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Cite this: DOI: 10.1039/c4sc02285h

# 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<sup>V</sup>(O)(6-COO<sup>-</sup>-tpa)](BF<sub>4</sub>)<sub>2</sub> (**1**; 6-COO<sup>-</sup>-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 achieved using ESI-MS spectrometry, electron paramagnetic resonance, UV-vis, and resonance Raman spectroscopies. The reduction potential ( $E_{\text{red}}$ ) 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<sup>II</sup>(bpy)<sub>3</sub>]<sup>2+</sup> (bpy = 2,2'-bipyridine). The reorganization energy ( $\lambda$ ) 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  $\lambda$  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<sup>-</sup> oxidized products in moderate yields as determined from <sup>1</sup>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 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 ( $E_{\text{ox}} = 1.22$  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.

Received 30th July 2014  
Accepted 17th October 2014

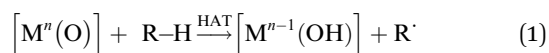
DOI: 10.1039/c4sc02285h

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## Introduction

Extensive efforts have been devoted to the preparation of high-valent metal–oxo complexes in order to understand their reactivity in the oxidative conversion of organic substrates.<sup>1–3</sup> 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 Cyt<sub>c</sub><sup>3</sup>.<sup>4–6</sup> These enzymatic reactions have been usually triggered by transferring formally a hydrogen

atom (H<sup>•</sup>) from organic substrates (R–H) to metal–oxo species ([M<sup>n</sup>(O)]) as the initial step as expressed by eqn (1), *i.e.*, hydrogen-atom transfer (HAT).



Mechanistic insights into HAT from a substrate to a high-valent 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.<sup>7</sup> 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.<sup>7</sup> Once a radical intermediate is formed by a HAT reaction from such a radical-clock 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.<sup>7</sup> Although such arguments should be valid only for specific

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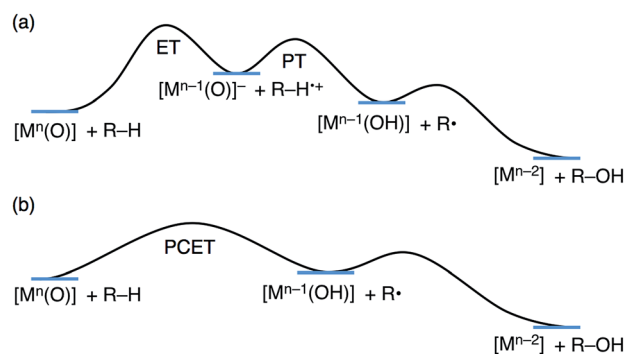
† Electronic supplementary information (ESI) available: Crystallographic data of **2** and **3** in CIF, ESI-TOF-MS, UV-vis, ESR, DFT calculations, <sup>1</sup>H NMR, and GC-MS data. CCDC 1017025 and 1017026. See DOI: 10.1039/c4sc02285h

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.<sup>8–10</sup> 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.<sup>9</sup> 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.<sup>8a,10b</sup> 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 ( $\lambda$ ) of metal-oxo complexes,  $pK_a$  of metal-oxo and metal-hydroxo species.<sup>11–15</sup>

The  $\lambda$  values of Fe(IV)-oxo<sup>16</sup> and Mn(IV)-oxo species<sup>17</sup> have been determined to be 2.37–2.74 eV and 2.27 eV, respectively. The relatively large  $\lambda$  values are interpreted as due to the structural change during ET due to the  $d\sigma$  character of the LUMO. When the smaller  $\lambda$  value of high-valent metal-oxo species is achieved, ET and PCET reactions would be accelerated. In order to reduce the structural change,  $d\pi$  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,<sup>18</sup> 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.<sup>19</sup> 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<sup>18a,19a,g</sup> and porphyrinoids.<sup>18b,c,19b,e</sup> The stabilization inevitably makes such Cr(V)-oxo complexes less reactive toward external organic substrates.<sup>18c,d</sup> Thereby, mechanistic investigation of the reactivity of those stabilized Cr(V)-oxo complexes has been limited to oxygen-atom



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

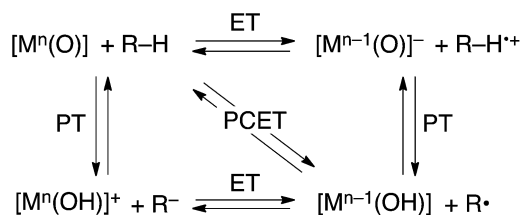
transfer reactions including epoxidation of alkenes,<sup>18a,19a,b</sup> and oxygenation of phosphines<sup>18d,19d,e</sup> and sulfides.<sup>19g</sup> In contrast, the lack of a characterizable but highly reactive Cr(V)-oxo complex, which is capable of HAT reactions from a variety of substrates, limits understanding of mechanisms of the reactions by Cr(V)-oxo complexes.<sup>18e,20</sup> 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 electron-donating ability.

We report herein the preparation, characterization and reactivity of a Cr(V)-oxo complex,  $[Cr^V(O)(6-COO^-tpa)]^{2+}$  (6-COO<sup>-</sup>-tpa<sup>21</sup> = *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 (CH<sub>3</sub>CN) 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. <sup>1</sup>H NMR spectra were recorded on a JEOL EX-270 spectrometer. ESR measurements were performed on a Bruker Bio Spin-EMXPlus9.5/2.7 spectrometer in CH<sub>3</sub>CN. 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). <sup>18</sup>O-labeled PhIO (PhI<sup>18</sup>O)<sup>22</sup> and deuterated benzyl alcohol derivatives<sup>23</sup> were synthesized as described in the literature. CH<sub>3</sub>CN was distilled over CaH<sub>2</sub> under Ar prior to use. THF was distilled from Na/benzophenone under Ar before use. Chemicals were used as received unless otherwise noted.



Scheme 1

### 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<sub>3</sub>CN (40 mL) was added to a solution of 6-(ethoxycarbonyl)-2-chloromethylpyridine<sup>24</sup> (2.20 g, 11.0 mmol) and Na<sub>2</sub>CO<sub>3</sub> (6.36 g, 60.0 mmol) in CH<sub>3</sub>CN (60 mL) and the mixture was refluxed for 24 h. After cooling, the mixture was filtered and CH<sub>3</sub>CN 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). <sup>1</sup>H NMR (CD<sub>3</sub>CN): 1.34 (t, *J* = 7 Hz, 3H, -CH<sub>2</sub>CH<sub>3</sub>), 3.80 (s, 4H, -CH<sub>2</sub>-py), 3.86 (s, 2H, -CH<sub>2</sub>-py-COOEt), 4.34 (q, *J* = 7 Hz, 2H, -CH<sub>2</sub>CH<sub>3</sub>), 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)<sup>21</sup>

NaOH (2.00 g, 50 mmol) in H<sub>2</sub>O (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% HClO<sub>4</sub> to pH ~4. Ethanol was removed using a rotary evaporator and the aqueous solution was extracted with CHCl<sub>3</sub> (3×) and then dried over MgSO<sub>4</sub>. By removing CHCl<sub>3</sub>, 6-COOH-tpa was obtained as a light brown liquid in 99% yield. <sup>1</sup>H NMR (CD<sub>3</sub>CN): 3.78 (s, 4H, CH<sub>2</sub>-py), 3.83 (s, 2H, -CH<sub>2</sub>-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]<sup>+</sup>).

### Synthesis of [Cr<sup>III</sup>(6-COO<sup>-</sup>-tpa)(Cl)](BF<sub>4</sub>) (2)

6-COOH-tpa (1.86 g, 5.59 mmol) was dissolved in distilled THF (40 mL) and to the solution was added CrCl<sub>2</sub> (482 mg, 3.92 mmol). The mixture was stirred overnight under Ar at 298 K. NH<sub>4</sub>BF<sub>4</sub> (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 CH<sub>3</sub>CN/diethyl ether. The target compound was obtained as a purple powder (641 mg, 1.16 mmol) in 30% yield. UV-vis (CH<sub>3</sub>CN): λ<sub>max</sub> (nm) = 393 (ε = 130 M<sup>-1</sup> cm<sup>-1</sup>), 554 (ε = 190 M<sup>-1</sup> cm<sup>-1</sup>). Anal. calcd for BC<sub>19</sub>F<sub>4</sub>H<sub>19</sub>N<sub>4</sub>O<sub>3</sub>ClCr: C, 43.41; H, 3.64; N, 10.66. Found: C, 43.18; H, 3.57; N, 10.66%.

### Synthesis of [Cr<sup>III</sup>(6-COO<sup>-</sup>-tpa)(BF<sub>4</sub>)](BF<sub>4</sub>) (3)

A solution containing [Cr<sup>III</sup>(6-COO<sup>-</sup>-tpa)Cl](BF<sub>4</sub>) (40 mg, 0.080 mmol) and AgBF<sub>4</sub> (22 mg, 0.12 mmol) in H<sub>2</sub>O (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<sub>3</sub>CN. 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<sub>3</sub>CN): λ<sub>max</sub> (nm) = 370 (ε = 120 M<sup>-1</sup> cm<sup>-1</sup>), 550 (ε = 180 M<sup>-1</sup> cm<sup>-1</sup>). Anal. calcd for B<sub>2</sub>C<sub>20</sub>F<sub>8</sub>H<sub>21</sub>N<sub>4</sub>O<sub>3.5</sub>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 CH<sub>3</sub>CN solution of 2. A pink single crystal of 3 was obtained by recrystallization from an CH<sub>3</sub>CN 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.<sup>25†</sup>

### Formation of Cr(v)-oxo complex, 1

[Cr<sup>V</sup>(O)(6-COO<sup>-</sup>-tpa)]<sup>2+</sup> (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<sub>3</sub>CN (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.<sup>26</sup> 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<sup>II</sup>(bpy)<sub>3</sub>]<sup>2+</sup> 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<sub>3</sub>CN, was added a substrate (benzyl alcohol and the deuterated derivatives) with various concentrations in CH<sub>3</sub>CN 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 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).

## Resonance Raman spectroscopy of complex 1

Samples were prepared by the following procedures. For  $[\text{Cr}^{\text{V}}(^{16}\text{O})(6\text{-COO}^-\text{-tpa})]^{2+}$ ,  $\text{PhI}^{16}\text{O}$  (5.5 mg, 25  $\mu\text{mol}$ ) was added to 2 mL of an  $\text{CD}_3\text{CN}$  solution containing **3** (2.8 mg, 4.9  $\mu\text{mol}$ ) and stirred for 35 min at 298 K under Ar. For  $[\text{Cr}^{\text{V}}(^{18}\text{O})(6\text{-COO}^-\text{-tpa})]^{2+}$ ,  $\text{PhI}^{18}\text{O}$  (5.5 mg, 25  $\mu\text{mol}$ ) was added to 2 mL of an  $\text{CD}_3\text{CN}$  solution containing **3** (2.8 mg, 4.9  $\mu\text{mol}$ ) and  $\text{H}_2^{18}\text{O}$  (5  $\mu\text{L}$ ) 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  $135^\circ$  scattering geometry.

## Electrochemical measurements

Second harmonic AC voltammetry (SHACV) and differential pulse voltammetry (DPV) measurements were carried out in  $\text{CH}_3\text{CN}$  containing 0.1 M  $\text{TBAPF}_6$  as an electrolyte at 298 K under Ar with a platinum working electrode, a platinum wire as a counter electrode, and  $\text{Ag}/\text{AgNO}_3$  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  $[\text{Cr}^{\text{V}}(\text{O})(6\text{-COO}^-\text{-tpa})]^{2+}$ ,  $[\text{Cr}^{\text{IV}}(\text{O})(6\text{-COO}^-\text{-tpa})]^+$ ,  $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})]^{2+}$  and  $[\text{Fe}^{\text{III}}(\text{O})(\text{TMC})]^+$  were optimized by using the hybrid B3LYP functional<sup>27</sup> without solvent effects. The Wachters-Hay basis set<sup>28,29</sup> was used for Fe and the 6-311+G\*\* basis set<sup>30</sup> for H, C, N and O atoms. The program used was Gaussian 09.<sup>31</sup>

# Results and discussion

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

The synthesis of a mononuclear Cr(v)-oxo complex,  $[\text{Cr}^{\text{V}}(\text{O})(6\text{-COO}^-\text{-tpa})](\text{BF}_4)_2$  (**1**), was accomplished by the procedure shown in Scheme 3. The synthetic method for the Cr(III) precursor complex,  $[\text{Cr}^{\text{III}}(6\text{-COO}^-\text{-tpa})(\text{Cl})](\text{BF}_4)$  (**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  $[\text{Cr}^{\text{III}}(6\text{-COO}^-\text{-tpa})(\text{Cl})]^+$ : 420.04) as shown in Fig. S1a in the ESI.† The crystal structure of **2** was determined by X-ray crystallography.

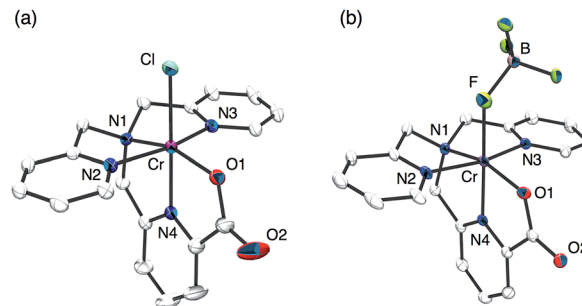
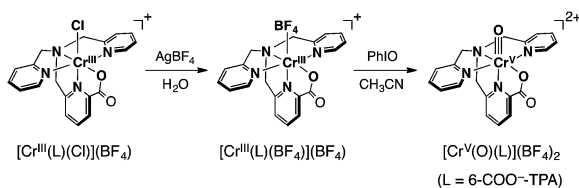


Fig. 1 ORTEP drawings of the cation moieties of (a)  $[\text{Cr}^{\text{III}}(6\text{-COO}^-\text{-tpa})(\text{Cl})](\text{BF}_4)$  (**2**) and (b)  $[\text{Cr}^{\text{III}}(6\text{-COO}^-\text{-tpa})(\text{BF}_4)](\text{BF}_4)$  (**3**) using 50% probability thermal ellipsoids with numbering schemes for the heteroatoms. Hydrogen atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) 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 ( $\text{\AA}$ ) 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)  $\text{\AA}$ , 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–N $_x$  ( $x = 1\text{--}4$ ) in  $[\text{Cr}^{\text{III}}(\text{Cl})_2(\text{tpa})]^+$  have been reported to fall in the range of 2.05–2.08  $\text{\AA}$ .<sup>32</sup>

Treatment of complex **2** with  $\text{AgBF}_4$  in  $\text{H}_2\text{O}$  resulted in the formation of  $[\text{Cr}^{\text{III}}(6\text{-COO}^-\text{-tpa})(\text{BF}_4)](\text{BF}_4)$  (**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  $\text{BF}_4^-$ . 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  $[\text{Cr}^{\text{III}}(6\text{-COO}^-\text{-tpa})(\text{F})]^+$ : 404.07) without any peak clusters due to the  $\text{BF}_4^-$ -bound Cr(III) complex as shown in Fig. S1b in the ESI.† The coordinated fluoride anion ( $\text{F}^-$ ) was presumably derived from decomposition of the  $\text{BF}_4^-$  anion in the ionization process of ESI-TOF-MS measurements.<sup>33</sup>

Reaction of **3** with iodobenzene (PhIO) in acetonitrile ( $\text{CH}_3\text{CN}$ ) 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.<sup>18d</sup> The stability of **1** in  $\text{CH}_3\text{CN}$  was evaluated by measuring the half-life ( $\tau_{1/2}$ ) at different temperatures ( $\tau_{1/2} \sim 20$  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  $[\text{Cr}^{\text{V}}(\text{O})(6\text{-COO}^-\text{-tpa})]^{2+}$ : 200.59), which was in good agreement with the calculated isotopic pattern (Fig. 2b). When  $\text{PhI}^{16}\text{O}$  was replaced by isotopically labeled  $\text{PhI}^{18}\text{O}$  with a small amount of  $\text{H}_2^{18}\text{O}$ , the peak cluster corresponding to  $^{18}\text{O}$ -labeled **1** shifted to  $m/z = 201.59$  (Fig. 2b).<sup>34</sup> Electron spin resonance (ESR)

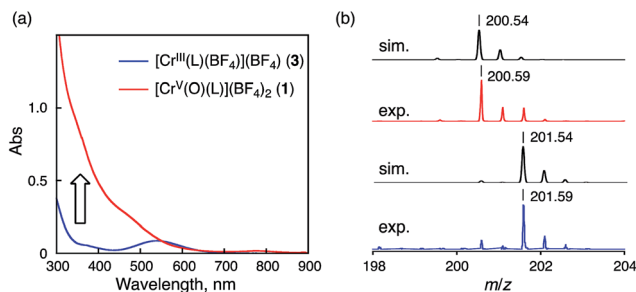


Fig. 2 (a) UV-vis spectral change observed upon addition of PhIO to **3** (0.5 mM) in CH<sub>3</sub>CN at 298 K. (b) Positive-ion ESI-TOF-MS of **1** (upper) and <sup>18</sup>O-labeled **1** (lower) in CH<sub>3</sub>CN. The black lines are simulated isotopic patterns.

measurements on **1** in CH<sub>3</sub>CN at 243 K and 100 K afforded a strong signal at  $g = 1.9756$ , assignable to that of a Cr(v) species ( $S = 1/2$ ),<sup>18,19</sup> which was different from that of complex **3** ( $S = 3/2$ )<sup>35</sup> in CH<sub>3</sub>CN 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  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  (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 CD<sub>3</sub>CN). As shown in Fig. 3, Raman scattering due to the Cr(v)-oxo moiety was observed at  $951 \text{ cm}^{-1}$ , which was comparable to that observed for a reported Cr(v)-oxo complex with a corrole derivative as a supporting ligand ( $986 \text{ cm}^{-1}$ ).<sup>37</sup> The peak of <sup>18</sup>O, which was formed by using PhI<sup>18</sup>O with a small amount of H<sub>2</sub><sup>18</sup>O, shifted to  $918 \text{ cm}^{-1}$ ; the isotopic shift ( $33 \text{ cm}^{-1}$ ) is fairly consistent with the calculated value ( $\Delta\nu = 41 \text{ cm}^{-1}$ ) as shown in Fig. 3.<sup>38</sup>

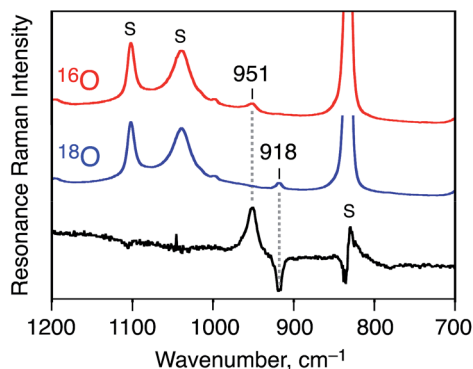


Fig. 3 Resonance Raman spectra of  $[\text{Cr}^{\text{V}}(^{16}\text{O})(6\text{-COO}^-\text{tpa})]^{2+}$  (red line),  $[\text{Cr}^{\text{V}}(^{18}\text{O})(6\text{-COO}^-\text{tpa})]^{2+}$  (blue line), and their differential spectrum (black line); measured at 236 K in CD<sub>3</sub>CN with 441.6 nm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

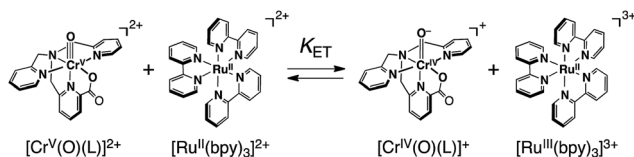
## Reduction potential of complex **1**

In order to determine the  $E_{\text{red}}$  value of **1** in the light of ET equilibrium,  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  was employed as an electron donor ( $E_{\text{ox}} = 1.06 \text{ V vs. SCE}$ ) in CH<sub>3</sub>CN.<sup>39</sup> Upon addition of  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  to an CH<sub>3</sub>CN solution containing **1** (0.15 mM), a UV-vis spectral change was observed at 298 K (Fig. S5 in ESI†). The final concentration of  $[\text{Fe}^{\text{III}}(\text{bpy})_3]^{3+}$  was 0.15 mM on the basis of the absorption coefficient ( $\epsilon_{650} = 300 \text{ M}^{-1} \text{ cm}^{-1}$ ),<sup>40a</sup> indicating that a stoichiometric ET reaction proceeded from  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  to **1**. ESR measurements clearly exhibited ET from  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  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  $[\text{Fe}^{\text{III}}(\text{bpy})_3]^{3+}$  (Fig. S6a in ESI†).<sup>41</sup> In this case, one-way ET from  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$  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  $[\text{Fe}^{\text{II}}(\text{bpy})_3]^{2+}$ , the ET reaction between **1** and  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$  ( $E_{\text{ox}} = 1.24 \text{ V}$ )<sup>42</sup> is found to be in ET equilibrium (Scheme 4), where the observed concentration of  $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$  ( $\epsilon_{675\text{nm}} = 420 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>40b</sup> produced in the ET reaction from  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$  to **1** increases with the increase in the initial concentration of  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$  ( $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}_0$ ) as shown in Fig. 4.<sup>16,43</sup> Formation of  $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$  was also confirmed by the detection of an ESR signal at  $g = 2.6$  as shown in Fig. S6b in the ESI.<sup>41†</sup> The ET equilibrium between complex **1** and  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$  indicates that the redox potential of **1** is close to that of  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$  according to the Nernst equation (eqn (2)), where  $F$  is the Faraday constant and  $K_{\text{et}}$  is an ET-equilibrium constant.<sup>16,43</sup> The  $K_{\text{et}}$  value was determined to be  $0.57 \pm 0.13$  at 243 K by fitting the plot according to a equation described in the literature<sup>16</sup> (red line), as shown in Fig. 4b. The apparent one-electron reduction potential ( $E_{\text{red}}$ ) of **1** ( $E_{\text{red}}(\mathbf{1})$ ) was then determined to be  $1.23 \pm 0.01 \text{ V}$  using eqn (2).

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

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



Scheme 4

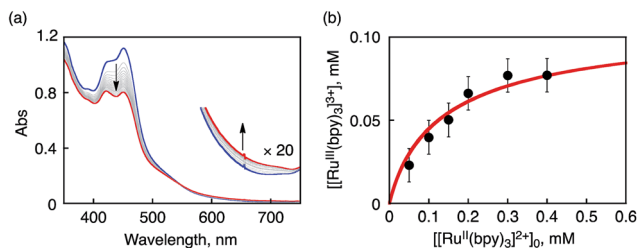


Fig. 4 (a) UV-vis spectral change observed upon addition of  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$  (0.1 mM) to an  $\text{CH}_3\text{CN}$  solution of **1** (0.1 mM) at 243 K. (b) Plot of concentration of  $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$  produced in electron transfer from  $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$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

on the reduction potential as observed in DPV measurements.<sup>45</sup>

When bromoferrocene ( $\text{BrFc}$ ;  $E_{1/2} = 0.54$  V) was employed as a one-electron donor, complex **1** (0.17 mM) consumed 2 eq. of  $\text{BrFc}$  in  $\text{CH}_3\text{CN}$  at 243 K on the basis of the absorption due to  $\text{BrFc}^+$  ( $\epsilon_{630} = 330 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>46</sup> This result indicated that two-electron reduction of **1** occurred to form a  $\text{Cr}(\text{III})$  species (Fig. S7 in ESI<sup>†</sup>). On the other hand, upon addition of 0.5 mM triphenylamine ( $\text{Ph}_3\text{N}$ ) as a one-electron donor ( $E_{\text{ox}} = 0.85$  V)<sup>47</sup> to an  $\text{CH}_3\text{CN}$  solution containing **1** (0.04 mM) in the absence of acid at 243 K, ET from  $\text{Ph}_3\text{N}$  to **1** occurred to form one equivalent of the one-electron oxidized product ( $\text{Ph}_3\text{N}^+$ ), which showed an absorption band at 650 nm observed by UV-vis spectroscopy (Fig. S8 in ESI<sup>†</sup>). Subsequently, addition of  $\text{HClO}_4$  (2 mM) to the reaction solution including  $\text{Ph}_3\text{N}$  resulted in additional formation of one more equivalent of  $\text{Ph}_3\text{N}^+$ , indicating that the two-electron reduction of **1** by  $\text{Ph}_3\text{N}$  occurred in the presence of  $\text{H}^+$ .<sup>48</sup> The formation of two equivalents of  $\text{Ph}_3\text{N}^+$  relative to **1** clearly indicates that **1** is the sole oxidant in the solution. In addition, the protonation of one-electron reduced  $\text{Cr}(\text{IV})$ -oxo complex leads to a positive shift of the  $E_{\text{red}}$  of  $\text{Cr}(\text{III/IV})$  beyond the  $E_{\text{ox}}$  value of  $\text{Ph}_3\text{N}$ . Thus two-electron oxidation of a substrate should be possible for **1** *via* the formation of  $[\text{Cr}^{\text{IV}}(\text{6-COO}^-\text{-tpa})(\text{OH})]^{2+}$ , which is a protonated species of the one-electron reduced species of **1**, in a PCET or ET/PT process.

### Determination of the $\lambda$ value of complex **1**

To gain kinetic insight into the ET reduction of **1** in  $\text{CH}_3\text{CN}$ , 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  $4\text{-Ph}^+$  as shown in Fig. 5a. The absorption band of  $4\text{-Ph}^+$  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 ( $k_{\text{obs}}$ ) for the oxidation of 4-Ph by **1** increase linearly with increasing concentrations of 4-Ph. The second-order rate constant ( $k_{\text{et}}$ ) 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,  $k_{\text{et}}$  values were determined for oxidation reactions of other phenol derivatives by **1** (Fig. S9

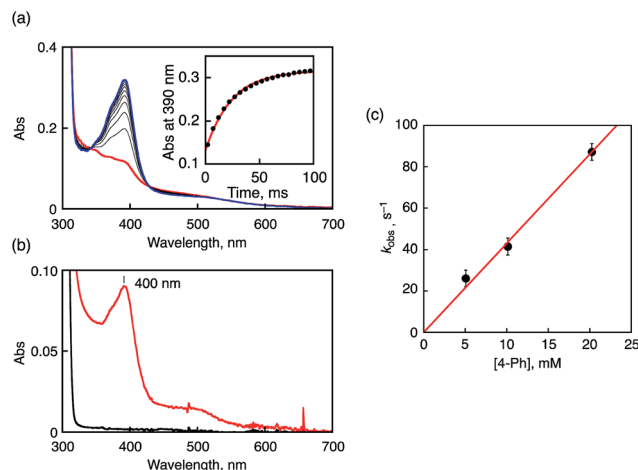


Fig. 5 (a) UV-vis spectral change upon addition of 4-Ph (10 mM) to **1** (0.1 mM) in  $\text{CH}_3\text{CN}$  at 233 K. Inset: the time profile at 390 nm due to  $4\text{-Ph}^+$ . (b) UV-vis spectrum of  $4\text{-Ph}^+$  produced by oxidizing 4-Ph with CAN in  $\text{CH}_3\text{CN}$  at 233 K. (c) Plots of  $k_{\text{obs}}$  vs.  $[4\text{-Ph}]$ .

in ESI<sup>†</sup>). The obtained  $k_{\text{et}}$  values are listed in Table 1, together with the oxidation potentials of phenol derivatives ( $E_{\text{ox}}$ ) determined by SHACV measurements and driving forces of ET ( $-\Delta G_{\text{et}} = -e(E_{\text{ox}} - E_{\text{red}}(\mathbf{1}))$ ). 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.<sup>49,50</sup>

The driving-force dependence of  $\log k_{\text{et}}$  for phenol derivatives is shown in Fig. 6, where the  $\log k_{\text{et}}$  values are plotted relative to the driving force of ET ( $-\Delta G_{\text{et}}$ ). The plot was analysed in light of the Marcus theory of adiabatic outer-sphere electron transfer (eqn (3)), where  $k_{\text{diff}}$  is the diffusion rate constant,  $k_{\text{B}}$  is the Boltzmann constant and  $Z [= (k_{\text{B}}T/h)(k_{\text{diff}}/k_{-\text{diff}})]$  is the collision frequency that is taken as  $1 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>51</sup> The  $k_{\text{diff}}$  value in  $\text{CH}_3\text{CN}$  is taken as  $2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>52</sup>

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

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

R-PhOH and naphthols	$E_{\text{ox}}/\text{V}$	$-\Delta G_{\text{et}}/\text{eV}$	$k_{\text{et}}/\text{M}^{-1} \text{ s}^{-1}$	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) <sub>2</sub>	1.39	-0.16	$(1.4 \pm 0.1) \times 10^4$	
2,4,6-Me <sub>3</sub>	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

<sup>a</sup> Determined by SHACV performed in  $\text{CH}_3\text{CN}$  at room temperature under Ar in the presence of TBAPF<sub>6</sub> (0.1 M) as an electrolyte (*vs.* SCE).

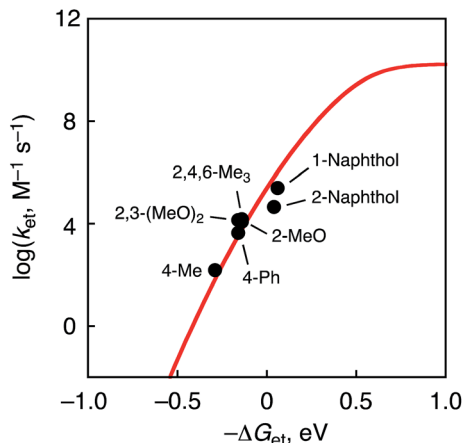


Fig. 6 Plots of  $\log k_{\text{et}}$  vs.  $-\Delta G_{\text{et}}$  in ET reactions from phenol derivatives to **1** at 233 K.

The reorganization energy of ET ( $\lambda$ ) of **1** was thus determined to be  $1.03 \pm 0.05$  eV in  $\text{CH}_3\text{CN}$  at 233 K on the basis of the Marcus plot in Fig. 6. The  $\lambda$  value of **1** is much smaller than that ( $2.37 \pm 0.04$  eV) of a non-heme Fe(IV)-oxo complex,  $[\text{Fe}^{\text{IV}}(\text{O})(\text{TMC})(\text{CH}_3\text{CN})]^{2+}$ .<sup>16</sup> This indicates that the structural change upon the ET reduction is much smaller for **1** than that for the Fe<sup>IV</sup>-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<sup>IV</sup>(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  $\pi^*$  orbital of the Cr–O bond (Fig. S12 in ESI<sup>†</sup>). Thus, the Cr–O bond (1.55 Å) was elongated to 1.63 Å upon the ET reduction (Fig. S13a in ESI<sup>†</sup>). On the other hand, in the case of the Fe(IV)-oxo complex ( $S = 1$ ), the LUMO has been reported to be the  $d_{x^2-y^2}$  orbital<sup>53</sup> and the equatorial Fe–N bonds (2.12–2.15 Å) were elongated to 2.24–2.29 Å (Fig. S13b in ESI<sup>†</sup>). 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<sup>IV</sup>-oxo complex (0.090 Å). Thus, the smaller structural change of **1** in the course of ET reactions to afford the smaller  $\lambda$  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<sup>†</sup>).<sup>54</sup> In addition, in the case of a Mn(v)(O) complex with a corrolazine derivative,<sup>55</sup> a smaller  $\lambda$  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  $\text{H}^+$  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)<sup>56</sup> that shows the oxidation potential ( $E_{\text{ox}}$ ) of 2.33 V (vs. SCE) as a substrate, complex **1** worked as a  $2e^-$ -

Table 2 One-electron oxidation potentials ( $E_{\text{ox}}$ ) of BA derivatives, driving force for ET ( $-\Delta G_{\text{et}}$ ), second-order rate constants ( $k_{\text{H}}$  or  $k_{\text{et}}$ ), and KIE values for the oxidation of benzyl alcohol derivatives with complex **1** in  $\text{CH}_3\text{CN}$  at 233 K

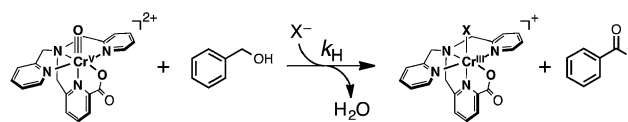
No.	R-BA	$E_{\text{ox}}^a/\text{V}$	$-\Delta G_{\text{et}}/\text{eV}$	$k_{\text{H}}$ or $k_{\text{et}}/\text{M}^{-1} \text{s}^{-1}$	KIE
1	4-NO <sub>2</sub>	2.88	-1.65	$1.4 \pm 0.1$	—
2	H	2.33	-1.10	$2.5 \pm 0.1$	5.4
3	4- <i>t</i> -Bu	2.07	-0.84	$5.4 \pm 0.3$	—
4	4-Me	2.05	-0.82	$5.2 \pm 0.2$	—
5	4-MeO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

<sup>a</sup> Determined by SHACV performed in  $\text{CH}_3\text{CN}$  at room temperature under Ar in the presence of TBAPF<sub>6</sub> (0.1 M) as an electrolyte (vs. SCE).

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

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 a  $\text{CH}_3\text{CN}$  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 ( $k_{\text{obs}}$ ) increased linearly with increasing concentrations of H-BA (Fig. 7b, red line). The second-order rate constant ( $k_{\text{H}}$ ) was determined to be  $2.5 \text{ M}^{-1} \text{ s}^{-1}$  from the slope of the linear plot. When H-BA was replaced by the corresponding deuterated compound at the benzylic position (benzyl alcohol-*d*<sub>2</sub>, H-BA-*d*<sub>2</sub>), a significant deceleration of the oxidation rate (blue line in Fig. 7b,  $k_{\text{D}} = 0.46 \text{ M}^{-1} \text{ s}^{-1}$ ) was observed, giving a kinetic isotope effect (KIE =  $k_{\text{H}}/k_{\text{D}}$ ) 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;  $E_{\text{ox}} = 1.58$  V) and 3,5-dimethoxy-4-methyl-BA (3,5-(MeO)<sub>2</sub>-4-Me-BA;  $E_{\text{ox}} = 1.49$  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 ( $-\Delta G_{\text{et}} < 0$ ).



Scheme 5

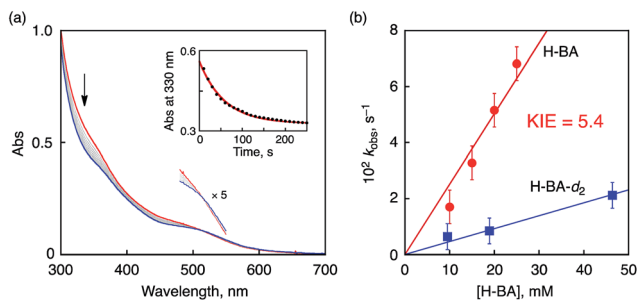


Fig. 7 (a) UV-vis spectral change observed upon addition of benzyl alcohol (10 mM) to **1** (0.1 mM) in  $\text{CH}_3\text{CN}$  at 233 K. Inset: the decay time profile of the absorbance at  $\lambda = 330$  nm due to **1**. (b) Concentration dependence of pseudo-first-order rate constants ( $k_{\text{obs}}$ ) 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,  $E_{\text{ox}} = 1.22$  V) is comparable to the  $E_{\text{red}}$  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 $^{\cdot+}$ ) as a new intermediate (Fig. 8a and Fig. S16 in ESI $^\dagger$ ).<sup>12a</sup>

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 ( $k_{\text{et}}$ ) of 3,4,5-(MeO) $_3$ -BA $^{\cdot+}$  was thus determined to be  $1.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$  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 $^{\cdot+}$  (Fig. 9a). The decay time profile

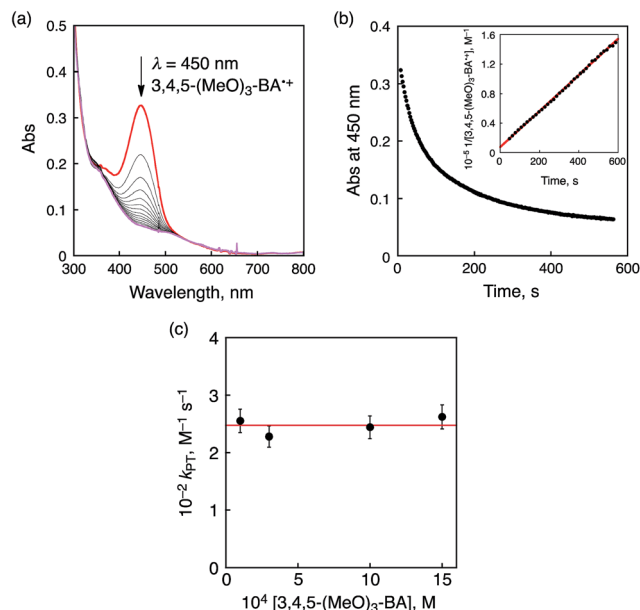


Fig. 9 (a) Following spectral changes observed in the oxidation of 3,4,5-(MeO) $_3$ -BA (1.0 mM) by **1** (0.1 mM) in  $\text{CH}_3\text{CN}$  at 233 K. (b) The decay time profile at  $\lambda = 450$  nm due to 3,4,5-(MeO) $_3$ -BA $^{\cdot+}$ . Inset: second-order plot. (c) Plots of  $k_{\text{PT}}$  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 $^{\cdot+}$  to a  $\text{Cr}^{\text{IV}}(\text{O})$  complex derived from one-electron reduction of **1**. The second-order rate constant ( $k_{\text{PT}}$ ) was determined to be  $2.5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ . It should be noted that the  $k_{\text{PT}}$  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 $^{\cdot+}$  to the  $\text{Cr}^{\text{IV}}(\text{O})$  complex to form 3,4,5-(MeO) $_3$ -BA $^{\cdot}$  and a  $\text{Cr}^{\text{IV}}(\text{OH})$  complex.

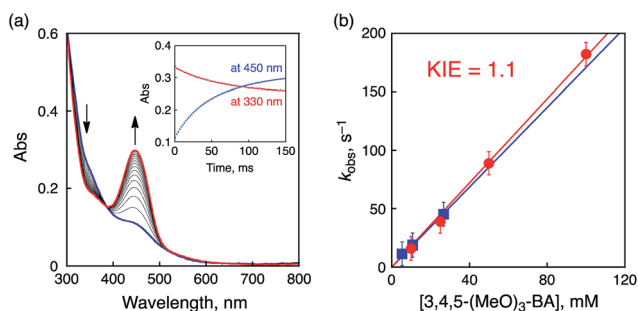


Fig. 8 (a) Spectral changes observed in the oxidation of 3,4,5-(MeO) $_3$ -BA (10 mM) by **1** (0.1 mM) in  $\text{CH}_3\text{CN}$  at 233 K. Inset: time profiles of the absorbance at  $\lambda = 330$  nm due to **1** and the absorbance at  $\lambda = 450$  nm due to 3,4,5-(MeO) $_3$ -BA $^{\cdot+}$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

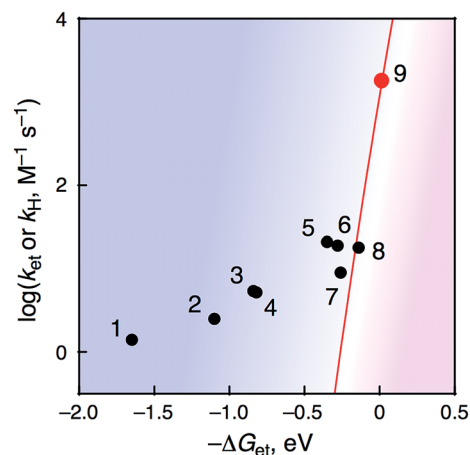


Fig. 10 Plots of  $\log k_{\text{H}}$  or  $\log k_{\text{et}} - \Delta G_{\text{et}}$  in HAT reactions of R-BA by **1** at 233 K.



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  $-\Delta G_{\text{et}}$  as shown in Fig. 10, a boundary was found around  $-\Delta G_{\text{et}} = -0.2$  eV. It should be noted that the KIE was still observed to be 6.8 in the case of 3,5-(MeO)<sub>2</sub>-4-Me-BA, although the  $-\Delta G_{\text{et}}$  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.<sup>12</sup>

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<sup>3+</sup>.<sup>12</sup> 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<sup>3+</sup>, 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 CH<sub>3</sub>CN at 233 K as shown in Fig. 11. In the case of R-BA, except for 3,4,5-(MeO)<sub>3</sub>-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)<sub>3</sub>-BA by **1** allowed us to observe the formation of 3,4,5-(MeO)<sub>3</sub>-BA<sup>•+</sup> as the intermediate in the course of the reaction. Then, deprotonation from 3,4,5-(MeO)<sub>3</sub>-BA<sup>•+</sup> is facilitated by the more basic Cr<sup>IV</sup>(O) complex to form 3,4,5-(MeO)<sub>3</sub>-BA<sup>•</sup>, 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 process<sup>57</sup> affording  $\alpha$ -diol intermediates, which undergo facile dehydration.

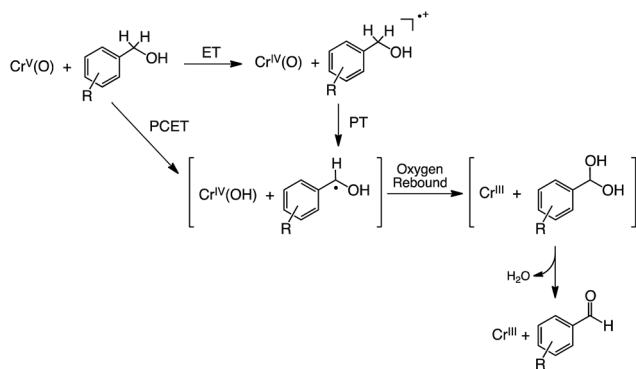


Fig. 11 Proposed mechanism for oxidation of R-BA by **1**.

## Conclusions

In conclusion, we have synthesized and characterized a reactive Cr(v)-oxo complex (**1**) by using a monoanionic pentadentate ligand (6-COO<sup>-</sup>-tpa). The  $E_{\text{red}}$  value of **1** was determined to be 1.23 V vs. SCE on the basis of analysis of the ET equilibrium with [Ru<sup>II</sup>(bpy)<sub>3</sub>]<sup>2+</sup>. 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<sup>IV</sup>(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  $-\Delta G_{\text{et}} = -0.2$  eV. The present study provides a standard for the elucidation of the reactivity of Cr(v)-oxo complexes in HAT reactions.

## Acknowledgements

This work was supported by a Grant-in-Aid (no. 24750052 and 24245011) from the Japan Society of Promotion of Science (JSPS, MEXT) of Japan and financial support from The Kurata Foundation.

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