Inorganic Chemistry

Tuning the Reactivity of Chromium(III)-Superoxo Species by **Coordinating Axial Ligands**

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Supporting Information

ABSTRACT: Metal-superoxo species have attracted much attention recently as key intermediates in enzymatic and biomimetic oxidation reactions. The effect(s) of axial ligands on the chemical properties of metal-superoxo complexes has never been explored previously. In this study, we synthesized and characterized chromium(III)-superoxo complexes bearing TMC derivatives with pendant pyridine and imidazole donors, such as $[Cr^{III}(O_2)]$ -(TMC-Py)]²⁺ (1, TMC-Py = 4,8,11-trimethyl-1-(2-pyridylmethyl)-1,4,8,11tetraazacyclotetradecane) and $[Cr^{III}(O_2)(TMC-Im)]^{2+}$ (2, TMC-Im = 4,8,11trimethyl-1-(2-methylimidazolmethyl)-1,4,8,11-tetraazacyclotetradecane). The reactivity of chromium(III)-superoxo complexes binding different axial ligands, such as 1, 2, and $[Cr^{III}(O_2)(TMC)(Cl)]^+$ (3, TMC = 1,4,8,11tetramethyl-1,4,8,11-tetraazacyclotetradecane), was then investigated in C-H bond activation and oxygen atom transfer reactions. Kinetic studies revealed that the reactivity of the Cr(III)-superoxo complexes depends on the axial



ligands, showing the reactivity order of 1 > 2 > 3 in those electrophilic oxidation reactions. It was also shown that there is a good correlation between the reactivity of the chromium(III)-superoxo complexes and their redox potentials, in which the redox potentials of the chromium(III)-superoxo complexes are in the order 1 > 2 > 3. DFT calculations reproduced the reactivity order between 1 and 3 in both C-H bond activation and oxygen atom transfer reactions, and the latter reaction is described using orbital interactions. The calculations are also in agreement with the experimentally obtained redox potentials. The present results provide the first example showing that the reactivity of metal-superoxo species can be tuned by the electron-donating ability of axial ligands bound trans to the metal-superoxo moiety.

INTRODUCTION

Synthetic metal-oxygen complexes, such as metal-superoxo, -peroxo, -hydroperoxo, and -oxo, have attracted much attention in the communities of bioinorganic and biological chemistry, since these metal-oxygen species are key intermediates in the dioxygen activation and oxidation reactions by metalloenzymes and their biomimetic compounds.^{1,2} A large number of highvalent metal-oxo complexes bearing heme and nonheme ligands have been synthesized and investigated intensively in various oxidation reactions for the past several decades.² Metal-peroxo and -hydroperoxo complexes have also been synthesized successfully and characterized spectroscopically and/or structurally, and their reactivities have been well-demonstrated in nucleophilic and electrophilic oxidation reactions.^{2g,3}

Metal-superoxo species have been recently proposed as active oxidants in enzymatic reactions, such as nonheme iron enzymes (e.g., isopenicillin N synthase, myo-inositol oxygenase, homoprotocatechuate 2,3-dioxygenase, and cysteine dioxygenases) and copper enzymes (e.g., peptidylglycine- α -amidating monooxygenase and dopamine β -monooxygenase).^{4,5} In biomimetic studies, a number of metal-superoxo complexes have been synthesized and characterized to understand the

structural and spectroscopic properties of the metal-superoxo intermediates in the enzymatic reactions.^{6,7} A notable example is the crystal structure of a synthetic nonheme iron(III)superoxo complex reported recently.8 Nonetheless, the chemistry of the metal-superoxo species is less clearly understood and remains to be elusive.

In the reactivity studies of metal-oxygen species, one of the frequently discussed subjects is the role of axial ligands in oxidation reactions by metal-oxygen species, since it has been shown that the axial ligands of heme enzymes, such as cytochromes P450 and peroxidases, play a significant role in tuning the enzyme's ability in oxidation reactions by high-valent iron(IV)-oxo porphyrin π -cation radical species (compound I).⁹ Thus, the axial ligand effect on the reactivities of high-valent iron(IV)-oxo species has been investigated intensively with synthetic iron-oxo complexes of heme and nonheme ligands, thereby demonstrating that the axial ligand indeed affects the reactivities of the iron-oxo complexes dramatically in hydrogen atom transfer (HAT) and oxygen atom transfer (OAT)

Received: September 8, 2015

reactions.^{10,11} The axial ligand effect has also been demonstrated in oxidative nucleophilic reactions by iron(III)- and manganese(III)-peroxo complexes, in which binding of electron-rich axial ligands increases the nucleophilic reactivity of the metal(III)-peroxo complexes.¹² However, such an axial ligand effect has never been explored in metal-superoxo species, probably due to the lesser availability of thermally stable and well-characterized metal-superoxo complexes for reactivity studies.

Recently, we reported the synthesis and spectroscopic and structural characterization of a thermally stable chromium(III)-superoxo complex, $[Cr^{III}(O_2)(TMC)(Cl)]^+$ (3, TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) (Scheme 1).¹³ This Cr(III)-superoxo complex was reactive

Scheme 1. Schematic Drawing of Macrocyclic Ligands and Chromium(III)-Superoxo Complexes Used in This Study



enough to be used in the reactions of HAT (e.g., the oxidation of xanthene, dihydroanthracene (DHA), cyclohexadiene (CHD), and fluorene) and OAT (e.g., the oxidation of phosphines and sulfides).¹³ In the present study, we synthesized chromium(III)-superoxo complexes bearing TMC derivatives with pendant pyridine and imidazole donors, such as $[Cr^{III}(O_2)(TMC-Py)]^{2+}$ (1, TMC-Py = 4,8,11-trimethyl-1-(2pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane) and $[Cr^{III}(O_2)(TMC-Im)]^{2+}$ (2, TMC-Im = 4,8,11-trimethyl-1-(2methylimidazolmethyl)-1,4,8,11-tetraazacyclotetradecane) (Scheme 1), and used these Cr(III)-superoxo complexes in the investigation of the axial ligand effect on the reactivity of metalsuperoxo species. We now report experimental and theoretical results showing that the reactivity of metal-superoxo species is significantly affected by the axial ligands coordinated trans to the metal-superoxo moiety in HAT and OAT reactions.

RESULTS AND DISCUSSION

The starting materials, $[Cr^{II}(TMC-Py)]^{2+}$ and $[Cr^{II}(TMC-Im)]^{2+}$, were prepared by reacting CrCl₂ with TMC-Py and TMC-Im, respectively, in CH₃CN under an inert atmosphere. Blue crystalline powders were isolated by adding NaClO₄ [Supporting Information (SI) Experimental Section for experimental details, and Figure S1 for UV–vis and cold spray ionization mass spectra (CSI-MS)]. The chromium(III)-superoxo complexes, $[Cr^{III}(O_2)(TMC-Py)]^{2+}$ (1) and $[Cr^{III}(O_2)(TMC-Im)]^{2+}$ (2), were then synthesized by bubbling O₂ into the solutions of $[Cr^{II}(TMC-Py)]^{2+}$ and $[Cr^{II}(TMC-Im)]^{2+}$, respectively, in CH₃CN at -10 °C, as reported previously for the synthesis of 3^{13} The intermediates 1 and 2 were metastable (e.g., ca. 5% decay for 1 h at -10 °C), allowing us to use them for spectroscopic characterization and reactivity studies.

The UV–vis spectrum of **1** shows an intense band at 320 nm ($\varepsilon = 2100 \text{ M}^{-1} \text{ cm}^{-1}$) and several weak bands at 455 nm ($\varepsilon = 130 \text{ M}^{-1} \text{ cm}^{-1}$), 527 nm ($\varepsilon = 170 \text{ M}^{-1} \text{ cm}^{-1}$), 605 nm ($\varepsilon = 60 \text{ M}^{-1} \text{ cm}^{-1}$), 624 nm ($\varepsilon = 50 \text{ M}^{-1} \text{ cm}^{-1}$), and 670 nm ($\varepsilon = 30 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 1a). The CSI-MS of **1** exhibits a prominent



Figure 1. (a) UV–vis spectrum of 1 (0.50 mM) in CH₃CN at -10 °C. Inset shows solution IR spectra of 1 prepared with ¹⁶O₂ (red line) and ¹⁸O₂ (blue line). (b) CSI-MS of 1 in CH₃CN at -10 °C. Insets show the observed isotope distribution patterns for {Cr(¹⁶O₂)(TMC-Py)(CIO₄)}⁺ (lower) and {Cr(¹⁸O₂)(TMC-Py)(CIO₄)}⁺ (upper). The peaks at m/z of 484.2 and 501.2 marked with asterisk are assigned to {Cr(TMC-Py)(CIO₄)}⁺ and {Cr(OH)(TMC-Py)-(CIO₄)}⁺, respectively.

ion peak at a mass-to-charge ratio (m/z) of 516.2 (Figure 1b), whose mass and isotope distribution pattern correspond to $\{Cr(O_2)(TMC-Py)(ClO_4)\}^+$ (calculated m/z of 516.2). When the reaction was carried out with isotopically labeled ¹⁸O₂, a mass peak corresponding to $\{Cr(^{18}O_2)(TMC-Py)(ClO_4)\}^+$ appeared at m/z of 520.2 (calculated m/z of 520.2) (Figure 1b, inset). The four mass unit shift on substitution of ¹⁶O with ¹⁸O indicates that the source of two oxygen atoms in 1 is molecular O₂. Compound 1 is EPR silent, and the effective magnetic moment of 1 ($\mu_{eff} = 3.3 \mu_B$ at $-40 \ ^{\circ}C$) indicates the spin state of S = 1 resulting from strong antiferromagnetic coupling between the Cr^{III} ("d³", $S = {}^{3}/{_2}$) and the superoxide ($S = {}^{1}/{_2}$).

The solution infrared (IR) spectrum of 1 was recorded in CH₃CN at -10 °C. Compound 1 prepared under an $^{16}O_2$ atmosphere exhibits an isotopically sensitive band at 1179 cm⁻¹, which shifts to 1113 cm⁻¹ when $^{18}O_2$ is used (Figure 1a, inset). The observed vibrational change is consistent with its assignment as an O–O stretching vibration on the basis of its $^{16-18}\Delta\nu$ value of 66 cm⁻¹ ($^{16-18}\Delta\nu_{calc}=67$ cm⁻¹). Comparable

signals were reported in the spectra of end-on chromium(III)superoxo complexes, such as $[Cr(O_2)(cyclam)(H_2O)]^{2+}$ (1134/1145 (doublet) cm⁻¹), $[Cr(O_2)(H_2O)_5]^{2+}$ (1166 cm⁻¹), and 3 (1170 cm⁻¹).^{13,16,17} However, the values are higher than those of side-on chromium(III)-superoxo complexes (1027–1104 cm⁻¹).^{14,18} The DFT calculated ¹⁶O–¹⁶O bond vibration frequency for 1 is slightly off at 1156 cm⁻¹, but on the other hand, so is its ¹⁸O–¹⁸O vibration (1089 cm⁻¹); i.e., the DFT calculated ^{16–18} $\Delta \nu_{calc} = 67$ cm⁻¹ matches the experiments. On the basis of the spectroscopic characterization and the calculations presented above, 1 is assigned as a chromium(III) complex with an "end-on" superoxo group, $[Cr^{III}(O_2)(TMC-Py)]^{2+}$.

Spectroscopic properties of **2** are similar to those of **1**. The UV–vis spectrum of **2** exhibits characteristic bands at 315 nm ($\varepsilon = 2100 \text{ M}^{-1} \text{ cm}^{-1}$), 450 nm ($\varepsilon = 170 \text{ M}^{-1} \text{ cm}^{-1}$), 515 nm ($\varepsilon = 170 \text{ M}^{-1} \text{ cm}^{-1}$), 600 nm ($\varepsilon = 60 \text{ M}^{-1} \text{ cm}^{-1}$), 628 nm ($\varepsilon = 70 \text{ M}^{-1} \text{ cm}^{-1}$), and 660 nm ($\varepsilon = 70 \text{ M}^{-1} \text{ cm}^{-1}$) (SI, Figure S2a). The CSI-MS of **2** shows a prominent signal at m/z of 519.2 (SI, Figure S2b), corresponding to $\{\text{Cr}(\text{O}_2)(\text{TMC-Im})(\text{CIO}_4)\}^+$ (calculated m/z of 519.2). The mass peak shifted to m/z of 523.2 (SI, Figure S2b, inset) when ¹⁸O₂ was used. Evan's method analysis of the ¹H NMR data indicates that **2** ($\mu_{\text{eff}} = 3.4 \mu_{\text{B}}$ at -40 °C) has the spin state of S = 1,¹⁵ which is EPR silent. The solution IR spectrum of **2** in CH₃CN shows an isotopically sensitive band at 1196 cm⁻¹, which shifts to 1128 cm⁻¹ on ¹⁸O-substitution (¹⁶⁻¹⁸ $\Delta \nu = 68 \text{ cm}^{-1}$; SI, Figure S2a, inset). The O–O stretching frequency of **2** is comparable to those of **1** (1179 cm⁻¹) and **3** (1170 cm⁻¹).^{13a,17}

The reactivities of chromium(III)-superoxo complexes bearing different axial ligands were investigated in HAT reactions (Scheme 2, left). Upon addition of CHD (40 equiv;

Scheme 2. Possible Mechanisms for the HAT and OAT Reactions of 2 with CHD (left) and PPh₃ (right), Respectively



80 mM) to 1 in CH₃CN at -10 °C, the characteristic UV–vis absorption bands of 1 disappeared through pseudo-first-order decay (SI, Figure S3), and product analysis of the reaction solution revealed the formation of benzene (85(5)%). In addition, [Cr^{III}(OH)(TMC-Py)]²⁺ was formed as a product, and [Cr^{III}(¹⁸OH)(TMC-Py)]²⁺ was produced when 1-¹⁸O was used (SI, Figure S4). The pseudo-first-order fitting of the kinetic data, monitored at 527 nm, yielded the k_{obs} value of $1.7(2) \times 10^{-2} \text{ s}^{-1}$ (SI, Figure S3, inset). The pseudo-first-order rate constant increased proportionally with the concentration of CHD, giving a second-order rate constant (k_2) of $2.2(2) \times 10^{-1}$ M⁻¹ s⁻¹ (Figure 2a). Similarly, a second-order rate constant of



Figure 2. Kinetic studies of the reaction of 1 (red line with red \blacktriangle), 2 (blue line with blue \bullet), and 3 (black line with black \blacksquare) with external substrates in CH₃CN at -10 °C. Plots of k_{obs} against the concentration of CHD (a) and PPh₃ (b) to determine second-order rate constants.

 $8.9(7) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ was determined in the reaction of 2 and CHD in CH₃CN at -10 °C (Figure 2a and SI, Figure S5). Hence, the order of the second-order rate constants for the different ligands was determined to be 1 > 2 > 3 (Table 1 and Figure 2a).^{13a} Product analysis of the final reaction mixture revealed the formation of [Cr^{III}(OH)(TMC-Im)]²⁺ (SI, Figure S6) and benzene (79(5)%).

Table 1. Second-Order Rate Constants in Substrate Oxidations and Electrochemical Data for Chromium(III)-Superoxo Complexes, 1–3, in CH₃CN at –10 °C

	$k_2 (M^{-1} s^{-1})$			
complex	CHD	PPh ₃	E _{1/2} (V) vs SCE	E _{pc} (V) vs SCE
1	$2.2(2) \times 10^{-1}$	$2.6(2) \times 10^2$	-0.17	-0.36
2	$8.9(7) \times 10^{-2}$	$8.1(7) \times 10$	-0.37	-0.42
3 ^{<i>a</i>}	$2.7(3) \times 10^{-2}$	$8.4(6) \times 10^{-1a}$	-0.52	-0.55

 a The values obtained in this study are the same as those reported in ref 13.

The axial ligand effect was also investigated for the OAT reactions by the chromium(III)-superoxo complexes (Scheme 2, right). Addition of triphenylphosphine (PPh₃) to the solutions of 1 and 2 caused the decay of the intermediates with the concomitant formation of the corresponding chromium(IV)-oxo complexes as detected by UV-vis and CSI-MS (SI, Figures S7 and S8). The product analysis of the reaction solutions with HPLC and ³¹P NMR revealed the

formation of OPPh₃ in a quantitative yield (Experimental Section). The pseudo-first-order rate constant increased proportionally with the concentration of PPh₃, giving k_2 values of 2.6(2) × 10² M⁻¹ s⁻¹ for 1 and 8.1(7) × 10 M⁻¹ s⁻¹ for 2 (Table 1 and Figure 2b), indicating that OAT from 1 to PPh₃ is ~3 times faster than that from 2 to PPh₃. Further, by comparing the second-order rate constants of 1 and 2 to that of 3 under the identical reaction conditions, we were able to demonstrate that 1 and 2 are about 100 times or more reactive than 3 in the oxidation of the phosphine and the reactivity order of the chromium(III)-superoxo complexes is 1 > 2 > 3 (Table 1 and Figure 2b). Thus, these results demonstrate that the reactivity of the chromium(III)-superoxo complexes in OAT reactions is modulated by the axial ligands bound *trans* to the superoxo group.

The cyclic voltammograms (CVs) of chromium(III)-superoxo complexes were investigated to gain insight into the axial ligand effect on the observed reactivities of the chromiumsuperoxo moiety. The redox potentials of chromium(III)superoxo complexes were determined to be $E_{1/2} = -0.17$ V versus SCE for 1, $E_{1/2} = -0.37$ V versus SCE for 2, and $E_{1/2} =$ -0.52 V versus SCE for 3 (Table 1) by the increase of scan rate because the cyclic voltammograms are all irreversible (SI, Figure S9). However, the data clearly show that the reduction peak potentials (E_{pc}) shift in the negative direction upon binding of more basic axial ligands, yielding the reduction peak potential order of 1 (-0.36 V vs SCE) > 2 (-0.42 V vs SCE) > 3 (-0.55 V vs SCE). The negative shifts observed are consistent with the introduction of electron-rich axial ligands trans to the superoxo group, resulting in the decrease of the reduction peak potentials (or redox potentials) of the chromium(III)-superoxo moiety. Such an axial ligand effect was observed in the reactivity of iron(IV)-oxo complexes.¹ Interestingly, we observed a good linear correlation between the E_{pc} values of the chromium(III)-superoxo complexes and the reaction rates of CHD and PPh₃ oxidation (Figure 3). To



Figure 3. Correlation between reactivities and reduction peak potentials of chromium(III)-superoxo complexes. Plots of log k_2 determined in the oxidation of CHD (blue line with blue ■) and PPh₃ (red line with red •) against the reduction peak potentials of 1–3 in CH₃CN at -10 °C.

conclude the reactivity trend of the chromium(III)-superoxo complexes, the one having the most positive potential shows the fast rates in the electrophilic oxidation reactions.

To correlate these results with theory, one-electron reduced species of 1 and 3 were calculated with density functional theory (DFT) calculations (see also SI, Tables S1-S15). Compound 2 was excluded from this theoretical study as the differences to 1 and 3 were considered too small for meaningful

comparisons (in terms of calculated reaction energies, *vide infra*). Interestingly, the one-electron reduced species of both 1 and 3 resulted in chromium(III)-peroxo species instead of chromium(II)-superoxo. The preferred spin states are, in both cases, high-spin ($S = \frac{3}{2}$). The electron affinities (i.e., the energy difference between the chromium(III)-peroxo and chromium(III)-superoxo structures) are 94.4 kcal/mol for 1 and 87.1 kcal/mol for 3. The difference of 7.3 kcal/mol corresponds to 0.32 V for one-electron transfer, in good agreement with the experimental CV difference of 0.35 V between 1 and 3.

Then, we attempted to reproduce the observed reactivity with DFT as well. The experimental reactivity order of the chromium(III)-superoxo complexes is 1 > 2 > 3, and 1 is 8-fold and 310-fold more reactive than 3 in HAT and OAT reactions, respectively (Table 1). Using the Eyring equation, these differences correspond to only about 1.1 and 3.0 kcal/mol in energy barrier differences at -10 °C, respectively. These differences are within error margins of DFT when compared directly to experiments. However, the comparisons here would be between two theoretically calculated rates on very similar structures using the same computational protocol, presumably raising the accuracy somewhat. Hence, if the calculations could support the experimental results by yielding the same reactivity trend, the combined results of experiments and theory would be convincing. Figure 4 shows the S = 1 transition states found



Figure 4. Examples of transition states for 1 (S = 1) in HAT (left) and OAT (right) reactions. Atom colors used are red for oxygen, blue for nitrogen, chrome for chromium, gray for carbon, green for phosphorus, and white for hydrogen.

in HAT and OAT reactions with 1. The S = 1 state of 1 is lower in energy at the reactant state than its S = 2 equivalent (by 4.7 kcal/mol). However, both spin states are approximately at the same energy level at the transition states (Figure 5 and SI, Tables S3 and S4). We have earlier reported the DFTcalculated HAT transition states for the CHD oxidation by 3 at 17.5 and 18.7 kcal/mol in S = 1 and S = 2 spin states, respectively, above the S = 1 ground state using the same computational protocol.^{13c} Here, the HAT transition states obtained for 1 are at 16.5 and 17.0 kcal/mol in respective spin states above the S = 1 ground state. Hence, the difference of 1.0 kcal/mol between the barriers of 1 and 3 in the S = 1 state (which are the lowest in energy, Figure 5) shows a good



Figure 5. Energy profiles for the HAT reaction from CHD (upper) and OAT reaction to $P(CH_3)_3$ (lower) by **1** and **3**. Full lines are S = 1 spin state curves, while dashed lines represent S = 2 spin states. Transition state values for the HAT reaction from CHD by **3** are taken from ref 13c.

correlation to the experimentally derived 1.1 kcal/mol difference. To gauge how much the different charges of the axial ligands affect the system, we added a counterion $([ClO_4]^-)$ to the modeling of S = 1 reactivity of 1 with CHD, thus making the total system charge the same as in 3 (i.e., 1+). The differences in reaction energies (Table S3), Mulliken spin density distribution (Table S8), and geometries (Table S13) between the systems with and without $[ClO_4]^-$ were found to be negligible. We therefore conclude that, despite the different ligand charges, the charge difference by itself does not contribute to the reactivity differences.

For the OAT reaction, the reactions of 1 and 3 with a model substrate $P(CH_3)_3$ were also calculated by DFT. The S = 1 and S = 2 spin states again show similar transition state heights (Figure 5 and SI, Tables S2 and S3). For the S = 2 reaction, there is a prereaction step where the substrate P donates about 0.6 spin to the superoxo moiety of 1 or 3, forming something akin to Cr^{III} -peroxo species before the OAT reaction itself. However, these prereaction species are only stable at low basis set level, and are not minima when energy is corrected by larger basis set (see Methods Section). Also, even though the transition state heights are similar, the end $Cr^{IV}O$ product is clearly preferred in its S = 1 spin state. Therefore, in order to utilize the S = 2 transition state, the system has to flip one electron spin at the beginning of the reaction, and do it once more after the reaction as well. The probability of this occurring

is likely not compensated by the small energy gained (0.4 kcal/mol) compared to performing this reaction in the S = 1 state. Thus, the energy barrier is assumed to be 10.0 kcal/mol (S = 1) for 1 and 13.3 kcal/mol (S = 1) for 3. Therefore, the difference of 3.3 kcal/mol also corresponds nicely to the experimentally derived 3.0 kcal/mol difference.

The nature of the O–O bond breaking reaction can be deduced from orbital analysis as well as the Mulliken spin density distributions (SI, Tables S5 and S6). The chromium-(III)-superoxo valence orbitals were described previously,^{13c} and the S = 1 configuration was described as three singly α -occupied orbitals on Cr (d_{xy} , d_{xz} , and d_{yz}) in combination with a singly β -occupied orbital π^*_y on the superoxo moiety (Figure 6). This latter orbital has an α occupation in the case of S = 2.



Figure 6. Orbital interactions during OAT interaction of the chromium(III)-superoxo species with P(CH₃)₃. The substrate lonepair sp³_{lp} orbital forms bonding $[\pi^*_y + sp^3_{lp}]$ and antibonding $[\pi^*_y - sp^3_{lp}]$ orbitals with π^*_y which upon O–O bond cleavage results in the O–P bonding orbital σ_y and the antibonding σ^*_y orbital. The electron in σ^*_y is subsequently used to fill the lone-pair orbitals of the O bound to P.

The orbital interactions are more clearly understood by investigating the two-step reaction of the S = 2 state first from a conceptual point of view. The first step involves interaction between the phosphorus sp³ lone-pair orbital with π^*_y on the O₂ moiety. This creates a bonding and antibonding orbital pair $[\pi^*_y + sp^3_{1p}]$ and $[\pi^*_y - sp^3_{1p}]$ (Figure 6). Upon O–O bond breaking, the bonding and antibonding σ_y/σ^*_y orbitals are kept between O–P; σ_y is doubly occupied, while σ^*_y is singly occupied. The lone electron in σ^*_y will be relocated to fill the lone-pair (lp) p-orbitals of the phosphor bound oxygen. In the S = 1 state, all this will occur simultaneously. This conceptual view can be made more complicated by invoking participation of metal d orbitals as well as hybridization in the reaction. Figure S10 in SI shows a more detailed view of the orbital transformations.

CONCLUSION

We have synthesized and characterized mononuclear chromium(III)-superoxo complexes bearing different axial ligands. We have also shown that the reactivity of the chromium(III)-superoxo complexes depends on the electron-donating ability of the axial ligands in electrophilic oxidation reactions; the observed reactivity order of 1 > 2 > 3 indicates that the electrophilicity of the chromium(III)-superoxo moiety can be tuned by the electron-donating ability of the axial ligands. The redox potential order of 1 > 2 > 3, determined by CV measurements, provides the definitive evidence supporting that the electron-rich chromium(III)-superoxo species is less reactive in the electrophilic oxidation reactions, as observed in high-valent metal-oxo species.^{2,11a} DFT calculations on 1 and 3, as well as their one-electron reduced species, confirm the above CV results. Also, the reactivity calculations surpassed the

expectations as the rate differences match closely to the experimental rates. The calculations also show that the transition states of both S = 1 and S = 2 states lie close to each other, in principle allowing the reaction to proceed in both spin states. Inspection of the participating orbitals shows that this is because the only difference between the spin states is in the π^*_y orbital (α or β spin), and at least in the initial stages of the reaction, no chromium orbitals are involved in both the spin states. Despite this, a reaction in the S = 1 spin state would avoid potentially complicated spin flips, particularly in the OAT reaction. We are currently investigating the axial ligand effect(s) on the chemical properties and reactivities of a mononuclear nonheme iron(III)-superoxo complex reported recently.⁸

METHODS SECTION

Materials. All chemicals obtained from Aldrich Chemical Co. were of the best available purity and used without further purification unless otherwise indicated. Solvents were dried according to published procedures and distilled under Ar prior to use.¹⁹ ¹⁸O₂ (98% ¹⁸O-enriched) was purchased from ICON Services Inc. (Summit, NJ). $[Cr(O_2)(TMC)(Cl)](Cl)\cdot 2CH_3CN$ was prepared according to the literature method. ^{13a} The TMC-Py and TMC-Im ligands, and $[Cr(TMC-Py)](ClO_4)_2$ and $[Cr(TMC-Im)](ClO_4)_2$, were prepared according to the literature method (see also SI Experimental Section for experimental details).²⁰

Instrumentation. UV-vis spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer equipped with a UNISOKU Scientific Instrument for low-temperature experiments. Cold spray ionization mass spectra (CSI-MS) were collected on a JEOL JMS-T100CS spectrometer. Solution infrared (IR) spectra were obtained on a Remspec 626 spectrometer in CH₃CN at -10 °C under Ar atmosphere. Electrochemical measurements were performed on a CH Instrument (CHI630B) electrochemical analyzer in deaerated CH₃CN in the presence of 0.1 M Bu₄NPF₆ as a supporting electrolyte. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm²) and a platinum wire as a counter electrode. The platinum working electrodes (BAS) were routinely polished with BAS polishing alumina suspension and rinsed with CH₃CN before use. The measured potentials were recorded as a function of Ag/Ag⁺ (0.01 M) reference electrode. All potentials (vs Ag/Ag^+) were converted to values versus SCE by adding 0.29 V.²¹ All electrochemical measurements were performed under Ar atmosphere. $^1\mathrm{H}$ and $^{31}\mathrm{P}$ NMR spectra for spin state measurements and product analyses, respectively, were measured with a Bruker AVANCE III 400 spectrometer. The effective magnetic moments were determined using the modified ¹H NMR method of Evans at -40 °C.¹⁵ A WILMAD coaxial insert (sealed capillary) tubes containing the blank acetonitrile d_3 solvent (with 1.0% TMS) only was inserted into the normal NMR tubes containing the complexes (4.0 mM) dissolved in acetonitrile- d_3 (with 0.03% TMS). The chemical shift of the TMS peak (and/or solvent peak) in the presence of the paramagnetic metal complexes was compared to that of the TMS peak (and/or solvent peak) in the inner coaxial insert tube. The effective magnetic moments were calculated using the equation, $\mu = 0.0618 (\Delta \nu T/2 f M)^{1/2}$, where f is the oscillator frequency (MHz) of the superconducting spectrometer, T is the absolute temperature, M is the molar concentration of the chromium complexes, and Δv is the difference in frequency (Hz) between the two reference signals.^{15c} CW-EPR spectra were taken at 5.0 K using an X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM). Low temperatures were achieved and controlled using an Oxford Instruments ESR900 liquid He quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. Product analysis was conducted with Waters Pump Series P580 equipped with a various wavelength UV-200 detector (HPLC).

Generation and Characterization of 1. Bubbling O₂ directly through a blue solution of $[Cr(TMC-Py)](ClO_4)_2$ (5.8 mg, 10 μ mol) in CH₃CN (2.0 mL) at -10 °C produces a violet intermediate, $[Cr(O_2)(TMC-Py)]^{2+}$ (1). $[Cr(^{18}O_2)(TMC-Py)]^{2+}$ was also prepared

by bubbling ¹⁸O₂ into a solution containing $[Cr(TMC-Py)](ClO_4)_2$ in CH₃CN at -10 °C. Spectroscopic data, including UV–vis, CSI-MS, and solution IR, were reported in Figure 1. *Caution!* Perchlorate salts are potentially explosive and should be handled with care!

Generation and Characterization of 2. Bubbling O₂ directly through a blue solution of $[Cr(TMC-Im)](ClO_4)_2$ (5.8 mg, 10 μ mol) in CH₃CN (2.0 mL) at -10 °C produces a violet intermediate, $[Cr(O_2)(TMC-Im)]^{2+}$ (2). $[Cr(^{18}O_2)(TMC-Im)]^{2+}$ was also prepared by bubbling $^{18}O_2$ into a solution containing $[Cr(TMC-Im)](ClO_4)_2$ in CH₃CN at -10 °C. Spectroscopic data, including UV–vis, CSI-MS, and solution IR, were reported in SI, Figure S2.

Reactivity Studies and Product Analysis. All reactions were run by monitoring UV-vis spectral changes of reaction solutions, and rate constants were determined by fitting the changes in absorbance at 527 nm for 1 and 515 nm for 2. Reactions were run at least in triplicate, and the data reported represent the average of these reactions. After the completion of reactions, pseudo-first-order fitting of the kinetic data allowed us to determine k_{obs} values. Products formed in the oxidation of PPh3 and CHD by 1 and 2 in CH3CN at $-10\ ^\circ\text{C}$ were analyzed by ¹H NMR and HPLC. Quantitative analysis was conducted on the basis of comparison between standard curves and authentic samples. In the oxidation of PPh₃ and CHD by 1, OPPh₃ (93(5)%)and benzene (85(5)%) were obtained as a major product. OPPh₃ (90(6)%) and benzene (79(5)5%) were formed as a sole product in the oxidation of PPh₃ and CHD by 2, respectively. Product yields in the oxidation of PPh3 were also confirmed by ³¹P NMR measurements.

Theoretical Methods. Geometry optimizations and frequency calculations have been done on an unrestricted ^UB3LYP/LanL2DZ level,²² except for Cl and P atoms which were assigned 6-311G*. Solvent (acetonitrile) effects were also added during optimizations through the CPCM scheme.²³ Single-point energy corrections has been done with the 6-311+G(d,p) basis set. Gaussian 09²⁴ was used throughout. Although the free energies (including dispersion²⁵) were calculated and included in SI, Tables S1–S5, we tend to favor bare electronic energies due to additional uncertainties introduced during free energy corrections.²⁶ Hence, all the energies mentioned in this text are electronic energies only.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02068.

Experimental and theoretical sections, and DFT details and coordinates (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

W.N. acknowledges the financial support from the NRF of KOREA through the CRI (NRF-2012R1A3A2048842) and GRL (NRF-2010-00353). K.-B.C. and Y.J.P. acknowledge Ministry of Science, ICT and Future Planning (NRF-2013R1A1A2062737 and NRF-2013R1A1A2061528, respectively). J.C. acknowledges the NRF (2014R1A1A2056051), the Ministry of Science, ICT and Future Planning (DGIST R&D Program 15-BD-0403 & 15-HRLA-02, KCRC

2014M1A8A1049320, and 2015M3D3A1064890), and the Ministry of Oceans and Fisheries (Marine Biotechnology Program 20150220) of Korea.

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(17) We have reported the O–O stretching frequency of 3 (1170/1104 cm⁻¹) using resonance Raman (rRaman) in ref 13a. We calculate here the O–O vibration frequencies for 3 with DFT as (1157/1091); i.e., $^{16-18}\Delta\nu_{\rm calc} = 66 \text{ cm}^{-1}$ matches the experiments. However, we could not obtain the rRaman data of 1 and 2 because of laser decomposition. The O–O stretches of 1 (1179/1113 cm⁻¹) and 2 (1196/1128 cm⁻¹) were obtained by solution IR spectroscopy. For comparison, the O–O stretch frequency of 3 (1170/1096 cm⁻¹), which is almost identical to the value obtained from rRaman, was also obtained using solution IR.

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