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Formation and characterization of a reactive chromium(v)-oxo complex: mechanistic insight into hydrogen-atom transfer reactions[†]

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A mononuclear Cr(v)-oxo complex, $[Cr^{V}(O)(6-COO^{-}tpa)](BF_{4})_{2}$ (1; 6-COO⁻-tpa = N,N-bis(2pyridylmethyl)-N-(6-carboxylato-2-pyridylmethyl)amine) was prepared through the reaction of a Cr(III) precursor complex with iodosylbenzene as an oxidant. Characterization of 1 was achieved using ESI-MS spectrometry, electron paramagnetic resonance, UV-vis, and resonance Raman spectroscopies. The reduction potential (E_{red}) of 1 was determined to be 1.23 V vs. SCE in acetonitrile based on analysis of the electron-transfer (ET) equilibrium between 1 and a one-electron donor, $[Ru^{II}(bpy)_3]^{2+}$ (bpy = 2,2'bipyridine). The reorganization energy (λ) of **1** was also determined to be 1.03 eV in ET reactions from phenol derivatives to 1 on the basis of the Marcus theory of ET. The smaller λ value in comparison with that of an Fe(iv)-oxo complex (2.37 eV) is caused by the small structural change during ET due to the $d\pi$ character of the electron-accepting LUMO of 1. When benzyl alcohol derivatives (R-BA) with different oxidation potentials were employed as substrates, corresponding aldehydes were obtained as the 2e⁻oxidized products in moderate yields as determined from ¹H NMR and GC-MS measurements. One-step UV-vis spectral changes were observed in the course of the oxidation reactions of BA derivatives by 1 and a kinetic isotope effect (KIE) was observed in the oxidation reactions for deuterated BA derivatives at the benzylic position as substrates. These results indicate that the rate-limiting step is a concerted proton-coupled electron transfer (PCET) from substrate to 1. In sharp contrast, in the oxidation of trimethoxy-BA ($E_{\rm ox} = 1.22$ V) by 1, trimethoxy-BA radical cation was observed by UV-vis spectroscopy. Thus, it was revealed that the mechanism of the oxidation reaction changed from one-step PCET to stepwise ET-proton transfer (ET/PT), depending on the redox potentials of R-BA.

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Introduction

Extensive efforts have been devoted to the preparation of highvalent metal–oxo complexes in order to understand their reactivity in the oxidative conversion of organic substrates.¹⁻³ Nonheme high-valent iron–oxo species have been identified as key intermediates in various enzymatic oxidations involving oxidative C–H bond cleavage, such as those of taurine:α-ketoglutarate dioxygenase and halogenase Cytc₃.⁴⁻⁶ These enzymatic reactions have been usually triggered by transferring formally a hydrogen atom (H[•]) from organic substrates (R–H) to metal–oxo species ([$M^n(O)$]) as the initial step as expressed by eqn (1), *i.e.*, hydrogen-atom transfer (HAT).

$$\left[\mathbf{M}^{n}(\mathbf{O})\right] + \mathbf{R} - \mathbf{H} \xrightarrow{\mathrm{HAT}} \left[\mathbf{M}^{n-1}(\mathbf{OH})\right] + \mathbf{R}^{\cdot}$$
(1)

Mechanistic insights into HAT from a substrate to a highvalent metal–oxo species in oxidative reactions have been gained using "radical clock" substrates, which usually involve a cyclopropane framework such as bicyclo[2.1.0]pentane and methylcyclopropane, for several decades.⁷ These radical-clock experiments have contributed to being able to discriminate the mechanisms of oxidation reactions by scrutinizing reaction products: whether radical-clock compounds are oxidized *via* concerted, radical, or cationic mechanisms.⁷ Once a radical intermediate is formed by a HAT reaction from such a radicalclock compound to a high-valent metal–oxo species, radical rearrangements or a ring-opening reaction occurs in competition with oxygen rebound to produce hydroxylated products.⁷ Although such arguments should be valid only for specific

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substrates, further details of HAT require a more general protocol to elucidate the mechanism for a wide range of substrates.

HAT reactions performed by $[M^n(O)]$ have been categorized into stepwise electron/proton transfer (ET/PT) as well as proton/ electron transfer (PT/ET), and concerted proton-coupled electron transfer (PCET), as shown in Scheme 1.8-10 High-valent metal-oxo species have been recognized to oxidize a C-H bond of a substrate by accepting an electron at the metal centre and a proton at the oxo ligand, respectively, in a concerted manner with a certain kinetic isotope effect.9 This concerted pathway can be recognized as a "PCET" mechanism in Scheme 1. The one-step PCET pathway is kinetically discriminate from the stepwise ET/PT pathway (Scheme 2). Thus, PCET reactions can occur, even if the electron transfer process from substrates to metal-oxo species is thermodynamically uphill.84,10b It has been suggested that whether a net hydrogen-atom transfer reaction proceeds via a one-step concerted pathway (PCET) or a stepwise pathway (ET/PT or PT/ET) depends on underlying parameters for both oxidants and substrates, including C-H bond dissociation energies of substrates, redox potentials and the reorganization energy (λ) of metal-oxo complexes, pK_a of metal-oxo and metal-hydroxo species.11-15

The λ values of Fe(rv)–oxo¹⁶ and Mn(rv)–oxo species¹⁷ have been determined to be 2.37–2.74 eV and 2.27 eV, respectively. The relatively large λ values are interpreted as due to the structural change during ET due to the d σ character of the LUMO. When the smaller λ value of high-valent metal–oxo species is achieved, ET and PCET reactions would be accelerated. In order to reduce the structural change, d π character of the LUMO should be required as is realized in Cr(v)–oxo species in the d¹ configuration. In addition, the spin state is fixed to be S = 1/2, regardless of ligands used.

Cr(v)-oxo complexes have been synthesized and characterized not only in relevance to high-valent Fe- and Mn-oxo complexes,¹⁸ which are mostly unstable, but also in the light of many examples in which they have been proposed as important reactive intermediates in oxidation reactions.¹⁹ Efforts have been rather devoted to elucidating the electronic structure and determining the crystal structures of Cr(v)-oxo complexes, which are stabilized using highly electron-donating ancillary ligands such as salen derivatives^{18*a*,19*a*,*g*} and porphyrinoids.^{18*b*,*c*,19*b*,*e*} The stabilization inevitably makes such Cr(v)-oxo complexes less reactive toward external organic substrates.^{18*c*,*d*} Thereby, mechanistic investigation of the reactivity of those stabilized Cr(v)-oxo complexes has been limited to oxygen-atom



Scheme 1





Scheme 2 Schematic energy diagrams of (a) stepwise ET/PT and (b) one-step PCET.

transfer reactions including epoxidation of alkenes,^{18a,19a,b} and oxygenation of phosphines^{18d,19d,e} and sulfides.^{19g} In contrast, the lack of a characterizable but highly reactive Cr(v)-oxo complex, which is capable of HAT reactions from a variety of substrates, limits understanding of mechanisms of the reactions by Cr(v)-oxo complexes.^{18e,20} In order to gain mechanistic insights into HAT reactions by a Cr(v)-oxo complex, the regulation of the electron density at a Cr(v) center should be important for balancing its stabilization and its reactivity by employing a multidentate ligand with moderate electrondonating ability.

We report herein the preparation, characterization and reactivity of a Cr(v)-oxo complex, $[Cr^{V}(O)(6-COO^{-}tpa)]^{2+}$ (6- $COO^{-}tpa^{21} = N,N$ -bis(2-pyridylmethyl)-*N*-(6-carboxylato-2-pyridylmethyl)amine; **1**), having a monoanionic pentadentate ligand. The Cr(v)-oxo complex **1** not only exhibits moderate stability to be spectroscopically characterized but also a high reduction potential enough to perform HAT reactions from a series of organic substrates, allowing us to discuss in detail the reactivity of Cr(v)-oxo complexes in HAT reactions for the first time.

Experimental

General

UV-vis absorption spectra were measured in acetonitrile (CH₃CN) on Shimadzu UV-3600 and Agilent 8453 spectrometers at various temperatures. ESI-TOF-MS spectra were obtained on an Applied Biosystems QSTAR Pulsar i-mass spectrometer. ¹H NMR spectra were recorded on a JEOL EX-270 spectrometer. ESR measurements were performed on a Bruker Bio SpinE-MXPlus9.5/2.7 spectrometer in CH₃CN. GC-MS data were obtained on a JEOL JMS-T100GCV spectrometer, equipped with a capillary gas chromatograph (Agilent 7890A, HP-5 (19091J-413) capillary column). ¹⁸O-labeled PhIO (PhI¹⁸O)²² and deuterated benzyl alcohol derivatives²³ were synthesized as described in the literature. CH₃CN was distilled over CaH₂ under Ar prior to use. THF was distilled from Na/benzophenone under Ar before use. Chemicals were used as received unless otherwise noted.

Synthesis of *N*,*N*-bis(2-pyridylmethyl)-*N*-(6-ethoxycarbonyl-2-pyridylmethyl)amine (6-COOEt-tpa)

Bis(2-pyridylmethyl)amine (2.38 g, 12.0 mmol) in CH₃CN (40 mL) was added to a solution of 6-(ethoxycarbonyl)-2-chloromethylpyridine²⁴ (2.20 g, 11.0 mmol) and Na₂CO₃ (6.36 g, 60.0 mmol) in CH₃CN (60 mL) and the mixture was refluxed for 24 h. After cooling, the mixture was filtered and CH₃CN was removed using a rotary evaporator to afford a deep brown oil. This crude material was purified on an alumina column, eluting with EtOAc/hexane (4/1 v/v), to give the ligand as a brown oil. The yield was 72% (2.88 g). ¹H NMR (CD₃CN): 1.34 (t, *J* = 7 Hz, 3H, -CH₂CH₃), 3.80 (s, 4H, -CH₂-py), 3.86 (s, 2H, -CH₂-py-COOEt), 4.34 (q, *J* = 7 Hz, 2H, -CH₂CH₃), 7.13 (dd, *J* = 5 Hz, 1 Hz, 2H, H4 of py), 7.56 (d, *J* = 8 Hz, 2H, H3 of py), 7.66 (dd, *J* = 5 Hz, 6 Hz, 2H, H5 of py), 7.8–7.9 (m, 3H, H3 and H4 and H5 of py–COOEt), 8.45 (d, *J* = 6 Hz, 2H, H6 of py).

Synthesis of bis(2-pyridylmethyl)(6-carboxyl-2-pyridylmethyl) amine (6-COOH-tpa)²¹

NaOH (2.00 g, 50 mmol) in H₂O (75 mL) was added to a solution of 6-(COOEt)-tpa (2.88 g, 8.0 mmol) in ethanol (75 mmol) and the mixture solution was refluxed for 20 h. After cooling, the solution was neutralized with 70% HClO₄ to pH ~4. Ethanol was removed using a rotatory evaporator and the aqueous solution was extracted with CHCl₃ (3×) and then dried over MgSO₄. By removing CHCl₃, 6-COOH-tpa was obtained as a light brown liquid in 99% yield. ¹H NMR (CD₃CN): 3.78 (s, 4H, CH₂– py), 3.83 (s, 2H, -CH₂–py-COOH), 7.15 (dd, J = 8 Hz, 6 Hz, 2H, H4 of py), 7.41 (m, 3H, H3 of py and H5 of py-COOH), 7.68 (t, J = 8 Hz, 2H, H5 of py), 7.79 (t, J = 8 Hz, 1H, H3 of py-COOH), 7.94 (d, J = 8 Hz, 1H, H6 of py-COOH), 8.52 (d, J = 6 Hz, 2H, H6 of py). ESI-MS (m/z): 333.1 ({M – H⁺}⁻).

Synthesis of [Cr^{III}(6-COO⁻-tpa)(Cl)](BF₄) (2)

6-COOH-tpa (1.86 g, 5.59 mmol) was dissolved in distilled THF (40 mL) and to the solution was added CrCl₂ (482 mg, 3.92 mmol). The mixture was stirred overnight under Ar at 298 K. NH₄BF₄ (472 mg, 4.5 mmol) was added and the mixture was stirred for a further 1 h under air. The precipitate was filtered and washed with THF and diethyl ether. The dark purple powder of the crude product was reprecipitated from CH₃CN/ diethyl ether. The target compound was obtained as a purple powder (641 mg, 1.16 mmol) in 30% yield. UV-vis (CH₃CN): λ_{max} (nm) = 393 (ε = 130 M⁻¹ cm⁻¹), 554 (ε = 190 M⁻¹ cm⁻¹). Anal. calcd for BC₁₉F₄H₁₉N₄O₃ClCr: C, 43.41; H, 3.64; N, 10.66. Found: C, 43.18; H, 3.57; N, 10.66%.

Synthesis of [Cr^{III}(6-COO⁻-tpa)(BF₄)](BF₄) (3)

A solution containing $[Cr^{III}(6\text{-}COO^{-}\text{-}tpa)Cl](BF_4)$ (40 mg, 0.080 mmol) and AgBF₄ (22 mg, 0.12 mmol) in H₂O (20 mL) was stirred at room temperature and then heated to 373 K. The temperature was kept for 6 h. The pink solution was filtered through a membrane filter to remove insoluble solids. The filtrate was evaporated to dryness and the residual solids were dissolved into CH₃CN. Vapor diffusion of ethyl acetate to the

solution allowed us to obtain pink crystals. The crystals obtained were washed with diethyl ether and then dried *in vacuo*. The target compound was obtained as pink crystals (31 mg, 0.055 mmol) in 69% yield. UV-vis (CH₃CN): λ_{max} (nm) = 370 ($\varepsilon = 120 \text{ M}^{-1} \text{ cm}^{-1}$), 550 ($\varepsilon = 180 \text{ M}^{-1} \text{ cm}^{-1}$). Anal. calcd for $B_2C_{20}F_8H_{21}N_4O_{3.5}$ Cr: C, 40.10; H, 3.53; N, 9.35. Found: C, 40.30; H, 3.47; N, 9.16%.

X-ray crystallography of 2 and 3

A purple single crystal of 2 was grown by vapor diffusion of THF into an CH₃CN solution of 2. A pink single crystal of 3 was obtained by recrystallization from an CH₃CN solution of 3 with vapor diffusion of ethyl acetate as a poor solvent. All measurements were performed at 120 K on a Bruker APEXII Ultra diffractometer. The structures were solved by a direct method (SIR-97) and expanded with a differential Fourier technique. All non-hydrogen atoms were refined anisotropically and the refinement was carried out with full matrix least squares on *F*. All calculations were performed using the Yadokari-XG crystallographic software package.²⁵†

Formation of Cr(v)-oxo complex, 1

 $[Cr^{V}(O)(6\text{-}COO^{-}\text{-}tpa)]^{2+}$ (1) was prepared *in situ* by the reaction of 3 (0.50 mM, 2.5 µmol) with iodosylbenzene (PhIO; 2.5 mM, 12.5 µmol) in CH₃CN (5 mL) at 298 K under air. While the resulting suspension was stirred for 60 min, a colour change from pink to yellowish brown was observed.²⁶ The yellowish brown solution was filtered to remove remaining PhIO. The concentration of 1 was determined to be $25 \pm 5\%$ (0.13 \pm 0.03 mM) by chemical titration with $[Fe^{II}(bpy)_3]^{2+}$ and double integration of the signal due to 1 against that of a standard radical (TEMPO radical) using ESR measurements.

Kinetic measurements

Kinetic measurements were performed on a UNISOKU RSP-2000 stopped-flow spectrometer equipped with a multi-channel photodiode array or an Agilent 8453 photodiode-array spectrophotometer or a Shimadzu UV-3600 spectrophotometer at 298 K. To a solution of the complex **1** (0.1 mM) in CH₃CN, was added a substrate (benzyl alcohol and the deuterated derivatives) with various concentrations in CH₃CN at various temperatures. The reactions were monitored by the decay of the absorption assigned to that of **1** at $\lambda = 330$ nm.

ESR measurements

ESR spectra were taken on a Bruker X-band spectrometer (EMXPlus9.5/2.7) with a liquid nitrogen or a liquid helium transfer system under non-saturating microwave power conditions (1.0 mW). The magnitude of the modulation was chosen to optimize the resolution and the signal to noise ratio (S/N) of the observed spectrum (modulation amplitude, 3–15 G; modulation frequency, 100 kHz).

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Resonance Raman spectroscopy of complex 1

Samples were prepared by the following procedures. For $[Cr^{V}(^{16}O)(6-COO^{-}-tpa)]^{2+}$, PhI¹⁶O (5.5 mg, 25 µmol) was added to 2 mL of an CD₃CN solution containing 3 (2.8 mg, 4.9 µmol) and stirred for 35 min at 298 K under Ar. For [Cr^V(¹⁸O)(6-COO⁻-tpa)]²⁺, PhI¹⁸O (5.5 mg, 25 µmol) was added to 2 mL of an CD₃CN solution containing 3 (2.8 mg, 4.9 µmol) and $H_2^{18}O(5 \ \mu L)$ and stirred for 35 min at 298 K under Ar. Resonance Raman scattering was carried out by excitation at 441.6 nm with a He-Cd Laser (KIMMON KOHA CO., LTD.). The scattered light was dispersed with a polychromator (MC-100DG, Ritsu Oyo Kogaku) and detected with a CCD detector (Symphony, HORIBA Jobin Yvon). The measurements were performed at 236 K using a spinning NMR tube at 135° scattering geometry.

Electrochemical measurements

Second harmonic AC voltammetry (SHACV) and differential pulse voltammetry (DPV) measurements were carried out in CH₃CN containing 0.1 M TBAPF₆ as an electrolyte at 298 K under Ar with a platinum working electrode, a platinum wire as a counter electrode, and Ag/AgNO₃ as a reference electrode. An AUTOLAB PGSTAT12 potentiometer was used for SHACV measurements and a BAS ALS-710D electrochemical analyzer for DPV measurements, respectively.

Computational methods

The structures of $[Cr^{V}(O)(6-COO^{-}-tpa)]^{2+}$, $[Cr^{IV}(O)(6-COO^{-}-tpa)]^{+}$, $[Fe^{IV}(O)(TMC)]^{2+}$ and $[Fe^{III}(O)(TMC)]^{+}$ were optimized by using the hybrid B3LYP functional²⁷ without solvent effects. The Wachters-Hay basis set^{28,29} was used for Fe and the 6-311+G** basis set30 for H, C, N and O atoms. The program used was Gaussian 09.31

Results and discussion

Preparation and characterization of a Cr(v)-oxo complex

The synthesis of a mononuclear Cr(v)-oxo complex, $[Cr^{V}(O)(6-COO^{-}-tpa)](BF_{4})_{2}$ (1), was accomplished by the procedure shown in Scheme 3. The synthetic method for the Cr(III) precursor complex, [Cr^{III}(6-COO⁻-tpa)(Cl)](BF₄) (2), was described in the experimental section. In the electrospray ionization TOF mass (ESI-TOF-MS) spectrum, the complex 2 exhibited a peak cluster at m/z = 420.10 (calcd for [Cr^{III} $(6-COO^{-}-tpa)(Cl)$ ⁺: 420.04) as shown in Fig. S1a in the ESI.[†] The crystal structure of 2 was determined by X-ray crystallography.

[CrIII(L)(CI)](BF₄) [CrIII(L)(BF₄)](BF₄) [CrV(O)(L)](BF4)2 (L = 6-COO--TPA) Scheme 3

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Fig. 1 ORTEP drawings of the cation moieties of (a) [Cr^{III}(6-COO⁻tpa)(Cl)](BF₄) (2) and (b) [Cr^{III}(6-COO⁻-tpa)(BF₄)](BF₄) (3) using 50% probability thermal ellipsoids with numbering schemes for the heteroatoms. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) for 2: Cr-Cl 2.2874(6), Cr-O1 1.959(2), Cr-N1 2.088(2), Cr-N2 2.048(2), Cr-N3 2.066(2), Cr-N4 1.978(2). Selected bond lengths (Å) for 3: Cr-F 1.986(2), Cr-O1 1.958(2), Cr-N1 2.079(2), Cr-N2 2.044(2), Cr-N3 2.046(2), Cr-N4 1.968(2).

Its ORTEP drawing is depicted in Fig. 1a and selected bond lengths are given in the figure caption. The bond length of Cr-N4 was 1.978(2) Å, which is shorter than those of Cr-N bonds for other pyridine rings. This result should be induced by a strong binding of the anionic carboxyl group to the Cr(III) centre and two successive five-membered chelate rings in the meridional geometry. Note the bond lengths of Cr-Nx (x = 1-4) in $[Cr^{III}(Cl)_2(tpa)]^+$ have been reported to fall in the range of 2.05– 2.08 Å.32

Treatment of complex 2 with AgBF₄ in H₂O resulted in the formation of $[Cr^{III}(6-COO^{-}-tpa)(BF_4)](BF_4)$ (3) via removing the chloro ligand. The structure of 3 was unambiguously determined by X-ray crystallography. As shown in Fig. 1b, the coordinated anionic ligand was identified as BF4-. The crystal structure suggests that the oxo ligand should be formed at the trans position to the pyridine moiety having the carboxyl group. In contrast, in the ESI-TOF-MS spectrum, the complex 3 unexpectedly exhibited a peak cluster at m/z =404.14 (calcd for [Cr^{III}(6-COO⁻-tpa)(F)]⁺: 404.07) without any peak clusters due to the BF₄⁻-bound Cr(III) complex as shown in Fig. S1b in the ESI.† The coordinated fluoride anion (F⁻) was presumably derived from decomposition of the BF₄⁻ anion in the ionization process of ESI-TOF-MS measurements.33

Reaction of 3 with iodosylbenzene (PhIO) in acetonitrile (CH₃CN) at 298 K resulted in a colour change from pink to yellowish brown, accompanying the spectral change as shown in Fig. 2a. This spectral feature is similar to that of a previously reported Cr(v)-oxo complex described in the literature.^{18d} The stability of 1 in CH₃CN was evaluated by measuring the halflifetime ($au_{1/2}$) at different temperatures ($au_{1/2} \sim 20$ min at 298 K and $\tau_{1/2}$ > 24 h at 243 K) (Fig. S2 in ESI†). The ESI-TOF-MS spectrum of 1 exhibited a peak cluster at m/z = 200.59 (calcd for $[Cr^{V}(O)(6-COO^{-}-tpa)]^{2+}$: 401.08), which was in good agreement with the calculated isotopic pattern (Fig. 2b). When PhI¹⁶O was replaced by isotopically labeled PhI¹⁸O with a small amount of H₂¹⁸O, the peak cluster corresponding to ¹⁸O-labeled 1 shifted to m/z = 201.59 (Fig. 2b).³⁴ Electron spin resonance (ESR)



Fig. 2 (a) UV-vis spectral change observed upon addition of PhIO to 3 (0.5 mM) in CH₃CN at 298 K. (b) Positive-ion ESI-TOF-MS of 1 (upper) and ¹⁸O-labeled 1 (lower) in CH₃CN. The black lines are simulated isotopic patterns.

measurements on **1** in CH₃CN at 243 K and 100 K afforded a strong signal at g = 1.9756, assignable to that of a Cr(v) species (S = 1/2),^{18,19} which was different from that of complex **3** $(S = 3/2)^{35}$ in CH₃CN at 10 K (see Fig. S3 in ESI[†]).

The formation yield of Cr(v)-oxo complex was calculated to be 20 \pm 3% on the basis of the spin amount obtained by double integration of the ESR signal against a standard (TEMPO radical) and 25 \pm 5% (ref. 36) based on the stoichiometry of the Cr(v)-oxo complex in an electron-transfer (ET) reaction from $[Fe^{II}(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) (*vide infra*).

In addition, the strong evidence to support the formation of 1 as a Cr(v)-oxo complex was obtained by resonance Raman spectroscopy (at 236 K, excitation at 441.6 nm in CD₃CN). As shown in Fig. 3, Raman scattering due to the Cr(v)-oxo moiety was observed at 951 cm⁻¹, which was comparable to that observed for a reported Cr(v)-oxo complex with a corrole derivative as a supporting ligand (986 cm⁻¹).³⁷ The peak of 1-¹⁸O, which was formed by using PhI¹⁸O with a small amount of H₂¹⁸O, shifted to 918 cm⁻¹; the isotopic shift (33 cm⁻¹) is fairly consistent with the calculated value ($\Delta \nu = 41$ cm⁻¹) as shown in Fig. 3.³⁸

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Fig. 3 Resonance Raman spectra of $[Cr^{V(16}O)(6-COO^{-}tpa)]^{2+}$ (red line), $[Cr^{V(18}O)(6-COO^{-}tpa)]^{2+}$ (blue line), and their differential spectrum (black line); measured at 236 K in CD₃CN with 441.6 nm excitation. The peaks marked with 'S' are ascribed to the bands due to the solvent.

Reduction potential of complex 1

In order to determine the $E_{\rm red}$ value of **1** in the light of ET equilibrium, $[{\rm Fe}^{\rm II}({\rm bpy})_3]^{2+}$ was employed as an electron donor $(E_{\rm ox} = 1.06 \text{ V} \text{ vs. SCE})$ in CH₃CN.³⁹ Upon addition of $[{\rm Fe}^{\rm II}({\rm bpy})_3]^{2+}$ to an CH₃CN solution containing **1** (0.15 mM), a UV-vis spectral change was observed at 298 K (Fig. S5 in ESI[†]). The final concentration of $[{\rm Fe}^{\rm II}({\rm bpy})_3]^{3+}$ was 0.15 mM on the basis of the absorption coefficient $(\varepsilon_{650} = 300 \text{ M}^{-1} \text{ cm}^{-1})$,^{40*a*} indicating that a stoichiometric ET reaction proceeded from $[{\rm Fe}^{\rm II}({\rm bpy})_3]^{2+}$ to **1**. ESR measurements clearly exhibited ET from $[{\rm Fe}^{\rm II}({\rm bpy})_3]^{2+}$ to **1**, where the signal at g = 1.98 due to **1** decreases, accompanied by an increase in a new signal at g = 2.6 due to $[{\rm Fe}^{\rm II}({\rm bpy})_3]^{3+}$ (Fig. S6a in ESI[†]).⁴¹ In this case, one-way ET from $[{\rm Fe}^{\rm II}({\rm bpy})_3]^{2+}$ to **1** occurs to indicate that the reduction potential of **1** is much higher than 1.06 V.

In sharp contrast to the case of $[Fe^{II}(bpy)_3]^{2+}$, the ET reaction between **1** and $[Ru^{II}(bpy)_3]^{2+}$ ($E_{ox} = 1.24 \text{ V}$)⁴² is found to be in ET equilibrium (Scheme 4), where the observed concentration of $[Ru^{III}(bpy)_3]^{3+}$ ($\varepsilon_{675nm} = 420 \text{ M}^{-1} \text{ cm}^{-1}$)^{40b} produced in the ET reaction from $[Ru^{II}(bpy)_3]^{2+}$ to **1** increases with the increase in the initial concentration of $[Ru^{II}(bpy)_3]^{2+}$ $([[Ru^{II}(bpy)_3]^{2+}]_0)$ as shown in Fig. 4.^{16,43} Formation of $[Ru^{III}(bpy)_3]^{3+}$ was also confirmed by the detection of an ESR signal at g = 2.6 as shown in Fig. S6b in the ESI.⁴¹[†] The ET equilibrium between complex **1** and $[Ru^{II}(bpy)_3]^{2+}$ indicates that the redox potential of **1** is close to that of $[Ru^{II}(bpy)_3]^{2+}$ according to the Nernst equation (eqn (2)), where F is the Faraday constant and Ket is an ET-equilibrium constant.^{16,43} The $K_{\rm et}$ value was determined to be 0.57 \pm 0.13 at 243 K by fitting the plot according to a equation described in the literature¹⁶ (red line), as shown in Fig. 4b. The apparent one-electron reduction potential (E_{red}) of **1** $(E_{red}$ (**1**)) was then determined to be 1.23 ± 0.01 V using eqn (2).

$$E_{\rm red} = E_{\rm ox} + (RT/F) \ln K_{\rm et}$$
⁽²⁾

The $E_{\rm red}$ (1) value is much higher than those of $\rm Cr^V(O)$ complexes reported so far,^{18,19} such as $[\rm Cr^V(O)(TpFPC)]$ ($E_{\rm red} = 0.11$ V vs. Ag/AgCl; TpFPC = tris(pentafluorophenyl)corrolato)^{18c} with a trianionic ligand and $[\rm Cr^V(O)(TMP)]^+$ ($E_{\rm red} = 0.76$ V vs. Ag/AgCl; TMP = tetramesitylporphyrinato) with a dianionic ligand,^{18b} although a $\rm Cr^V(O)$ complex with a macrocyclic ligand (1,4,8,11-tetraazacyclotetradecane) has been proposed to exhibit a higher $E_{\rm red}$ value (>1.34 V vs. SCE) in the presence of HClO₄.⁴⁴ In the case of 1, the addition of a proton showed not so much influence (~+0.1 V)

 $[Cr^{V}(O)(L)]^{2+} [Ru^{II}(bpy)_{3}]^{2+} [Cr^{IV}(O)(L)]^{+} [Ru^{II}(bpy)_{3}]^{2+}$

Scheme 4



Fig. 4 (a) UV-vis spectral change observed upon addition of $[Ru^{II}(bpy)_3]^{2+}$ (0.1 mM) to an CH₃CN solution of 1 (0.1 mM) at 243 K. (b) Plot of concentration of $[Ru^{III}(bpy)_3]^{3+}$ produced in electron transfer from $[Ru^{II}(bpy)_3]^{2+}$ to 1 in CH₃CN at 243 K *vs.* initial concentration of $[Ru^{II}(bpy)_3]^{2+}$, $[[Ru^{II}(bpy)_3]^{2+}]_0$.

on the reduction potential as observed in DPV measurements.⁴⁵

When bromoferrocene (BrFc; $E_{1/2} = 0.54$ V) was employed as a one-electron donor, complex 1 (0.17 mM) consumed 2 eq. of BrFc in CH₃CN at 243 K on the basis of the absorption due to $BrFc^+$ ($\varepsilon_{630} = 330 \text{ M}^{-1} \text{ cm}^{-1}$).⁴⁶ This result indicated that twoelectron reduction of 1 occurred to form a Cr(III) species (Fig. S7 in ESI[†]). On the other hand, upon addition of 0.5 mM triphenylamine (Ph₃N) as a one-electron donor ($E_{ox} = 0.85 \text{ V}$)⁴⁷ to an CH₃CN solution containing 1 (0.04 mM) in the absence of acid at 243 K, ET from Ph₃N to 1 occurred to form one equivalent of the one-electron oxidized product (Ph_3N^{+}) , which showed an absorption band at 650 nm observed by UV-vis spectroscopy (Fig. S8 in ESI[†]). Subsequently, addition of HClO₄ (2 mM) to the reaction solution including Ph₃N resulted in additional formation of one more equivalent of Ph_3N^{+} , indicating that the twoelectron reduction of 1 by Ph₃N occurred in the presence of H⁺.48 The formation of two equivalents of Ph_3N^{++} relative to 1 clearly indicates that 1 is the sole oxidant in the solution. In addition, the protonation of one-electron reduced Cr(w)-oxo complex leads to a positive shift of the $E_{\rm red}$ of Cr(m/n) beyond the $E_{\rm ox}$ value of Ph₃N. Thus two-electron oxidation of a substrate should be possible for 1 via the formation of $[Cr^{IV}(6-COO^{-}-tpa)(OH)]^{2+}$, which is a protonated species of the one-electron reduced species of 1, in a PCET or ET/PT process.

Determination of the λ value of complex 1

To gain kinetic insight into the ET reduction of **1** in CH₃CN, phenol derivatives (R-PhOH and naphthols) were employed as electron donors. In the case of 4-phenylphenol (4-Ph), ET rates were determined on the basis of the increase of the absorption band at 400 nm due to 4-Ph⁺⁺ as shown in Fig. 5a. The absorption band of 4-Ph⁺⁺ agreed with that observed in the independent experiment using a strong one-electron oxidant such as ammonium hexanitratocerate(IV) (CAN) as shown in Fig. 5b. The pseudo-first-order rate constants (k_{obs}) for the oxidation of 4-Ph by **1** increase linearly with increasing concentrations of 4-Ph. The second-order rate constant (k_{et}) was determined to be $4.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ from the slope of the linear plot as depicted in Fig. 5c. Similarly, k_{et} values were determined for oxidation reactions of other phenol derivatives by **1** (Fig. S9



Fig. 5 (a) UV-vis spectral change upon addition of 4-Ph (10 mM) to 1 (0.1 mM) in CH₃CN at 233 K. Inset: the time profile at 390 nm due to 4-Ph⁺⁺. (b) UV-vis spectrum of 4-Ph⁺⁺ produced by oxidizing 4-Ph with CAN in CH₃CN at 233 K. (c) Plots of k_{obs} vs. [4-Ph].

in ESI[†]). The obtained $k_{\rm et}$ values are listed in Table 1, together with the oxidation potentials of phenol derivatives ($E_{\rm ox}$) determined by SHACV measurements and driving forces of ET ($-\Delta G_{\rm et}$ = $-e(E_{\rm ox} - E_{\rm red}$ (1))). Judging from the kinetic isotope effect values (KIE = 1.0–1.1), the reactions between 1 and phenol derivatives proceed *via* ET followed by PT rather than one-step PCET.^{49,50}

The driving-force dependence of log $k_{\rm et}$ for phenol derivatives is shown in Fig. 6, where the log $k_{\rm et}$ values are plotted relative to the driving force of ET $(-\Delta G_{\rm et})$. The plot was analysed in light of the Marcus theory of adiabatic outer-sphere electron transfer (eqn (3)), where $k_{\rm diff}$ is the diffusion rate constant, $k_{\rm B}$ is the Boltzmann constant and $Z = (k_{\rm B}T/h)(k_{\rm diff}/k_{\rm -diff})$ is the collision frequency that is taken as $1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$.⁵¹ The $k_{\rm diff}$ value in CH₃CN is taken as $2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.⁵²

$$\frac{1}{k_{\rm et}} = \frac{1}{k_{\rm diff}} + \frac{1}{Z \, \exp\left[-(\lambda/4)(1 + \Delta G_{\rm et}/\lambda)^2 / k_{\rm B}T\right]}$$
(3)

Table 1 One-electron oxidation potentials (E_{ox}) of phenol derivatives, driving forces of ET ($-\Delta G_{et}$), ET rate constants (k_{et}), and KIE values in ET reactions from phenol derivatives to **1** at 233 K

| R-PhOH and naphthols | $E_{\rm ox}^{\ a}/{\rm V}$ | $-\Delta G_{\rm et}/{ m eV}$ | $k_{\rm et}/{\rm M}^{-1}~{\rm s}^{-1}$ | KIE |
|------------------------|----------------------------|------------------------------|--|-----|
| 4-Me | 1.52 | -0.29 | $(1.5\pm0.1)	imes10^2$ | |
| 4-Ph | 1.39 | -0.16 | $(4.3 \pm 0.2) \times 10^3$ | 1.1 |
| 2,3-(MeO) ₂ | 1.39 | -0.16 | $(1.4 \pm 0.1) \times 10^4$ | |
| 2,4,6-Me ₃ | 1.37 | -0.14 | $(1.5 \pm 0.1) \times 10^4$ | |
| 2-MeO | 1.37 | -0.14 | $(1.2 \pm 0.1) \times 10^4$ | |
| 2-Naphthol | 1.19 | 0.04 | $(4.5 \pm 0.2) \times 10^4$ | |
| 1-Naphthol | 1.17 | 0.06 | $(2.5\pm0.1)	imes10^5$ | 1.0 |
| | | | | |

^{*a*} Determined by SHACV performed in CH₃CN at room temperature under Ar in the presence of TBAPF₆ (0.1 M) as an electrolyte (*vs.* SCE).



Fig. 6 Plots of log k_{et} vs. $-\Delta G_{et}$ in ET reactions from phenol derivatives to 1 at 233 K.

The reorganization energy of ET (λ) of **1** was thus determined to be 1.03 \pm 0.05 eV in CH₃CN at 233 K on the basis of the Marcus plot in Fig. 6. The λ value of **1** is much smaller than that (2.37 \pm 0.04 eV) of a non-heme Fe(IV)-oxo complex, [Fe^{IV}(O)(TMC)(CH₃CN)]²⁺.¹⁶ This indicates that the structural change upon the ET reduction is much smaller for 1 than that for the Fe^{IV}-oxo complex. In order to argue the structural change during the ET reaction, DFT calculations were performed to estimate the structural difference between complex 1 and the corresponding $Cr^{IV}(O)$ complex by comparing bond lengths around the Cr centres. As a result, the LUMO of 1 was revealed to localize on the d_{xy} orbital involved in the π^* orbital of the Cr–O bond (Fig. S12 in ESI[†]). Thus, the Cr-O bond (1.55 Å) was elongated to 1.63 Å upon the ET reduction (Fig. S13a in ESI[†]). On the other hand, in the case of the Fe($_{IV}$)-oxo complex (S = 1), the LUMO has been reported to be the d_{x2-y2} orbital⁵³ and the equatorial Fe-N bonds (2.12-2.15 Å) were elongated to 2.24-2.29 Å (Fig. S13b in ESI[†]). The average of the change of coordination bond lengths around the metal centres is smaller for 1 (0.044 Å) than that for the Fe^{IV}-oxo complex (0.090 Å). Thus, the smaller structural change of 1 in the course of ET reactions to afford the smaller λ value should be due to the fact that the LUMO of 1 is a $d\pi$ orbital as suggested by DFT calculations (Fig. S12 in ESI^{\dagger}).⁵⁴ In addition, in the case of a Mn(v)(O) complex with a corrolazine derivative,⁵⁵ a smaller λ value (1.53 eV) has been reported; in this case, the Mn(v) centre also accepts an electron into a $d\pi$ orbital.

Impact of redox potentials of substrates on their oxidation by 1

Complex 1, showing a high reduction potential, is expected to be an efficient oxidant for HAT reactions (eqn (1)) because a Cr(v)-oxo complex is capable of accepting not only e⁻ at the Cr(v) centre but also H⁺ at the terminal oxo ligand upon the reduction as mentioned above. We examined HAT reactions from substrates listed in Table 2 to 1. First, in the case of benzyl alcohol (H-BA)⁵⁶ that shows the oxidation potential (E_{ox}) of 2.33 V (ν s. SCE) as a substrate, complex 1 worked as a 2e⁻-

Table 2 One-electron oxidation potentials ($E_{\rm ox}$) of BA derivatives, driving force for ET ($-\Delta G_{\rm et}$), second-order rate constants ($k_{\rm H}$ or $k_{\rm et}$), and KIE values for the oxidation of benzyl alcohol derivatives with complex **1** in CH₃CN at 233 K

| No. | R-BA | $E_{\rm ox}^{\ a}/V$ | $-\Delta G_{\rm et}/{\rm eV}$ | $k_{\rm H}$ or $k_{\rm et}/{ m M}^{-1}~{ m s}^{-1}$ | KIE |
|-----|------------------------------|----------------------|-------------------------------|---|-----|
| | | | | | |
| 1 | $4-NO_2$ | 2.88 | -1.65 | 1.4 ± 0.1 | |
| 2 | Н | 2.33 | -1.10 | 2.5 ± 0.1 | 5.4 |
| 3 | 4- <i>t</i> -Bu | 2.07 | -0.84 | 5.4 ± 0.3 | — |
| 4 | 4-Me | 2.05 | -0.82 | 5.2 ± 0.2 | _ |
| 5 | 4-MeO | 1.58 | -0.35 | 21 ± 1 | 12 |
| 6 | 3,5-(MeO) ₂ -4-Me | 1.49 | -0.26 | 19 ± 1 | 6.8 |
| 7 | 3,5-(MeO) ₂ | 1.49 | -0.26 | 9.0 ± 0.5 | — |
| 8 | 2,3,4-(MeO) ₃ | 1.37 | -0.14 | 16 ± 1 | — |
| 9 | 3,4,5-(MeO) ₃ | 1.22 | 0.01 | 1800 ± 50 | 1.1 |
| 10 | 2,5-(MeO) ₂ | 1.20 | 0.03 | Too fast | — |
| | | | | | |

^{*a*} Determined by SHACV performed in CH_3CN at room temperature under Ar in the presence of $TBAPF_6$ (0.1 M) as an electrolyte (*vs.* SCE).

oxidant to afford benzaldehyde as the sole product (Scheme 5), as identified and quantified by ¹H NMR and GC-MS measurements (Fig. S14 and 15 in ESI[†]).

To elucidate the reaction mechanism of HAT reactions from H-BA derivatives to 1, a kinetic analysis was conducted on the basis of spectroscopic measurements. The addition of an excess amount of H-BA to an CH₃CN solution of 1 resulted in the decay of the absorption derived from 1 with an isosbestic point at 515 nm, as shown in Fig. 7a. The decay time profile of the absorption at 330 nm due to 1 obeyed pseudo-first-order kinetics (inset of Fig. 7a). The pseudo-first-order rate constant (k_{obs}) increased linearly with increasing concentrations of H-BA (Fig. 7b, red line). The second-order rate constant $(k_{\rm H})$ was determined to be 2.5 M^{-1} s⁻¹ from the slope of the linear plot. When H-BA was replaced by the corresponding deuterated compound at the benzylic position (benzyl alcohol- d_2 , H-BA- d_2), a significant deceleration of the oxidation rate (blue line in Fig. 7b, $k_D = 0.46 \text{ M}^{-1} \text{ s}^{-1}$) was observed, giving a kinetic isotope effect (KIE = $k_{\rm H}/k_{\rm D}$) of 5.4 at 233 K.

Similarly, kinetic analysis was made on the oxidation reactions of BA derivatives having substituents (R) on the aromatic ring of H-BA (R-BA) to afford corresponding benzaldehydes as the sole products. In the case of 4-methoxy-BA (4-MeO-BA; $E_{\rm ox} = 1.58$ V) and 3,5-dimethoxy-4-methyl-BA (3,5-(MeO)₂-4-Me-BA; $E_{\rm ox} = 1.49$ V) used as substrates, KIE values were also determined to be 12 and 6.8, respectively, as listed in Table 2. The observed KIE values suggest that the oxidation reactions of R-BA should be initiated by a one-step PCET reaction from substrates to the Cr(v)-oxo complex rather than an ET oxidation, since ET reactions are difficult under highly endothermic situations $(-\Delta G_{\rm et} < 0)$.



Scheme 5



Fig. 7 (a) UV-vis spectral change observed upon addition of benzyl alcohol (10 mM) to 1 (0.1 mM) in CH₃CN at 233 K. Inset: the decay time profile of the absorbance at $\lambda = 330$ nm due to **1**. (b) Concentration dependence of pseudo-first-order rate constants (k_{obs}) for the reaction of **1** with H-BA (red) and benzyl alcohol- d_2 (blue).

The oxidation potentials of the substrates listed in Table 2 as no. 1-8 are much higher than the reduction potential of 1, however, the oxidation potential of 3,4,5-trimethoxy-BA (3,4,5-(MeO)₃-BA, $E_{ox} = 1.22$ V) is comparable to the E_{red} of 1. In the course of the oxidation of 3,4,5-(MeO)₃-BA with 1, a new absorption band appeared at 450 nm, which was assigned to 3,4,5-(MeO)₃-BA radical cation (3,4,5-(MeO)₃-BA⁺) as a new intermediate (Fig. 8a and Fig. S16 in ESI[†]).^{12a}

A time profile of the decay of the absorption at 330 nm (inset of Fig. 8a, red line) due to 1 coincides with that of the rise of the absorption at 450 nm (inset of Fig. 8a, blue line). The formation rate constant (k_{et}) of 3,4,5-(MeO)₃-BA⁺ was thus determined to be 1.8 \times $10^3~M^{-1}~s^{-1}$ by changing the concentration of 3,4,5-(MeO)₃-BA as shown in Fig. 8b (red line with filled circles). This indicates that ET from 3,4,5-(MeO)₃-BA to 1 occurs faster than PCET because of the low oxidation potential of 3,4,5-(MeO)₃-BA. In addition, negligible KIE (1.1) was observed for deuterated $3,4,5-(MeO)_3$ -BA $(3,4,5-(MeO)_3$ -BA- $d_2)$ at the benzylic position (Fig. 8b, blue line with filled squares) to exclude a PCET pathway in the oxidation.

A subsequent reaction of ET from 3,4,5-(MeO)₃-BA to 1 was analyzed by the decay of the absorption at 450 nm due to $3,4,5-(MeO)_3-BA^{+}$ (Fig. 9a). The decay time profile



Fig. 8 (a) Spectral changes observed in the oxidation of 3,4,5-(MeO)₃-BA (10 mM) by 1 (0.1 mM) in CH₃CN at 233 K. Inset: time profiles of the absorbance at $\lambda = 330$ nm due to **1** and the absorbance at $\lambda = 450$ nm due to $3,4,5-(MeO)_3-BA^{+}$. (b) Plots of k_{obs} vs. $[3,4,5-(MeO)_3-BA$ (red) or 3,4,5-(MeO)3-BA-d2 (blue)].



Fig. 9 (a) Following spectral changes observed in the oxidation of 3,4,5-(MeO)₃-BA (1.0 mM) by 1 (0.1 mM) in CH₃CN at 233 K. (b) The decay time profile at $\lambda = 450$ nm due to 3,4,5-(MeO)₃-BA⁺⁺. Inset: second-order plot. (c) Plots of k_{PT} vs. [3,4,5-(MeO)₃-BA].

obeyed second-order kinetics as shown in Fig. 9b and thus we assumed that this process should be a proton transfer (PT) process from 3,4,5-(MeO)₃-BA⁺⁺ to a Cr^{IV}(O) complex derived from one-electron reduction of 1. The secondorder rate constant $(k_{\rm PT})$ was determined to be 2.5 \times 10² M^{-1} s⁻¹. It should be noted that the k_{PT} values show no dependence on the concentration of 3,4,5-(MeO)₃-BA (Fig. 9c). Therefore, we conclude that the second step is accounted for by intermolecular PT from 3,4,5-(MeO)₃-BA⁺⁺ to the Cr^{IV}(O) complex to form 3,4,5-(MeO)₃-BA' and a Cr^{IV}(OH) complex.



Fig. 10 Plots of log $k_{\rm H}$ or log $k_{\rm et} - \Delta G_{\rm et}$ in HAT reactions of R-BA by 1 at 233 K.

All kinetic parameters obtained for PCET or ET reactions from R-BA to 1 at 233 K are summarized in Table 2. When the rate constants were plotted against $-\Delta G_{\rm et}$ as shown in Fig. 10, a boundary was found around $-\Delta G_{\rm et} = -0.2$ eV. It should be noted that the KIE was still observed to be 6.8 in the case of 3,5-(MeO)₂-4-Me-BA, although the $-\Delta G_{\rm et}$ value (-0.26 eV) is close to the mechanistic borderline. This phenomenon clearly represents the first example of alteration of the oxidation mechanism (one-step PCET or stepwise ET/PT) of organic substrates by using a metal-oxo complex without any additives to control the reactivity.¹²

Recently, Fukuzumi and co-workers have reported a mechanistic borderline, which discriminates between one-step PCET and stepwise ET/PT mechanisms in the oxidation of benzyl alcohol derivatives by non-heme Fe(IV)-oxo complexes in the presence and absence of Sc^{3+} .¹² In the one-step PCET reactions, the oxidized products are also different: radical coupling products and corresponding aldehydes in the presence and absence of Sc^{3+} , respectively. In sharp contrast to the case of Fukuzumi and co-workers, the present study provides apparently the same net hydrogen-atom transfer reaction to afford corresponding benzaldehydes *via* either a PCET or ET/PT pathway under the same conditions, without perturbation of the reactivity of metal-oxo species by additives.

Based on these results, we propose a mechanism for the oxidation of R-BA by 1 in CH₃CN at 233 K as shown in Fig. 11. In the case of R-BA, except for 3,4,5-(MeO)₃-BA, one-step PCET occurs to yield H-atom abstracted species and showing a considerable KIE. In sharp contrast to this, the oxidation of 3,4,5-(MeO)₃-BA by 1 allowed us to observe the formation of $3,4,5-(MeO)_3-BA^{+}$ as the intermediate in the course of the reaction. Then, deprotonation from 3,4,5-(MeO)₃-BA⁺ is facilitated by the more basic Cr^{IV}(O) complex to form 3,4,5-(MeO)₃-BA', which should be the same intermediate derived from one-step PCET. Although such a mechanistic difference may often result in the formation of different oxidized products, the oxidation of R-BA by 1 provides only the corresponding aldehydes as the two-electron oxidized products via an oxygen-rebound process57 affording α -diol intermediates, which undergo facile dehydration.

Conclusions

In conclusion, we have synthesized and characterized a reactive Cr(v)-oxo complex (1) by using a monoanionic pentadentate ligand (6-COO⁻-tpa). The $E_{\rm red}$ value of 1 was determined to be 1.23 V vs. SCE on the basis of analysis of the ET equilibrium with $[{\rm Ru}^{\rm II}({\rm bpy})_3]^{2+}$. The reorganization energy of ET from phenols to 1 has been determined to be 1.03 \pm 0.05 eV, which is much smaller than that for a non-heme Fe^{IV}(O) complex, due to the smaller structural change upon one-electron reduction. When a series of benzyl alcohol derivatives were employed as substrates of oxidation by 1, we found a mechanistic borderline between one-step PCET and stepwise ET/PT around $-\Delta G_{\rm et} = -0.2$ eV. The present study provides a standard for the elucidation of the reactivity of Cr(v)-oxo complexes in HAT reactions.

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Fig. 11 Proposed mechanism for oxidation of R-BA by 1.

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