

Supporting Information

For

Formation of the *syn* Isomer of $[\text{Fe}^{\text{IV}}(\text{O}_{\text{anti}})(\text{TMC})(\text{NCMe})]^{2+}$ in the Reaction of Lewis Acids with the Side-on Bound Peroxo Ligand in $[\text{Fe}^{\text{III}}(\eta^2\text{-O}_2)(\text{TMC})]^+$

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Experimental Section:

General Considerations

All reagents were purchased from commercial sources and used as received, unless otherwise noted. The complex, $\text{Fe}^{\text{II}}(\text{TMC})(\text{OTf})_2$,¹ and iodosylbenzene ($\text{C}_6\text{H}_5\text{IO}$)² were synthesized according to previously published procedures. The complex $[\text{Fe}^{\text{III}}(\eta^2\text{-O}_2)(\text{TMC})](\text{ClO}_4)$ was synthesized following an earlier reported procedure with a minor variation.³ All moisture and oxygen sensitive compounds were prepared using standard Schlenk-line techniques, and a nitrogen-filled glove box was used for any subsequent manipulation and storage of these compounds.

Physical Methods

NMR spectra were recorded in deuterated solvents using either Varian Inova/Bruker 400 or 300 MHz spectrometers, and chemical shifts (ppm) were referenced to residual protic solvent peaks. UV-vis spectroscopic measurements were performed using a HP8453A diode array spectrometer equipped with a cryostat from Unisoku Scientific Instruments (Osaka, Japan). Electrospray-ionization mass spectrometry (ESI-MS) experiments were carried out on a Bruker BioTOF II mass spectrometer using a spray chamber voltage of 4000 V and a carrier gas temperature of 25 °C.

Synthesis of $[\text{Fe}^{\text{III}}(\eta^2\text{-O}_2)(\text{TMC})](\text{ClO}_4)$ (2): To the methanolic solution of $\text{Fe}^{\text{II}}(\text{TMC})(\text{OTf})_2$ (20 mg in 2 mL) at -40 °C was added 10 equiv. of H_2O_2 and 20 equiv. of Et_3N , and the solution was stirred for 30 min to give greenish-blue solution. To this solution was added 10 equiv. of the solid NaClO_4 followed by cold diethyl ether (10 mL, kept at -40 °C) to precipitate out **2** as purple solid. The solvents were carefully decanted and the solid was dried under vacuum at -10 °C. The dried solid was further washed several times with cold diethyl ether to remove any unreacted Et_3N and H_2O_2 .

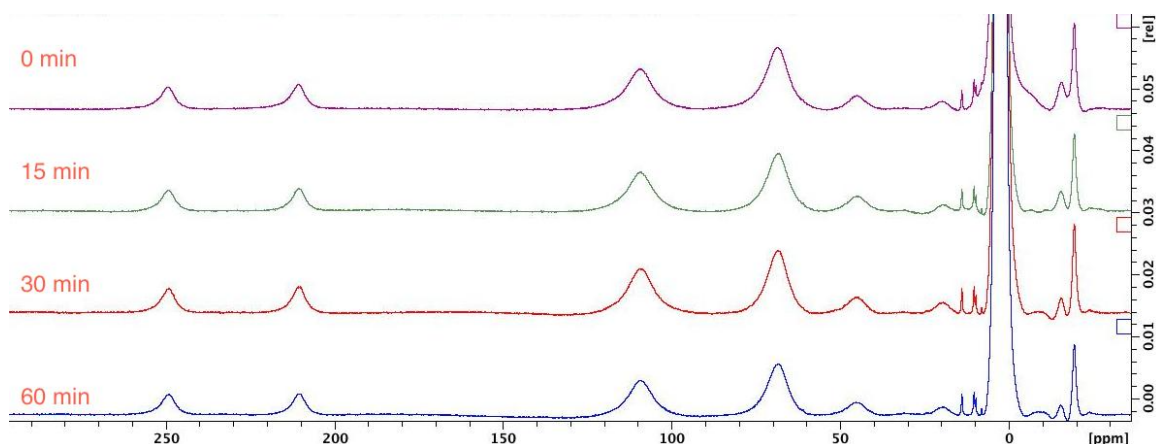


Figure S1. ^1H -NMR spectra of species **2**, recorded in CD_3CN at $-10\text{ }^\circ\text{C}$ over a period of one hour. The resonances at 68 and 109 ppm correspond to the N-Me protons with line widths (full width at half maximum, FWHM) of 3000 and 3200 Hz respectively. There was no evident change observed in the spectra during this period.

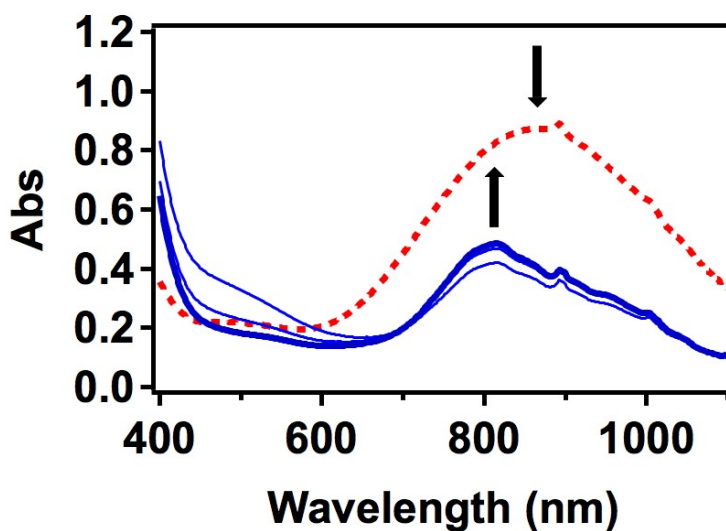


Figure S2. UV-vis spectral change upon addition of 1 equiv. of $[\text{NO}][\text{SbF}_6]$ to an acetonitrile solution of **2** (1.5 mM, red dotted line) at $-10\text{ }^\circ\text{C}$ to give **1S**.

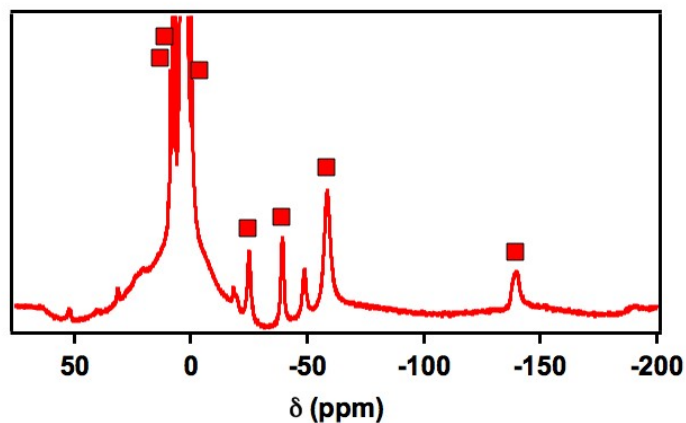


Figure S3. ^1H -NMR spectra of **1S** (marked with “■”) from the reaction of **2** (10 mM) with 1 equiv. of $[\text{NO}][\text{SbF}_6]$ at $-10\text{ }^\circ\text{C}$ in CD_3CN . Integration of the N-Me resonances (-48 for **1A** and -55 ppm for **1S**) gives a ratio of $\sim 5:1$ for **1S/1A**.

References:

1. J.-U. Rohde, J.-H. In, M. H. Lim, W. W. Brennessel, M. R. Bukowski, A. Stubna, E. Münck, W. Nam and L. Que, Jr., *Science*, 2003, **299**, 1037-1039.
2. Saltzman, H.; Sharefkin, J. G. *Org. Synth.*, 1963, **43**, 60-61.
3. F. Li, K. M. Van Heuvelen, K. K. Meier, E. Münck and L. Que, Jr., *J. Am. Chem. Soc.*, 2013, **135**, 10198-10201.