)-Oxo Complexes. *Inorg. Chem.* 1990, 29 (10), 1907–1915.
- (65). Nemykin VN; Basu P Oxygen Atom Transfer Reactivity from a Dioxo-Mo(VI) Complex to Tertiary Phosphines: Synthesis, Characterization, and Structure of Phosphoryl Intermediate Complexes. *Inorg. Chem.* 2005, 44 (21), 7494–7502. [PubMed: 16212375]
- (66). Gago S; Gomes AC; Cunha-Silva L; Pillinger M; Gonçalves IS; Almeida Paz FA A Novel Dinuclear Mo^{VI} Complex with Tris(3,5-Dimethyl-1H-Pyrazol-1-yl)methane. *Acta Crystallogr.* 2012, C68 (3), m73–m75.
- (67). Miessler GL; Fischer PJ; Tarr DA 3.2.3 Electronegativity and Atomic Size Effects In *Inorganic Chemistry*; Pearson Education: Upper Saddle River, NJ, 2014; pp 59–60.

- (68). Xiao Z; Gable RW; Wedd AG; Young CG The Cis-dioxomolybdenum(V) Radical Anion, [(HB(Me₂C₂N₃)₂)MoO₂(SPh)]⁻. J. Chem. Soc., Chem. Commun. 1994, 1994 (11), 1295–1296.
- (69). Sundermeyer J; Putterlik J; Pritzkow H Tris(3,5-Dimethyl-1-Pyrazolyl)boranato-Substituierte Alkyl(dioxo)-, Methylenephosphoranyl(dioxo)- and σ -Allyl(dioxo)-Komplexe Des Molybdäns Und Wolframs. Chem. Ber. 1993, 126 (2), 289–296.
- (70). Tolman CA Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis. Chem. Rev. 1977, 77 (3), 313–348.
- (71). Xiao Z; Bruck MA; Doyle C; Enemark JH; Grittini C; Gable RW; Wedd AG; Young CG Dioxomolybdenum(VI) Complexes of Tripodal Nitrogen-Donor Ligands: Syntheses and Spectroscopic, Structural, and Electrochemical Studies, Including the Generation of EPR-Active Molybdenum(V) Species in Solution. Inorg. Chem. 1995, 34 (24), 5950–5962.
- (72). Baum AE; Lindeman SV; Fiedler AT Mononuclear Iron-(Hydro/semi)quinonate Complexes Featuring Neutral and Charged Scorpionates: Synthetic Models of Intermediates in the Hydroquinone Dioxygenase Mechanism. Eur. J. Inorg. Chem. 2016, 15–16, 2455–2464.
- (73). Smith PD; Millar AJ; Young CG; Ghosh A; Basu P Detection, Isolation, and Characterization of Intermediates in Oxygen Atom Transfer Reactions in Molybdoenzyme Model Systems. J. Am. Chem. Soc. 2000, 122 (38), 9298–9299.
- (74). Nemykin VN; Laskin J; Basu P Isolation, Characterization of an Intermediate in an Oxygen Atom-Transfer Reaction, and the Determination of the Bond Dissociation Energy. J. Am. Chem. Soc. 2004, 126 (28), 8604–8605. [PubMed: 15250684]
- (75). Millar AJ; Doonan CJ; Smith PD; Nemykin VN; Basu P; Young CG Oxygen Atom Transfer in Models for Molybdenum Enzymes: Isolation and Structural, Spectroscopic, and Computational Studies of Intermediates in Oxygen Atom Transfer from Molybdenum(VI) to Phosphorus(III). Chem. - A Eur. J. 2005, 11 (11), 3255–3267.
- (76). Kail BW; Pérez LM; Zari SD; Millar AJ; Young CG; Hall MB; Basu P Mechanistic Investigation of the Oxygen-Atom-Transfer Reactivity of Dioxo-Molybdenum(VI) Complexes. Chem. - A Eur. J. 2006, 12 (28), 7501–7509.
- (77). Sengar RS; Nemykin VN; Basu P Synthesis, Electrochemistry, Geometric and Electronic Structure of Oxo-Molybdenum Compounds Involved in an Oxygen Atom Transferring System. J. Inorg. Biochem. 2008, 102 (4), 748–756. [PubMed: 18187198]
- (78). Keith JM; Tomi ZD; Zari SD; Hall MB Oxygen Atom Transfer Catalysis: Ligand Effects on the Key Reaction Barrier in Molybdenum(VI) Dioxo Systems. J. Mol. Catal. A Chem. 2010, 324 (1–2), 15–23.
- (79). Basu P; Kail BW; Young CG Influence of the Oxygen Atom Acceptor on the Reaction Coordinate and Mechanism of Oxygen Atom Transfer from the Dioxo-Mo(VI) Complex, TpiPrMoO₂(OPh), to Tertiary Phosphines. Inorg. Chem. 2010, 49 (11), 4895–4900. [PubMed: 20433155]
- (80). Basu P; Kail BW; Adams AK; Nemykin VN Quantitation of the Ligand Effect in Oxo-Transfer Reactions of Dioxo-Mo(VI) Trispyrazolyl Borate Complexes. Dalton Trans. 2013, 42 (9), 3071–3081. [PubMed: 23212540]
- (81). Izumi Y; Glaser T; Rose K; McMaster J; Basu P; Enemark JH; Hedman B; Hodgson KO; Solomon EI Ligand K-Edge and Metal L-Edge X-Ray Absorption Spectroscopy and Density Functional Calculations of Oxomolybdenum Complexes with Thiolate and Related Ligands: Implications for Sulfite Oxidase. J. Am. Chem. Soc. 1999, 121 (43), 10035–10046.
- (82). Bersuker IB Electronic Structure and Properties of Transition Metal Compounds: Introduction to the Theory, 2nd Edn; John Wiley & Sons: Hoboken, NJ, 2010.
- (83). Carey FA; Sunberg RJ 3.3.2 Correlation Between Thermodynamic and Kinetic Aspects of Reactions In Advanced Organic Chemistry Part A: Structure and Mechanisms; Springer: New York, NY, 2007; pp 288–289.
- (84). Hermet J; Torrent M; Bottin F; Dezanneau G; Geneste G Oxide Ion and Proton Transport in Gd-Doped Barium Cerate: A Combined First-Principles and Kinetic Monte Carlo Study. J. Mater. Chem. A 2014, 2 (24), 9055–9066.
- (85). Roy S; Goedecker S; Hellmann V Bell-Evans-Polanyi Principle for Molecular Dynamics Trajectories and Its Implications for Global Optimization. Phys. Rev. E 2008, 77 (5), 56707.

- (86). The first step of these OAT reactions is rate-limiting.
- (87). Kennepohl P; Solomon EI Electronic Structure Contributions to Electron-Transfer Reactivity in Iron–Sulfur Active Sites: 2. Reduction Potentials. *Inorg. Chem.* 2003, 42 (3), 689–695. [PubMed: 12562182]
- (88). Qiu JA; Wilson HL; Rajagopalan KV Structure-Based Alteration of Substrate Specificity and Catalytic Activity of Sulfite Oxidase from Sulfite Oxidation to Nitrate Reduction. *Biochemistry* 2012, 51 (6), 1134–1147. [PubMed: 22263579]
- (89). Wu SY; Rothery RA; Weiner JH Pyranopterin Coordination Controls Molybdenum Electrochemistry in *Escherichia Coli* Nitrate Reductase. *J. Biol. Chem.* 2015, 290 (41), 25164–25173. [PubMed: 26297003]

Figure 1. ORTEP diagram (50% probability thermal ellipsoids) of the X-ray crystal structure of [Tpm*MoO₂Cl](ClO₄) (**2**).

Figure 2.
Cyclic voltammogram of **2**.

Figure 3.

Top panel: UV-visible spectra of the reaction between 0.5 mM **2** (black solid line) and 5 equiv. PPh_3 in CH_3CN at -40°C , including UV-visible spectra of **3** (red solid line) and **4** (blue solid line). Bottom panel: the time trace of this reaction.

Figure 4.

Plots of k_{form} (Top) and k_{decay} (Bottom) vs. $[\text{PPh}_3]$ monitored at 692 nm (black square) and 795 nm (red circle). Reaction conditions: 0.5 mM **2** in CH_3CN at -40°C .

Figure 5.

Eyring plot for the reaction of 0.5 mM **2** and 10 mM PPh₃ in EtCN between –30 to –60 °C monitored at 692 nm for k_{form} (top panel) and k_{decay} (bottom panel).

Figure 6. Electrostatic potential energy surfaces computed for $[\text{TpmMoO}_2\text{Cl}]^+$ (left), TpMoO_2Cl (center), and PPh_3 (right). The isovalue has been set at $0.0004 \text{ au}/\text{\AA}^3$.

Figure 7.

Reaction coordinate diagram of the first step of the OAT reaction in the Tpm and Tp systems. Reactant energies have been normalized to $E = 0$ for comparative purposes.

Figure 8.

Fragment molecular orbital (FMO) description of reactivity at the OAT TS for the reaction of PPh_3 with $[(\text{TpM})\text{MoO}_2\text{Cl}]^+$ (left) and $(\text{Tp})\text{MoO}_2\text{Cl}$ (right).

Figure 9.

A schematic illustration of relative activation energy and thermodynamic driving force of the first step of OAT reaction for the Tpm* system (blue line) vs. Tp* system (red line). Dotted lines highlight an earlier TS for the system (blue) that possesses a lower activation barrier and a greater thermodynamic driving force.

Tp* Ligand
hydrotris(3,5-dimethyl-1-
pyrazolyl)borate

Tpm* Ligand
tris(3,5-dimethyl-1-
pyrazolyl)methane

Scheme 1.

Scheme 2.

Method of measuring carbon- (or boron-) based cone angle (θ) of Tpm* ligand (or Tp* ligand), with $\theta = 2/3(\theta_1 + \theta_2 + \theta_3)$, as well as molybdenum-based cone angle (β), with $\beta = 2/3(\beta_1 + \beta_2 + \beta_3)$.⁷⁰

Scheme 4.

Table 1.

Comparison of IR features.

Complex	$\nu(\text{Mo=O})$ (cm ⁻¹)	Ref
1	944, 905	This work
2	951, 912	This work
Tp*Mo ^{VI} O ₂ Cl	930, 898	39
Tp*Mo ^{VI} O ₂ (SPh)	921, 894	39
Tp*Mo ^{VI} O ₂ (OPh)	922, 896	39
Tp ^{Pr} *Mo ^{VI} O ₂ (OAr)	930, 905	59
Tp*Mo ^{VI} O ₂ (SAr)	~930, ~900	60
[Tp ^m *Mo ^{VI} O ₂ Cl]BF ₄	951, 916 ^b	61
[Tp ^m *Mo ^{VI} O ₂ Cl]Cl	946, 912 ^b	62
(L ₀)Mo ^{VI} O ₂ Cl ₂ ^a	943, 906 ^b	62
(L ₁)Mo ^{VI} O ₂ Cl ₂ ^a	943, 916	62
[(Tp ^m)Mo ^{VI} O ₂ Cl]Cl	953, 920 ^b	62
[(Tp ^m)Mo ^{VI} O ₂ Br]Br	948, 918 ^b	62
Tp ^{Pr} *Mo ^{VI} OS(OAr)	910	63
[(Tp ^m) ₂ Mo ^{VI} O ₄ (μ ₂ -O)](BF ₄) ₂	945, 916	61
Tp*Mo ^V OCl ₂	958	64
(Tp*) ₂ Mo ^V O ₂ Cl ₂ (μ ₂ -O)	954	64
Tp*MoO ^{IV} Cl(OPR ₃)	945–955	65
Tp*Mo ^{IV} O(SAr)(OPR ₃)	~945	60

^aL₀ = 3,5-dimethylpyrazole; L₁ = 2,2-di(1-pyrazolyl)propane.^bNo crystal structure was reported.

Table 2.Crystal data and structural refinement for [Tpm*MoO₂Cl](MoO₂Cl₃) (**1**) and [Tpm*MoO₂Cl](ClO₄) (**2**).

Empirical formula	1	2
Formula weight	699.96	561.23
Space group	<i>I4₁cd</i>	<i>P2₁/n</i>
Unit cell dimensions	a = 27.539(3) Å	a = 12.632(2) Å
	b = 27.539(3) Å	b = 10.344(2) Å
	c = 13.1280(14) Å	c = 16.682(3) Å
	α = 90°	α = 90°
	β = 90°	β = 105.696°
	γ = 90°	γ = 90°
Volume	9956(2)	2098.4(5)
Z	16	4
Crystal size	0.42×0.19×0.17 mm ³	0.19×0.075×0.02 mm ³
Reflections collected	45522	20967
Data / restraints / parameters	5499/420/373	3826/655/363
Goodness-of-fit on <i>F</i> ²	1.062	1.059
Final <i>R</i> indices	<i>R</i> 1 = 3.53%	<i>R</i> 1 = 3.72%
	<i>wR</i> 2 = 9.05%	<i>wR</i> 2 = 7.87%
<i>R</i> indices (all data)	<i>R</i> 1 = 3.84%	<i>R</i> 1 = 5.06%
	<i>wR</i> 2 = 9.31%	<i>wR</i> 2 = 8.37%
Largest diff. peak and hole	1.049 and	0.501 and
	−0.84 e.Å ^{−3}	−0.532 e.Å ^{−3}

Table 3.Selected bond distances (Å) for **1** and **2**.

	1		2
Bond Distances (Å)			
Mo1–O1	1.752(11)	Mo1A–O1A	1.672(7)
Mo1–O2	1.742(5)	Mo1A–O2A	1.681(7)
Mo1–Cl1	2.209(3)	Mo1A–Cl1A	2.316(3)
Mo1–N1	2.220(5)	Mo1–N1	2.176(4)
Mo1–N3	2.282(5)	Mo1–N3	2.329(4)
Mo1–N5	2.304(5)	Mo1–N5	2.324(4)
Bond Angles (°)			
∠O1–Mo1–O2	102.8(4)	∠O1A–Mo1A–O2A	105.5(7)
∠O1–Mo1–N5	90.4(4)	∠O1A–Mo1A–N5	88.1(4)
∠O2–Mo1–N1	90.5(2)	∠O2A–Mo1A–N1	91.9(5)
∠N1–Mo1–N5	76.68(19)	∠N1–Mo1A–N5	76.23(14)
∠Cl1–Mo1–O2	100.94(18)	∠Cl1A–Mo1A–O2A	101.4(5)
∠Cl1–Mo1–O1	101.4(4)	∠Cl1A–Mo1A–O1A	100.2(4)
∠Cl1–Mo1–N1	160.55(14)	∠Cl1A–Mo1A–N1	158.10(17)
∠Cl1–Mo1–N5	88.33(16)	∠Cl1A–Mo1A–N5	86.52(13)
∠N3–Mo1–O1	164.3(4)	∠N3–Mo1A–O1A	162.8(4)
∠N3–Mo1–O2	88.2(2)	∠N3–Mo1A–O2A	88.9(5)
∠N3–Mo1–N1	77.45(18)	∠N3–Mo1A–N1	77.07(13)
∠N3–Mo1–N5	76.54(18)	∠N3–Mo1A–N5	76.12(14)
∠Cl1–Mo1–N3	87.15(14)	∠Cl1A–Mo1A–N3	85.84(12)
∠O1–Mo1–N1	91.2(4)	∠O1A–Mo1A–N1	92.7(4)
∠O2–Mo1–N5	161.84(19)	∠O2A–Mo1A–N5	162.5(5)

Table 4.

Comparison of bond distances and ligand bite angles of *cis*-dioxo Mo(VI) complexes of Tpm* and Tp* ligands.

	1	2	{Tpm*Mo ^{VI} O ₂ }(μ-O) O}{[Mo ^{VI} O ₂ (Tpm*)]} ²⁻ ^a	[(Tpm*Mo ^{VI} O ₂)(μ-O) O}{[Mo ^{VI} O ₂ (Tpm*)]} ²⁻ ^a	{Tpm*Mo ^{VI} O ₂ }(μ-O) [Mo ^{VI} O ₂ (O)(H ₂ O)] ^a	Tp*Mo ^{VI} O ₂ (SPH)	Tp*Mo ^{VI} O ₂ (S- <i>p</i> -OMe)	Tp*Mo ^{VI} O ₂ (NCS)	Tp*Mo ^{VI} O ₂ (Me)
Mo=O	1.742, 1.752	1.672, 1.681	1.706, 1.706	1.680, 1.698	1.699, 1.721	1.742, 1.742	1.692, 1.697	1.694, 1.704	1.712, 1.736
Mo-N	2.220, 2.282, 2.304	2.176, 2.324, 2.329	2.258, 2.299, 2.299	2.230, 2.310, 2.314	2.286, 2.329, 2.336	2.277, 2.334, 2.410	2.157, 2.324, 2.349	2.162, 2.291, 2.293	2.169, 2.336, 2.344
Mo-X	2.209	2.316	1.854	1.887	1.810	2.442	2.420	2.000	2.169
θ ^b	143.54	143.35	143.75	144.97	143.27	135.06	140.22	139.08	138.55
β ^b	91.77	91.23	90.77	91.05	89.17	93.67	94.73	95.16	94.02
Ref	This work		⁶⁶	⁶¹	⁶¹	⁶⁸	⁶⁰	³⁹	⁶⁹

^a Only metrical parameters of one Tpm*-coordinated {Mo^{VI}O₂} center of each binuclear complex are documented in this table.

^b See Scheme 3 for the method of measuring θ and β.

Table 5.

Redox potential of **2** in CH₃CN relative to Fc⁺/Fc, in comparison with *cis*-Mo^{VI}O₂ compounds supported by the anionic Tp* ligand.

	$E_{1/2}$ (mV)	E_{pp} (mV)	i_{pa}/i_{pc}	Ref
2 ^a	−660	182	0.71	This work
Tp*MoO ₂ Cl	−1010	230	0.5	71
Tp*MoO ₂ Br	−870	<i>b</i>	<i>b</i>	71
Tp*MoO ₂ (SPh)	−1150	66	1.02	71
Tp*MoO ₂ (OPh)	−1270	73	0.99	71
Tp ^{dt} MoO ₂ (Cl)	−890	82	0.77	71

^a. Cyclic Voltammograms of **2** were collected at 100 mV■S^{−1} in anhydrous CH₃CN using 0.1 M KPF₆.

^b. The observed wave is completely irreversible.

Table 6.UV-visible spectra of Mo^{IV} complexes in MeCN solution.

	UV-vis spectra λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)	Ref
[Tpm*Mo ^{VI} O ₂ Cl](ClO ₄) (2)	213 (54000), 250sh ^a (14000), 282 (9300)	This work
Tp*Mo ^{VI} O ₂ Cl	211 (48000), 250sh ^a (11000), 284 (10000)	³⁹ , this work
[Tpm*Mo ^{IV} O(OPPh ₃)(Cl)](ClO ₄) (3)	795 (140), 445 (400), 370 (2330)	This work
Tp*Mo ^{IV} O(OPPh ₃)(Cl)	840 (130), 465 (290), 330 (2300)	This work
Tp*Mo ^{IV} O(OPMe ₃)(Cl)	820 (58), 422 (111), 329 (1060)	⁶⁵
Tp*Mo ^{IV} O(OPMe ₃)(SPh)	760 (165), 411 (716)	⁷⁷
Tp*Mo ^{IV} O(OPEt ₃)(Cl)	826 (54), 427 (114), 332 (1129)	⁶⁵
Tp*Mo ^{IV} O(OPPhMe ₂)(Cl)	826 (41), 440 (92), 353 (762)	⁶⁵
[Tpm*Mo ^{IV} O(NCCH ₃)(Cl)](ClO ₄) (4)	810sh ^a (70), 690 (105), 340 (2400)	This work
Tp*Mo ^{IV} O(NCCH ₃)(Cl)	870sh ^a (32), 723 (65), 373 (213), 320 (2167)	⁶⁵
Tp*Mo ^{IV} O(NCCH ₃)(SPh)	762 (96), 643 (96), 375sh ^a (785)	⁷⁷

^a
sh = shoulder

Table 7.

Activation parameters for the first and second steps of OAT reactions in Tpm* and Tp* systems.

Conversion	$H^\ddagger$ (kJ/mol)	$S^\ddagger$ [J/(mol•T)]	Reference
$2 + \text{PPh}_3 \rightarrow 3^a$	22 (2)	−158 (8)	This work
$\text{Tp}^*\text{Mo}^{\text{VI}}\text{O}_2\text{Cl} + \text{PPh}_3 \rightarrow \text{Tp}^*\text{Mo}^{\text{IV}}(\text{O})(\text{OPPh}_3)\text{Cl}^a$	32 (1)	−170 (4)	This work
$\text{Tp}^*\text{Mo}^{\text{VI}}\text{O}_2\text{X} + \text{PR}_3 \rightarrow \text{Tp}^*\text{Mo}^{\text{IV}}\text{O}(\text{OPR}_3)(\text{X})^b$	Between 34 and 83	Between −36 and −184	60,75,79,80
$3 + \text{EtCN} \rightarrow 4^{\text{EtCN}} + \text{OPPh}_3^{a,c}$	51 (2)	−69 (6)	This work
$\text{Tp}^*\text{Mo}^{\text{IV}}(\text{O})(\text{OPPh}_3)\text{Cl} + \text{EtCN} \rightarrow \text{Tp}^*\text{Mo}^{\text{IV}}\text{O}(\text{NCEt})\text{Cl} + \text{OPPh}_3^a$	90 (2)	23 (6)	This work
$\text{Tp}^*\text{Mo}^{\text{IV}}\text{O}(\text{OPR}_3)(\text{X}) + \text{CH}_3\text{CN} \rightarrow \text{Tp}^*\text{Mo}^{\text{IV}}\text{O}(\text{NCCH}_3)(\text{X}) + \text{OPR}_3^b$	Between 56 ^d and 109	Between −126 and 69	60,75,79,80

^aReaction in EtCN.

^binclude both Tp* and Tp^{Pr} data; X = chloride, substituted phenolate or thiophenolate; PR₃ = tertiary phosphines including PMe₃, PMe₂Ph, PMePh₂, PPh₃, PEt₃, PEt₂Ph, PEtPh₂, and PⁿBu₃. Reaction in CH₃CN.

^c4^{EtCN} = [Tpm*Mo^{IV}O(NCCH₂CH₃)(Cl)] ClO₄.

^dThe following transformation: [Tp^{Pr}Mo^{IV}O(OPh)(OPMe₃)] + CH₃CN → [Tp^{Pr}Mo^{IV}O(OPh)(NCCH₃)] + OPMe₃ has a relatively small $H^\ddagger$ of 56 kJ/mol, while the rest of transformations have $H^\ddagger$ values ranging from 66 to 109 kJ/mol.

Table 8.

OAT reaction rates of the Tpm* and Tp* system.

	$k_{2\text{ form}}$ value ($\text{s}^{-1}\text{M}^{-1}$) for the first step: $\{\text{Mo}^{\text{VI}}\text{O}_2\} + \text{PPh}_3 \rightarrow \{\text{Mo}^{\text{IV}}(\text{O})(\text{OPPh}_3)\}^a$	k_{decay} value (s^{-1}) for the second step: $\{\text{Mo}^{\text{IV}}(\text{O})(\text{OPPh}_3)\} + \text{CH}_3\text{CN} \rightarrow$ $\{\text{Mo}^{\text{IV}}\text{O}(\text{NCCH}_3)\} + \text{OPPh}_3^a$
L = Tpm*	84(4)	$4.8(2) \times 10^{-3}$
L = Tp*	$0.16(2)^b$	Very slow ^c

^aReaction condition: 0.2 mM **2** or [Tp*MoO₂Cl] in anhydrous CH₃CN at -40 °C with 1 to 5 mM PPh₃.^bSee Figure S2.^cThere was no sign of any decay of [Tp*Mo^{IV}O(OPPh₃)Cl] for at least 3.5 hours at -40 °C. For a more quantitative comparison of the observed reaction rates of the second-step of OAT, we measured k_{decay} of both systems at -15 °C in EtCN: k_{decay} was determined to be $5.8(1) \times 10^{-2} \text{ s}^{-1}$ when L = Tpm*, and $7.6(3) \times 10^{-5} \text{ s}^{-1}$ for Tp* system.

Table 9.

Selected angles for computed (or crystallographically characterized) TS and intermediate structures.^a

	Tpm PPh₃	Tp PPh₃	Tp[*] PMe₃	Tp^{iPr} PMe₃
O–P–C bond angle (°)	[133.8] {111.4}	[142.0] {112.6}	{113.7}	[153.0] {114.5}
O–Mo–O–P dihedral angle (°)	[87.5] {63.92}	[90.2] {62.21}	{47.44}	[79.6] {60.5}
Mo–O–P bond angle (°)	[131.2] {148.2}	[132.4] {150.6}	{133.7}	[121.3] {126.4}
Ref	This work		⁷⁴	⁷⁶

^a[TS] {intermediate}. The intermediate herein refers to computed [(Tpm)MoOCl(OPPh₃)]⁺ for the Tpm system and (Tp)MoO₂Cl(OPPh₃) for the Tp system of this work, crystal structure of Tp^{*}MoO(Cl)(OPMe₃) for Tp^{*} system in Ref ⁷⁴, and computed Tp^{iPr}MoO(OPh)(OPMe₃) for Tp^{iPr} system in Ref ⁷⁶.