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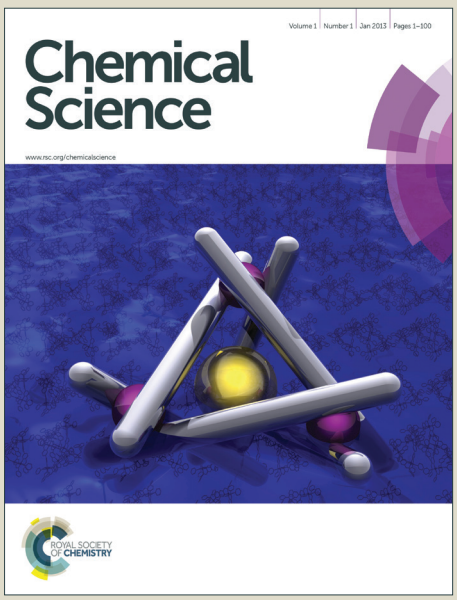

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ARTICLE

Formation and Characterization of a Reactive Chromium(V)-Oxo Complex: A Mechanistic Insight into Hydrogen-Atom Transfer Reactions

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A mononuclear Cr(V)-oxo complex, $[Cr^{V}(O)(6\text{-}COO^{-}\text{-tpa})](BF_4)_2$ (**1**; 6-COO^{-}-tpa = *N*,*N*-bis(2-pyridylmethyl)-*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 made by 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 the analysis of electron-transfer (ET) equilibrium between **1** and a one-electron donor, $[Ru^{II}(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine). 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 dπ 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 by ^{1}H 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 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_{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.

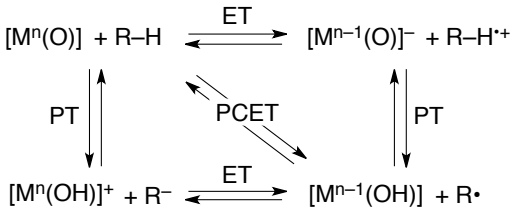
Introduction

Extensive efforts have been devoted to preparation of high-valent metal-oxo complexes in order to understand their reactivity in oxidative conversion of organic substrates.[1-3] Non-heme 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 Cytc_3.[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).

$$[M^{n}(O)] + R\text{–}H \xrightarrow{HAT} [M^{n-1}(OH)] + R\bullet \qquad (1)$$

Mechanistic insights into HAT from a substrate to a high-valent metal-oxo species in oxidative reactions have been gained by "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 discriminate 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 radical-clock compound to 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 substrates, further details of

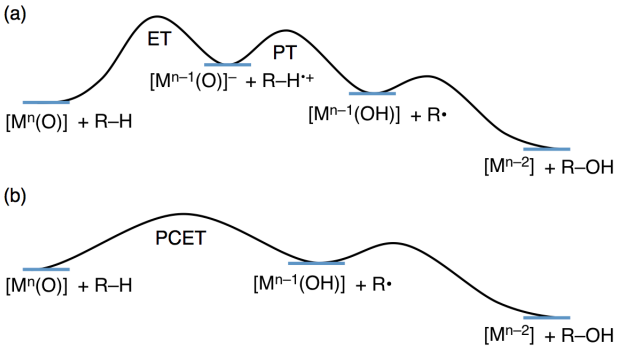
Scheme 1



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 showing 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 discriminated from 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.[8a,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 reorganization energy (λ) of metal-oxo complexes, pK_a of metal-oxo and metal-hydroxo species.[11-15]

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



The λ values of Fe(IV)-oxo[16] and Mn(IV)-oxo species[17] have been determined to be 2.37–2.74 eV and 2.27 eV, respectively. The relatively large λ values are interpreted as the structural change during ET due to the dσ 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, a dπ character of the LUMO should be required as is realized in Cr(V)-oxo species in the d^1 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 crystal structures of Cr(V)-oxo complexes, which are stabilized using highly electron-donating ancillary ligands such as salen derivatives[18a,19a,g] and porphyrinoids.[18b,c,19b,e] The stabilization inevitably makes such Cr(V)-oxo complexes less reactive toward external organic substrates.[18c,d] Thereby, mechanistic investigation on the reactivity of those stabilized Cr(V)-oxo complexes has been limited to oxygen-atom transfer reactions including epoxidation of alkenes,[18a,19a,b] 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 multi-dentate ligand with moderate electron-donating ability.

We report herein preparation, characterization and reactivity of a Cr(V)-oxo complex, $[Cr^V(O)(6\text{-}COO^-\text{-}tpa)]^{2+}$ (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 on the reactivity of Cr(V)-oxo complexes in HAT reactions for the first time.

Experimental

General.

UV-vis absorption spectra were measured in acetonitrile (CH_3CN) 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. ^{1}H NMR spectra were recorded on a JEOL EX-270 spectrometer. ESR measurements were performed on a Bruker Bio SpinEMXPlus9.5/2.7 spectrometer in CH_3CN. 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). ^{18}O-labeled PhIO ($PhI^{18}O$)[22] and deuterated benzyl alcohol derivatives[23] were synthesized as described in the literature. CH_3CN was distilled over CaH_2 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 CH_3CN (40 mL) was added to a solution of 6-(ethoxycarbonyl)-2-chloromethyl- pyridine[24] (2.20 g, 11.0 mmol) and Na_2CO_3 (6.36 g, 60.0 mmol) in CH_3CN (60 mL) and the mixture was refluxed for 24 h. After cooling, the mixture was filtered and CH_3CN was removed by a rotary evaporator to afford a deep brown oil. This crude material was purified on an alumina column eluted with EtOAc/hexane (4/1 v/v) to give the ligand as a brown oil. The yield was 72% (2.88 g). ^{1}H NMR (CD_3CN): 1.34 (t, J = 7 Hz, 3H, -CH_2CH_3), 3.80 (s, 4H, -CH_2-py), 3.86 (s, 2H, -CH_2-py-COOEt), 4.34 (q, J = 7 Hz, 2H, -CH_2CH_3), 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-pyridyl methyl)amine (6-COOH-tpa).[21]

NaOH (2.00 g, 50 mmol) in H_2O (75 mL) was added into 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 by 70% $HClO_4$ to be pH ~ 4. Ethanol was removed by a rotatory evaporator and the aqueous solution was extracted by $CHCl_3$ (3 times) and then dried over $MgSO_4$. By removing $CHCl_3$, 6-COOH-TPA was obtained as a light brown liquid in 99% yield. ^{1}H NMR (CD_3CN): 3.78 (s, 4H, CH_2-py), 3.83 (s, 2H, -CH_2-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)](BF_4) (2).

6-COOH-tpa (1.86 g, 5.59 mmol) was dissolved in distilled THF (40 mL) and to the solution was added $CrCl_2$ (482 mg, 3.92 mmol). The mixture was stirred overnight under Ar at 298 K. NH_4BF_4 (472 mg, 4.5 mmol) was added and the mixture was stirred for further 1 hour under air. The precipitate was filtered and washed with THF and diethyl ether. Dark purple powder of the crude product was reprecipitated from CH_3CN/diethyl ether. The target compound was obtained as a purple powder (641 mg, 1.16 mmol) in 30% yield. UV-Vis (CH_3CN): λ_{max} (nm) = 393 (ε = 130 M^{-1} cm^{-1}), 554 (ε = 190 M^{-1} cm^{-1}). Anal. Calcd for $BC_{19}F_4H_{19}N_4O_3ClCr$: 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)(BF_4)](BF_4) (3).

A solution containing $[Cr^{III}$(6-COO^--tpa)Cl](BF_4) (40 mg, 0.080 mmol) and $AgBF_4$ (22 mg, 0.12 mmol) in H_2O (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 CH_3CN. 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 (CH_3CN): λ_{max} (nm) = 370 (ε = 120 M^{-1} cm^{-1}), 550 (ε = 180 M^{-1} 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 on 2 and 3.

A purple single crystal of **2** was grown by vapor diffusion of THF into an CH_3CN solution of **2**. A pink single crystal of **3** was obtained by recrystallization from an CH_3CN 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 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] Crystallographic details are available in the cif format as ESI†.

Formation of a Cr(V)-oxo complex, 1.

$[Cr^V(O)$(6-COO^--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 CH_3CN (5 mL) at 298 K under air. While the resulting suspension was stirred for 60 min, the 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 ± 5% (0.13 ± 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 CH_3CN, was added a substrate (benzyl alcohol and the deuterated derivatives) with various concentrations in CH_3CN at various temperatures. The reactions were monitored by the decay of the absorption assigned to that of **1** at λ = 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 nonsaturating 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).

Resonance Raman spectroscopy on complex 1.

Samples were prepared by the following procedures. For $[Cr^{V}(^{16}O)(6\text{-}COO^{-}\text{-}tpa)]^{2+}$, $PhI^{16}O$ (5.5 mg, 25 μmol) was added to 2 mL of an CD_3CN solution containing **3** (2.8 mg, 4.9 μmol) and stirred for 35 min at 298 K under Ar. For $[Cr^{V}(^{18}O)(6\text{-}COO^{-}\text{-}tpa)]^{2+}$, $PhI^{18}O$ (5.5 mg, 25 μmol) was added to 2 mL of an CD_3CN solution containing **3** (2.8 mg, 4.9 μmol) and $H_2{}^{18}O$ (5 μL) and stirred for 35 min at 298 K under Ar. Resonance Raman scattering was excited 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 CH_3CN containing 0.1 M $TBAPF_6$ as an electrolyte at 298 K under Ar with a platinum working electrode, a platinum wire as a counter electrode, and $Ag/AgNO_3$ 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 $[Cr^{V}(O)\ (6\text{-}COO^{-}\text{-}tpa)]^{2+}$, $[Cr^{IV}(O)(6\text{-}COO^{-}\text{-}tpa)]^{+}$, $[Fe^{IV}(O)(TMC)]^{2+}$ and $[Fe^{III}(O)(TMC)]^{+}$ were optimized by using the hybrid B3LYP functional[27] without solvent effects. The Wachters-Hay basis set[28,29] was used for Fe and the 6-311+G** basis set[30] for H, C, N and O atoms. The program used is Gaussian 09.[31]

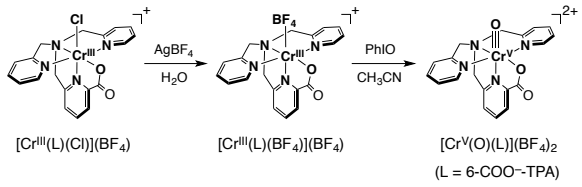
Results and discussion

Preparation and characterization of a Cr(V)-oxo complex.

The synthesis of a mononuclear Cr(V)-oxo complex, $[Cr^{V}(O)(6\text{-}COO^{-}\text{-}tpa)](BF_4)_2$ (**1**) was accomplished by the procedure shown in Scheme 3. A synthetic method for a Cr(III) precursor complex, $[Cr^{III}(6\text{-}COO^{-}\text{-}tpa)(Cl)](BF_4)$ (**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 $[Cr^{III}(6\text{-}COO^{-}\text{-}tpa)(Cl)]^{+}$: 420.04) as shown in Fig. S1a in ESI†. The crystal structure of **2** was determined by X-ray crystallography. Its ORTEP drawing is depicted in Fig. 1a and selected bond lengths are given in the Fig. 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 $[Cr^{III}(Cl)_2(tpa)]^{2+}$ have been reported to fall in the range of 2.05–2.08 Å.[32]

Treatment of complex **2** with $AgBF_4$ in H_2O resulted in the formation of $[Cr^{III}(6\text{-}COO^{-}\text{-}tpa)(BF_4)](BF_4)$ (**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 BF_4^{-}. 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 $[Cr^{III}(6\text{-}COO^{-}\text{-}tpa)(F)]^{+}$: 404.07) without any peak clusters due to the BF_4^{-}-bound Cr(III) complex as shown in Fig. S1b in ESI†. The coordinated fluoride anion (F^{-}) was presumably

Scheme 3



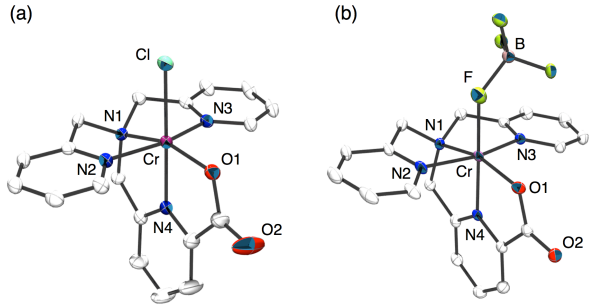


Fig. 1 ORTEP drawings of the cation moieties of (a) $[Cr^{III}(6\text{-}COO^{-}\text{-}tpa)(Cl)](BF_4)$ (**2**) and (b) $[Cr^{III}(6\text{-}COO^{-}\text{-}tpa)(BF_4)](BF_4)$ (**3**) using 50% probability thermal ellipsoids with numbering schemes for the heteroatoms. Hydrogen atoms are omitted for clarity. 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).

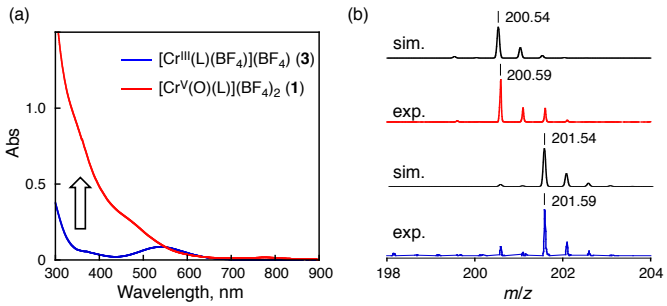


Fig. 2 (a) UV-vis spectral change observed upon addition of PhIO to **3** (0.5 mM) in CH_3CN at 298 K. (b) Positive-ion ESI-TOF-MS of **1** (upper) and ^{18}O-labeled **1** (lower) in CH_3CN. The black lines are simulated isotopic patterns.

derived from decomposition of the BF_4^- anion in the ionization process of ESI-TOF-MS measurements.[33]

Reaction of **3** with iodosylbenzene (PhIO) in acetonitrile (CH_3CN) 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 CH_3CN was evaluated by measuring the half-lifetime ($t_{1/2}$) at different temperatures ($t_{1/2}$ ~ 20 min at 298 K and $t_{1/2}$ > 24 hours 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 $[Cr^V(O)(6\text{-}COO^-\text{-tpa})]^{2+}$: 401.08), which was in good agreement with the calculated isotopic pattern (Fig. 2b). When $PhI^{16}O$ was replaced by isotopically labeled $PhI^{18}O$ with a small amount of $H_2{}^{18}O$, the peak cluster corresponding to ^{18}O-labeled **1** shifted to m/z = 201.59 (Fig. 2b).[34] Electron spin resonance (ESR) measurements on **1** in CH_3CN 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 CH_3CN at 10 K (see Fig. S3 in ESI†).

The formation yield of Cr(V)-oxo complex was calculated to be 20 ± 3% on the basis of the spin amount obtained by double integration of the ESR signal against a standard (TEMPO radical) and 25 ± 5%[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*).

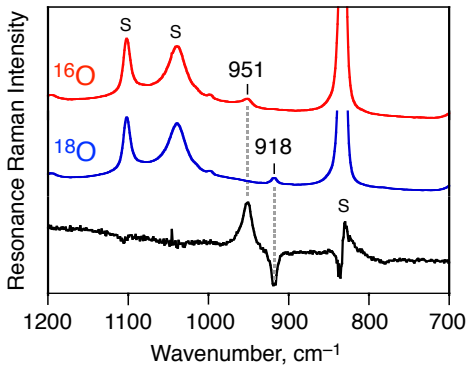


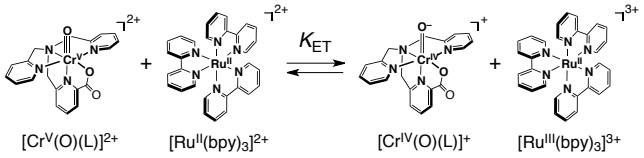
Fig. 3 Resonance Raman spectra of $[Cr^V(^{16}O)(6\text{-}COO^-\text{-TPA})]^{2+}$ (red line), $[Cr^V(^{18}O)(6\text{-}COO^-\text{-TPA})]^{2+}$ (blue line), and their differential spectrum (black line); measured at 236 K in CD_3CN with 441.6 nm excitation. The peaks marked with 'S' are ascribed to the bands due to the solvent.

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 CD_3CN). As shown in Fig. 3, a 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**-^{18}O, which was formed by using $PhI^{18}O$ with a small amount of $H_2{}^{18}O$, 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]

Reduction potential of complex 1.

In order to determine the E_{red} value of **1** in the light of ET equilibrium, $[Fe^{II}(bpy)_3]^{2+}$ was employed as an electron donor (E_{ox} = 1.06 V *vs.* SCE) in CH_3CN.[39] Upon addition of $[Fe^{II}(bpy)_3]^{2+}$ to an CH_3CN solution containing **1** (0.15 mM), UV-vis spectral change was observed at 298 K (Fig. S5 in ESI†). The final concentration of $[Fe^{III}(bpy)_3]^{3+}$ was 0.15 mM on the basis of the absorption coefficient (ε_{650} = 300 M^{-1} cm^{-1})[40a], indicating that a stoichiometric ET reaction proceeded from $[Fe^{II}(bpy)_3]^{2+}$ to **1**. ESR measurements clearly exhibited ET from $[Fe^{II}(bpy)_3]^{2+}$ to **1**, where the signal at g = 1.98 due to **1** decreases, accompanied by an increase a new signal at g = 2.6 due to $[Fe^{III}(bpy)_3]^{3+}$ (Fig. S6a in ESI†).[41] In this case, one-way ET from $[Fe^{II}(bpy)_3]^{2+}$ to **1** occurs to indicate that the reduction

Scheme 4



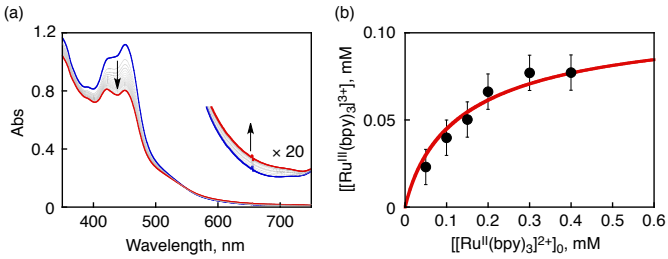


Fig. 4 (a) UV-vis spectral change observed upon addition of $[Ru^{II}(bpy)_3]^{2+}$ (0.1 mM) to an CH_3CN solution of **1** (0.1 mM) at 243 K. (b) Plot of concentration of $[Ru^{III}(bpy)_3]^{3+}$ produced in electron transfer from $[Ru^{II}(bpy)_3]^{2+}$ to **1** in CH_3CN at 243 K *vs.* initial concentration of $[Ru^{II}(bpy)_3]^{2+}$, $[[Ru^{II}(bpy)_3]^{2+}]_0$.

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 V)[42] is found to be in ET equilibrium (Scheme 4), where the observed concentration of $[Ru^{III}(bpy)_3]^{3+}$ (ε_{675nm} = 420 M^{-1} 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 ESR signal at g = 2.6 as shown in Fig. S6b in 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 K_{et} is an ET-equilibrium constant.[16,43] The K_{et} value was determined to be 0.57 ± 0.13 at 243 K by fitting the plot according to a equation described in the literature[16] (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).

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

The E_{red}(**1**) value is much higher than those of $Cr^{V}(O)$ complexes reported so far,[18,19] such as $[Cr^{V}(O)(TpFPC)]$ (E_{red} = 0.11 V *vs.* Ag/AgCl; TpFPC = tris(pentafluorophenyl)-corrolato)[18c] with a trianionic ligand and $[Cr^{V}(O)(TMP)]^{+}$ (E_{red} = 0.76 V *vs.* Ag/AgCl; TMP = tetramesitylporphinato) with a dianionic ligand,[18b] although a $Cr^{V}(O)$ complex with a macrocyclic ligand (1,4,8,11-tetraazacyclotetradecane) has been proposed to exhibit a higher E_{red} value (> 1.34 V *vs.* SCE) in the presence of $HClO_4$.[44] In the case of **1**, the addition of proton showed not so much influence (~ +0.1 V) 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 CH_3CN at 243 K on the basis of the absorption due to $BrFc^{+}$ (ε_{630} = 330 M^{-1} cm^{-1}).[46] This result indicated that two-electron reduction of **1** occurred to form a Cr(III) species (Fig. S7 in ESI†). On the contrary, upon addition of 0.5 mM triphenylamine (Ph_3N) as a one-electron donor (E_{ox} = 0.85 V)[47] to an CH_3CN solution containing **1** (0.04 mM) in the absence of acid at 243 K, ET from Ph_3N to **1** occurred to form one equivalent of the one-electron oxidized product ($Ph_3N^{\bullet+}$), which showed an absorption band at 650 nm observed by UV-vis spectroscopy (Fig. S8 in ESI†). Subsequently, addition of $HClO_4$ (2 mM) to the reaction solution including Ph_3N resulted in additional formation of one more equivalent of $Ph_3N^{\bullet+}$, indicating that the two-electron reduction of **1** by Ph_3N occurred in the presence of H^{+}.[48] The formation of two equivalents of $Ph_3N^{\bullet+}$ relative to **1** clearly indicates that **1** is the sole oxidant in the solution. In addition, the protonation of one-electron reduced Cr(IV)-oxo complex leads to positive shift of E_{red} of Cr(III/IV) beyond the E_{ox} value of Ph_3N. Thus two-electron oxidation of a substrate should be possible for **1** *via* the formation of $[Cr^{IV}(6\text{-}COO^{-}\text{-}TPA)(OH)]^{2+}$, which is a protonated species of the one-electron reduced species of **1**, in a PCET or ET/PT process.

Determination of λ value of complex 1.

To gain kinetic insight into the ET reduction of **1** in CH_3CN, phenol derivatives (R-PhOH and naphtols) 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 $4\text{-}Ph^{\bullet+}$ as shown in Fig. 5a. The absorption band of $4\text{-}Ph^{\bullet+}$ 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 × 10^{3} M^{-1} 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 in ESI†). The obtained k_{et} values are listed in Table 1, together with the oxidation potentials of phenol

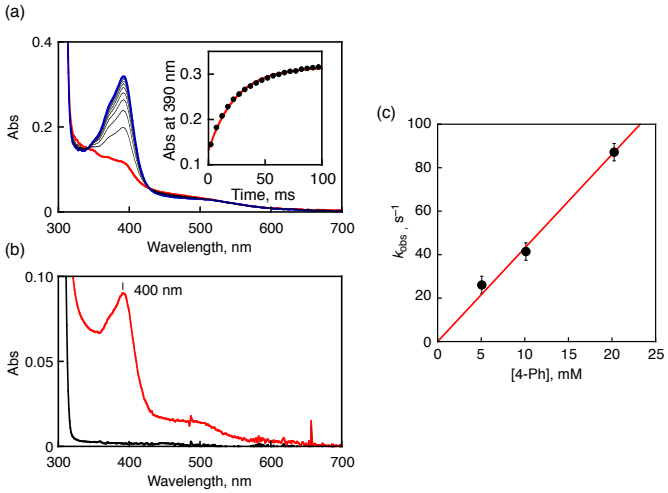


Fig. 5 (a) UV-vis spectral change upon addition of 4-Ph (10 mM) to **1** (0.1 mM) in CH_3CN at 233 K. Inset: The time profile at 390 nm due to $4\text{-}Ph^{\bullet+}$. (b) UV-vis spectrum of $4\text{-}Ph^{\bullet+}$ produced by oxidizing 4-Ph with CAN in CH_3CN at 233 K (c) Plots of k_{obs} *vs.* [4-Ph].

derivatives (E_{ox}) determined by SHACV measurements and driving forces of ET ($-\Delta G_{et} = -e(E_{ox} - E_{red}(\mathbf{1}))$). 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 logk_{et} for phenol derivatives is shown in Fig. 6, where the logk_{et} values are plotted relative to the driving force of ET ($-\Delta G_{et}$). The plot was analysed in light of the Marcus theory of adiabatic outer-sphere electron transfer (eqn (3)), where k_{diff} is the diffusion rate constant, k_B is the Boltzmann constant and Z [= $(k_BT/h)(k_{diff}/k_{-diff})$] is the collision frequency that is taken as 1 × 10^{11} M^{-1} s^{-1}.[51] The k_{diff} value in CH_3CN is taken as 2.0 × 10^{10} M^{-1} s^{-1}.[52]

$$\frac{1}{k_{et}} = \frac{1}{k_{diff}} + \frac{1}{Z\exp[-(\lambda/4)(1 + \Delta G_{et}/\lambda)^2/k_BT]} \quad (3)$$

The reorganization energy of ET (λ) of **1** was thus determined to be 1.03 ± 0.05 eV in CH_3CN 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 ± 0.04 eV) of a non-heme Fe(IV)-oxo complex, $[Fe^{IV}(O)(TMC)(CH_3CN)]^{2+}$.[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 contrary, in the case of the Fe(IV)-oxo complex (S = 1), the LUMO has been reported to be the d_{x2-y2} orbital[53] and the equatorial Fe-N bonds (2.12-2.15 Å) were elongated to 2.24-2.29 Å (Fig. S13b in ESI†). The

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 naphtols	E_{ox}, V[a]	$-\Delta G_{et}$, eV	k_{et}, M^{-1} s^{-1}	KIE
4-Me	1.52	–0.29	$(1.5 \pm 0.1) \times 10^2$	
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	$(2.5 \pm 0.1) \times 10^5$	1.0

[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).

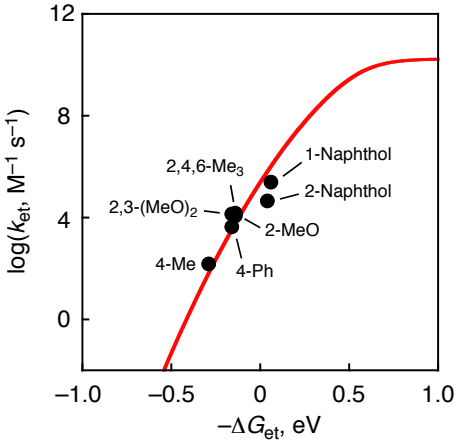


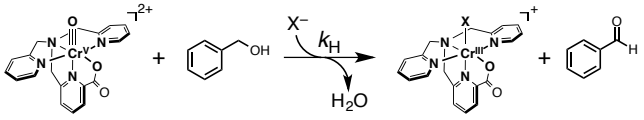
Fig. 6 Plots of logk_{et} *vs.* $-\Delta G_{et}$ in ET reactions from phenol derivatives to **1** at 233 K.

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 dπ orbital as suggested by DFT calculations (Fig. S12 in ESI†).[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 dπ 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 (*vs.* SCE) as a substrate, complex **1** worked as a $2e^-$-oxidant to afford benzaldehyde as the sole product (Scheme 5) as identified and quantified by ^{1}H NMR and GC-MS

Scheme 5



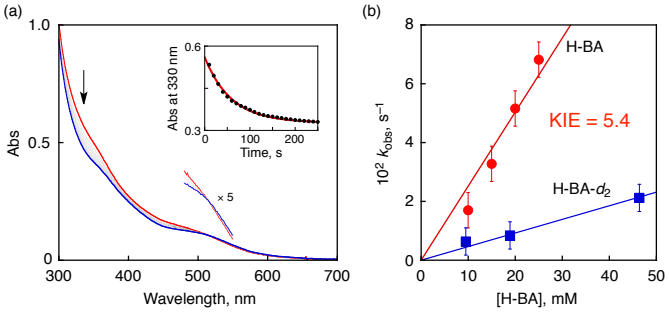


Fig. 7 (a) UV-vis spectral change observed upon addition of benzyl alcohol (10 mM) to **1** (0.1 mM) in CH_3CN at 233 K. Inset: The decay time profile of the absorbance at λ = 330 nm due to **1**. (b) Concentration dependence of pseudo-first-order rate constants (k_{obs}) for the reaction of **1** with H-BA (red) and benzyl alcohol-d_2 (blue).

measurements (Fig. S14, 15 in ESI†).

To elucidate the reaction mechanism of HAT reactions from H-BA derivatives to **1**, the kinetic analysis was conducted on the basis of spectroscopic measurements. The addition of an excess amount of H-BA to an CH_3CN 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_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 M^{-1} s^{-1}) was observed, giving a kinetic isotope effect (KIE = k_H/k_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_{ox} = 1.58 V) and 3,5-dimethoxy-4-methyl-BA (3,5-$(MeO)_2$-4-Me-BA; E_{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 hard to occur under highly endothermic situations ($-\Delta G_{et} < 0$).

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 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

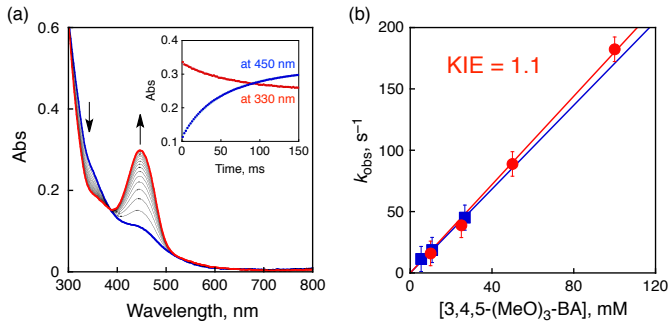


Fig. 8 (a) Spectral changes observed in the oxidation of 3,4,5-$(MeO)_3$-BA (10 mM) by **1** (0.1 mM) in CH_3CN at 233 K. Inset: Time profiles of the absorbance at λ = 330 nm due to **1** and the absorbance at λ = 450 nm due to 3,4,5-$(MeO)_3$-$BA^{\bullet+}$. (b) Plots of k_{obs} *vs.* [3,4,5-$(MeO)_3$-BA (red) or 3,4,5-$(MeO)_3$-BA-d_2 (blue)].

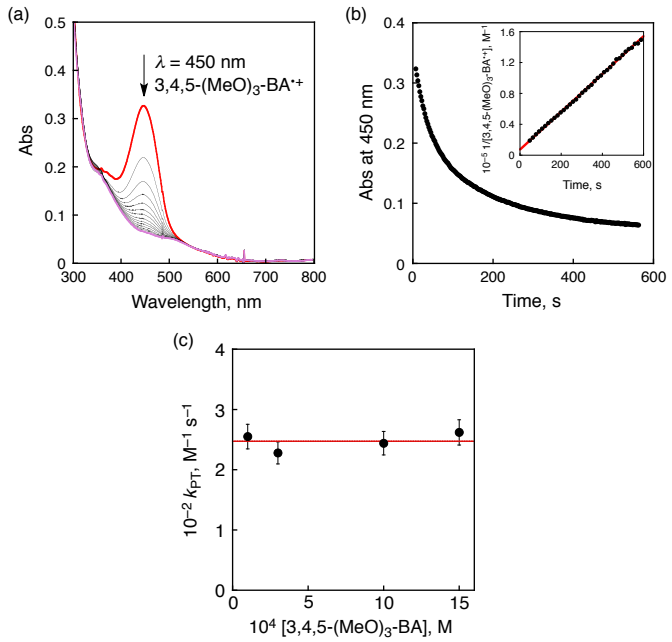


Fig. 9 (a) Following spectral changes observed in the oxidation of 3,4,5-$(MeO)_3$-BA (1.0 mM) by **1** (0.1 mM) in CH_3CN at 233 K. (b) The decay time profile at λ = 450 nm due to 3,4,5-$(MeO)_3$-$BA^{\bullet+}$. Inset: Second-order plot. (c) Plots of k_{PT} *vs.* [3,4,5-$(MeO)_3$-BA].

3,4,5-$(MeO)_3$-BA radical cation (3,4,5-$(MeO)_3$-$BA^{\bullet+}$) 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-$(MeO)_3$-$BA^{\bullet+}$ was thus determined to be 1.8×10^3 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-$(MeO)_3$-$BA^{\bullet+}$ (Fig. 9a). The decay time profile 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-$(MeO)_3$-$BA^{\bullet+}$ to a $Cr^{IV}(O)$ complex derived from one-electron reduction of **1**. The second-order rate constant (k_{PT}) was determined to be 2.5×10^2 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 intermolecular PT from 3,4,5-$(MeO)_3$-$BA^{\bullet+}$ to the $Cr^{IV}(O)$ complex to form 3,4,5-$(MeO)_3$-$BA^{\bullet}$ and a $Cr^{IV}(OH)$ complex.

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 $-\Delta G_{et}$ as shown in Fig. 10, a boundary was found around $-\Delta G_{et} = -0.2$ eV. It should be noted that KIE was still observed to be 6.8 in the case of 3,5-$(MeO)_2$-4-Me-BA, although the $-\Delta G_{et}$ value (–0.26 eV) is close to the mechanistic borderline. This phenomenon clearly represents the first example of alteration of the oxidation mechanisms (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 coworkers 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

Table 2 One-electron oxidation potentials (E_{ox}) of BA derivatives, driving force for ET ($-\Delta G_{et}$), second-order rate constants (k_H or k_{et}), and KIE values for oxidation of benzyl alcohol derivatives with complex **1** in CH_3CN at 233 K.

no.	R-BA	E_{ox}, V[a]	$-\Delta G_{et}$, eV	k_H or k_{et}, M^{-1} s^{-1}	KIE
1	4-NO_2	2.88	–1.65	1.4 ± 0.1	–
2	H	2.33	–1.10	2.5 ± 0.1	5.4
3	4-*t*-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).

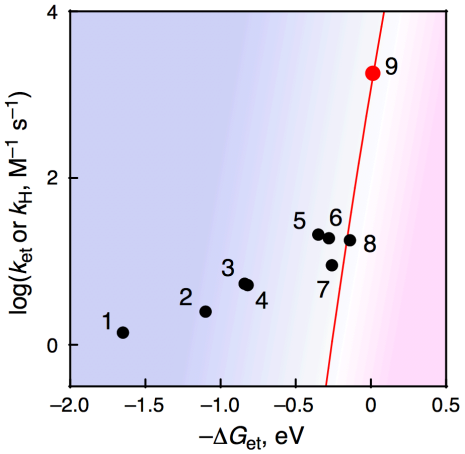


Fig. 10 Plots of logk_H or logk_{et} $-\Delta G_{et}$ in HAT reactions of R-BA by **1** at 233 K.

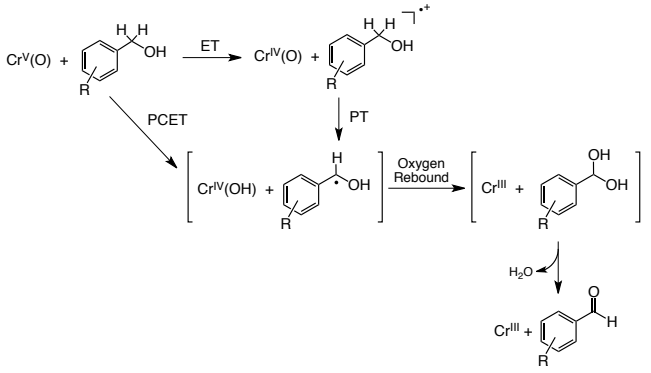


Fig. 11 Proposed mechanism for oxidation of R-BA by **1**.

of Fukuzumi and coworkers, the present study provides apparently the same net hydrogen-atom transfer reaction to afford corresponding benzaldehydes *via* either 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 CH_3CN 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 with showing 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$^{\bullet+}$ as the intermediate in the course of the reaction. Then, deprotonation from 3,4,5-$(MeO)_3$-BA$^{\bullet+}$ is facilitated by the more basic Cr^{IV}(O) complex to form 3,4,5-$(MeO)_3$-BA$^{\bullet}$, 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 oxygen-rebound process[57] 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_{red} value of **1** was determined to be 1.23 V *vs.* SCE on the basis of analysis of the ET equilibrium with $[Ru^{II}(bpy)_3]^{2+}$. The reorganization energy of ET from phenols to **1** has been determined to be 1.03 ± 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 have found a mechanistic borderline between one-step PCET and stepwise ET/PT around $-\Delta G_{et}$ = –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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† Electronic Supplementary Information (ESI) available: crystallographic data of **2** and **3** in CIF, ESI-TOF-MS, UV-vis, ESR, DFT calculations, ^{1}H NMR, and GC-MS data. CCDC 1017025 and 1017026. See DOI: 10.1039/b000000x/

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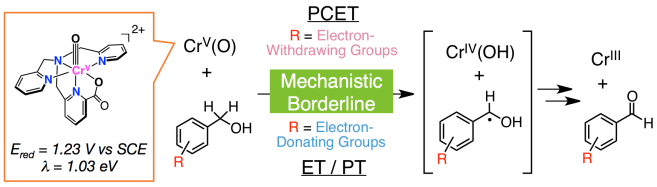
TOC entry



Mechanistic insights were gained into hydrogen-atom-transfer reactions from benzyl alcohol derivatives with different oxidation potentials to a highly reactive Cr(V)-oxo complex to reveal switching of reaction mechanisms.