

## Supporting Information

### **Chromium(V)-Oxo and Chromium(III)-Superoxo Complexes Bearing a Macrocyclic TMC Ligand in Hydrogen Atom Abstraction Reactions**

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## Experimental Section

**Materials and Instrumentation.** All chemicals obtained from Aldrich Chemical Co. were the best available purity and used without further purification unless otherwise indicated. Solvents were dried according to published procedures and distilled under Ar prior to use.<sup>[1]</sup> H<sub>2</sub><sup>18</sup>O (95% <sup>18</sup>O-enriched) was purchased from ICON Services Inc. (Summit, NJ, USA). Iodosylbenzene (PhIO), [Cr(TMC)(Cl)](Cl)·2CH<sub>3</sub>CN, and [Cr(TMC)(O<sub>2</sub>)(Cl)](Cl)·2CH<sub>3</sub>CN were prepared according to the literature methods.<sup>[2,3]</sup>

UV-vis spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer equipped with a UNISOKU Scientific Instruments for low-temperature experiments or with a circulating water bath. Fast reactions were monitored using a Hi-Tech Scientific SF-61 DX2 cryogenic stopped-flow spectrometer equipped with a Xe arc lamp and a KinetaScan diode array rapid scanning unit. Electrospray ionization mass spectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQ<sup>TM</sup> Advantage MAX quadrupole ion trap instrument, by infusing samples directly into the source using a manual method. The spray voltage was set at 4.2 kV and the capillary temperature at 80 °C. Resonance Raman spectra were obtained using a liquid nitrogen cooled CCD detector (CCD-1024×256-OPEN-1LS, HORIBA Jobin Yvon) attached to a 1-m single polychromator (MC-100DG, Ritsu Oyo Kogaku) with a 1200 grooves/mm holographic grating. An excitation wavelength of 406.7 nm was provided by a Kr<sup>+</sup> laser (Spectra Physics, BeamLok 2060-RM), with 20 mW power at the sample point. All measurements were carried out with a spinning cell (1000 rpm) at -20 °C. Raman shifts were calibrated with indene, and the accuracy of the peak positions of the Raman bands was ±1 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra were measured with Bruker DPX-400 spectrometer. CW-EPR spectra were taken at 4.3 K using an X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM). Low temperatures were achieved and controlled using an Oxford Instruments ESR900 liquid He quartz cryostat with an Oxford Instruments ITC503 temperature and gas flow controller. Product analysis was performed with an Agilent Technologies 6890N gas chromatograph (GC) and Thermo Finnigan (Austin, Texas, USA) FOCUS DSQ (dual stage quadrupole) mass spectrometer interfaced with Finnigan FOCUS gas chromatograph (GC-MS). Crystallographic analysis was conducted with a SMART APEX CCD equipped with a Mo X-ray tube at the Crystallographic Laboratory of Ewha Womans University.

**Synthesis and Characterization of [Cr(TMC)(CH<sub>3</sub>CN)](ClO<sub>4</sub>)<sub>2</sub>.** [Cr(TMC)(Cl)](Cl)·2CH<sub>3</sub>CN (0.092 g, 0.2 mmol) was dissolved in CH<sub>3</sub>CN (3 mL), to which was added NaClO<sub>4</sub> (0.098 g, 0.8 mmol). The reaction solution was allowed to stand for a few days under N<sub>2</sub>. After slow diffusion of diethyl ether to the resulting solution, blue crystals suitable for X-ray analysis were isolated (Figure S1). Crystalline yield: 0.067 g (61 %). UV-vis (CH<sub>3</sub>CN): λ<sub>max</sub> (ε) = 659 nm (80 M<sup>-1</sup> cm<sup>-1</sup>).

**Synthesis and Characterization of [Cr(TMC)(O)(OCH<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub> (2-(ClO<sub>4</sub>)<sub>2</sub>).** Treatment of [Cr(TMC)(CH<sub>3</sub>CN)](ClO<sub>4</sub>)<sub>2</sub> (8.8 mg, 0.016 mmol) in CH<sub>3</sub>CN (1 mL) with 2 equiv PhIO in CH<sub>3</sub>OH (200

$\mu\text{L}$ ) at  $-30\text{ }^{\circ}\text{C}$  afforded the formation of a dark orange solution. Slow diffusion of diethyl ether dark to the resulting solution afforded orange crystals suitable for X-ray analysis. Crystalline yield: 0.0059 g (56 %). Spectroscopic data, including UV-vis, EPR, ESI-MS, and resonance Raman, were reported in Figure 1.  $[\text{Cr}(\text{TMC})(^{18}\text{O})(\text{OCH}_3)]^{2+}$  (**2**- $^{18}\text{O}$ ) was prepared by adding 2 equiv PhIO, dissolved in  $\text{CH}_3\text{OH}$  (200  $\mu\text{L}$ ) in the presence of  $\text{H}_2^{18}\text{O}$  (10  $\mu\text{L}$ ), to a solution containing  $[\text{Cr}(\text{TMC})(\text{CH}_3\text{CN})(\text{ClO}_4)_2]$  (8.8 mg, 0.016 mmol) in  $\text{CH}_3\text{CN}$  (1 mL) at  $-30\text{ }^{\circ}\text{C}$ .

**Reactivity Studies.** All reactions were run monitoring UV-vis spectral changes of reaction solutions, and rate constants were determined by fitting the changes in absorbance at 549 nm for **1** and 446 nm for **2**. Reactions were run at least in triplicate, and the data reported represent the average of these reactions. The isolated crystalline sample of **2** was used in kinetic studies, such as the oxidation of CHD under stoichiometric conditions in  $\text{CH}_3\text{CN}$  at  $30\text{ }^{\circ}\text{C}$ . For the stopped-flow experiments, the raw kinetic data were treated with KinetAsyst 3 (Hi-Tech Scientific) and Specfit/32 Global Analysis System software from Spectrum software Associates. The purity of substrates was checked with GC and GC-MS prior to use. Products were analyzed by injecting the reaction mixture directly into GC and GC-MS. Products were identified by comparing with authentic samples, and product yields were determined by comparison against standard curves prepared with authentic samples and using decane as an internal standard.

**X-ray Crystallography.** Single crystals of **2**- $(\text{ClO}_4)_2$  were picked from solutions by a nylon loop (Hampton Research Co.) on a hand made copper plate mounted inside a liquid  $\text{N}_2$  Dewar vessel at *ca.*  $-40\text{ }^{\circ}\text{C}$  and mounted on a goniometer head in a  $\text{N}_2$  cryostream. Data collections were carried out on a Bruker SMART APEX II CCD diffractometer equipped with a monochromator in the  $\text{Mo K}\alpha$  ( $\lambda = 0.71073\text{ \AA}$ ) incident beam. The CCD data were integrated and scaled using the Bruker-S SAINT software package, and the structure was solved and refined using SHELXTL V 6.12.<sup>[4]</sup> Hydrogen atoms were located in the calculated positions for **2**- $(\text{ClO}_4)_2$ . Crystal data for **2**- $(\text{ClO}_4)_2$ :  $\text{C}_{15}\text{H}_{35}\text{Cl}_2\text{CrN}_4\text{O}_{10}$ , Orthorhombic, *Pnma*,  $Z = 4$ ,  $a = 14.2150(4)$ ,  $b = 9.7664(3)$ ,  $c = 16.4588(5)\text{ \AA}$ ,  $V = 2284.96(12)\text{ \AA}^3$ ,  $\mu = 0.794\text{ mm}^{-1}$ ,  $\rho_{\text{calcd}} = 1.611\text{ g/cm}^3$ ,  $R_1 = 0.0486$ ,  $wR_2 = 0.2095$  for 2378 unique reflections, 166 variables. The crystallographic data for **2**- $(\text{ClO}_4)_2$  are listed in Table S1, and Table S2 lists the selected bond distances and angles. CCDC-812941 for **2**- $(\text{ClO}_4)_2$  contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## References

- [1] *Purification of Laboratory Chemicals*; W. L. F. Armarego, D. D. Perrin, Eds.; Pergamon Press: Oxford, 1997.

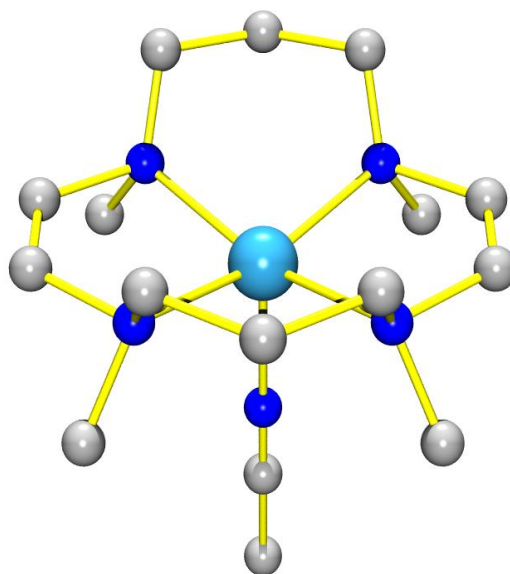
- [2] *Organic Syntheses*, H. Saltzman, J. G. Sharefkin, Eds.; Wiley, New York, 1973, Collect. Vol. V, p. 658.
- [3] J. Cho, J. Woo, W. Nam, *J. Am. Chem. Soc.* **2010**, *132*, 5958-5959.
- [4] G. M. Sheldrick, *SHELXTL/PC*. Version 6.12 for Windows XP. 2001, Bruker AXS Inc., Madison, Wisconsin, USA.

**Table S1.** Crystallographic data and structure refinements for  $[\text{Cr}^{\text{V}}(\text{TMC})(\text{O})(\text{OCH}_3)](\text{ClO}_4)_2, \mathbf{2}-(\text{ClO}_4)_2$ .

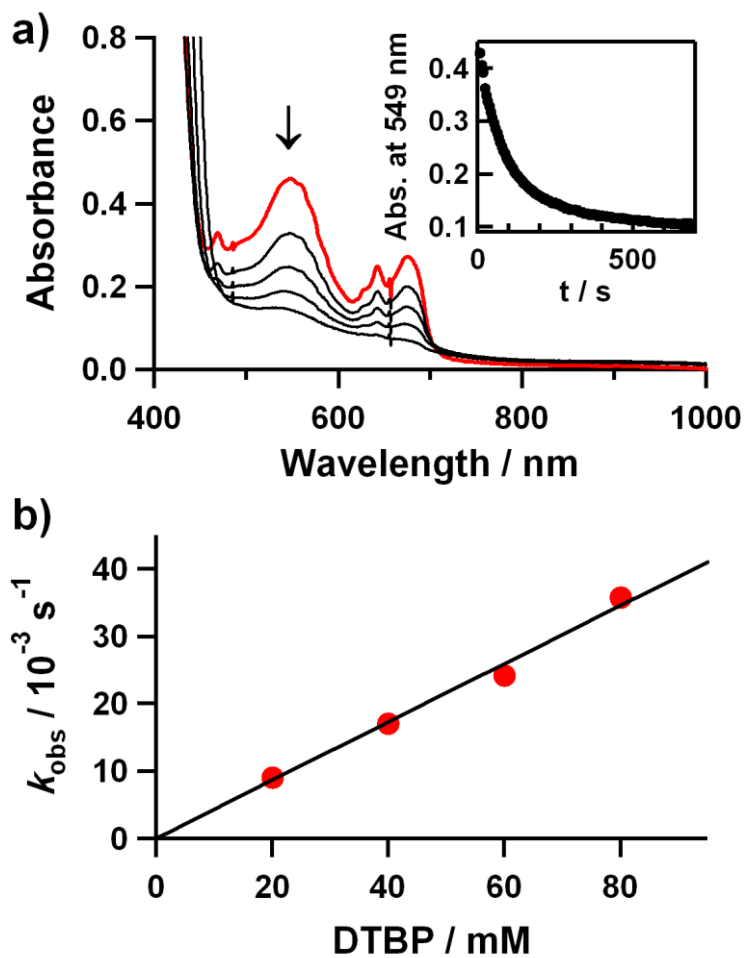
	$\mathbf{2}-(\text{ClO}_4)_2$
Empirical formula	$\text{C}_{15}\text{H}_{35}\text{Cl}_2\text{CrN}_4\text{O}_{10}$
Formula weight	554.37
Temperature (K)	100(2)
Wavelength ( $\text{\AA}$ )	0.71073
Crystal system	Orthorhombic
space group	<i>Pnma</i>
Unit cell dimensions	
<i>a</i> ( $\text{\AA}$ )	14.2150(4)
<i>b</i> ( $\text{\AA}$ )	9.7664(3)
<i>c</i> ( $\text{\AA}$ )	16.4588(5)
$\alpha$ ( $^\circ$ )	90
$\beta$ ( $^\circ$ )	90
$\gamma$ ( $^\circ$ )	90
Volume ( $\text{\AA}^3$ )	2284.96(12)
Z	4
$d_{\text{calcd}}$ ( $\text{g}/\text{cm}^{-3}$ )	1.611
$\mu$ ( $\text{mm}^{-1}$ )	0.794
Reflections collected	34238
Independent reflections [ <i>R</i> (int)]	2378 [0.0329]
Restraints	0
Parameters	166
Goodness-of-fit on $F^2$	1.164
Final <i>R</i> [ $I > 2\sigma(I)$ ]	0.0486
Final <i>wR</i> [ $I > 2\sigma(I)$ ]	0.2021

**Table S2.** Selected bond distances and angles for  $[\text{Cr}^{\text{V}}(\text{TMC})(\text{O})(\text{OCH}_3)](\text{ClO}_4)_2 \cdot 2-(\text{ClO}_4)_2$ .

Bond distances (Å)			
Cr1-O1	1.604(3)	Cr1-O2	1.765(3)
Cr1-N1	2.122(2)	Cr1-N2	2.148(2)
Bond angles (°)			
O1-Cr1-O2	178.39(13)	O1-Cr1-N1	85.99(9)
O1-Cr1-N2	89.03(9)	O2-Cr1-N1	92.97(9)
O2-Cr1-N2	92.07(9)	N1-Cr1-N1'	98.61(12)
N1-Cr1-N2	174.15(9)	N1-Cr1-N2'	174.15(9)
N2-Cr1-N2'	92.77(13)	C9-O2-Cr1	176.7(3)

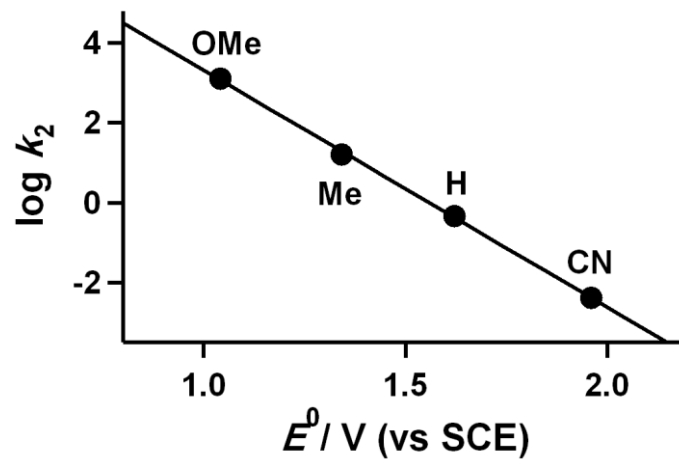


**Fig. S1.** Ball and stick model of the  $[\text{Cr}(\text{TMC})(\text{CH}_3\text{CN})]^{2+}$  cation in  $[\text{Cr}(\text{TMC})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$  (C, gray; N, blue; Cr, sky blue). Crystals suitable for X-ray analysis were obtained using  $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$  (vapour diffusion). Although the crystal structure of  $[\text{Cr}(\text{TMC})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$  is plagued by problems associated with the high degree of disorder, the data were sufficient to confirm a 5-coordinate Cr(II) site in an approximate square pyramidal geometry, similar to that of  $[\text{Cr}(\text{TMC})(\text{Cl})](\text{Cl}) \cdot 2\text{CH}_3\text{CN}$ .<sup>[3]</sup>

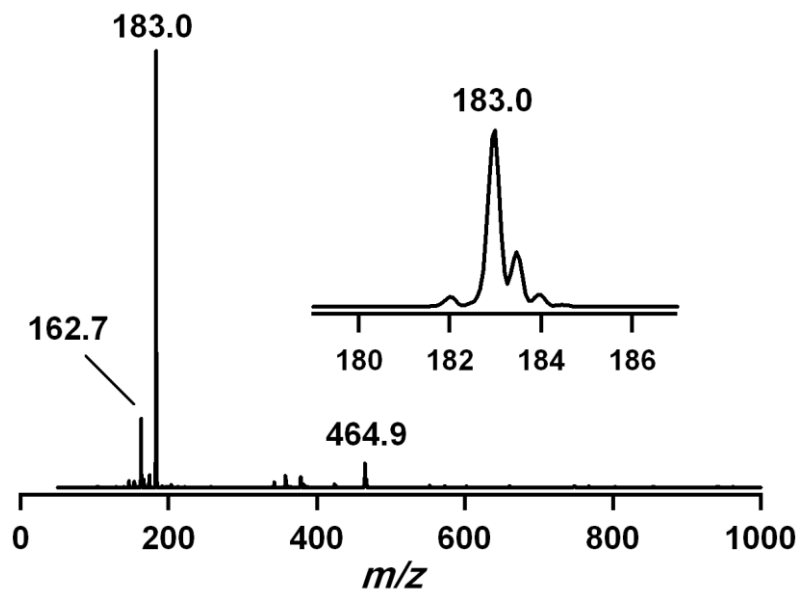


**Fig. S2.** Reaction of  $[\text{Cr}^{\text{III}}(\text{TMC})(\text{O}_2)(\text{Cl})]^+$  (**1**) with 2,6-di-*tert*-butylphenol (DTBP) in  $\text{CH}_3\text{CN}$  at  $-40^\circ\text{C}$ . a) UV-vis spectral changes of **1** (2 mM) upon addition of 10 equiv of DTBP. Inset shows the time course of the absorbance at 549 nm. b) Plot of  $k_{\text{obs}}$  against DTBP concentration to determine a second-order rate constant.

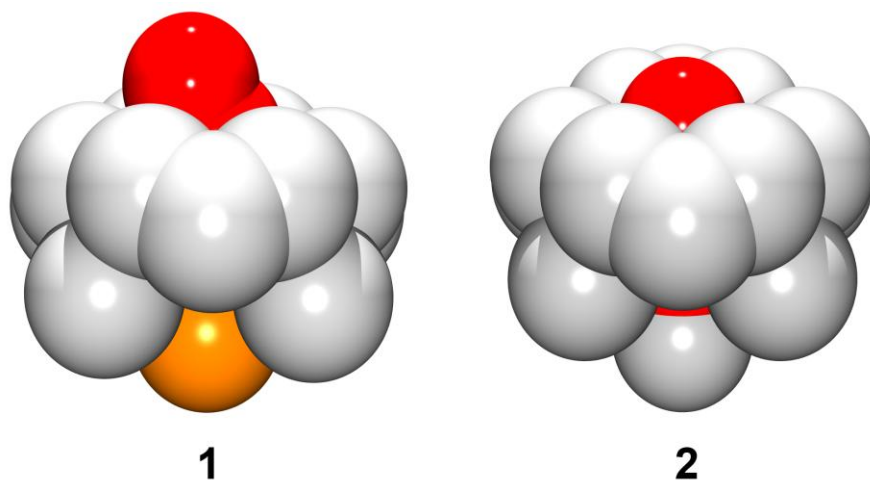




**Fig. S3.** Plot of  $\log k_2$  of **1** against O-H redox potentials of *para*-Y-2,6-*t*Bu<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>OH in CH<sub>3</sub>CN at –40 °C. The data (*p*-OMe, 1.04 V; *p*-Me, 1.34 V; *p*-H, 1.62 V; *p*-CN, 1.96 V) were determined by SHACV in CH<sub>3</sub>CN.



**Fig. S4.** ESI-MS taken after the completion of the reaction of  $[\text{Cr}^{\text{V}}(\text{TMC})(\text{O})(\text{OCH}_3)]^{2+}$  (**2**) with cyclohexadiene (CHD) in  $\text{CH}_3\text{CN}$  at 30 °C: Mass peaks at 162.7, 183.0 and 464.9 are assigned to  $[\text{Cr}^{\text{III}}(\text{TMC})(\text{OH})]^{2+}$ ,  $[\text{Cr}^{\text{III}}(\text{TMC})(\text{OH})(\text{CH}_3\text{CN})]^{2+}$  and  $[\text{Cr}^{\text{III}}(\text{TMC})(\text{OH})(\text{ClO}_4)]^+$ , respectively.



**Fig. S5.** Comparison of space-filling models of  $[\text{Cr}^{\text{III}}(\text{TMC})(\text{O}_2)(\text{Cl})]^+$  (**1**) and  $[\text{Cr}^{\text{V}}(\text{TMC})(\text{O})(\text{OCH}_3)]^{2+}$  (**2**) derived from their single crystal structures (oxygen, red; carbon, gray; chloride, orange).