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Supporting Information

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Characterization of a High-Spin Non-Heme $\{FeNO\}^8$ Complex: Implications for the Reactivity of Iron Nitroxyl Species in Biology**

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Synthesis. In general, reactions were performed using inert gas (Schlenk) techniques. Preparation and handling of air sensitive materials was carried out under nitrogen atmosphere in an MBraun glovebox equipped with a circulating purifier (O_2, H_2O < 0.1 ppm). Solvents and reagents were purchased and used as supplied except as follows. All solvents were dried over CaH_2, distilled, and freeze-pump-thawed to remove dioxygen. Nitric oxide (Cryogenic Gases Inc., 99.5%) was purified by passing through an ascarite II column (NaOH on silica) and then through a cold trap at -60°C in order to remove higher nitrogen oxide impurities. Nitric oxide-^{15}NO (Cambridge Isotope Labs, 98+% ^{15}N) was used without further purification. Bis(pentamethylcyclopentadienyl)cobalt(II) (CoCp*$_2$) was purified by vacuum sublimation at approximately 50°C and stored in the dark under inert atmosphere at -33°C prior to use.

Chlorotetramethylformamidinium chloride[1] and 1,1,1-tris{2-[*N*^{2}-(1,1,3,3-tetramethylguanidinio)]ethyl}amine[2] (TMG$_3$tren) were synthesized following reported procedures.

[Fe(TMG$_3$tren)(CH$_3$CN)](OTf)$_2$. In a procedure modified from the literature[2], 410 mg iron(II) trifluoromethanesulfonate (1.16 mmol) and 559 mg TMG$_3$tren (1.27 mmol, 1.09 equivalents) were combined in 4 mL CH_3CN in a glovebox. The reaction was stirred for 2 hours, and then filtered to remove impurities. Approximately 25 mL diethyl ether was added to the filtrate, and the reaction was allowed to precipitate at -33°C overnight. The resulting white solid was isolated by vacuum filtration and washed with diethyl ether. Yield: 807

[1] M. P. Lanci, V. V. Smirnov, C. J. Cramer, E. V. Gauchenova, J. Sundermeyer, J. P. Roth, *J. Am. Chem. Soc.* **2007**, *129*, 14697-14709.
[2] H. Wittmann, V. Raab, A. Schorm, J. Plackmeyer, J. Sundermeyer, *Eur. J. Inorg. Chem.* **2001**, 1937-1948.

mg, 83.4%. FT-IR (KBr pellet, see Figure S2): 2899, 2272 [ν(C≡N)], 1557 [ν(C=N)], 1398, 1265, 1164, 1145, 1029, 637 cm^{-1}. ^{1}H NMR (400 MHz, CD_3CN, all peaks appear as broad singlets): δ = 210.0 (3H), 86.0 (3H), 60.4 (3H), 33.8 (9H), 20.7 (9H), 10.0 (9H), -13.0 (9H) ppm.

[Fe(TMG_3tren)(NO)]$(OTf)_2$ (1). In a dry Schlenk flask, 830 mg [Fe(TMG_3tren)(CH_3CN)]$(OTf)_2$ were taken up in 3 mL CH_3CN. The solution was exposed to excess NO gas, causing a color change from clear to black. The reaction was stirred under NO atmosphere for 1 hour, at which point approximately 40 mL diethyl ether were added. The reaction was allowed to precipitate overnight at -33°C. The solution was filtered through a Schlenk frit, yielding a microcrystalline black solid. Yield: 640 mg, 78.1%. UV-Vis (CH_3CN, see Figure 1): 368 nm (ε=6,272) $M^{-1}cm^{-1}$), 569 nm (ε=336 $M^{-1}cm^{-1}$), 800 nm (ε=143 $M^{-1}cm^{-1}$). FT-IR (KBr pellet, see Figure S1): 2941, 1730 [ν(N=O), ν(^{15}N=O)=1700], 1544 [ν(C=N)], 1402, 1263, 1165, 1144, 1028, 637 cm^{-1}. (Note that ν(N-O) for solid **1** varies between 1730 cm^{-1} and 1745 cm^{-1} depending on the conditions of the preparation. Regardless, the complex shows ν(N-O) = 1748 cm^{-1} when redissolved in CH_2Cl_2 or CH_3CN solution.) ^{1}H NMR (400 MHz, CD_3CN, all signals appear as broad singlets, see Figure S8): δ= 191.8 (3H), 164.2 (3H), 92.4 (3H), 39.7 (12H), 37.6 (12H), 32.8 (12H), 9.0 (3H) ppm. Anal. Calcd. For $C_{23}H_{48}F_6FeN_{11}O_7S_2$: C, 33.50; H, 5.87; N, 18.68. Found: C, 33.50; H, 5.90; N, 18.64.

Red plate crystals suitable for x-ray diffraction were grown by vapor diffusion of diethyl ether into a concentrated CH_2Cl_2 solution of **1** at -33°C.

Electrochemical generation of 2. Under inert atmosphere, 30.7 mg (37.2 μmol) **1** were dissolved in 9.0 mL of 0.1 M NBu_4ClO_4 in CH_3CN. Using a two-compartment bulk electrolysis cell (described below), the sample was reduced at -1.0 V vs Ag wire until 1.05 equivalents of charge (3.3 C) had been passed, giving **2**. UV-Vis (CH_3CN, see Figure 1): 360 nm (ε=1912 $M^{-1}cm^{-1}$), 703 nm (ε=120 M^{-1} cm^{-1}); FT-IR (CH_3CN solution, see Figure S4): 1620 [ν(N=O)], 1561 [ν(C=N)] cm^{-1}.

Chemical generation of 2. Under inert atmosphere, 12.0 mg (14.6 μmol) **1** were dissolved in 1.6 mL degassed CD_3CN. The resulting solution was added to 4.8 mg (14.6 μmol) $CoCp^*_2$ and the solution was agitated until all solid had dissolved, giving **2**. ^{1}H NMR (400 MHz, CD_3CN, all signals appear as broad singlets, see Figure S9): δ= 97.0 (3H), 50.9 (3H), 39.3 (3H), 18.5 (12H), -7.6 (12H) ppm; FT-IR (CD_3CN solution, see Figure S6): 1620 [ν(N=O)], 1561 [ν(C=N)], 1525 [ν(C=N)] cm^{-1}.

Physical measurements. Infrared spectra of solid samples were obtained from KBr disks on a Perkin-Elmer BX spectrometer, and the IR spectra of solution samples were obtained in cells equipped with CaF_2 windows on the same instrument. Proton NMR spectra were recorded on a Varian MR 400 MHz instrument. Solution magnetic susceptibility measurements were determined on the same instrument at 295 K using the Evans method.[3] TMS was used as an internal reference. Diamagnetic corrections were determined from Pascal's constants. Electronic absorption spectra were recorded using an Analytical Jena Specord 600 instrument. Electron paramagnetic resonance spectra were measured on a Bruker X-Band EMX spectrometer equipped with an Oxford Instruments

[3] a) D.F. Evans *J. Chem. Soc.* **1959**, 2003-2005. b) E.M. Schubert *J. Chem. Ed.* **1992**, *69*, 62. c) G.A. Bain, J.F Berry *J. Chem. Ed.* **2008**, *85*, 532-536.

liquid helium cryostat. EPR spectra were obtained on frozen solutions using 20 mW microwave power and 100 kHz field modulation with the amplitude set to 1 G. EPR spectra were fit using the program SpinCount (Mike Hendrich, Carnegie Mellon). Elemental analysis was carried out by Atlantic Microlab, Inc. (Norcross, GA).

Cyclic voltammograms were obtained from a CH instruments CHI600E electrochemical workstation using a three component system consisting of a glassy carbon working electrode, a platinum counter electrode, and a silver wire pseudo-reference electrode. CVs were measured in 0.1 M tetrabutylammonium perchlorate in CH_3CN. Potentials were corrected to Fc/Fc^+ using an internal ferrocene standard (Fc/Fc^+= +624 mV vs SHE). IR spectroelectrochemistry experiments were performed using a solution IR cell with CaF_2 windows as previously described.[4] Electrodes consist of an 8 x 10 mm Pt mesh (100 mesh, 99.9%, Aldrich) for the working, 3 x 10 mm Pt mesh for the counter, and Ag wire (0.1 mm diameter, 99.9%, Aldrich) as a pseudo-reference electrode. Bulk electrolysis was performed using carbon felt working and counter electrodes and a silver wire reference electrode. The counter compartment, containing electrolyte and excess ferrocene as a sacrificial oxidant, was separated from the working compartment by a fine glass frit. All electrochemical manipulations were performed in a glovebox (<0.1 ppm O_2).

Crystal Structure Determination. A crystal of dimensions 0.11 x 0.04 x 0.02 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 1815 images were collected with an oscillation width of 1.0° in ω. The exposure time was 1 sec. for the low angle images, 4 sec. for high angle. The integration of the data yielded a total of 7165 reflections to a maximum 2θ value of 136.48° of which 7165 were independent and 6771 were greater than $2\sigma(I)$. The final cell constants (Table S6) were based on the xyz centroids of 25090 reflections above 10σ (I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0[5a] and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package[5b], using the space group P2(1)/n with Z = 4 for the formula $C_{24}H_{50}N_{11}O_7F_6S_2Cl_2Fe$. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0367 and wR2 = 0.0940 [based on I > 2σ(I)], R1 = 0.0386 and wR2 = 0.0955 for all data. Additional details are presented in Tables S6-S10. CCDC 945365 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Computational Methods. Of all the functionals surveyed, TPSS/TZVP provides the best agreement with the experimentally observed structural parameters of **1** and the spectroscopic data on **1** and **2** (Table S2). However, gradient-corrected functionals such as TPSS tend to overestimate metal-ligand covalency, which can lead to

[4] a) Z. Wei, M.D. Ryan *Inorg. Chem.* **2010**, *49*, 6948-6954 b) L. E. Goodrich, S. Roy, E. E. Alp, J. Zhao, M. Y. Hu, N. Lehnert, *Inorg. Chem.* **2013**, *52*, 7766-7780

[5] a) CrystalClear Expert 2.0 r12, Rigaku Americas and Rigaku Corporation (2011), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan b) G.M. Sheldrick SHELXTL, v. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.

significant spin quenching and a flawed spin-density distribution.[6] Thus, in order to examine bonding, the hybrid functional B3LYP, which has been used previously to study other $\{FeNO\}^7$ and $\{FeNO\}^8$ systems, was employed.[7] To facilitate comparison between the $\{FeNO\}^7$ and $\{FeNO\}^8$ complexes, the canonical orbitals for the broken symmetry solution were transformed into unrestricted corresponding orbitals (UCOs).[8] Note that because of the UCO transformation, the orbital energies are not well-defined.

All geometry optimizations and frequency calculations were performed with the Gaussian09 program package.[9] Molecular orbitals were obtained from B3LYP/TZVP broken symmetry single-point calculations on the TPSS/TZVP-optimized geometries using the ORCA program package.[10] Molecular orbitals were plotted using the orca_plot tool and visualized using GaussView (electron density isosurface threshold=0.05).

[6] L. E. Goodrich, F. Paulat, V. K. K. Praneeth, N. Lehnert, *Inorg. Chem.* **2010**, *49*, 6293-6316.
[7] S. Ye, J. C. Price, E. W. Barr, M. T. Green, J. M. Bollinger, C. Krebs, F. Neese, *J. Am. Chem. Soc.* **2010**, *132*, 4739-4751.
[8] F. Neese, *J. Phys. Chem. Solids* **2004**, *65*, 781-785.
[9] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian09,* revision A.02, Gaussian, Inc. Wallingford CT, 2009.
[10] F. Neese, *ORCA* version 2.1.9; Max-Planck Institut feur Bioanorganische Chemie: Meulheim/Ruhr, Germany, 2004.

Comparison of Basicity of 2 to Low-Spin (Heme) Complexes.

Regardless of spin state, the reduction of $\{FeNO\}^7$ systems should lead to an increase in the basicity of the NO moiety due to the increased electron density in the Fe-NO unit. It is thus of interest to determine the relative basicity of high- and low-spin complexes. However, no experimental pK_a values for biological or biomimetic low-spin (or high-spin) $\{FeNO\}^8$ complexes have been reported. The only biological complex for which even an approximate value is known is the ferrous HNO adduct of myoglobin, which shows long-term solution stability up to a pH of 10, indicating $pK_a \geq 10$.[11] Note that a pK_a of 7.7 was determined for $[Fe^{II}(CN)_5(HNO)]^{3-}$ by ^1H NMR, although this likely has limited relevance to biological systems.[12]

In order to probe the difference in basicity between high- and low-spin systems, DFT calculations were employed. Geometry optimizations were performed on **2** ($\{FeNO\}^8$) and **3** ($\{FeHNO\}^8$, S=2). In order to replicate the coordination environment of the myoglobin HNO adduct, a 6-coordinate heme model was constructed using porphine bound to 1-methylimidazole, ($[Fe(P)(MI)(NO)]^-$ and [Fe(P)(MI)(NHO)]).[13] Geometries were optimized at the BP86/TZVP level and energies were calculated at the B3LYP/TZVP level. Thermal and entropic corrections to ΔE to obtain the Gibbs energy (ΔG) were obtained from BP86/TZVP frequency calculations.

pK_a values were calculated using a standard thermodynamic cycle[14] where the free energy of the deprotonation of the $\{FeHNO\}^8$ is given by

$$\Delta G_{aq} = \Delta G_{gas} + \Delta G_{solv}(A^-) + \Delta G_{solv}(H^+) - \Delta G_{solv}(HA)$$

ΔG_{gas} is the gas-phase free energy change given by

$$\Delta G_{gas} = G(A^-) + G(H^+) - G(HA)$$

where the gaseous free energy of the proton $G(H^+) = -6.28$ kcal/mol is taken from experiment.[14] ΔG_{gas} was converted from the gaseous standard state (1 atm) to solution standard state (1 mol/L) by addition of the conversion factor RTln(24.46) (1.89 kcal/mol) to the gas-phase energies. Because the value of $\Delta G_{solv}(H^+)$ is not known to high accuracy in non-aqueous media, all calculations were performed assuming an aqueous environment in order to use the experimental-theoretical value $\Delta G_{solv}(H^+) = -265.9$ kcal/mol.[15] Solvation free energies ΔG_{solv} were calculated using the SMD solvent model[16] (ε=78.3553, corresponding to water) as implemented in Gaussian09.[9] pK_a values were then calculated from ΔG_{aq} using the relation

$$pK_a = \Delta G_{aq} / [RT\ln(10)]$$

It should be noted that absolute pK_a values are difficult to determine computationally, as a high degree of accuracy in energy is required. (As has been noted in the literature[14], an error of as little as 1.4 kcal/mol in ΔG gives an error of 1 pK_a unit.) However, general trends in pK_a values are typically well-reproduced provided the errors in calculated energies for the two systems are similar. The DFT calculations can therefore provide a qualitative

[11] R. Lin, P. J. Farmer, *J. Am. Chem. Soc.* **2000**, *122*, 2393-2394.
[12] A.C. Montenegro, V.T. Amorebieta, L.D. Slep, D.F. Martin, F. Roncaroli, D.H. Murgida, S.E. Bari, J.A. Olabe *Angew. Chem. Int. Ed.* **2009**, *48*, 4213-4216.
[13] L.E. Goodrich, N. Lehnert *J. Inorg. Biochem.* **2013**, *118*, 179-186
[14] See, for example, M.D. Liptak, G.C. Shields *J. Am. Chem. Soc.* **2001**, *123*, 7314-7319
[15] M.D. Tissandier, K.A. Cowen, W.Y. Feng, E. Gundlach, M.J. Cohen, A.D. Earhart, J.V. Coe *J. Phys. Chem. A* **1998**, *102*, 7787-7794
[16] A.V. Marenich, C.J. Cramer, D.G. Truhlar *J. Phys. Chem. B* **2009**, *113*, 6378-6396

assessment of whether the high-spin system **2** or the low-spin system $[Fe(P)(MI)(NO)]^-$ would be expected to be more basic. The DFT calculations yield pK_a(**2**) = 13 and $pK_a([Fe(P)(MI)(NHO)])$ = 21, *indicating that high-spin **2** is distinctively less basic than low-spin heme $\{FeNO\}^8$ complexes.* However, further studies are required to validate this result experimentally.

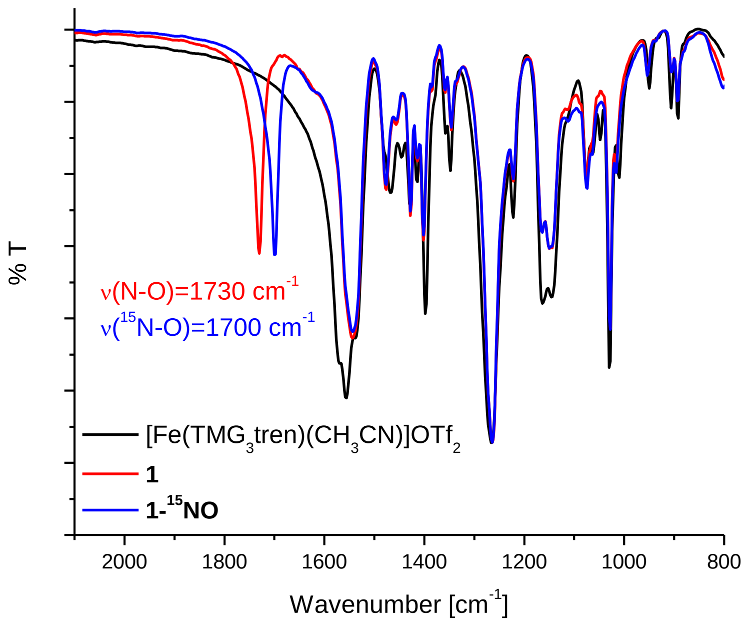


Figure S1. IR spectrum of solid [Fe(TMG$_3$tren)(CH$_3$CN)](OTf)$_2$, **1**-NO, and **1**-^{15}NO embedded in a KBr matrix.

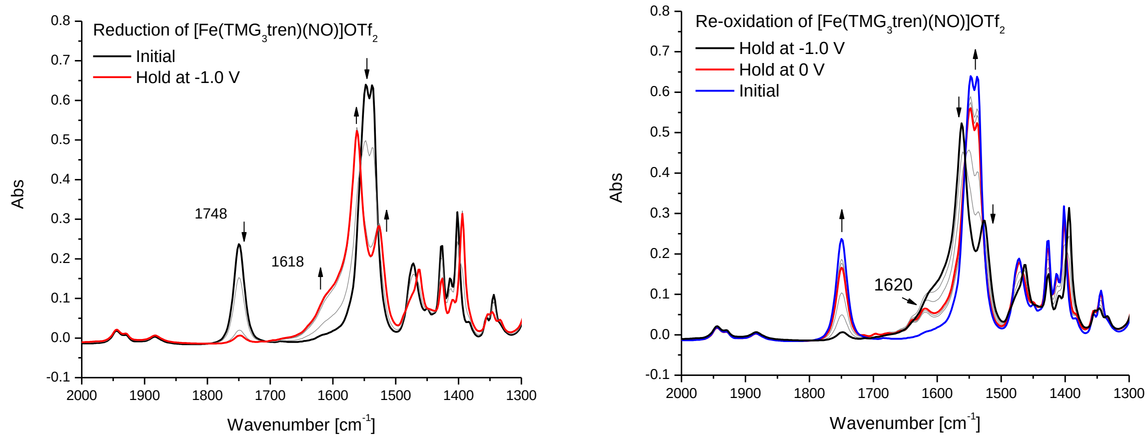


Figure S2. IR spectroelectrochemical reduction of **1** to **2** at -1.0 V vs Ag wire and re-oxidation at 0 V vs Ag wire.

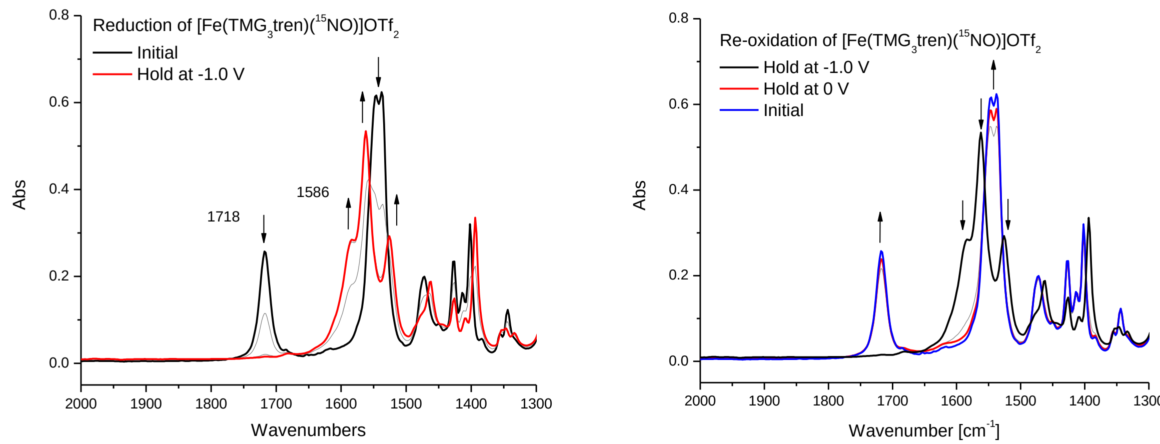


Figure S3. IR spectroelectrochemical reduction of **1-^{15}NO** to **2-^{15}NO** at -1.0 V vs Ag wire, and re-oxidation at 0 V vs Ag wire.

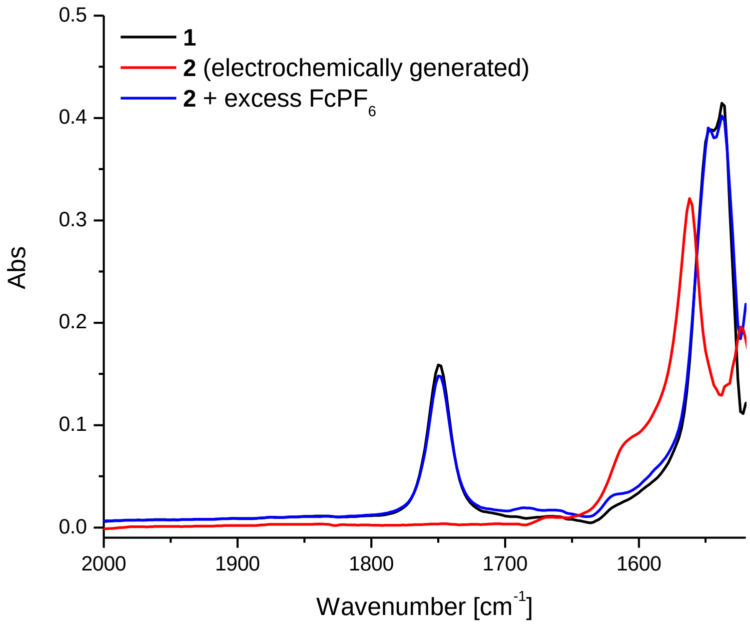


Figure S4. Solvent and electrolyte background-corrected solution IR of the product of _**bulk electrolysis**_ of **1** to **2** at -1.0 V vs Ag wire in 0.1 M NBu_4ClO_4 in CH_3CN, shown with reoxidation of **2** to **1** with $FcPF_6$.

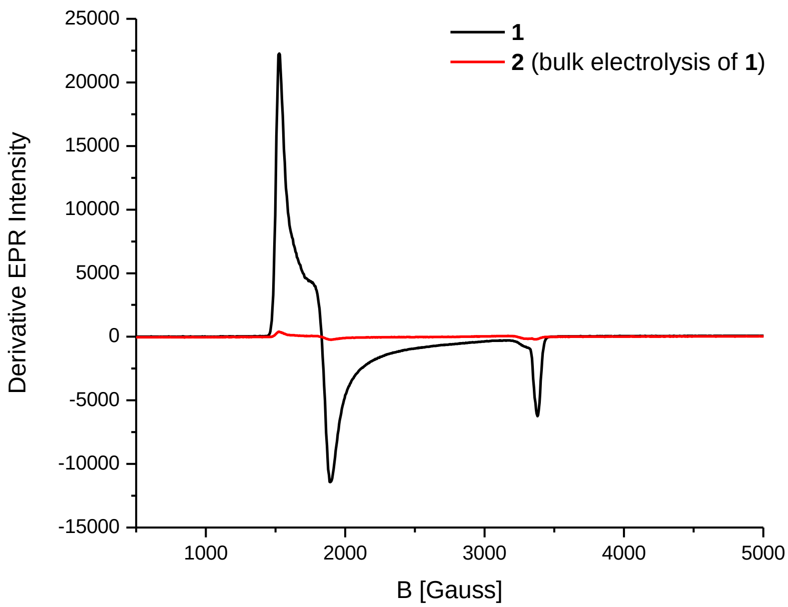


Figure S5. EPR of frozen **1** at 4.2 K in 1:1 propionitrile:butyronitrile containing 0.1 M NBu_4ClO_4 before (black) and after (red) bulk electrolysis at -1.0 V vs Ag wire.

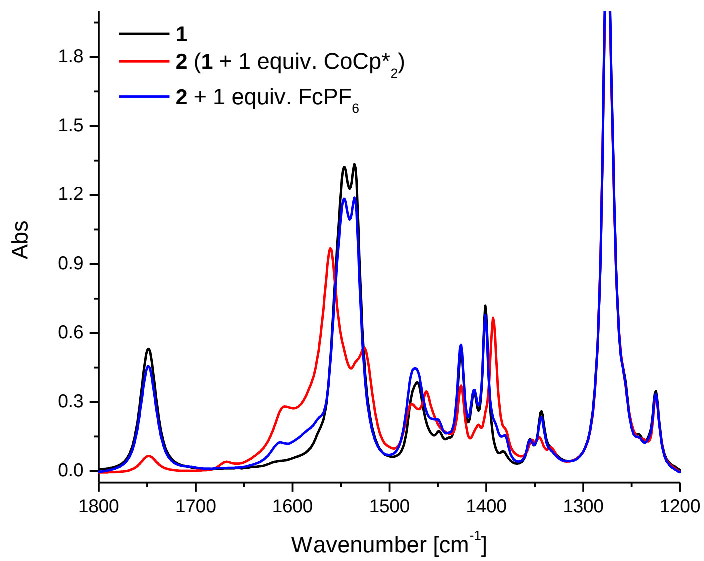


Figure S6. Solution IR (CD_3CN) of $CoCp^*_2$-reduced **1**, shown with re-oxidation of **2** to **1** with $FcPF_6$.

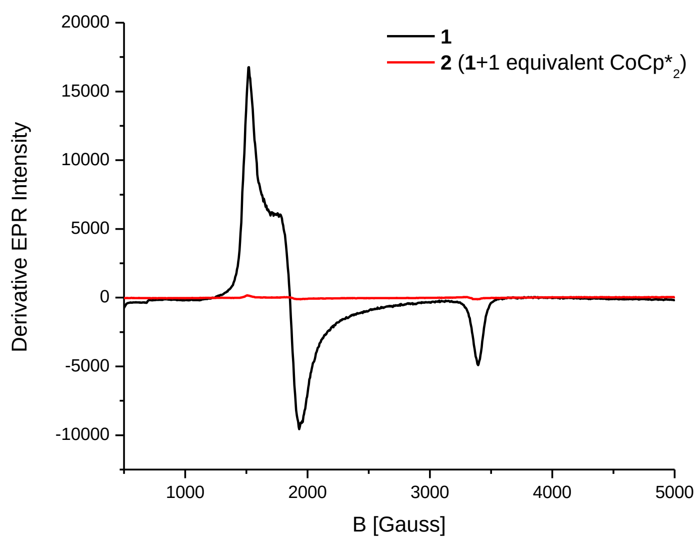


Figure S7. EPR of frozen CH_2Cl_2 solution of **1** reduced with 1 equivalent of $CoCp^*_2$.

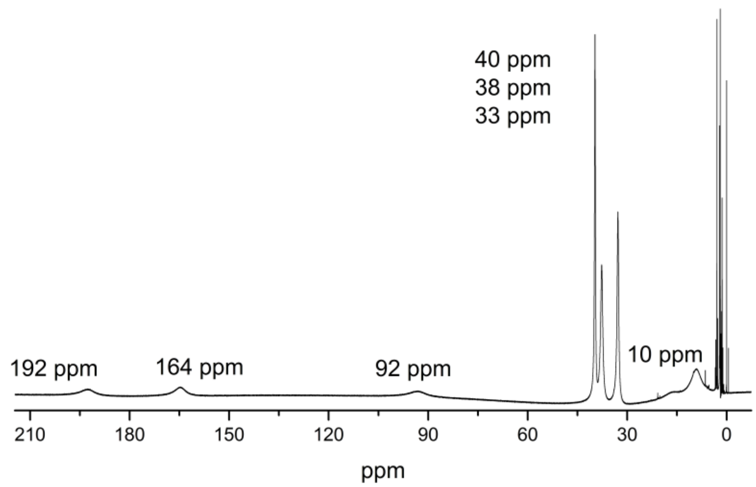


Figure S8. ^{1}H NMR spectrum (CD_3CN, 400 MHz) of **1**

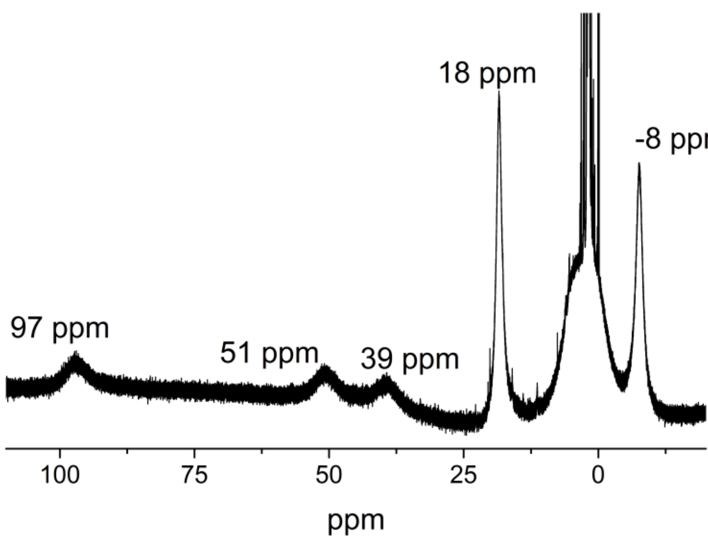


Figure S9. ^{1}H NMR spectrum (CD_3CN, 400 MHz) of **2** ($CoCp^*_2$-reduced **1**)

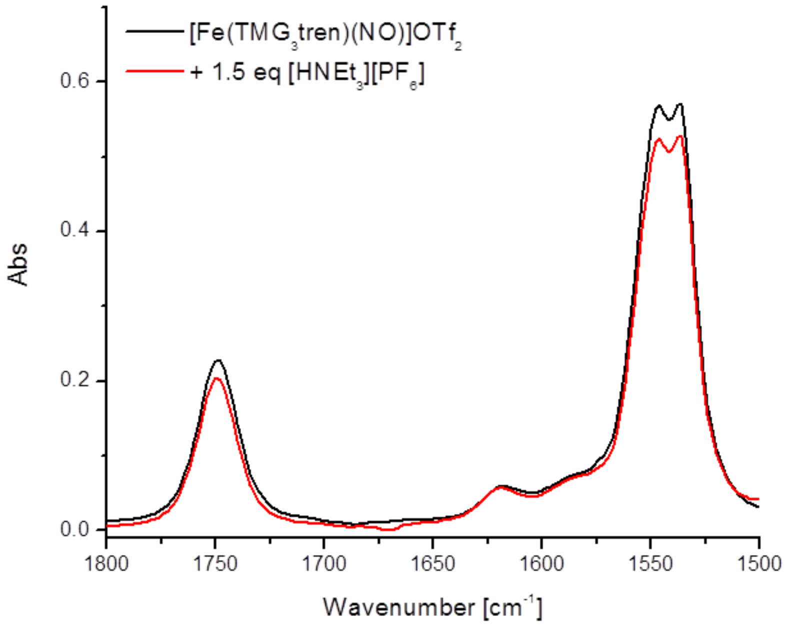
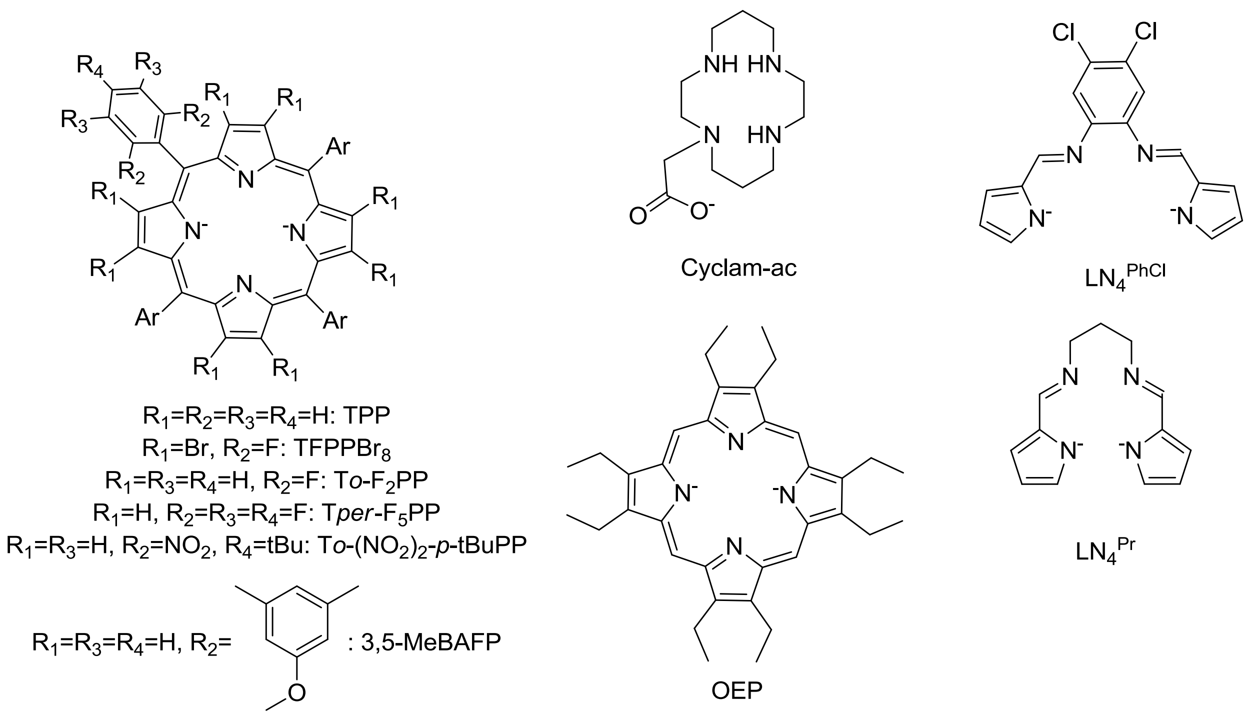


Figure S10. Solution IR of **1** before and after addition of $[HNEt_3][PF_6]$ in propionitrile. The data show that the complex is stable in the presence of a weak acid, as evident from the N-O stretching band at 1750 cm^{-1}.

Table S1. Comparison of **1** and **2** to <u>*low-spin*</u> $\{FeNO\}^8$ complexes

Complex	**$\{FeNO\}^7$ ν(N-O) [cm^{-1}]**	**$\{FeNO\}^8$ ν(N-O) [cm^{-1}]**	**Δν(N-O) [cm^{-1}]**	**Ref.**
[Fe(TPP)(NO)] $^{0/-}$	1681	1496	185	1
[Fe(OEP)(NO)] $^{0/-}$	1670	1441	229	2
[Fe(TFPPBr$_8$)(NO)] $^{0/-}$	1715	1550	166	3
[Fe(T*o*-F$_2$PP)(NO)] $^{0/-}$	1687	1473	214	4
[Fe(T*per*-F$_5$PP)(NO)] $^{0/-}$	1699	~1500	199	4
[Fe(T*o*-(NO$_2$)$_2$-*p*-tBuPP)(NO)] $^{0/-}$	1693	1482	211	4
[Fe(3,5-Me-BAFP)(NO)] $^{0/-}$	1684	1466	218	4
[Fe(LN$_4^{Pr}$)(NO)] $^{0/-}$	1704	1604	100	5
[Fe(LN$_4^{PhCl}$)(NO)] $^{0/-}$	1720	1580	140	6
[Fe(cyclam-ac)(NO)] $^{+/0}$	1607	1271	336	7
[Fe(TMG$_3$tren)(NO)] $^{2+/+}$ **(1/2)**	1748	1618	130	*This work*

Chart S1. Ligands used in the synthesis of low-spin $\{FeNO\}^8$ complexes



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[2] Z. Wei, M. D. Ryan, *Inorg. Chem.* **2010**, *49*, 6948-6954
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[4] L. E. Goodrich, S. Roy, E. E. Alp, J. Zhao, M. Y. Hu, N. Lehnert, *Inorg. Chem.* **2013**, *52*, 7766-7780
[5] A. K. Patra, K. S. Dube, B. C. Sanders, G. C. Papaefthymiou, J. Conradie, A. Ghosh, T. C. Harrop, *Chem. Sci.* **2012**, *3*, 364-369
[6] B. C. Sanders, A. K. Patra, T. C. Harrop, *J. Inorg. Biochem.* **2013**, *118*, 115-127.
[7] R. Garcia-Serres, C. A. Grapperhaus, E. Bothe, E. Bill, T. Weyhermüller, F. Neese, K. Wieghardt, *J. Am. Chem. Soc.* **2004**, *126*, 5138-5153.

Table S2. Comparison of DFT-calculated parameters of **1** and **2** to experimental parameters using the B3LYP, OLYP, BP86, and TPSS functionals. All calculations were performed with the TZVP basis set.

	{FeNO}^{7}					{FeNO}^{8}		
	Expt	**BP86**	**TPSS**	**OLYP**	**B3LYP**	**BP86**	**TPSS**	**OLYP**
Fe-N [Å]	1.75	1.72	1.73	1.76	1.77	1.69	1.71	1.72
N-O [Å]	1.15	1.18	1.18	1.17	1.18	1.21	1.21	1.19
Fe-N-O	167.96	151.32	153.34	164.27	178.24	151.73	156.87	166.76
Avg. Fe-N_{guan} [Å]	2.04	2.08	2.07	2.15	2.09	2.15	2.15	2.28
Avg. N=C [Å]	1.33	1.35	1.35	1.35	1.35	1.33	1.32	1.32
Fe-N_{amine} [Å]	2.25	2.24	2.23	2.28	2.26	2.33	2.36	2.37
ν(N-O)	1741	1702	1722	1797	1870	1599	1628	1703
ν(Fe-N)	497	574	562	469	479	419, 563	496	456

Table S3. Comparison of Muliken atomic spin densities calculated at the TPSS/TZVP level for **1** and **2**. The change in spin density on the guanidinium atoms of the TMG_3tren ligand is relatively small, which demonstrates that the reduction is based in the Fe-NO unit, and not in the ligand.

	{FeNO}^{7} (1)	**{FeNO}^{8} (2)**
Fe	3.008	2.643
N (NO)	-0.210	-0.425
O (NO)	-0.204	-0.314
N (C=N)	0.063	0.007
C (C=N)	0.007	-0.010
N (C=N)	0.055	0.019
C (C=N)	0.008	-0.014
N (C=N)	0.087	0.007
C (C=N)	0.013	0.018
Total Fe/NO	2.594	1.904
Total TMG_3tren	0.406	0.096

Table S4. DFT-optimized (TPSS/TZVP) coordinates of **1**

	x	y	z
Fe	-0.03659	-0.00695	0.29193
N	-0.04781	0.05348	-1.43599
N	-0.03416	-0.05067	2.51746
N	1.25607	-1.62852	0.62932
N	-2.05389	-0.29919	0.64416
N	0.74674	1.84783	0.64116
N	3.04494	-3.02774	-0.10305
N	1.05846	-2.934	-1.31278
N	-4.13141	-1.16388	-0.13821
N	-3.1413	0.65509	-1.20495
N	1.14097	4.09016	-0.05365
N	2.16613	2.32846	-1.17434
C	0.58605	-1.3367	2.94838
H	-0.178	-2.1159	2.88065
H	0.91838	-1.27408	3.99404
C	1.74395	-1.68609	2.02263
H	2.57613	-0.98848	2.18963
H	2.11323	-2.68814	2.27046
C	1.78735	-2.5039	-0.24066
C	4.18068	-2.25917	0.42199
H	3.93214	-1.19923	0.44695
H	5.03684	-2.40204	-0.24608
H	4.46594	-2.59264	1.42658
C	3.35645	-4.42788	-0.44394
H	2.43289	-4.98494	-0.60104
H	3.89733	-4.87424	0.39704
H	3.98494	-4.49705	-1.33894
C	1.67438	-3.27101	-2.60426
H	2.70453	-2.91556	-2.62598
H	1.10952	-2.77158	-3.39892
H	1.65815	-4.35055	-2.79335
C	-0.38602	-3.15752	-1.23686
H	-0.72028	-2.94915	-0.2212
H	-0.60318	-4.20222	-1.4923
H	-0.92149	-2.50681	-1.93616
C	-1.45181	0.04314	2.9697
H	-1.74941	1.09462	2.93699
H	-1.55277	-0.30933	4.00557
C	-2.33132	-0.76114	2.02265
H	-2.11936	-1.83208	2.13888

H	-3.38536	-0.60976	2.28186
C	-3.08928	-0.28472	-0.21715
C	-3.96519	-2.55827	0.2923
H	-2.90802	-2.81939	0.29298
H	-4.48792	-3.2069	-0.41862
H	-4.38678	-2.72544	1.29014
C	-5.52003	-0.77634	-0.4488
H	-5.59072	0.30764	-0.53639
H	-6.16152	-1.10615	0.37489
H	-5.87127	-1.24507	-1.37466
C	-3.73058	0.38979	-2.52593
H	-3.89927	-0.68038	-2.64563
H	-3.02462	0.72598	-3.29291
H	-4.67619	0.92632	-2.66372
C	-2.68048	2.02995	-0.99265
C	0.76285	1.12565	2.96563
H	1.82103	0.8568	2.91261
H	0.52555	1.38385	4.00709
C	0.49309	2.29698	2.03173
H	-0.54015	2.64628	2.15757
H	1.15044	3.13307	2.29453
C	1.32668	2.74279	-0.18623
C	-0.13768	4.67925	0.36494
H	-0.91775	3.92002	0.34228
H	-0.40179	5.47756	-0.33695
H	-0.07147	5.10931	1.37103
C	2.22255	5.06604	-0.2848
H	3.17927	4.54869	-0.35594
H	2.25403	5.75004	0.56953
H	2.05128	5.65123	-1.19489
C	2.29719	3.03911	-2.45656
H	1.49585	3.77054	-2.55663
H	2.2104	2.30709	-3.26586
H	3.26693	3.54198	-2.54035
C	3.00701	1.13843	-1.03729
H	2.89854	0.74487	-0.02772
H	4.05157	1.41664	-1.22137
H	2.71792	0.36826	-1.76097
O	-0.06564	0.61859	-2.47004
H	-1.86003	2.27754	-1.67418
H	-2.34594	2.133	0.03923
H	-3.51145	2.72034	-1.18237

Table S5. DFT-optimized (TPSS/TZVP) coordinates of **2**

	x	**y**	**z**
Fe	0.00101	-0.06804	0.13615
N	-0.06792	0.07398	-1.56191
N	0.04882	-0.1136	2.49505
N	1.95124	-0.95566	0.62481
N	-1.77427	-1.16118	0.63266
N	-0.17462	1.99108	0.62203
N	4.18254	-1.41246	-0.10377
N	2.3601	-2.33078	-1.22422
N	-3.32885	-2.82283	-0.09899
N	-3.30138	-0.71247	-1.08798
N	-0.74801	4.23562	0.04832
N	0.91486	3.11438	-1.13558
C	1.22677	-0.90182	2.93233
H	0.95529	-1.96119	2.88853
H	1.49901	-0.66342	3.97334
C	2.4026	-0.65721	1.98924
H	2.73591	0.38682	2.0855
H	3.24692	-1.29284	2.28977
C	2.80801	-1.52725	-0.20457
C	4.83383	-0.17258	0.31739
H	4.10299	0.63446	0.34324
H	5.61494	0.08722	-0.40813
H	5.30024	-0.26963	1.30657
C	5.08989	-2.51841	-0.42472
H	4.51105	-3.42935	-0.57868
H	5.7799	-2.67195	0.4141
H	5.68293	-2.31102	-1.32549
C	2.94129	-2.28191	-2.56932
H	3.77836	-1.58359	-2.58359
H	2.18311	-1.93556	-3.28286
H	3.2929	-3.27246	-2.88326
C	1.09431	-3.05107	-1.1175
H	0.84106	-3.15388	-0.06132
H	1.2194	-4.04513	-1.5648
H	0.28043	-2.52381	-1.62891
C	-1.22012	-0.73772	2.94905
H	-1.98764	0.04049	2.99114
H	-1.1102	-1.16097	3.95997
C	-1.65736	-1.80323	1.95075
H	-0.91607	-2.61656	1.93982

H	-2.61177	-2.23998	2.27294
C	-2.75802	-1.5629	-0.15917
C	-2.53455	-4.02347	0.15296
H	-1.47527	-3.78382	0.06294
H	-2.7854	-4.78471	-0.59654
H	-2.72537	-4.44528	1.14906
C	-4.76751	-3.04096	-0.27401
H	-5.27865	-2.07834	-0.30958
H	-5.15326	-3.61525	0.57764
H	-4.98584	-3.59924	-1.19416
C	-3.70779	-1.16018	-2.42306
H	-3.49579	-2.22415	-2.5327
H	-3.13778	-0.60692	-3.17851
H	-4.7785	-0.98705	-2.59102
C	-3.30882	0.73265	-0.87791
C	0.14142	1.30092	2.92842
H	1.19134	1.60386	2.87718
H	-0.19543	1.41749	3.97137
C	-0.67113	2.18969	1.99066
H	-1.73634	1.92746	2.06724
H	-0.56742	3.23482	2.3101
C	-0.01818	3.07085	-0.1292
C	-2.16851	4.22099	0.391
H	-2.55201	3.20514	0.30505
H	-2.71674	4.86303	-0.31052
H	-2.35114	4.59007	1.40946
C	-0.14805	5.56484	-0.0922
H	0.92981	5.46504	-0.22387
H	-0.34213	6.14874	0.81655
H	-0.56594	6.11085	-0.94862
C	0.65219	3.76695	-2.42131
H	-0.34709	4.20223	-2.4141
H	0.70376	3.02096	-3.22331
H	1.3888	4.55572	-2.62027
C	2.14764	2.33922	-1.06915
H	2.23917	1.91574	-0.069
H	2.99887	3.00111	-1.27937
H	2.14585	1.52062	-1.79793
O	-0.44813	0.49791	-2.6241
H	-2.57863	1.23374	-1.52209
H	-3.063	0.93009	0.1652
H	-4.3108	1.11921	-1.10617

Figure S11. Crystal structure of **1 x CH_2Cl_2** shown with atom labels

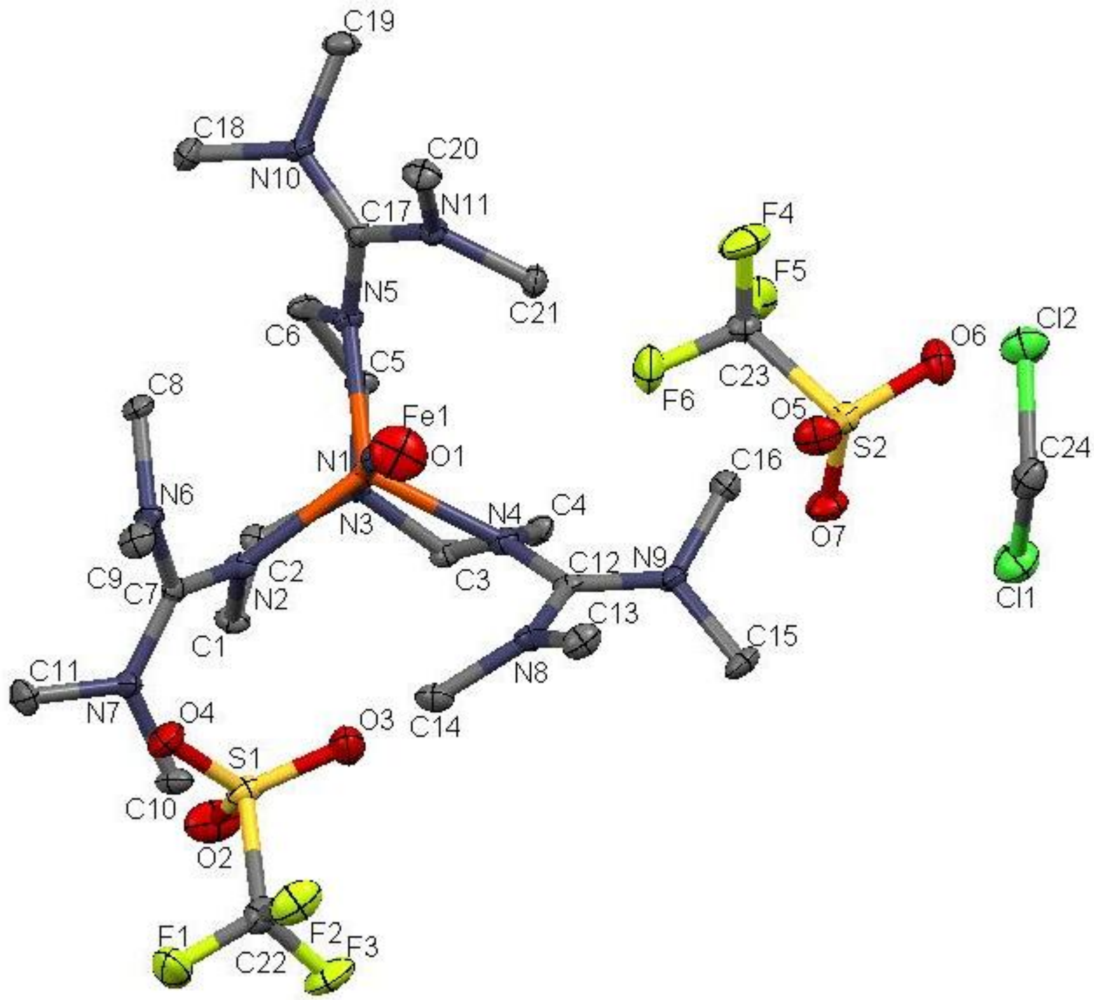

Table S6. Crystal data and structure refinement for [Fe(TMG$_3$tren)(NO)](OTf)$_2$•CH$_2$Cl$_2$

Empirical formula	C_{24} H_{50} Cl_2 F_6 Fe N_{11} O_7 S_2	
Formula weight	909.62	
Temperature	85(2) K	
Wavelength	1.54178 Å	
Crystal system, space group	Monoclinic, P2(1)/n	
Unit cell dimensions	a = 9.0027(2) Å	alpha = 90 deg.
	b = 22.4142(4) Å	beta = 100.504(7) deg.
	c = 19.8307(14) Å	gamma = 90 deg.
Volume	3934.5(3) Å^3	
Z, Calculated density	4, 1.536 Mg/m^3	
Absorption coefficient	6.062 mm^{-1}	
F(000)	1892	
Crystal size	0.11 x 0.04 x 0.02 mm	
Theta range for data collection	3.00 to 68.24 deg.	
Limiting indices	-10<=h<=10, -27<=k<=27, -18<=l<=23	
Reflections collected / unique	52071 / 7165 [R(int) = 0.0624]	
Completeness to theta = 68.24	99.7 %	
Absorption correction	semi-empirical, from equivalents	
Max. and min. transmission	0.909 and 0.549	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7165 / 0 / 490	
Goodness-of-fit on F^2	1.115	
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0940	
R indices (all data)	R1 = 0.0386, wR2 = 0.0955	
Largest diff. peak and hole	0.427 and -0.414 e.Å^{-3}	

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [Fe(TMG$_3$tren)(NO)](OTf)$_2$•CH$_2$Cl$_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Fe(1)	1487(1)	2126(1)	6822(1)	10(1)
S(1)	7136(1)	701(1)	8713(1)	19(1)
S(2)	5565(1)	1190(1)	4069(1)	18(1)
Cl(1)	399(1)	78(1)	3171(1)	36(1)
Cl(2)	1416(1)	1165(1)	2584(1)	33(1)
O(1)	4658(2)	2109(1)	6746(1)	42(1)
O(2)	5683(2)	636(1)	8906(1)	36(1)
O(3)	7127(2)	687(1)	7986(1)	30(1)
O(4)	8091(2)	1148(1)	9088(1)	27(1)
O(5)	7147(2)	1146(1)	4355(1)	28(1)
O(6)	5193(2)	1258(1)	3337(1)	28(1)
O(7)	4590(2)	790(1)	4357(1)	26(1)
C(1)	-27(2)	1699(1)	7937(1)	15(1)
C(2)	-1271(2)	2065(1)	7507(1)	16(1)
C(3)	-1573(2)	1539(1)	6407(1)	15(1)
C(4)	-657(2)	1422(1)	5850(1)	16(1)
C(5)	-1687(2)	2632(1)	6434(1)	15(1)
C(6)	-611(2)	3151(1)	6621(1)	16(1)
C(7)	2587(2)	1967(1)	8341(1)	13(1)
C(8)	3272(3)	2996(1)	8082(1)	17(1)
C(9)	5265(2)	2285(1)	8561(1)	20(1)
C(10)	2216(3)	977(1)	8845(1)	19(1)
C(11)	3528(3)	1767(1)	9567(1)	23(1)
C(12)	1882(2)	1039(1)	5956(1)	13(1)
C(13)	4539(2)	684(1)	6175(1)	20(1)
C(14)	3130(3)	764(1)	7126(1)	20(1)
C(15)	2049(3)	204(1)	5159(1)	21(1)
C(16)	994(3)	1174(1)	4714(1)	18(1)
C(17)	1693(2)	3372(1)	6220(1)	13(1)
C(18)	1398(3)	4214(1)	6988(1)	20(1)
C(19)	1718(3)	4407(1)	5797(1)	22(1)
C(20)	4110(2)	3505(1)	5810(1)	20(1)
C(21)	2379(3)	2695(1)	5350(1)	17(1)
C(22)	8090(3)	5(1)	9016(1)	22(1)
C(23)	5077(3)	1915(1)	4383(1)	19(1)
C(24)	1969(3)	461(1)	2951(1)	26(1)
N(1)	3432(2)	2155(1)	6835(1)	14(1)
N(2)	1432(2)	1944(1)	7822(1)	14(1)
N(3)	-1023(2)	2086(1)	6790(1)	13(1)
N(4)	954(2)	1431(1)	6170(1)	14(1)
N(5)	863(2)	2966(1)	6470(1)	13(1)
N(6)	3658(2)	2397(1)	8340(1)	14(1)
N(7)	2775(2)	1589(1)	8884(1)	16(1)
N(8)	3121(2)	840(1)	6395(1)	16(1)
N(9)	1649(2)	817(1)	5312(1)	15(1)

N(10)	1578(2)	3966(1)	6328(1)	16(1)
N(11)	2681(2)	3198(1)	5819(1)	14(1)
F(1)	8276(2)	-52(1)	9691(1)	41(1)
F(2)	9452(2)	-29(1)	8842(1)	34(1)
F(3)	7316(2)	-471(1)	8736(1)	35(1)
F(4)	5902(2)	2350(1)	4185(1)	37(1)
F(5)	3622(2)	2048(1)	4150(1)	29(1)
F(6)	5295(2)	1927(1)	5069(1)	31(1)

Table S8. Bond lengths [Å] and angles [°] for $[Fe(TMG_3tren)(NO)](OTf)_2 \bullet CH_2Cl_2$.

Fe(1)-N(1)	1.7478(19)
Fe(1)-N(4)	2.0246(18)
Fe(1)-N(2)	2.0346(19)
Fe(1)-N(5)	2.0506(18)
Fe(1)-N(3)	2.2502(18)
S(1)-O(2)	1.4354(19)
S(1)-O(4)	1.4376(18)
S(1)-O(3)	1.4405(19)
S(1)-C(22)	1.829(3)
S(2)-O(5)	1.4367(17)
S(2)-O(6)	1.4374(19)
S(2)-O(7)	1.4433(17)
S(2)-C(23)	1.822(2)
Cl(1)-C(24)	1.775(3)
Cl(2)-C(24)	1.770(3)
O(1)-N(1)	1.154(3)
C(1)-N(2)	1.479(3)
C(1)-C(2)	1.518(3)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-N(3)	1.482(3)
C(2)-H(2B)	0.9900
C(2)-H(2C)	0.9900
C(3)-N(3)	1.479(3)
C(3)-C(4)	1.517(3)
C(3)-H(3B)	0.9900
C(3)-H(3C)	0.9900
C(4)-N(4)	1.474(3)
C(4)-H(4B)	0.9900
C(4)-H(4C)	0.9900
C(5)-N(3)	1.483(3)
C(5)-C(6)	1.515(3)
C(5)-H(5B)	0.9900
C(5)-H(5C)	0.9900
C(6)-N(5)	1.472(3)
C(6)-H(6B)	0.9900
C(6)-H(6C)	0.9900
C(7)-N(2)	1.323(3)
C(7)-N(7)	1.355(3)
C(7)-N(6)	1.365(3)
C(8)-N(6)	1.455(3)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-N(6)	1.455(3)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-N(7)	1.459(3)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800

C(10)-H(10C)	0.9800
C(11)-N(7)	1.456(3)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-N(4)	1.335(3)
C(12)-N(9)	1.351(3)
C(12)-N(8)	1.359(3)
C(13)-N(8)	1.465(3)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-N(8)	1.458(3)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-N(9)	1.466(3)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-N(9)	1.464(3)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-N(5)	1.329(3)
C(17)-N(11)	1.354(3)
C(17)-N(10)	1.356(3)
C(18)-N(10)	1.456(3)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-N(10)	1.466(3)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-N(11)	1.462(3)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-N(11)	1.456(3)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-F(1)	1.323(3)
C(22)-F(2)	1.336(3)
C(22)-F(3)	1.339(3)
C(23)-F(4)	1.327(3)
C(23)-F(6)	1.339(3)
C(23)-F(5)	1.341(3)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
N(1)-Fe(1)-N(4)	99.14(8)
N(1)-Fe(1)-N(2)	101.24(8)

N(4)-Fe(1)-N(2)	115.02(7)
N(1)-Fe(1)-N(5)	100.51(8)
N(4)-Fe(1)-N(5)	118.08(7)
N(2)-Fe(1)-N(5)	117.54(7)
N(1)-Fe(1)-N(3)	179.24(8)
N(4)-Fe(1)-N(3)	80.28(7)
N(2)-Fe(1)-N(3)	79.47(7)
N(5)-Fe(1)-N(3)	79.37(7)
O(2)-S(1)-O(4)	114.90(12)
O(2)-S(1)-O(3)	115.18(13)
O(4)-S(1)-O(3)	115.22(11)
O(2)-S(1)-C(22)	102.86(11)
O(4)-S(1)-C(22)	102.95(11)
O(3)-S(1)-C(22)	103.18(11)
O(5)-S(2)-O(6)	115.90(11)
O(5)-S(2)-O(7)	115.58(11)
O(6)-S(2)-O(7)	114.70(11)
O(5)-S(2)-C(23)	102.14(11)
O(6)-S(2)-C(23)	103.00(11)
O(7)-S(2)-C(23)	102.60(10)
N(2)-C(1)-C(2)	107.36(17)
N(2)-C(1)-H(1A)	110.2
C(2)-C(1)-H(1A)	110.2
N(2)-C(1)-H(1B)	110.2
C(2)-C(1)-H(1B)	110.2
H(1A)-C(1)-H(1B)	108.5
N(3)-C(2)-C(1)	109.34(18)
N(3)-C(2)-H(2B)	109.8
C(1)-C(2)-H(2B)	109.8
N(3)-C(2)-H(2C)	109.8
C(1)-C(2)-H(2C)	109.8
H(2B)-C(2)-H(2C)	108.3
N(3)-C(3)-C(4)	109.90(17)
N(3)-C(3)-H(3B)	109.7
C(4)-C(3)-H(3B)	109.7
N(3)-C(3)-H(3C)	109.7
C(4)-C(3)-H(3C)	109.7
H(3B)-C(3)-H(3C)	108.2
N(4)-C(4)-C(3)	107.85(18)
N(4)-C(4)-H(4B)	110.1
C(3)-C(4)-H(4B)	110.1
N(4)-C(4)-H(4C)	110.1
C(3)-C(4)-H(4C)	110.1
H(4B)-C(4)-H(4C)	108.4
N(3)-C(5)-C(6)	109.41(17)
N(3)-C(5)-H(5B)	109.8
C(6)-C(5)-H(5B)	109.8
N(3)-C(5)-H(5C)	109.8
C(6)-C(5)-H(5C)	109.8
H(5B)-C(5)-H(5C)	108.2
N(5)-C(6)-C(5)	107.16(17)
N(5)-C(6)-H(6B)	110.3
C(5)-C(6)-H(6B)	110.3
N(5)-C(6)-H(6C)	110.3

C(5)-C(6)-H(6C)	110.3
H(6B)-C(6)-H(6C)	108.5
N(2)-C(7)-N(7)	124.04(19)
N(2)-C(7)-N(6)	118.78(19)
N(7)-C(7)-N(6)	117.17(19)
N(6)-C(8)-H(8A)	109.5
N(6)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
N(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
N(6)-C(9)-H(9A)	109.5
N(6)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(6)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
N(7)-C(10)-H(10A)	109.5
N(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
N(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(7)-C(11)-H(11A)	109.5
N(7)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
N(7)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(4)-C(12)-N(9)	123.05(19)
N(4)-C(12)-N(8)	120.0(2)
N(9)-C(12)-N(8)	116.98(19)
N(8)-C(13)-H(13A)	109.5
N(8)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
N(8)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
N(8)-C(14)-H(14A)	109.5
N(8)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
N(8)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
N(9)-C(15)-H(15A)	109.5
N(9)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
N(9)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
N(9)-C(16)-H(16A)	109.5
N(9)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
N(9)-C(16)-H(16C)	109.5

H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
N(5)-C(17)-N(11)	119.70(19)
N(5)-C(17)-N(10)	123.3(2)
N(11)-C(17)-N(10)	116.99(19)
N(10)-C(18)-H(18A)	109.5
N(10)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
N(10)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
N(10)-C(19)-H(19A)	109.5
N(10)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
N(10)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
N(11)-C(20)-H(20A)	109.5
N(11)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
N(11)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
N(11)-C(21)-H(21A)	109.5
N(11)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
N(11)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
F(1)-C(22)-F(2)	107.7(2)
F(1)-C(22)-F(3)	107.7(2)
F(2)-C(22)-F(3)	106.24(19)
F(1)-C(22)-S(1)	112.33(17)
F(2)-C(22)-S(1)	111.19(17)
F(3)-C(22)-S(1)	111.43(17)
F(4)-C(23)-F(6)	107.37(19)
F(4)-C(23)-F(5)	107.39(19)
F(6)-C(23)-F(5)	107.39(18)
F(4)-C(23)-S(2)	111.76(16)
F(6)-C(23)-S(2)	111.46(16)
F(5)-C(23)-S(2)	111.24(16)
Cl(2)-C(24)-Cl(1)	110.83(13)
Cl(2)-C(24)-H(24A)	109.5
Cl(1)-C(24)-H(24A)	109.5
Cl(2)-C(24)-H(24B)	109.5
Cl(1)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	108.1
O(1)-N(1)-Fe(1)	167.96(19)
C(7)-N(2)-C(1)	119.27(18)
C(7)-N(2)-Fe(1)	126.50(15)
C(1)-N(2)-Fe(1)	113.84(13)
C(3)-N(3)-C(2)	111.77(17)
C(3)-N(3)-C(5)	111.90(17)
C(2)-N(3)-C(5)	111.34(17)

C(3)-N(3)-Fe(1)	106.75(12)
C(2)-N(3)-Fe(1)	107.48(13)
C(5)-N(3)-Fe(1)	107.29(12)
C(12)-N(4)-C(4)	118.53(18)
C(12)-N(4)-Fe(1)	128.38(14)
C(4)-N(4)-Fe(1)	112.70(13)
C(17)-N(5)-C(6)	118.17(17)
C(17)-N(5)-Fe(1)	128.18(14)
C(6)-N(5)-Fe(1)	112.94(13)
C(7)-N(6)-C(8)	121.94(18)
C(7)-N(6)-C(9)	122.79(18)
C(8)-N(6)-C(9)	115.19(18)
C(7)-N(7)-C(11)	122.54(19)
C(7)-N(7)-C(10)	123.59(19)
C(11)-N(7)-C(10)	113.85(18)
C(12)-N(8)-C(14)	122.09(18)
C(12)-N(8)-C(13)	123.07(19)
C(14)-N(8)-C(13)	114.85(18)
C(12)-N(9)-C(16)	122.33(18)
C(12)-N(9)-C(15)	122.62(19)
C(16)-N(9)-C(15)	115.05(18)
C(17)-N(10)-C(18)	122.71(19)
C(17)-N(10)-C(19)	121.88(19)
C(18)-N(10)-C(19)	115.31(18)
C(17)-N(11)-C(21)	122.18(18)
C(17)-N(11)-C(20)	123.03(18)
C(21)-N(11)-C(20)	114.77(18)

Table S9. Anisotropic displacement parameters ($Å^2 \times 10^4$) for [Fe(TMG$_3$tren)(NO)](OTf)$_2$•CH$_2$Cl$_2$. The anisotropic displacement factor exponent takes the form:

$$-2 \pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$$

	U11	U22	U33	U23	U13	U12
Fe(1)	10(1)	8(1)	12(1)	1(1)	1(1)	0(1)
S(1)	18(1)	15(1)	24(1)	-1(1)	6(1)	1(1)
S(2)	17(1)	16(1)	21(1)	-2(1)	4(1)	0(1)
Cl(1)	34(1)	31(1)	41(1)	-3(1)	5(1)	-7(1)
Cl(2)	31(1)	27(1)	40(1)	4(1)	4(1)	7(1)
O(1)	16(1)	57(1)	54(1)	5(1)	12(1)	3(1)
O(2)	20(1)	31(1)	62(1)	6(1)	18(1)	4(1)
O(3)	39(1)	27(1)	22(1)	-2(1)	4(1)	4(1)
O(4)	35(1)	17(1)	29(1)	-6(1)	6(1)	-4(1)
O(5)	17(1)	28(1)	37(1)	4(1)	1(1)	5(1)
O(6)	26(1)	37(1)	20(1)	-6(1)	4(1)	-5(1)
O(7)	28(1)	18(1)	34(1)	2(1)	11(1)	-6(1)
C(1)	12(1)	17(1)	18(1)	4(1)	2(1)	-2(1)
C(2)	12(1)	18(1)	19(1)	2(1)	4(1)	0(1)
C(3)	11(1)	13(1)	21(1)	0(1)	1(1)	-3(1)
C(4)	14(1)	14(1)	20(1)	-3(1)	0(1)	-1(1)
C(5)	13(1)	13(1)	18(1)	3(1)	3(1)	3(1)
C(6)	16(1)	13(1)	20(1)	2(1)	4(1)	3(1)
C(7)	14(1)	11(1)	14(1)	-1(1)	4(1)	2(1)
C(8)	21(1)	9(1)	20(1)	-1(1)	4(1)	-2(1)
C(9)	15(1)	20(1)	24(1)	0(1)	0(1)	-1(1)
C(10)	19(1)	13(1)	23(1)	5(1)	0(1)	0(1)
C(11)	28(1)	24(1)	13(1)	1(1)	-4(1)	-1(1)
C(12)	15(1)	7(1)	18(1)	1(1)	3(1)	-3(1)
C(13)	14(1)	18(1)	29(1)	-2(1)	4(1)	1(1)
C(14)	21(1)	17(1)	22(1)	5(1)	2(1)	2(1)
C(15)	23(1)	10(1)	29(1)	-5(1)	7(1)	-2(1)
C(16)	21(1)	16(1)	17(1)	-1(1)	3(1)	-1(1)
C(17)	15(1)	10(1)	13(1)	0(1)	-2(1)	0(1)
C(18)	26(1)	15(1)	20(1)	-5(1)	5(1)	-1(1)
C(19)	27(1)	13(1)	25(1)	6(1)	6(1)	0(1)
C(20)	16(1)	21(1)	24(1)	3(1)	5(1)	-3(1)
C(21)	20(1)	17(1)	14(1)	-4(1)	2(1)	0(1)
C(22)	21(1)	20(1)	26(1)	-4(1)	5(1)	-1(1)
C(23)	18(1)	17(1)	22(1)	2(1)	4(1)	-1(1)
C(24)	25(1)	23(1)	28(1)	-5(1)	1(1)	3(1)
N(1)	17(1)	12(1)	13(1)	0(1)	1(1)	-1(1)
N(2)	10(1)	13(1)	17(1)	2(1)	1(1)	-1(1)
N(3)	13(1)	11(1)	15(1)	1(1)	1(1)	0(1)
N(4)	12(1)	12(1)	16(1)	0(1)	0(1)	-1(1)
N(5)	12(1)	10(1)	17(1)	1(1)	3(1)	1(1)
N(6)	13(1)	12(1)	15(1)	0(1)	1(1)	-1(1)
N(7)	18(1)	13(1)	15(1)	2(1)	1(1)	-1(1)

N(8)	15(1)	12(1)	20(1)	1(1)	4(1)	2(1)
N(9)	18(1)	9(1)	18(1)	-1(1)	2(1)	0(1)
N(10)	23(1)	9(1)	18(1)	0(1)	5(1)	-1(1)
N(11)	14(1)	14(1)	15(1)	-1(1)	4(1)	-1(1)
F(1)	64(1)	34(1)	24(1)	5(1)	6(1)	17(1)
F(2)	21(1)	28(1)	54(1)	-4(1)	8(1)	6(1)
F(3)	35(1)	16(1)	53(1)	-5(1)	1(1)	-6(1)
F(4)	43(1)	17(1)	56(1)	1(1)	21(1)	-6(1)
F(5)	23(1)	32(1)	32(1)	-1(1)	1(1)	12(1)
F(6)	35(1)	36(1)	21(1)	-10(1)	1(1)	5(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $[Fe(TMG_3tren)(NO)](OTf)_2 \bullet CH_2Cl_2$

	x	y	z	U(eq)
H(1A)	-97	1727	8428	18
H(1B)	-121	1275	7797	18
H(2B)	-2266	1883	7523	19
H(2C)	-1266	2475	7694	19
H(3B)	-2652	1586	6199	19
H(3C)	-1479	1195	6726	19
H(4B)	-928	1029	5634	19
H(4C)	-868	1733	5491	19
H(5B)	-2666	2722	6573	18
H(5C)	-1872	2569	5932	18
H(6B)	-987	3507	6348	19
H(6C)	-519	3249	7114	19
H(8A)	3678	3061	7662	25
H(8B)	3708	3289	8429	25
H(8C)	2171	3041	7983	25
H(9A)	5423	1864	8687	30
H(9B)	5653	2536	8959	30
H(9C)	5800	2380	8187	30
H(10A)	1322	952	9061	29
H(10B)	3005	712	9084	29
H(10C)	1947	856	8363	29
H(11A)	4513	1569	9677	34
H(11B)	2907	1651	9903	34
H(11C)	3671	2201	9580	34
H(13A)	4649	249	6174	31
H(13B)	5388	859	6492	31
H(13C)	4527	838	5712	31
H(14A)	2114	836	7220	30
H(14B)	3839	1048	7387	30
H(14C)	3444	356	7263	30
H(15A)	2990	206	4976	31
H(15B)	1238	31	4818	31
H(15C)	2188	-35	5580	31
H(16A)	-34	1035	4534	27
H(16B)	1614	1133	4358	27
H(16C)	963	1594	4848	27
H(18A)	1365	3888	7315	30
H(18B)	456	4442	6932	30
H(18C)	2253	4476	7160	30
H(19A)	2680	4620	5923	32
H(19B)	881	4692	5756	32
H(19C)	1688	4203	5358	32
H(20A)	4065	3705	5367	30
H(20B)	4937	3214	5878	30

H(20C)	4286	3802	6179	30
H(21A)	3074	2368	5514	26
H(21B)	2525	2818	4892	26
H(21C)	1336	2560	5327	26
H(24A)	2752	517	3367	31
H(24B)	2412	219	2620	31