

## Supplementary Information

### Reactivity of a Cobalt(III)-Hydroperoxo Complex in Electrophilic Reactions†

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## Experimental Section

### Synthesis of Ligands

**3,6,9,15-tetraazabicyclo[9,3,1]pentadeca-1(15),11,13-triene (pyclen).** **pyclen** was synthesized by a modification of a previously reported procedure.<sup>[1],[2]</sup> To a stirred DMF solution of 2,6-bis(chloromethyl)pyridine (2.2 g, 12.3 mmol) and K<sub>2</sub>CO<sub>3</sub> (5.1 g, 37.1 mmol) was slowly added 1,4,7-tris(p-tosylsulfonyl)-1,4,7-triazaheptane (7.0 g, 12.3 mmol). Upon stirring for 12 hours, excess of ice water was added to the mixture until white precipitate formed. The precipitate was collected by filtration. This white powder in H<sub>2</sub>SO<sub>4</sub> were heated at reflux (80 ~ 100 °C). An ordinary work-up treatment of the reaction mixture with NaOH followed by extraction with CHCl<sub>3</sub> and evaporation gave an organic product, as a yellow oil. Yield: 0.79 g (31%), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.21(4H, s, CH<sub>2</sub>), 2.65 (4H, t, CH<sub>2</sub>), 3.92 (4H, s, CH<sub>2</sub>), 6.96 (2H, d, PyH), 7.48 (1H, t, PyH). ESI-MS (in CH<sub>3</sub>CN): *m/z* 207.2 [M + H]<sup>+</sup>.

**3,6,9-trimethyl-3,6,9-triaza-1(2,6)-pyridinacyclodecaphane (Me<sub>3</sub>-TPADP).** Formaldehyde 37% (3.1 ml, 40.3 mmol) and formic acid (3.1 ml, 40.3 mmol) was slowly added to **pyclen** (0.79 g, 3.83 mmol) in an ice bath over 30 mins, and stirring over 1 hour in an ice bath. The mixture solvent was then heated at reflux (100 ~ 120 °C). An ordinary work-up treatment of the reaction mixture with NaOH followed by extraction with CH<sub>2</sub>Cl<sub>2</sub> and evaporation gave an organic product, as a yellow oil.<sup>[3]</sup> Yield: 0.88 g (93%), <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.15 (3H, s, CH<sub>3</sub>), 2.46-2.62 (14H, m, CH<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>), 3.77 (4H, s, PyCH<sub>2</sub>), 7.11 (2H, m, PyH), 7.57 (1H, t, PyH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 400 MHz): δ 157.8, 136.8, 62.7, 67.9, 53.2, 52.4, 45.2, 44.7. ESI-MS (in CH<sub>3</sub>CN): *m/z* 249.2 [M + H]<sup>+</sup>.

### Preparation of a Precursor Complex

**[Co(Me<sub>3</sub>-TPADP)(CH<sub>3</sub>CN)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.** Me<sub>3</sub>-TPADP (0.18 g, 0.5 mmol) was added to a CH<sub>3</sub>CN solution of Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.12 g, 0.5 mmol). The mixture was stirred for 12 hours, giving a purple solution. Diethyl ether (40 mL) was added to the the resulting solution to yield a violet powder, which was collected by filtration, washed with diethyl ether, and dried in vacuo. Yield: 0.15 g (87%). UV-vis (CH<sub>3</sub>CN): λ<sub>max</sub> (ε) = 498 nm (80 M<sup>-1</sup> cm<sup>-1</sup>). ESI-MS (CH<sub>3</sub>CN): *m/z* 174.2 for [Co(Me<sub>3</sub>-TPADP)(CH<sub>3</sub>CN)]<sup>2+</sup>, *m/z* 194.7 for [Co(Me<sub>3</sub>-TPADP)(CH<sub>3</sub>CN)<sub>2</sub>]<sup>2+</sup>, and *m/z* 406.2 for [Co(Me<sub>3</sub>-TPADP)(ClO<sub>4</sub>)]<sup>+</sup>. Anal. Calcd for C<sub>18</sub>H<sub>30</sub>Cl<sub>2</sub>CoN<sub>6</sub>O<sub>8</sub>: C, 36.75; H, 5.14; N, 14.29. Found: C, 37.03; H, 5.103; N, 14.29. μ<sub>eff</sub> = 4.5 BM. X-ray crystallographically suitable crystals were obtained by slow diffusion of Et<sub>2</sub>O into a solution of the complex in CH<sub>3</sub>CN. Crystalline yield: 0.23 g (44%).

**Table S1.** Crystal Data and Structure Refinements for [Co(Me<sub>3</sub>-TPADP)(CH<sub>3</sub>CN)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1**-(ClO<sub>4</sub>)<sub>2</sub>).

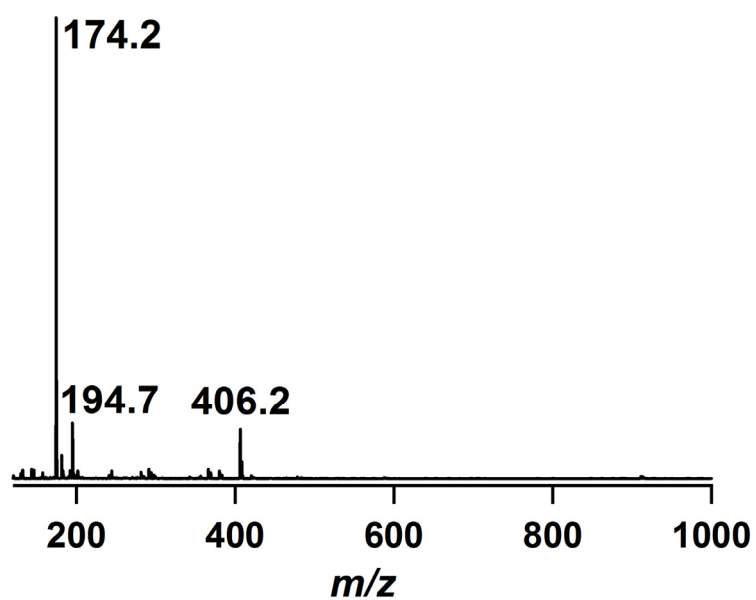
	<b>1</b> -(ClO <sub>4</sub> ) <sub>2</sub>
Empirical formula	C <sub>18</sub> H <sub>30</sub> Cl <sub>2</sub> CoN <sub>6</sub> O <sub>8</sub>
Formula weight	588.31
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system/space group	monoclinic, <i>P2<sub>1</sub>/n</i>
Unit cell dimensions	
<i>a</i> (Å)	15.7400(3)
<i>b</i> (Å)	19.7237(4)
<i>c</i> (Å)	16.3257(3)
<i>α</i> (°)	90.00
<i>β</i> (°)	97.6290(10)
<i>γ</i> (°)	90.00
Volume (Å <sup>3</sup> )	5023.47(17)
<i>Z</i>	8
Calculated density (g/cm <sup>-3</sup> )	1.556
Absorption coefficient (mm <sup>-1</sup> )	0.951
Reflections collected	12456
Independent reflections [ <i>R</i> (int)]	641 [0.0155]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	12456/0/641
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.019
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0345, <i>wR</i> <sub>2</sub> = 0.0890
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0384, <i>wR</i> <sub>2</sub> = 0.0926

**Table S2.** Selected bond distances (Å) and angles (°) for [Co(Me<sub>3</sub>-TPADP)(CH<sub>3</sub>CN)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**1A**-(ClO<sub>4</sub>)<sub>2</sub> and **1B**-(ClO<sub>4</sub>)<sub>2</sub>).

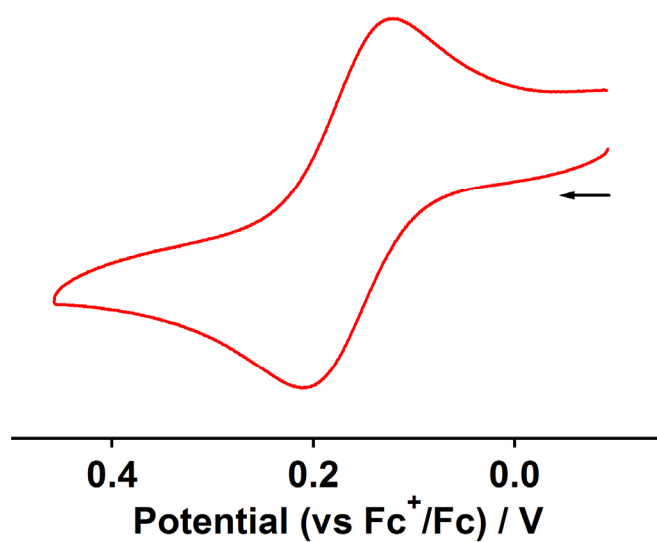
Bond Distances (Å)			
<b>1A</b> -(ClO <sub>4</sub> ) <sub>2</sub>		<b>1B</b> -(ClO <sub>4</sub> ) <sub>2</sub>	
Co1-N1	2.0574(14)	Co2-N7	2.0485(14)
Co1-N2	2.1999(14)	Co2-N8	2.1997(14)
Co1-N3	2.2108(14)	Co2-N9	2.2227(14)
Co1-N4	2.2050(14)	Co2-N10	2.1951(14)
Co1-N5	2.0514(15)	Co2-N11	2.0570(15)
Co1-N6	2.1151(15)	Co2-N12	2.1329(15)
Bond Angles (°)			
<b>1A</b> -(ClO <sub>4</sub> ) <sub>2</sub>		<b>1B</b> -(ClO <sub>4</sub> ) <sub>2</sub>	
N1-Co1-N2	78.56(5)	N7-Co2-N8	78.79(6)
N1-Co1-N3	90.66(5)	N7-Co2-N9	90.86(5)
N1-Co1-N4	78.82(5)	N7-Co2-N10	79.01(5)
N1-Co1-N5	177.17(6)	N7-Co2-N11	176.06(6)
N1-Co1-N6	87.70(5)	N7-Co2-N12	87.30(6)
N2-Co1-N3	81.91(5)	N8-Co2-N9	82.59(5)
N2-Co1-N4	152.06(5)	N8-Co2-N10	152.23(5)
N2-Co1-N5	101.96(6)	N8-Co2-N11	100.38(6)
N2-Co1-N6	95.15(6)	N8-Co2-N12	100.66(6)
N3-Co1-N4	82.19(5)	N9-Co2-N10	81.28(5)
N3-Co1-N5	92.16(6)	N9-Co2-N11	92.85(6)
N3-Co1-N6	176.87(5)	N9-Co2-N12	175.88(6)
N4-Co1-N5	101.45(6)	N10-Co2-N11	102.85(6)
N4-Co1-N6	100.10(6)	N10-Co2-N12	94.74(6)
N5-Co1-N6	89.48(6)	N11-Co2-N12	89.08(6)

**Table S3.** Geometric parameters and Mayer bond orders for  $S = 1$  Fe<sup>IV</sup>=O,  $S = 1/2$  Co<sup>IV</sup>=O, and  $S = 3/2$  Co<sup>IV</sup>=O complexes.

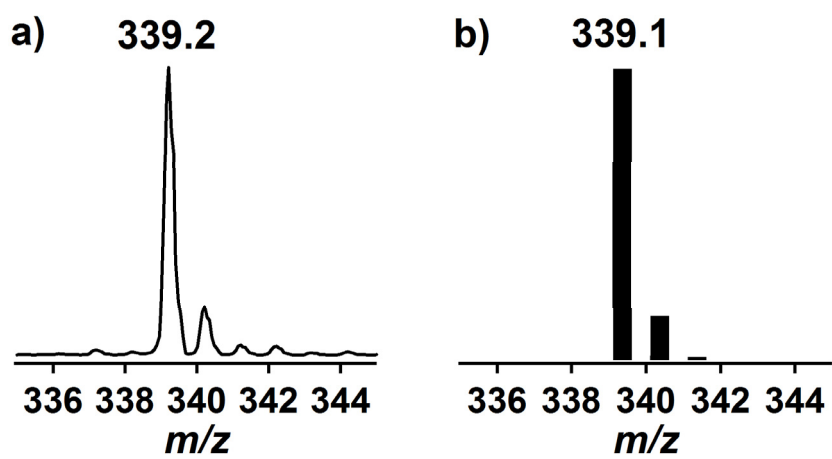
	$S = 1/2$ Co <sup>IV</sup> =O	$S = 3/2$ Co <sup>IV</sup> =O	$S = 1$ Fe <sup>IV</sup> =O
M-O length (Å)	1.79	1.62	1.64
M-O Mayer bond order	1.14	1.85	1.39
M-L <sub>equatorial</sub> length (average)	2.03	2.17	2.07
M-L <sub>equatorial</sub> Mayer bond order (total)	2.29	1.74	2.16



**Figure S1.** ESI-MS of **1** in CH<sub>3</sub>CN at 25 °C. Mass peaks at 174.2, 194.7 and 406.2 are assigned to [Co(Me<sub>3</sub>-TPADP)(CH<sub>3</sub>CN)]<sup>2+</sup>, [Co(Me<sub>3</sub>-TPADP)(CH<sub>3</sub>CN)<sub>2</sub>]<sup>2+</sup> and [Co(Me<sub>3</sub>-TPADP)(ClO<sub>4</sub>)]<sup>+</sup>, respectively.

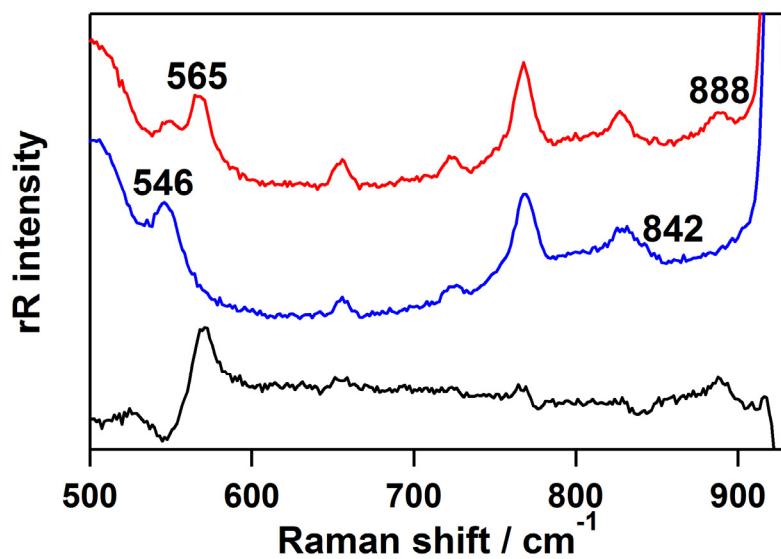


**Figure S2.** Cyclic voltammogram of **1** in CH<sub>3</sub>CN (1 mM) containing 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> at room temperature (working electrode, Pt; counter electrode, Pt; reference electrode, Ag/Ag<sup>+</sup>; scan rate = 100 mV).

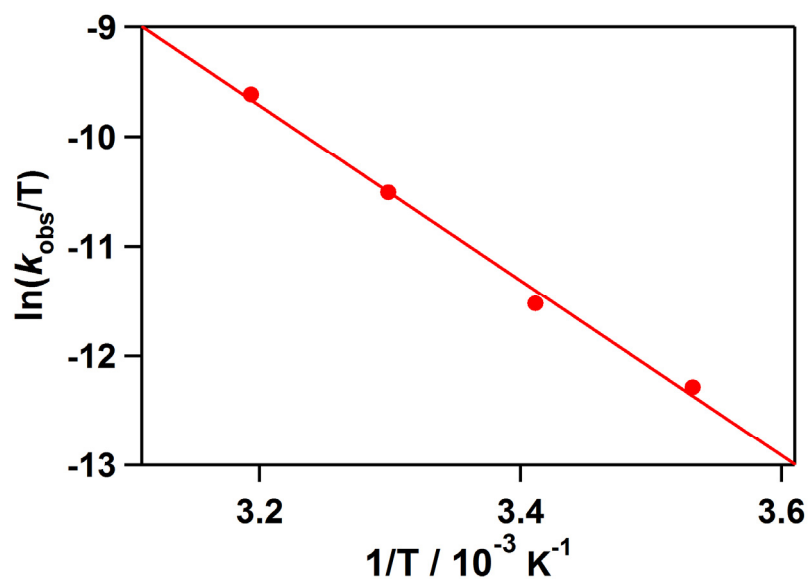


**Figure S3.** (a) Experimental and (b) calculated ESI-MS of  $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{O}_2)]^+$  (2).

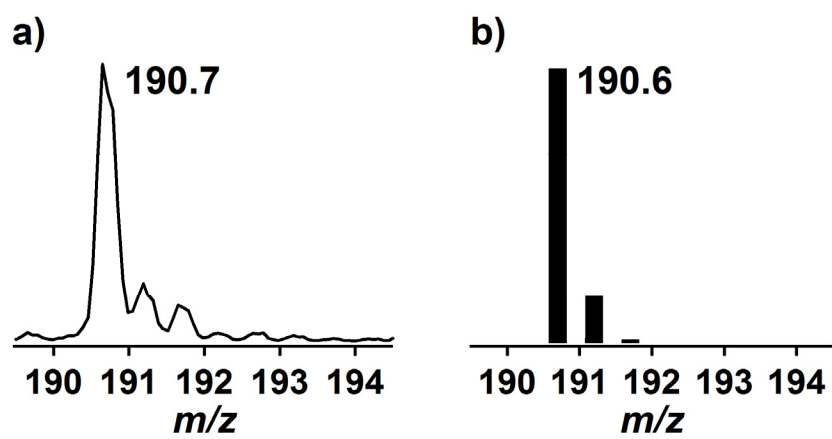




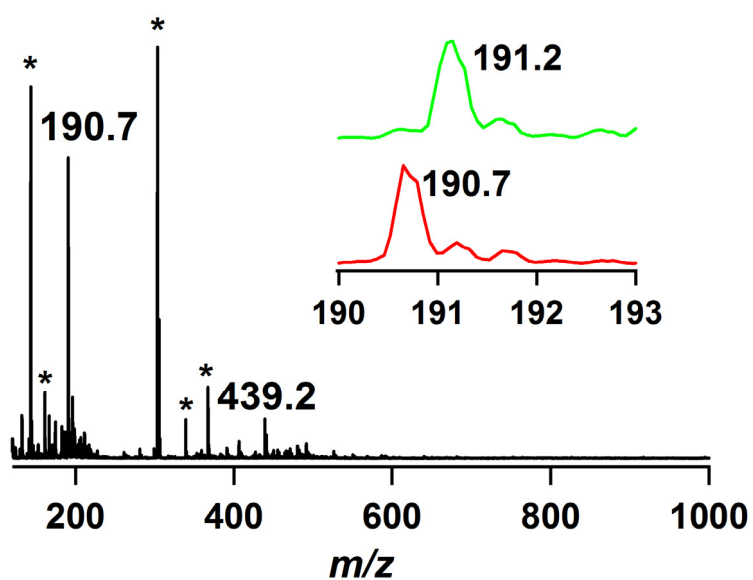
**Figure S4.** Resonance Raman spectra of **2** prepared with  $\text{H}_2^{16}\text{O}_2$  (red line) and  $\text{H}_2^{18}\text{O}_2$  (blue line) obtained upon excitation at 355 nm in  $\text{CH}_3\text{CN}$  at  $-30\text{ }^\circ\text{C}$ . Black line shows subtraction of the spectra prepared with  $\text{H}_2^{16}\text{O}_2$  and  $\text{H}_2^{18}\text{O}_2$ .



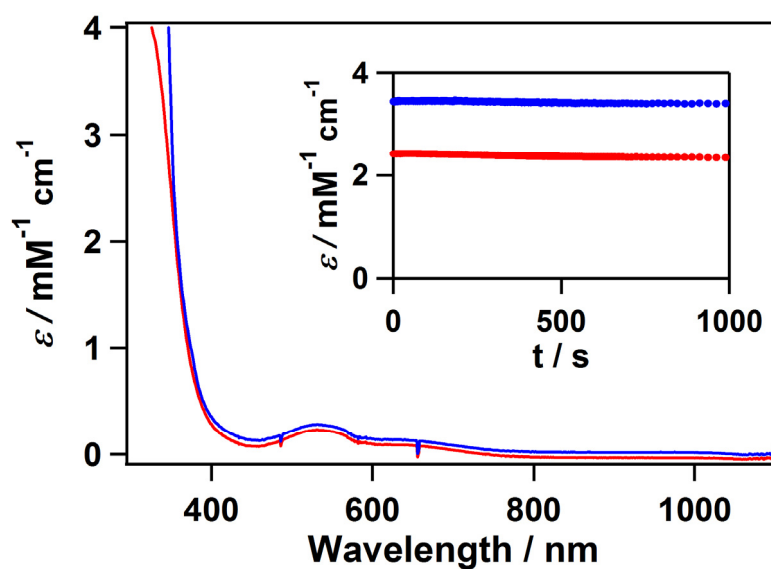
**Figure S5.** Plot of first-order rate constants against  $1/T$  to determine activation parameters for the decay of **3** (0.5 mM).



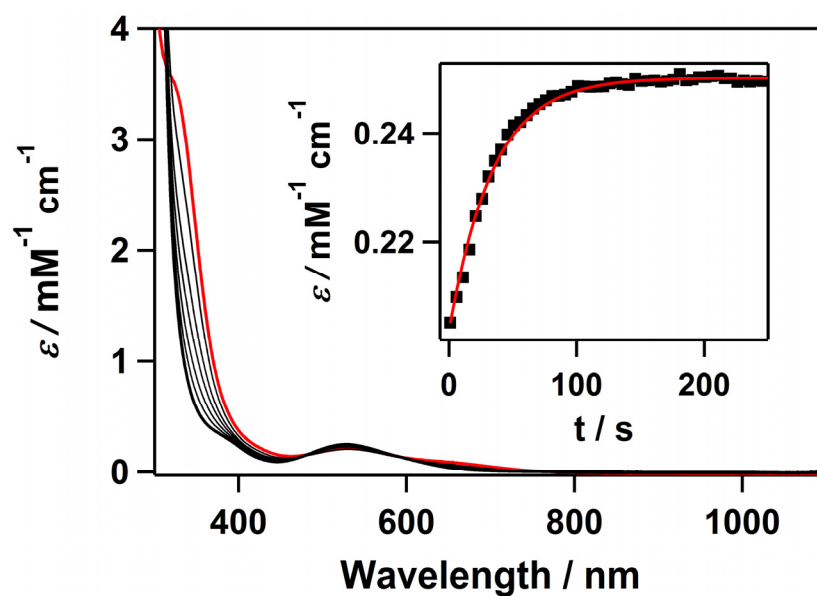
**Figure S6.** (a) Experimental and (b) calculated ESI-MS of  $[\text{Co}(\text{Me}_3\text{-TPADP})(\text{O}_2\text{H})(\text{CH}_3\text{CN})]^{2+}$  (**3**).



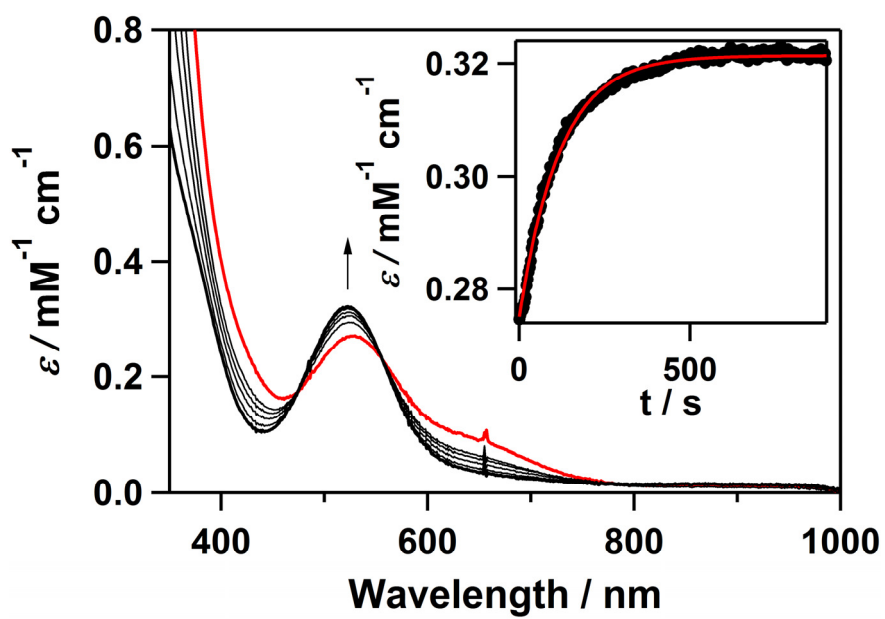
**Figure S7.** ESI-MS of **3** in CH<sub>3</sub>CN at -40 °C. Asterisks are some unidentified species due to the thermal instability. Insets show the observed isotope distribution patterns for [Co(Me<sub>3</sub>-TPADP)(<sup>16</sup>O<sub>2</sub>H)(CH<sub>3</sub>CN)]<sup>2+</sup> (lower) and [Co(Me<sub>3</sub>-TPADP)(<sup>16</sup>O<sub>2</sub><sup>2</sup>H)(CH<sub>3</sub>CN)]<sup>2+</sup> (upper, calcd *m/z* 191.1).



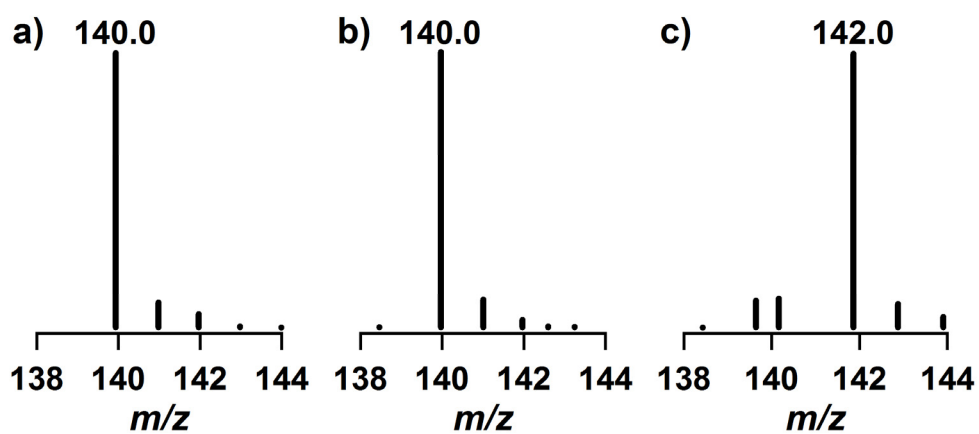
**Figure S8.** UV-vis spectral changes of **3** (0.5 mM) upon addition of 100 equiv of cyclohexadiene (red line) and xanthene (blue line) in  $\text{CH}_3\text{CN}$  at  $-40^\circ\text{C}$ . Inset shows the time course of the absorbance at 350 nm.



**Figure S9.** UV-vis spectral changes of **3** (0.5 mM) upon addition of 10 equiv of PPh<sub>3</sub> at –20 °C. Inset shows the time course of the absorbance at 523 nm and its first-order fitting (red line).

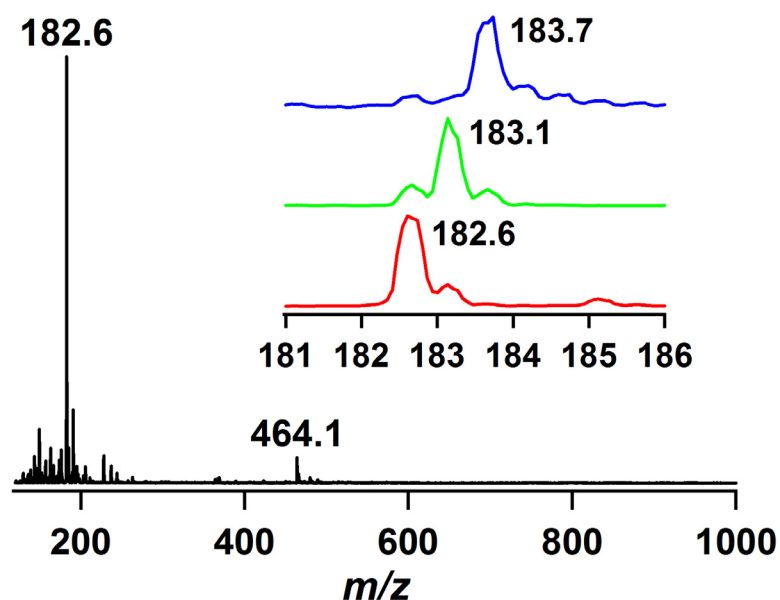


**Figure S10.** UV-vis spectral changes of **3** (0.5 mM) upon addition of 25 equiv of thioanisole at  $-40$  °C. Inset shows the time course of the absorbance at 523 nm and its first-order fitting (red line).

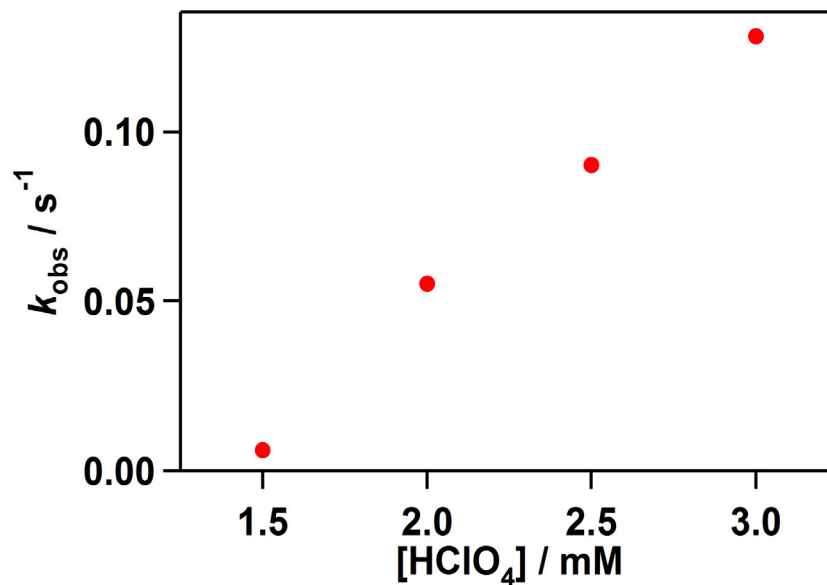


**Figure S11.** GC-MS spectra of  $\text{PhS(O)CH}_3$ ; (a) standard  $\text{PhS}^{(16)\text{O}}\text{CH}_3$ , (b)  $\text{PhS}^{(16)\text{O}}\text{CH}_3$  obtained from the reaction of **3** with  $\text{PhSCH}_3$ , and (c)  $\text{PhS}^{(18)\text{O}}\text{CH}_3$  obtained from the reaction of  $^{18}\text{O}$ -labeled **3** with  $\text{PhSCH}_3$ .

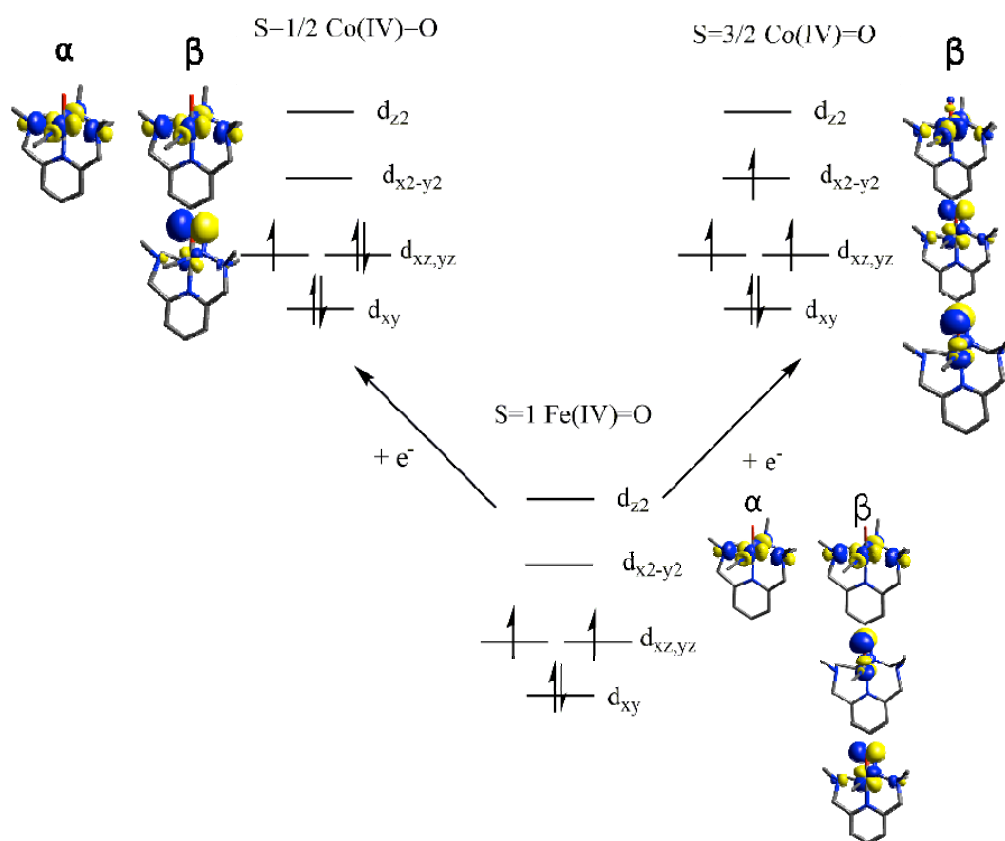




**Figure S12.** ESI-MS taken after the completion of the reaction of **3** with thioanisole in CH<sub>3</sub>CN at –20 °C, showing the formation of a Co(III)-hydroxo complex: Mass peaks at *m/z* of 182.6 and 464.1 are assigned to [Co(Me<sub>3</sub>-TPADP)(OH)(CH<sub>3</sub>CN)]<sup>2+</sup> (calcd *m/z* 182.6) and [Co(Me<sub>3</sub>-TPADP)(OH)(CH<sub>3</sub>CN)(ClO<sub>4</sub>)]<sup>+</sup> (calcd *m/z* 464.1), respectively. Insets show the observed isotope distribution patterns for [Co(Me<sub>3</sub>-TPADP)(OH)(CH<sub>3</sub>CN)]<sup>2+</sup> (red line), [Co(Me<sub>3</sub>-TPADP)(O<sup>2</sup>H)(CH<sub>3</sub>CN)]<sup>2+</sup> (green line, calcd *m/z* 183.1), [Co(Me<sub>3</sub>-TPADP)(<sup>18</sup>OH)(CH<sub>3</sub>CN)]<sup>2+</sup> (blue line, calcd *m/z* 183.6).



**Figure S13.** Plot of pseudo-first-order rate constants ( $k_{\text{obs}}$ ) against concentrations of  $\text{HClO}_4$  in the reactions of adding 25 equiv of thioanisole to different equivalent of  $\text{HClO}_4$  with  $[\text{Co}^{\text{III}}(\text{Me}_3\text{-TPADP})(\text{O}_2)]^+$  (**2**) (0.5 mM) at  $-40\text{ }^\circ\text{C}$ .



**Figure S14.** Unoccupied orbitals (excluding  $d_{22}$ ) and electronic structure schemes for  $S = 1$   $\text{Fe}^{\text{IV}}=\text{O}$ ,  $S = 1/2$   $\text{Co}^{\text{IV}}=\text{O}$ , and  $S = 3/2$   $\text{Co}^{\text{IV}}=\text{O}$  complexes.

## References

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- [3] Serrano-Plana, J.; Oloo, W. N.; Acosta-Rueda, L.; Meier, K. K.; Verdejo, B.; García-España, E.; Basallote, M. G.; Münck, E.; Que, L., Jr.; Company, A.; Costas, M. Trapping a Highly Reactive Nonheme Iron Intermediate That Oxygenates Strong C–H Bonds with Stereoretention. *J. Am. Chem. Soc.* **2015**, 137, 15833-15842.