Supplemental Material for:

Metal-Assisted Oxygen Atom Addition to an Fe(III)-Thiolate.

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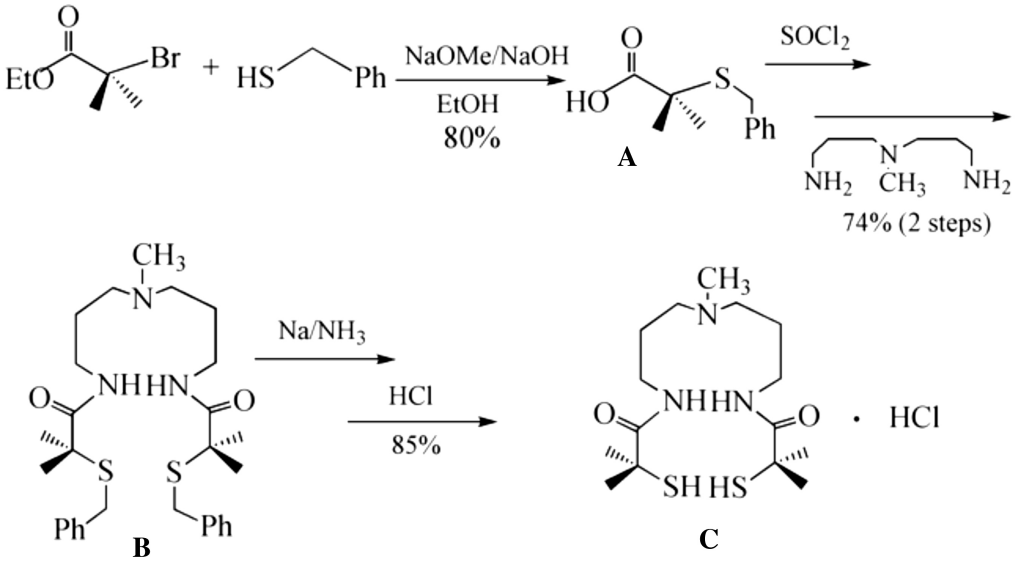
Experimental Details

Synthetic Route to Thiol Ligand $(HS^{Me})_2(N^{Me})(HN^{amide})_2$(Pr,Pr)•HCl (C). The protonated bis–thiol bis–carboxamide ligand, $(HS^{Me})_2(N^{Me})(HN^{amide})_2$(Pr,Pr)•HCl (**C**), was synthesized in reasonable yields according to the three step synthesis outlined in Scheme S1. Addition of benzyl mercaptan to ethyl 2-bromo-2-methyl propionate in the presence of base afforded **A** in 80% yield. In situ formation of the thionyl chloride derivative of **7**, followed by the addition of 3,3'-diamino-*N*-methyldipropylamine yielded benzyl-protected Pr,Pr amide–($Bz_2S_2^{Me2}N^{Me}N_2^{amide}$) (**B**). Deprotection of the sulfurs using Na/NH_3 followed by the addition of HCl afforded the hydrochloride salt of $(HS^{Me})_2(N^{Me})(HN^{amide})_2$(Pr,Pr) (**C**), as determined by ESI-MS (Figure S-6) and elemental analysis. Evidence for the presence of the free thiols was obtained by ^{1}H-NMR (Figure S-7 and Figure S-8) and FT-IR spectroscopy (ν_{SH}= 2496 cm^{-1}, Figure S-9).



Scheme S1.

Synthesis of 2-benzylsulfanyl-2-methyl propionic acid (A). To a stirred solution of ethyl 2-bromo-2-methyl propionate (15.0 mL, 102.5 mmol) in EtOH (340 mL) was added NaOMe (5.5 g,

102.5 mmol) followed by benzyl mercaptan (12.0 mL, 102.2 mmol). After stirring at 90 °C for 3.5 h, NaOH (5.3 g, 133.3 mmol) was added. The solution was filtered, and the solid recovered was washed with the minimum amount of EtOH. The solid was dissolved in H_2O (25 mL), and concentrated HCl was added dropwise until the solution reached pH=2. After filtration, the solid was dried *in vacuo* overnight to afford **A** (17.3 g, 81.2, 80%) as a white powder. ^{1}H NMR ($CDCl_3$, 301 MHz): δ 7.35-7.32 (m, 5H), 3.93 (s, 2H), 1.60 (s, 6H). ESI-MS calcd for $[C_{11}H_{14}O_2S + Na]^+$: 233.3, found 233.0.

Synthesis of benzyl-protected $Bz_2S_2^{Me2}N^{Me}(HN)_2^{amide}$(Pr,Pr) (B). To a stirred solution of 2-benzylsulfanyl-2-methyl propionic acid (**7**, 10.0 g, 47.6 mmol), placed in an ambient temperature H_2O bath, was added thionyl chloride (17.0 mL, 233.1 mmol). After 30 min, the excess thionyl chloride was removed under *vacuo*. The crude acid chloride derivative, 2-benzylsulfanyl-2-methyl-propionyl chloride, was used immediately in the next step without further purification.

To a stirred solution of 2-benzylsulfanyl-2-methyl-propionyl chloride (10.8 g, 47.4 mmol) in acetone (25 mL) at ambient temperature was added 3,3'-diamino-*N*-methyldipropylamine (7.7 mL, 47.8 mmol) followed by Et_3N (20.0 mL, 143.5 mmol). After stirring for 6 h, saturated aqueous NH_4Cl (20 mL) was added. The aqueous layer was extracted (3 x 20 mL) with Et_2O. The combined organic layers were washed with H_2O and brine (20 mL each), dried over Na_2SO_4, and concentrated *in vacuo* to yield **B** (17.2 g, 32.5 mmol, 74% (2 steps)) as a light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.46 (m, 2H), 7.36-7.20 (m, 10H), 3.74 (s, 4H), 3.22 (m, 4H), 2.40 (t, 4H), 2.21 (s, 3H), 1.64 (m, 4H), 1.54 (s, 12H); IR (KBr pellet): 3352 (N-H), 1651 (C=O) cm^{-1}; ESI-MS calcd for $C_{29}H_{43}N_3O_2S_2$: 529.8, found 530.6.

Synthesis of Thiol Ligand $(HS^{Me})_2(N^{Me})(HN^{amide})_2$(Pr,Pr) hydrochloride (C). To a stirred solution of liquid ammonia (~50 mL), sodium metal (200 mg) was added to afford an intense blue solution. To this blue solution was added 1 mL aliquots of a solution of **B** (10.0 g, 18.9 mmol) dissolved in diethyl ether (12 mL). Additional sodium was periodically added in small proportions to maintain the deep blue color of the solution. The completion of the reaction was assumed once the solution maintained its deep blue color for more than 30 min. The reaction was then quenched with NH_4Cl (200 mg), and the remaining liquid ammonia was evaporated under a stream of N_2. The resulting solid was dissolved in MeOH (15 mL), and conc. HCl was then added until the solution reached pH=2. The solution was concentrated *in vacuo*, the solid obtained redissolved in CH_3CN (15 mL), then filtered and the solvent evaporated under reduced pressure to afford a light brown glassy paste. Trituration with Et_2O yielded **C** (5.6 g, 16.0 mmol, 85%) as a white powder. ^{1}H NMR (D_2O, 301 MHz): δ 3.15 (t, 4H), 2.97 (m, 4H), 2.68 (s, 3H), 2.03 (s, 2H), 1.77 (m, 4H), 1.38 (s, 12H); IR (KBr pellet): 3349 (N-H), 2496 (S-H), 1640 (C=O) cm^{-1}; ESI-MS calcd for $C_{15}H_{31}N_3O_2S_2$: 349.6, found 350.4; Anal. Calcd. for $C_{15}H_{32}N_3O_2S_2Cl$: C, 46.7; H, 8.4; N, 10.9. Found: C, 46.3; H, 8.4; N, 11.0.

Supplemental Figures

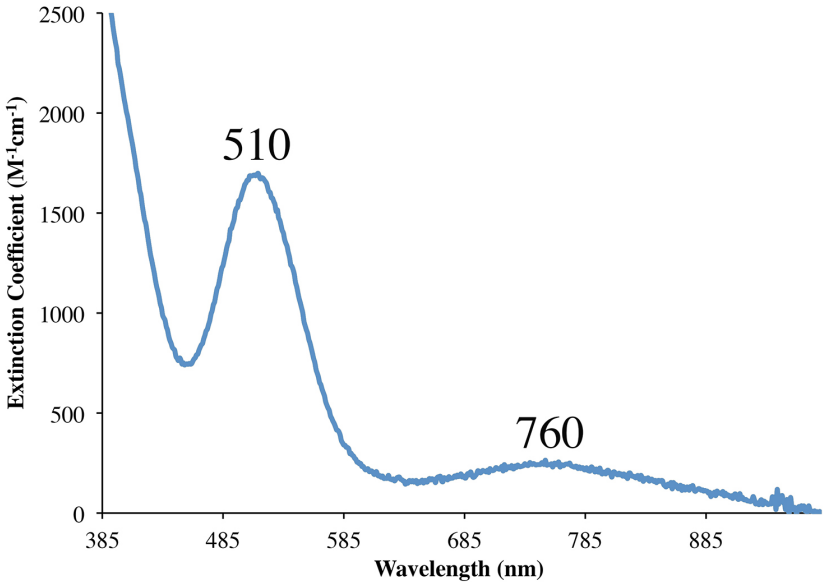


Figure S-1. Quantitative electronic absorption spectrum of [Fe^{III}(η^2-$S^{Me2}O$)($S^{Me2}N_3$(Pr,Pr)](PF_6) **(5)** in MeOH at 298 K.

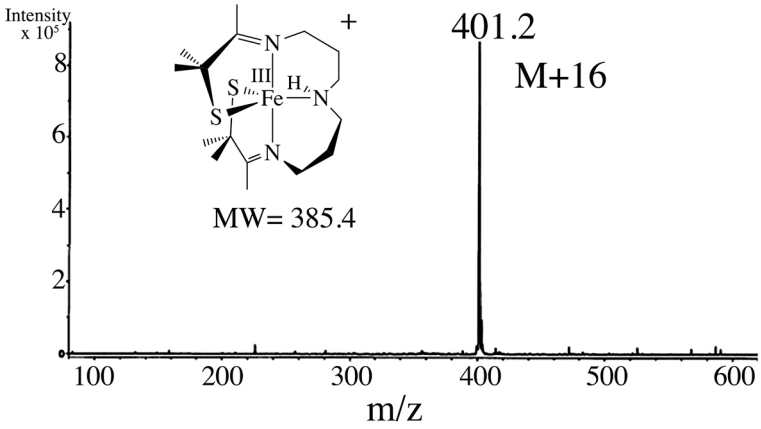


Figure S-2. ESI-MS of the product obtained upon addition of PhIO to **2** in MeOH, demonstrating that the m/z increases by 16, relative to the parent compound, consistent with the addition of an oxo atom.

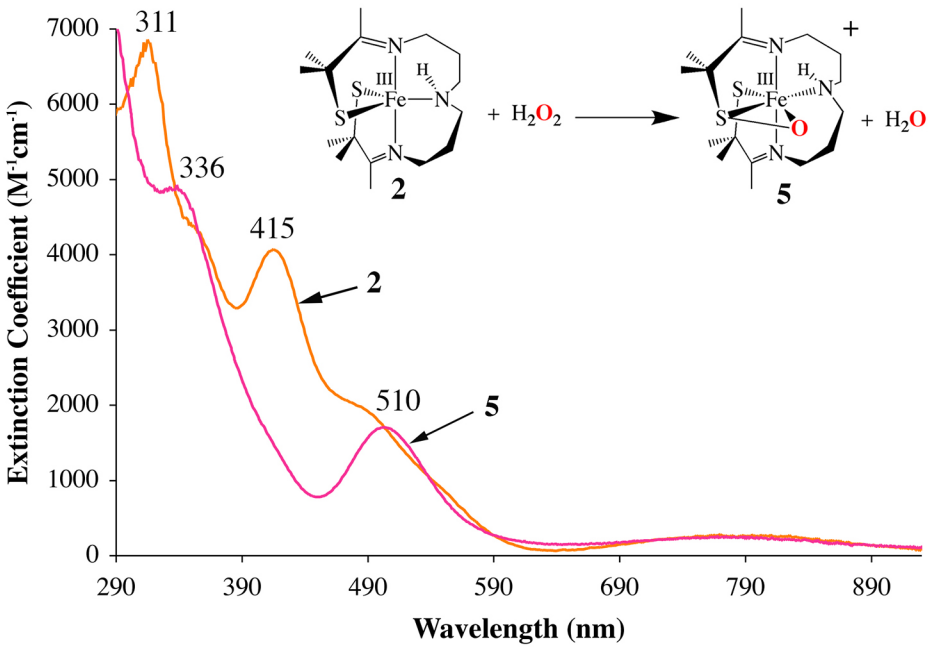


Figure S-3. Electronic absorption spectrum of $[Fe^{III}(S_2{}^{Me2}N_3(Pr,Pr))]^+$ (**2**) and the magenta product formed upon addition of 1 equiv of H_2O_2 in MeOH.

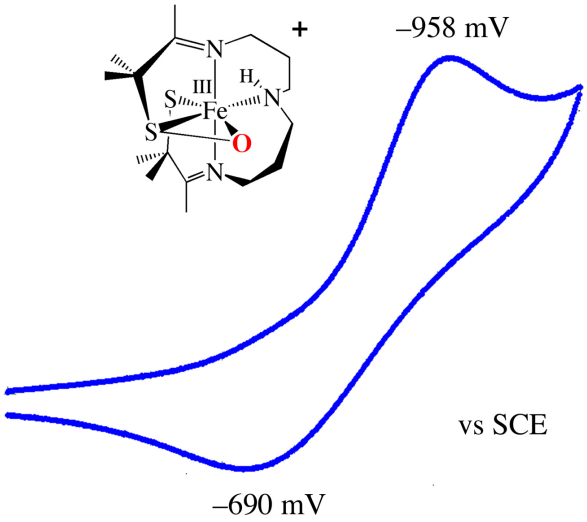


Figure S–4. Cyclic voltammogram of $[Fe^{III}(\eta^2\text{-}S^{Me2}O)(S^{Me2})N_3(Pr,Pr)]^+$ **(5)** in MeCN at 298 K (0.1 M $(Bu_4N)PF_6$, glassy carbon electrode, 150 mV/sec scan rate). Peak potentials versus SCE indicated.

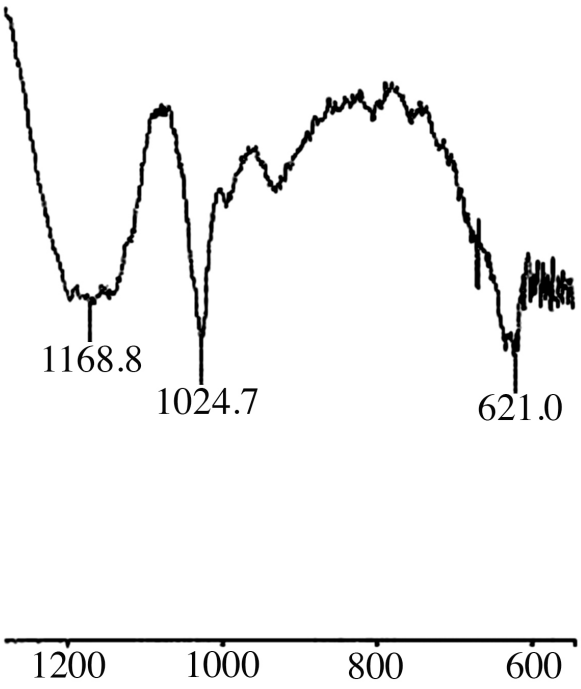


Figure S-5. IR spectrum of [$Fe^{III}(\eta^2$-$S^{Me2}O)(S^{Me2}N_3(Pr,Pr)]$(Cl) (**5**) (KBr pellet).

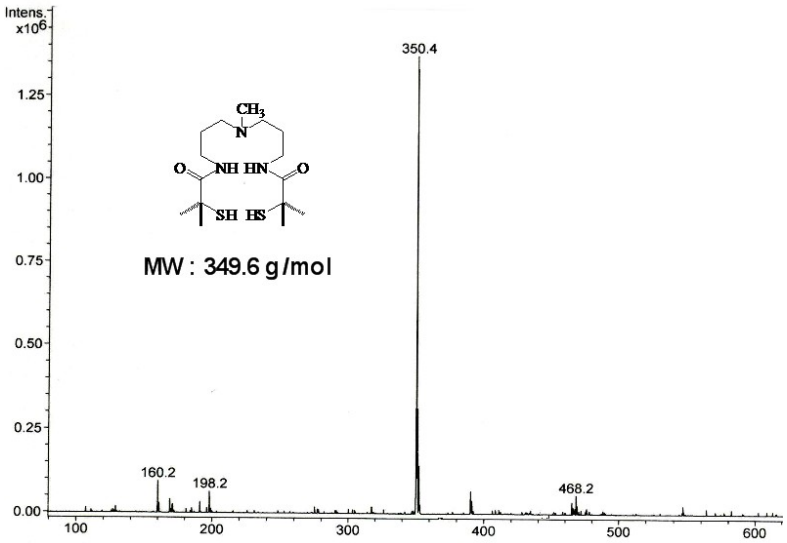


Figure S–6. ESI mass spec of (Pr,Pr) amide–$(S^{Me}H)_2(N^{Me})(N^{amide}H)_2$ (**C**) ligand.

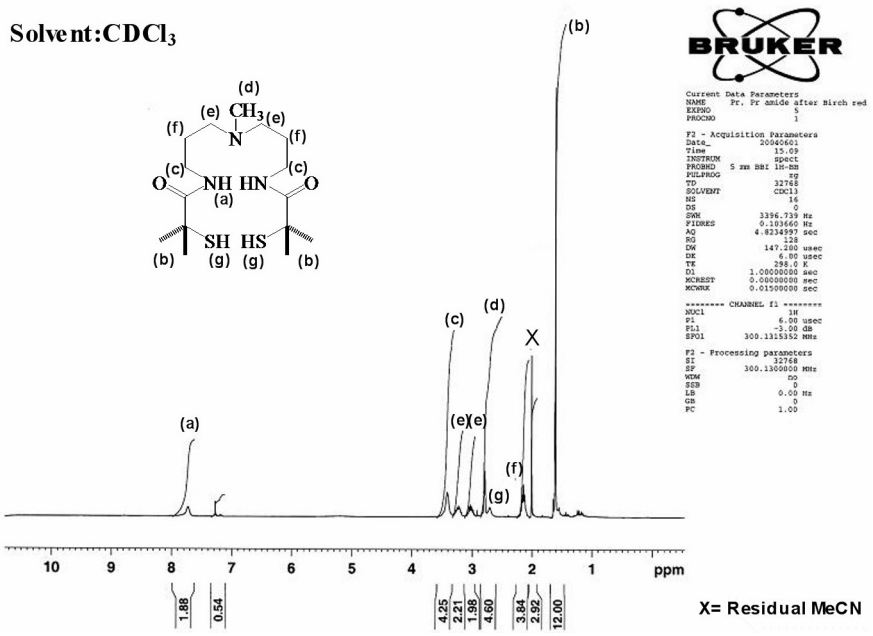


Figure S–7. ^{1}H NMR of (Pr,Pr) amide–$(S^{Me}H)_2(N^{Me})(N^{amide}H)_2$ (**C**) ligand in $CDCl_3$.

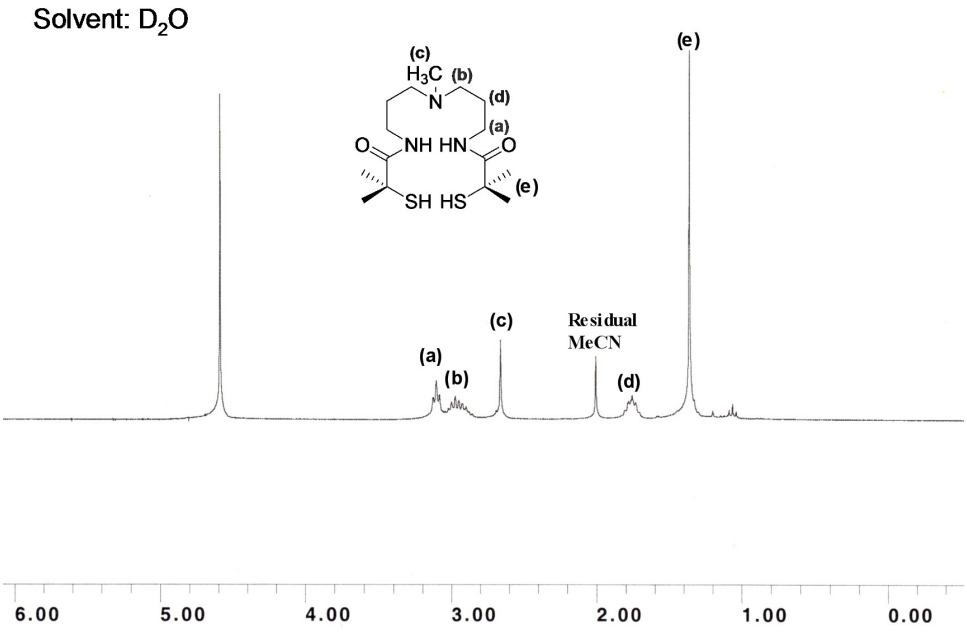


Figure S–8. ^{1}H NMR of (Pr,Pr) amide–$(S^{Me}H)_2(N^{Me})(N^{amide}H)_2$ (**C**) in D_2O.

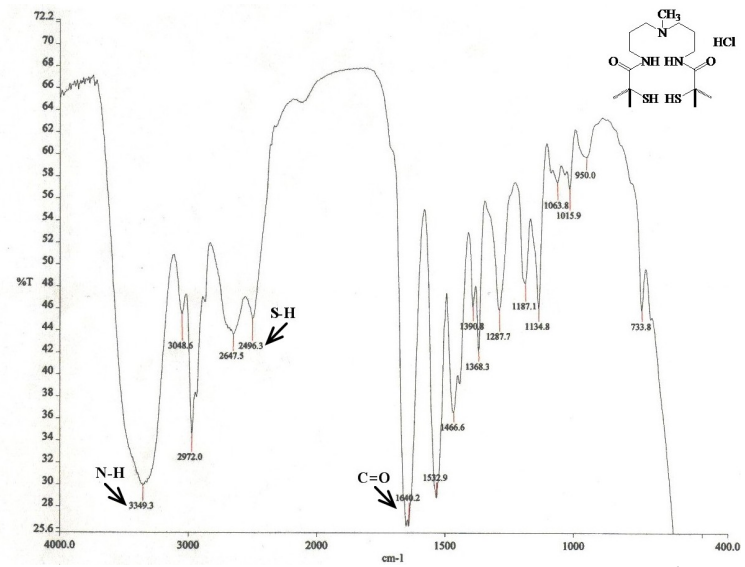


Figure S–9. IR spectrum of (Pr,Pr) amide–$(S^{Me}H)_2(N^{Me})(N^{amide}H)_2$ (**C**) ligand, showing the ν_{SH} stretch at 2496 cm^{-1}.

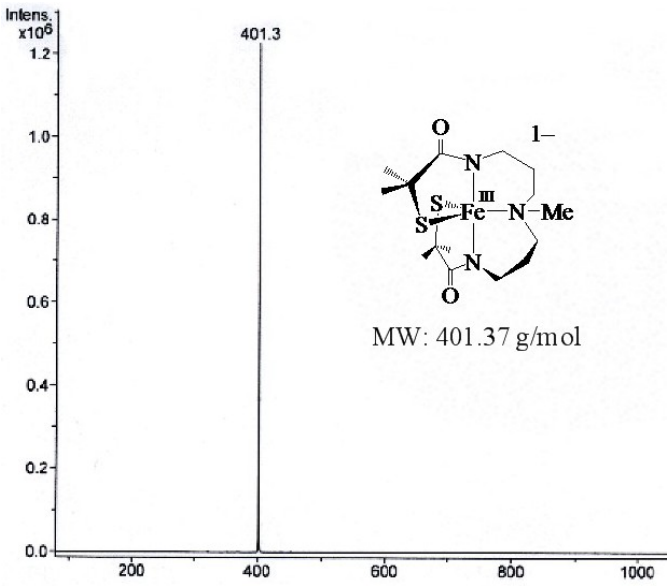


Figure S–10. ESI mass spec of $(Et_4N)[Fe^{III}S_2{}^{Me2}N^{Me}N_2{}^{amide}(Pr,Pr)]$ (**8**).

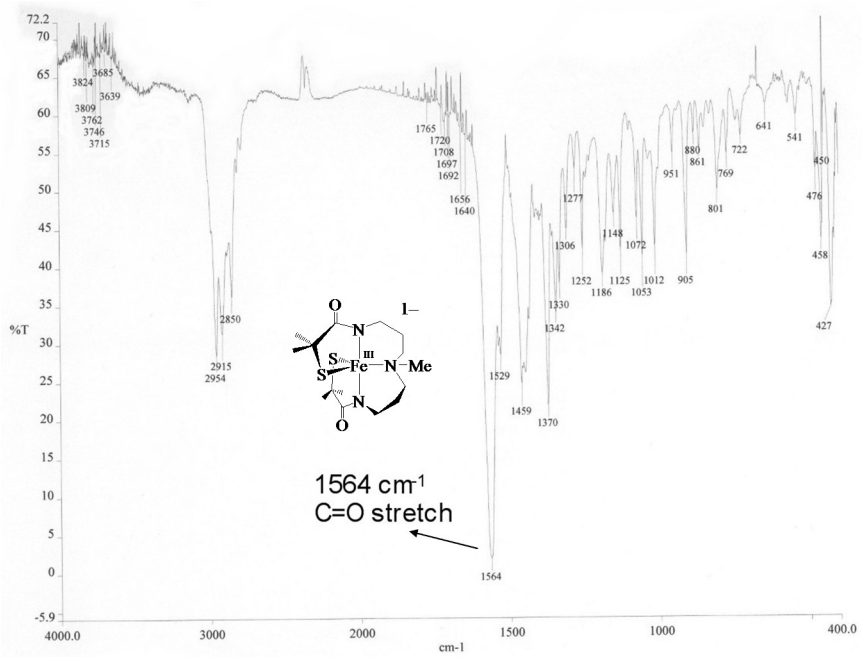


Figure S-11. IR spectrum of $(Et_4N)[Fe^{III}S_2{}^{Me2}N^{Me}N_2{}^{amide}(Pr,Pr)]$ (**8**) (KBr pellet).

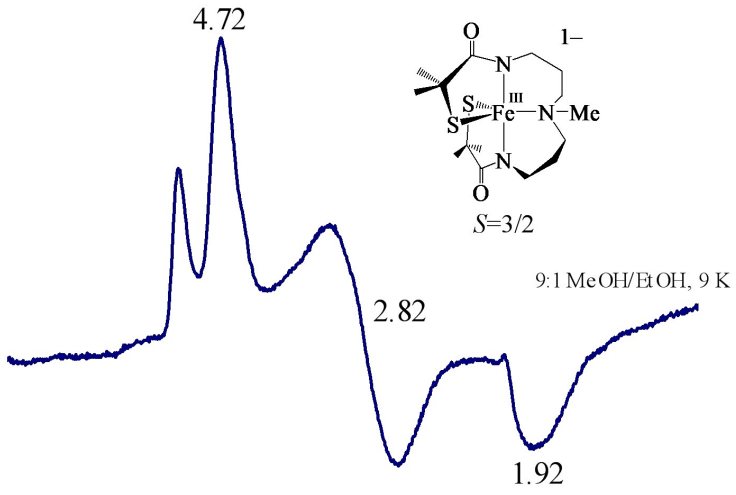


Figure S-12. X-band EPR spectrum of $(Et_4N)[Fe^{III}S_2{}^{Me2}N^{Me}N_2{}^{amide}(Pr,Pr)]$ (**8**) in MeOH/EtOH glass at 7 K.

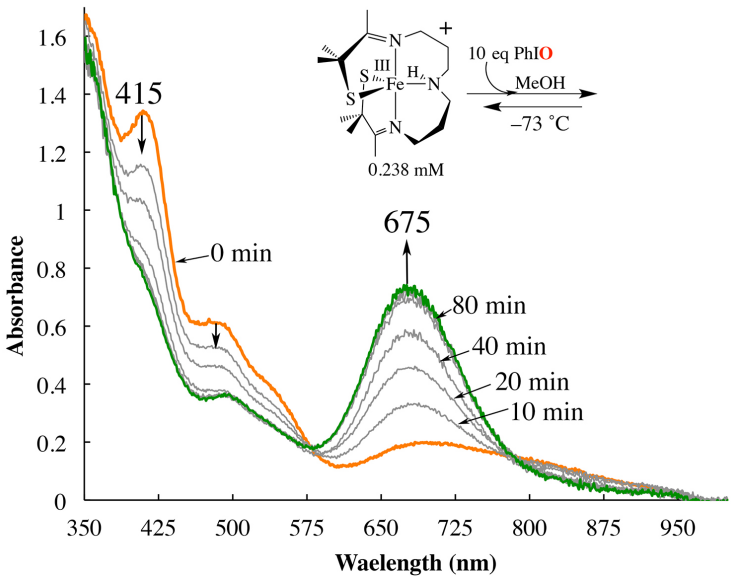


Figure S-13. Monitoring the formation of a green intermediate via the addition of 10 equiv of iodosylbenzene (PhIO) to $[Fe^{III}(S_2{}^{Me2}N_3(Pr,Pr))]^+$ (**2**) in MeOH at -73 ˚C.

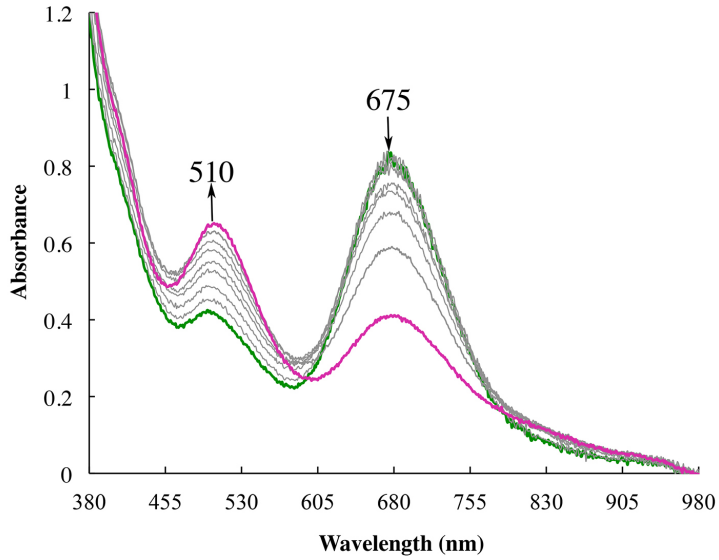


Figure S-14. Monitoring the conversion of the intermediate formed in the reaction between 10 equiv of iodosylbenzene (PhIO) and five-coordinate $[Fe^{III}(S_2{}^{Me2}N_3(Pr,Pr))]^+$ (**2**) (MeOH at -73 ˚C) to sulfenate-ligated **5**.

Supplemental Tables.

Table S-1. Metrical Parameters for DFT-Optimized versus Crystallographically-Determined Structures **2** and **8**.

$[Fe^{III}(S_2{}^{Me2}N_3(Pr, Pr,))]^+$ (**2**)						
	Bond Length (Å) (Exp.)	Bond Length (Å) (Opt.)	% Difference	Bond Angles	Bond Angles (degrees, Exp.)	Bond Angles (degrees, Opt.)
Fe-S1	2.161	2.119	1.96	S1-Fe-S2	121	116.9
Fe-S2	2.133	2.105	1.32	S1-Fe-N2	106.5	103.5
Fe-N1	1.954	1.935	0.98	N1-Fe-N2	86.2	87.4
Fe-N2	2.048	2.024	1.18	N1-Fe-N3	178.1	177.3
Fe-N3	1.967	1.951	0.82			
$[Fe^{III}S_2{}^{Me2}N^{Me}N_2{}^{amide}(Pr, Pr)]^{1-}$ (**8**)						
	Bond Length (Å) (Exp.)	Bond Length (Å) (Opt.)	% Difference	Bond Angles	Bond Angles (degrees, Exp.)	Bond Angles (degrees, Opt.)
Fe-S1	2.230	2.201	1.31	S1-Fe-S2	144.4	140.6
Fe-S2	2.210	2.207	0.14	S1-Fe-N2	107.1	111.2
Fe-N1	1.934	1.920	0.73	N2-Fe-N3	89.0	88.6
Fe-N2	2.212	2.240	1.26	S1-Fe-N3	96.1	94.1
Fe-N3	1.924	1.917	0.36	N1-Fe-N3	177.8	176.8

Table S-2. Crystal data and structure refinement for $[Fe^{III}(\eta^2\text{-}S^{Me2}O)(S^{Me2}N_3(Pr,Pr)](PF_6)$ (**5**).

Empirical formula	C16 H31 F6 Fe N3 O P S2
Formula weight	546.38
Temperature	130(2) K
Wavelength	0.71073 A
Crystal description/color	plate / red
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 12.3550(5)A α = 90 deg.
	b = 15.3070(8)A β = 123.147(3) deg.
	c = 14.8020(7)A γ = 90 deg.
Volume	2343.79(19) A^3
Z, Calculated density	4, 1.548 Mg/m^3
Absorption coefficient	0.950 mm^-1
F(000)	1132
Crystal size	0.24 x 0.24 x 0.05 mm
Reflections for indexing	306
Theta range for data collection	3.06 to 28.34 deg.
Index ranges	-16<=h<=16, -18<=k<=20, -19<=l<=19
Reflections collected /	
	unique 9378/5215 [R(int)= 0.0698]
Completeness to	theta = 25.00 96.1%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9540 and 0.8040
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5215/1/271
Goodness-of-fit on F^2	S = 1.001
S = root(sum(w*D*D)/(n-p)), where D = (Fo*Fo - Fc*Fc)	
Final R indices [I>2sigma(I)]	*R1 = 0.0721, wR2 = 0.1759
R indices (all data)	R1 = 0.1459, *wR2 = 0.2040
*Report these R factors.	
R1 = sum||Fo|-|Fc||/sum|Fo|, wR2= root(sum(w*D*D)/sum(w*Fo*Fo)), where D = (Fo*Fo - Fc*Fc)	
Weighting scheme	
calc w=1/[\s^2^(Fo^2^)+(0.1019P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3	
Largest diff. peak and hole	0.816 and -0.785 e.A^-3

Table S-3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [Fe^{III}(η^2-$S^{Me2}O$)($S^{Me2}N_3$(Pr,Pr)](PF_6) (**5**). U(eq) is defined as one third of the trace ofthe orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	4979(1)	3460(1)	2934(1)	45(1)
S(1)	3757(1)	3102(1)	1268(1)	65(1)
S(2)	5442(1)	4828(1)	3152(1)	58(1)
P(1)	9348(1)	1373(1)	1921(1)	50(1)
F(1)	9504(4)	1476(2)	925(3)	69(1)
F(2)	9176(3)	1268(2)	2910(3)	65(1)
F(3)	10002(4)	427(2)	2187(3)	73(1)
F(4)	7950(3)	955(2)	1137(3)	67(1)
F(5)	8695(3)	2322(2)	1653(3)	60(1)
F(6)	10730(3)	1803(3)	2693(3)	79(1)
O(1)	4081(4)	2346(3)	1958(4)	88(2)
N(1)	3364(4)	3663(3)	2878(4)	54(1)
N(2)	5887(5)	2775(3)	4349(4)	58(1)
N(3)	6600(4)	3297(3)	3018(3)	43(1)
C(1)	2207(5)	3506(4)	935(5)	55(2)
C(2)	1979(6)	4348(4)	295(6)	86(2)
C(3)	1160(5)	2823(4)	222(5)	59(2)
C(4)	2252(5)	3697(4)	1942(5)	55(2)
C(5)	1000(5)	3892(4)	1849(6)	73(2)
C(6)	3350(6)	3835(5)	3850(6)	73(2)
C(7)	4648(7)	3609(4)	4895(6)	71(2)
C(8)	5160(6)	2716(4)	4873(5)	65(2)
C(9)	6388(5)	1908(4)	4315(5)	60(2)
C(10)	7435(5)	1960(4)	4064(5)	60(2)
C(11)	6988(5)	2381(4)	3009(5)	52(1)
C(12)	7353(4)	3937(3)	3137(4)	39(1)
C(13)	8655(4)	3817(4)	3302(4)	46(1)
C(14)	6920(4)	4854(3)	3127(4)	44(1)
C(15)	7966(5)	5369(4)	4159(5)	57(2)
C(16)	6616(6)	5315(4)	2099(5)	66(2)

Table S-4. Bond lengths [A] and angles [deg] for [Fe^{III}(η^2-$S^{Me2}O$)($S^{Me2}N_3$(Pr,Pr)](PF_6) (**5**).

Fe(1)-N(3)	1.954(4)
Fe(1)-N(1)	1.976(4)
Fe(1)-N(2)	2.044(5)
Fe(1)-O(1)	2.115(4)
Fe(1)-S(1)	2.1420(17)
Fe(1)-S(2)	2.1477(17)
S(1)-O(1)	1.447(6)
S(1)-C(1)	1.806(5)
S(2)-C(14)	1.847(4)
P(1)-F(4)	1.596(4)
P(1)-F(6)	1.587(4)
P(1)-F(1)	1.596(3)
P(1)-F(2)	1.599(3)
P(1)-F(3)	1.599(4)
P(1)-F(5)	1.603(3)
N(1)-C(4)	1.314(7)
N(1)-C(6)	1.472(7)
N(2)-C(8)	1.475(6)
N(2)-C(9)	1.477(7)
N(2)-H(2)	0.9301
N(3)-C(12)	1.295(6)
N(3)-C(11)	1.484(7)
C(1)-C(4)	1.489(8)
C(1)-C(2)	1.532(8)
C(1)-C(3)	1.544(8)
C(2)-H(2A)	0.9799
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-H(3A)	0.9801
C(3)-H(3B)	0.9799
C(3)-H(3C)	0.9800
C(4)-C(5)	1.507(7)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(7)	1.540(10)
C(6)-H(6A)	0.9899
C(6)-H(6B)	0.9900
C(7)-C(8)	1.514(9)
C(7)-H(7A)	0.9901
C(7)-H(7B)	0.9899
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.531(7)

C(9)-H(9A)	0.9901
C(9)-H(9B)	0.9901
C(10)-C(11)	1.489(8)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(14)	1.499(7)
C(12)-C(13)	1.501(6)
C(13)-H(13A)	0.9799
C(13)-H(13B)	0.9801
C(13)-H(13C)	0.9800
C(14)-C(16)	1.526(8)
C(14)-C(15)	1.570(7)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9799
C(16)-H(16C)	0.9800
N(3)-Fe(1)-N(1)	178.00(19)
N(3)-Fe(1)-N(2)	84.29(17)
N(1)-Fe(1)-N(2)	95.7(2)
N(3)-Fe(1)-O(1)	94.44(17)
N(1)-Fe(1)-O(1)	87.56(18)
N(2)-Fe(1)-O(1)	94.3(2)
N(3)-Fe(1)-S(1)	95.37(13)
N(1)-Fe(1)-S(1)	86.08(15)
N(2)-Fe(1)-S(1)	134.02(15)
O(1)-Fe(1)-S(1)	39.72(16)
N(3)-Fe(1)-S(2)	86.28(13)
N(1)-Fe(1)-S(2)	91.89(14)
N(2)-Fe(1)-S(2)	113.24(15)
O(1)-Fe(1)-S(2)	152.32(17)
S(1)-Fe(1)-S(2)	112.62(8)
O(1)-S(1)-C(1)	108.0(3)
O(1)-S(1)-Fe(1)	69.14(19)
C(1)-S(1)-Fe(1)	101.6(2)
C(14)-S(2)-Fe(1)	101.76(17)
F(4)-P(1)-F(6)	179.2(2)
F(4)-P(1)-F(1)	89.8(2)
F(6)-P(1)-F(1)	89.9(2)
F(4)-P(1)-F(2)	89.56(18)
F(6)-P(1)-F(2)	90.7(2)
F(1)-P(1)-F(2)	179.4(2)
F(4)-P(1)-F(3)	90.9(2)
F(6)-P(1)-F(3)	89.9(2)
F(1)-P(1)-F(3)	91.01(17)

F(2)-P(1)-F(3)	89.16(18)
F(4)-P(1)-F(5)	89.17(18)
F(6)-P(1)-F(5)	90.0(2)
F(1)-P(1)-F(5)	88.89(18)
F(2)-P(1)-F(5)	90.94(17)
F(3)-P(1)-F(5)	179.9(2)
S(1)-O(1)-Fe(1)	71.1(2)
C(4)-N(1)-C(6)	117.4(4)
C(4)-N(1)-Fe(1)	120.0(4)
C(6)-N(1)-Fe(1)	122.6(4)
C(8)-N(2)-C(9)	110.5(4)
C(8)-N(2)-Fe(1)	114.8(4)
C(9)-N(2)-Fe(1)	115.5(3)
C(8)-N(2)-H(2)	104.9
C(9)-N(2)-H(2)	104.9
Fe(1)-N(2)-H(2)	104.9
C(12)-N(3)-C(11)	120.4(4)
C(12)-N(3)-Fe(1)	123.1(3)
C(11)-N(3)-Fe(1)	116.4(3)
C(4)-C(1)-C(2)	110.3(5)
C(4)-C(1)-C(3)	112.1(5)
C(2)-C(1)-C(3)	110.2(5)
C(4)-C(1)-S(1)	109.8(4)
C(2)-C(1)-S(1)	105.4(4)
C(3)-C(1)-S(1)	108.8(4)
C(1)-C(2)-H(2A)	109.5
C(1)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	109.5
C(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(1)-C(3)-H(3A)	109.5
C(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
N(1)-C(4)-C(1)	119.6(4)
N(1)-C(4)-C(5)	122.2(6)
C(1)-C(4)-C(5)	118.2(5)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(1)-C(6)-C(7)	112.3(5)
N(1)-C(6)-H(6A)	109.1

C(7)-C(6)-H(6A)	109.2
N(1)-C(6)-H(6B)	109.1
C(7)-C(6)-H(6B)	109.2
H(6A)-C(6)-H(6B)	107.9
C(6)-C(7)-C(8)	113.6(6)
C(6)-C(7)-H(7A)	108.8
C(8)-C(7)-H(7A)	108.9
C(6)-C(7)-H(7B)	108.9
C(8)-C(7)-H(7B)	108.9
H(7A)-C(7)-H(7B)	107.7
N(2)-C(8)-C(7)	109.7(5)
N(2)-C(8)-H(8A)	109.7
C(7)-C(8)-H(8A)	109.7
N(2)-C(8)-H(8B)	109.7
C(7)-C(8)-H(8B)	109.7
H(8A)-C(8)-H(8B)	108.2
N(2)-C(9)-C(10)	112.8(4)
N(2)-C(9)-H(9A)	109.0
C(10)-C(9)-H(9A)	109.1
N(2)-C(9)-H(9B)	109.0
C(10)-C(9)-H(9B)	109.0
H(9A)-C(9)-H(9B)	107.8
C(9)-C(10)-C(11)	113.5(5)
C(9)-C(10)-H(10A)	108.8
C(11)-C(10)-H(10A)	108.9
C(9)-C(10)-H(10B)	108.9
C(11)-C(10)-H(10B)	108.9
H(10A)-C(10)-H(10B)	107.7
N(3)-C(11)-C(10)	109.7(4)
N(3)-C(11)-H(11A)	109.8
C(10)-C(11)-H(11A)	109.7
N(3)-C(11)-H(11B)	109.7
C(10)-C(11)-H(11B)	109.8
H(11A)-C(11)-H(11B)	108.2
N(3)-C(12)-C(14)	118.8(4)
N(3)-C(12)-C(13)	123.7(5)
C(14)-C(12)-C(13)	117.4(4)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.4
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-C(16)	109.6(4)
C(12)-C(14)-C(15)	111.1(4)
C(16)-C(14)-C(15)	111.2(5)
C(12)-C(14)-S(2)	109.3(3)
C(16)-C(14)-S(2)	108.8(4)

C(15)-C(14)-S(2)	106.7(3)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.4
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(14)-C(16)-H(16A)	109.4
C(14)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(14)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S-5. Anisotropic displacement parameters (A^2 x 10^3) for [Fe^{III}(η^2-$S^{Me2}O$)($S^{Me2}N_3$(Pr,Pr)](PF_6) (**5**). 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)	35(1)	47(1)	58(1)	-5(1)	29(1)	-5(1)
S(1)	40(1)	89(1)	67(1)	-13(1)	30(1)	-3(1)
S(2)	43(1)	50(1)	92(1)	-11(1)	44(1)	0(1)
P(1)	51(1)	47(1)	63(1)	1(1)	38(1)	6(1)
F(1)	97(3)	60(2)	83(2)	8(2)	70(2)	13(2)
F(2)	65(2)	72(2)	69(2)	3(2)	44(2)	12(2)
F(3)	96(3)	51(2)	107(3)	16(2)	78(2)	22(2)
F(4)	66(2)	64(2)	75(2)	-11(2)	41(2)	-12(2)
F(5)	73(2)	42(2)	72(2)	0(2)	45(2)	10(2)
F(6)	56(2)	78(3)	93(3)	7(2)	36(2)	-6(2)
O(1)	82(3)	67(3)	117(4)	-35(2)	56(3)	-24(2)
N(1)	49(3)	48(3)	87(4)	-19(2)	51(3)	-10(2)
N(2)	70(3)	49(3)	74(3)	-10(2)	52(3)	-7(2)
N(3)	38(2)	40(3)	53(3)	2(2)	27(2)	6(2)
C(1)	39(3)	43(3)	75(4)	6(3)	27(3)	2(2)
C(2)	61(4)	55(4)	115(6)	27(4)	31(4)	-6(3)
C(3)	40(3)	39(3)	84(4)	1(3)	25(3)	-2(2)
C(4)	38(3)	36(3)	100(5)	-8(3)	43(3)	-5(2)
C(5)	49(3)	57(4)	117(6)	-12(4)	49(4)	1(3)
C(6)	58(4)	85(5)	97(5)	-28(4)	55(4)	-15(3)
C(7)	89(5)	70(5)	88(5)	-24(4)	70(4)	-19(4)
C(8)	69(4)	68(4)	73(4)	-4(3)	48(3)	-16(3)
C(9)	58(3)	42(3)	75(4)	4(3)	34(3)	-8(3)
C(10)	55(3)	38(3)	95(5)	-3(3)	45(3)	2(3)
C(11)	45(3)	44(3)	72(4)	0(3)	36(3)	-1(2)
C(12)	36(3)	43(3)	38(3)	2(2)	20(2)	0(2)
C(13)	34(3)	42(3)	64(3)	-5(3)	28(2)	-3(2)
C(14)	34(3)	45(3)	58(3)	1(2)	29(2)	1(2)
C(15)	51(3)	38(3)	88(4)	-8(3)	42(3)	-7(3)
C(16)	54(3)	65(4)	81(4)	33(3)	38(3)	22(3)

Table S-6. Hydrogen coordinates (x 10^4) and isotropic Displacement parameters (A^2 x 10^3) for [Fe^{III}(η^2-$S^{Me2}O$)($S^{Me2}N_3$(Pr,Pr)](PF_6) (**5**).

	x	y	z	U(eq)
H(2)	6617	3102	4822	69
H(2A)	2637	4781	760	104
H(2B)	2034	4223	-327	104
H(2C)	1119	4580	45	104
H(3A)	301	3080	-81	71
H(3B)	1256	2644	-366	71
H(3C)	1257	2313	660	71
H(5A)	1099	4423	2257	87
H(5B)	313	3978	1089	87
H(5C)	774	3401	2141	87
H(6A)	3155	4460	3865	88
H(6B)	2654	3487	3816	88
H(7A)	4538	3634	5508	85
H(7B)	5296	4055	5020	85
H(8A)	4431	2302	4470	78
H(8B)	5733	2494	5618	78
H(9A)	6748	1615	5020	72
H(9B)	5664	1547	3758	72
H(10A)	7739	1361	4064	72
H(10B)	8180	2293	4645	72
H(11A)	6244	2053	2420	62
H(11B)	7692	2372	2878	62
H(13A)	8583	3408	2763	55
H(13B)	8972	4382	3226	55
H(13C)	9261	3584	4027	55
H(15A)	8730	5467	4130	69
H(15B)	7610	5932	4188	69
H(15C)	8211	5027	4805	69
H(16A)	6033	4950	1473	79
H(16B)	6199	5877	2034	79
H(16C)	7419	5414	2129	79

Table S-7. Crystal data and structure refinement for $(Et_4N)[Fe^{III}S_2{}^{Me2}N^{Me}N_2{}^{amide}(Pr,Pr)]$ (**8**).

Empirical formula	C23 H47 Fe N4 O2 S2
Formula weight	531.62
Temperature	130(2) K
Wavelength	0.71073 A
Crystal description/color	prism / black
Crystal system, space group	Orthorhombic, P n a 21
Unit cell dimensions	a = 17.9580(3)A alpha = 90 deg. b = 8.5610(6)A beta = 90 deg. c = 18.1560(7)A gamma = 90 deg.
Volume	2791.3(2) A^3
Z, Calculated density	4, 1.265 Mg/m^3
Absorption coefficient	0.715 mm^-1
F(000)	1148
Crystal size	0.48 x 0.44 x 0.36 mm
Reflections for indexing	857
Theta range for data collection	2.27 to 28.63 deg.
Index ranges	-23<=h<=23, -11<=k<=11, -23<=l<=23
Reflections collected / unique	6353 / 6353 [R(int) = 0.063]
Completeness to theta = 25.00	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7828 and 0.7252
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6353 / 1 / 326

```
Goodness-of-fit on F^2           S = 0.940
S = root(sum(w*D*D)/(n-p)), where D = (Fo*Fo - Fc*Fc)

Final R indices [I>2sigma(I)]   *R1 = 0.0477, wR2 = 0.1075
R indices (all data)             R1 = 0.0868, *wR2 = 0.1219
*Report these R factors.
R1 = sum||Fo|-|Fc||/sum|Fo|, wR2= root(sum(w*D*D)/sum(w*Fo*Fo)),
where D = (Fo*Fo - Fc*Fc)

Weighting scheme
calc w=1/[\s^2^(Fo^2^)+(0.0686P)^2^+0.0000P] where P=(Fo^2^+2Fc^2^)/3

Largest diff. peak and hole     0.598 and -0.351 e.A^-3
```

Table S-8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $(Et_4N)[Fe^{III}S_2{}^{Me2}N^{Me}N_2{}^{amide}(Pr,Pr)]$ (**8**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Fe(1)	1378(1)	743(1)	1648(1)	39(1)
S(1)	420(1)	-795(1)	1941(1)	44(1)
S(2)	1820(1)	2369(1)	810(1)	48(1)
O(1)	-135(2)	3094(3)	2899(2)	51(1)
O(2)	2867(2)	-1470(3)	329(2)	54(1)
N(2)	2176(2)	637(4)	2574(2)	48(1)
N(1)	838(2)	2358(3)	2168(2)	44(1)
N(3)	1948(2)	-840(3)	1150(2)	43(1)
N(4)	221(2)	-4171(3)	-64(2)	39(1)
C(1)	-766(2)	1095(4)	1590(3)	46(1)
C(2)	-716(2)	79(5)	2877(2)	50(1)
C(3)	-255(2)	679(4)	2237(2)	41(1)
C(4)	160(2)	2162(4)	2471(2)	42(1)
C(5)	1265(2)	3735(5)	2403(2)	52(1)
C(6)	1800(2)	3336(6)	3021(3)	64(1)
C(7)	2431(4)	2214(9)	2756(4)	53(2)
C(7B)	1850(6)	1567(16)	3184(6)	60(4)
C(8)	1837(4)	-118(10)	3227(4)	57(2)
C(8B)	2901(6)	1328(18)	2370(7)	67(4)
C(9)	2843(4)	-274(10)	2361(4)	58(2)
C(9B)	2253(7)	-962(16)	2811(7)	64(4)
C(10)	2667(3)	-2027(6)	2167(3)	74(1)
C(11)	2093(2)	-2269(4)	1564(3)	53(1)
C(12)	2396(2)	-561(4)	575(2)	44(1)
C(13)	2258(2)	995(4)	170(2)	42(1)
C(14)	2998(2)	1680(5)	-92(2)	53(1)
C(15)	1766(2)	707(5)	-487(2)	50(1)
C(16)	-473(2)	-3308(4)	-309(2)	45(1)
C(17)	-519(2)	-1610(5)	-85(2)	51(1)
C(18)	312(2)	-4096(4)	775(2)	45(1)
C(19)	-367(2)	-4533(5)	1213(2)	49(1)
C(20)	168(2)	-5868(4)	-283(2)	43(1)
C(21)	108(3)	-6173(5)	-1102(3)	58(1)
C(22)	889(2)	-3364(4)	-417(2)	45(1)
C(23)	1622(2)	-4194(5)	-317(3)	51(1)

Table S-9. Bond lengths [A] and angles [deg] for $(Et_4N)[Fe^{III}S_2{}^{Me2}N^{Me}N_2{}^{amide}(Pr,Pr)]$ (**8**).

Fe(1)-N(3)	1.924(3)
Fe(1)-N(1)	1.934(3)
Fe(1)-S(2)	2.2100(12)
Fe(1)-N(2)	2.212(3)
Fe(1)-S(1)	2.2302(10)
S(1)-C(3)	1.830(4)
S(2)-C(13)	1.831(4)
O(1)-C(4)	1.233(4)
O(2)-C(12)	1.232(5)
N(2)-C(9B)	1.442(13)
N(2)-C(7)	1.463(8)
N(2)-C(8B)	1.477(11)
N(2)-C(9)	1.481(8)
N(2)-C(8)	1.481(7)
N(2)-C(7B)	1.484(13)
N(1)-C(4)	1.347(5)
N(1)-C(5)	1.469(5)
N(3)-C(12)	1.340(5)
N(3)-C(11)	1.460(5)
N(4)-C(20)	1.510(4)
N(4)-C(16)	1.516(5)
N(4)-C(22)	1.525(4)
N(4)-C(18)	1.534(5)
C(1)-C(3)	1.532(6)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.516(5)
C(2)-H(2A)	0.9800
C(2)-H(2B)	0.9800
C(2)-H(2C)	0.9800
C(3)-C(4)	1.532(5)
C(5)-C(6)	1.517(6)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7B)	1.546(15)
C(6)-C(7)	1.561(9)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(6)-H(6C)	0.9600
C(6)-H(6D)	0.9600
C(7)-C(8B)	1.334(15)
C(7)-C(7B)	1.413(12)
C(7)-H(7A)	0.9900

C(7)-H(7B)	0.9900
C(7)-H(8BB)	1.2211
C(7B)-C(8)	1.444(16)
C(7B)-H(7BA)	0.9601
C(7B)-H(7BB)	0.9600
C(8)-C(9B)	1.285(15)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(8B)-C(9)	1.376(16)
C(8B)-H(8BA)	0.9600
C(8B)-H(8BB)	0.9600
C(8B)-H(8BC)	0.9600
C(9)-C(9B)	1.461(14)
C(9)-C(10)	1.573(9)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(9B)-C(10)	1.658(16)
C(9B)-H(9BA)	0.9600
C(9B)-H(9BB)	0.9600
C(10)-C(11)	1.518(7)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(10)-H(10C)	0.9600
C(10)-H(10D)	0.9600
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.541(5)
C(13)-C(15)	1.505(6)
C(13)-C(14)	1.528(5)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.511(5)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(19)	1.503(5)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800

C(20)-C(21)	1.513(6)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.507(6)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
N(3)-Fe(1)-N(1)	177.83(14)
N(3)-Fe(1)-S(2)	85.93(10)
N(1)-Fe(1)-S(2)	93.76(10)
N(3)-Fe(1)-N(2)	89.03(14)
N(2)-Fe(1)-N(1)	89.03(14)
S(2)-Fe(1)-N(2)	108.43(9)
N(3)-Fe(1)-S(1)	96.14(10)
N(1)-Fe(1)-S(1)	85.37(9)
S(2)-Fe(1)-S(1)	144.40(5)
N(2)-Fe(1)-S(1)	107.14(9)
C(3)-S(1)-Fe(1)	100.01(12)
C(13)-S(2)-Fe(1)	100.75(13)
C(9B)-N(2)-C(7)	141.1(6)
C(9B)-N(2)-C(8B)	111.7(8)
C(7)-N(2)-C(8B)	54.0(6)
C(9B)-N(2)-C(9)	60.0(6)
C(7)-N(2)-C(9)	107.0(4)
C(8B)-N(2)-C(9)	55.5(6)
C(9B)-N(2)-C(8)	52.1(6)
C(7)-N(2)-C(8)	110.5(5)
C(8B)-N(2)-C(8)	137.6(6)
C(9)-N(2)-C(8)	108.2(5)
C(9B)-N(2)-C(7B)	108.9(8)
C(7)-N(2)-C(7B)	57.3(5)
C(8B)-N(2)-C(7B)	108.7(7)
C(9)-N(2)-C(7B)	142.8(6)
C(8)-N(2)-C(7B)	58.3(6)
C(9B)-N(2)-Fe(1)	109.2(5)
C(7)-N(2)-Fe(1)	109.7(3)
C(8B)-N(2)-Fe(1)	111.3(5)
C(9)-N(2)-Fe(1)	110.3(3)
C(8)-N(2)-Fe(1)	111.1(3)
C(7B)-N(2)-Fe(1)	106.9(5)
C(4)-N(1)-C(5)	116.9(3)
C(4)-N(1)-Fe(1)	124.3(2)
C(5)-N(1)-Fe(1)	117.0(3)

C(12)-N(3)-C(11)	116.3(3)
C(12)-N(3)-Fe(1)	124.1(3)
C(11)-N(3)-Fe(1)	116.3(3)
C(20)-N(4)-C(16)	109.8(3)
C(20)-N(4)-C(22)	112.0(3)
C(16)-N(4)-C(22)	107.6(3)
C(20)-N(4)-C(18)	108.0(3)
C(16)-N(4)-C(18)	111.0(3)
C(22)-N(4)-C(18)	108.4(3)
C(3)-C(1)-H(1A)	109.5
C(3)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(3)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-H(2A)	109.5
C(3)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5
C(3)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5
H(2B)-C(2)-H(2C)	109.5
C(2)-C(3)-C(4)	109.5(3)
C(2)-C(3)-C(1)	109.9(3)
C(4)-C(3)-C(1)	108.1(3)
C(2)-C(3)-S(1)	110.7(3)
C(4)-C(3)-S(1)	109.3(3)
C(1)-C(3)-S(1)	109.4(3)
O(1)-C(4)-N(1)	124.4(3)
O(1)-C(4)-C(3)	120.2(3)
N(1)-C(4)-C(3)	115.4(3)
N(1)-C(5)-C(6)	111.4(4)
N(1)-C(5)-H(5A)	109.3
C(6)-C(5)-H(5A)	109.3
N(1)-C(5)-H(5B)	109.3
C(6)-C(5)-H(5B)	109.3
H(5A)-C(5)-H(5B)	108.0
C(5)-C(6)-C(7B)	113.5(5)
C(5)-C(6)-C(7)	111.8(4)
C(5)-C(6)-H(6A)	109.7
C(7B)-C(6)-H(6A)	57.1
C(7)-C(6)-H(6A)	108.7
C(5)-C(6)-H(6B)	109.3
C(7B)-C(6)-H(6B)	137.2
C(7)-C(6)-H(6B)	109.2
H(6A)-C(6)-H(6B)	108.0
C(5)-C(6)-H(6C)	109.1
C(7B)-C(6)-H(6C)	108.4
C(7)-C(6)-H(6C)	57.7

H(6A)-C(6)-H(6C)	141.1
H(6B)-C(6)-H(6C)	55.5
C(5)-C(6)-H(6D)	109.5
C(7B)-C(6)-H(6D)	106.8
C(7)-C(6)-H(6D)	138.7
H(6A)-C(6)-H(6D)	54.0
H(6B)-C(6)-H(6D)	56.9
H(6C)-C(6)-H(6D)	109.5
C(8B)-C(7)-N(2)	63.5(6)
C(7B)-C(7)-N(2)	62.1(6)
C(8B)-C(7)-C(6)	166.1(8)
C(7B)-C(7)-C(6)	62.4(7)
N(2)-C(7)-C(6)	114.2(5)
C(8B)-C(7)-H(6C)	140.2
C(7B)-C(7)-H(6C)	97.6
N(2)-C(7)-H(6C)	150.5
C(8B)-C(7)-H(7A)	60.3
C(7B)-C(7)-H(7A)	153.9
N(2)-C(7)-H(7A)	105.1
C(6)-C(7)-H(7A)	109.4
H(6C)-C(7)-H(7A)	83.9
C(8B)-C(7)-H(7B)	82.1
C(7B)-C(7)-H(7B)	97.4
N(2)-C(7)-H(7B)	108.4
C(6)-C(7)-H(7B)	111.0
H(6C)-C(7)-H(7B)	94.6
H(7A)-C(7)-H(7B)	108.5
N(2)-C(7)-H(8BB)	97.5
C(6)-C(7)-H(8BB)	126.8
H(6C)-C(7)-H(8BB)	97.9
H(7B)-C(7)-H(8BB)	96.6
C(8)-C(7B)-N(2)	60.8(6)
C(8)-C(7B)-C(6)	171.0(9)
N(2)-C(7B)-C(6)	113.9(8)
C(8)-C(7B)-H(7BA)	69.0
N(2)-C(7B)-H(7BA)	110.4
C(6)-C(7B)-H(7BA)	108.3
H(6A)-C(7B)-H(7BA)	77.9
C(7)-C(7B)-H(7BB)	92.4
C(8)-C(7B)-H(7BB)	81.7
N(2)-C(7B)-H(7BB)	107.4
C(6)-C(7B)-H(7BB)	107.2
H(6A)-C(7B)-H(7BB)	95.0
H(7BA)-C(7B)-H(7BB)	109.5
C(9B)-C(8)-C(7B)	121.3(8)
C(9B)-C(8)-N(2)	62.4(6)
C(7B)-C(8)-N(2)	60.9(5)
C(9B)-C(8)-H(7BA)	148.4

N(2)-C(8)-H(7BA)	88.8
C(9B)-C(8)-H(8A)	81.5
C(7B)-C(8)-H(8A)	98.9
N(2)-C(8)-H(8A)	104.5
H(7BA)-C(8)-H(8A)	120.4
C(9B)-C(8)-H(8B)	54.7
C(7B)-C(8)-H(8B)	149.4
N(2)-C(8)-H(8B)	99.8
H(7BA)-C(8)-H(8B)	125.2
H(8A)-C(8)-H(8B)	109.5
C(9B)-C(8)-H(8C)	163.8
C(7B)-C(8)-H(8C)	69.9
N(2)-C(8)-H(8C)	123.3
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7B)-C(8)-H(9BA)	119.2
N(2)-C(8)-H(9BA)	83.7
H(7BA)-C(8)-H(9BA)	156.3
H(8B)-C(8)-H(9BA)	78.2
H(8C)-C(8)-H(9BA)	148.3
C(7B)-C(8)-H(9BB)	148.7
N(2)-C(8)-H(9BB)	93.0
H(7BA)-C(8)-H(9BB)	132.8
H(8A)-C(8)-H(9BB)	104.7
H(8C)-C(8)-H(9BB)	119.4
H(9BA)-C(8)-H(9BB)	70.2
C(7)-C(8B)-C(9)	121.7(9)
C(7)-C(8B)-N(2)	62.5(6)
C(9)-C(8B)-N(2)	62.4(6)
C(7)-C(8B)-H(7A)	45.6
C(9)-C(8B)-H(7A)	152.8
N(2)-C(8B)-H(7A)	94.0
C(9)-C(8B)-H(7B)	116.5
N(2)-C(8B)-H(7B)	83.2
H(7A)-C(8B)-H(7B)	70.1
C(7)-C(8B)-H(8BA)	90.8
C(9)-C(8B)-H(8BA)	90.1
N(2)-C(8B)-H(8BA)	109.3
H(7A)-C(8B)-H(8BA)	111.6
H(7B)-C(8B)-H(8BA)	51.6
C(7)-C(8B)-H(8BB)	61.8
C(9)-C(8B)-H(8BB)	160.3
N(2)-C(8B)-H(8BB)	110.6
H(7B)-C(8B)-H(8BB)	78.9
H(8BA)-C(8B)-H(8BB)	109.5
C(7)-C(8B)-H(8BC)	159.8
C(9)-C(8B)-H(8BC)	60.1
N(2)-C(8B)-H(8BC)	108.5

H(7A)-C(8B)-H(8BC)	122.3
H(7B)-C(8B)-H(8BC)	160.9
H(8BA)-C(8B)-H(8BC)	109.5
H(8BB)-C(8B)-H(8BC)	109.5
C(7)-C(8B)-H(9B)	154.1
N(2)-C(8B)-H(9B)	94.1
H(7A)-C(8B)-H(9B)	133.6
H(7B)-C(8B)-H(9B)	156.2
H(8BA)-C(8B)-H(9B)	108.4
H(8BB)-C(8B)-H(9B)	123.6
C(8B)-C(9)-C(9B)	116.7(9)
C(8B)-C(9)-N(2)	62.1(6)
C(9B)-C(9)-N(2)	58.7(6)
C(8B)-C(9)-C(10)	165.7(8)
C(9B)-C(9)-C(10)	66.1(7)
N(2)-C(9)-C(10)	113.5(5)
C(9B)-C(9)-H(8BC)	153.3
N(1)-C(9)-H(8BC)	95.0
C(10)-C(9)-H(8BC)	128.7
C(8B)-C(9)-H(9A)	84.1
C(9B)-C(9)-H(9A)	94.5
N(2)-C(9)-H(9A)	108.5
C(10)-C(9)-H(9A)	110.0
H(8BC)-C(9)-H(9A)	98.9
C(8B)-C(9)-H(9B)	61.5
C(9B)-C(9)-H(9B)	156.6
N(2)-C(9)-H(9B)	106.8
C(10)-C(9)-H(9B)	109.8
H(9A)-C(9)-H(9B)	108.1
C(8B)-C(9)-H(10C)	139.4
C(9B)-C(9)-H(10C)	103.0
N(2)-C(9)-H(10C)	145.7
H(8BC)-C(9)-H(10C)	96.9
H(9A)-C(9)-H(10C)	101.3
H(9B)-C(9)-H(10C)	78.8
C(8)-C(9B)-N(2)	65.5(7)
C(8)-C(9B)-C(9)	121.6(11)
N(2)-C(9B)-C(9)	61.3(6)
C(8)-C(9B)-C(10)	169.7(10)
N(2)-C(9B)-C(10)	110.8(8)
C(9)-C(9B)-C(10)	60.2(6)
N(2)-C(9B)-H(8A)	84.2
C(9)-C(9B)-H(8A)	110.8
C(10)-C(9B)-H(8A)	149.9
C(8)-C(9B)-H(8B)	48.1
N(2)-C(9B)-H(8B)	97.7
C(9)-C(9B)-H(8B)	156.4
C(10)-C(9B)-H(8B)	125.8

H(8A)-C(9B)-H(8B)	75.0
C(8)-C(9B)-H(9BA)	80.7
N(2)-C(9B)-H(9BA)	108.6
C(9)-C(9B)-H(9BA)	94.5
C(10)-C(9B)-H(9BA)	109.5
H(8B)-C(9B)-H(9BA)	103.1
C(8)-C(9B)-H(9BB)	64.6
N(2)-C(9B)-H(9BB)	108.9
C(9)-C(9B)-H(9BB)	156.1
C(10)-C(9B)-H(9BB)	109.5
H(8A)-C(9B)-H(9BB)	88.5
H(9BA)-C(9B)-H(9BB)	109.5
C(8)-C(9B)-H(10B)	146.2
N(2)-C(9B)-H(10B)	146.9
C(9)-C(9B)-H(10B)	91.6
H(8A)-C(9B)-H(10B)	125.6
H(8B)-C(9B)-H(10B)	103.6
H(9BA)-C(9B)-H(10B)	91.0
H(9BB)-C(9B)-H(10B)	88.1
C(11)-C(10)-C(9)	115.3(4)
C(11)-C(10)-C(9B)	106.2(5)
C(9)-C(10)-C(9B)	53.7(5)
C(11)-C(10)-H(10A)	108.0
C(9)-C(10)-H(10A)	107.8
C(9B)-C(10)-H(10A)	145.7
C(11)-C(10)-H(10B)	109.0
C(9)-C(10)-H(10B)	108.9
C(9B)-C(10)-H(10B)	62.3
H(10A)-C(10)-H(10B)	107.6
C(11)-C(10)-H(10C)	111.2
C(9)-C(10)-H(10C)	56.0
C(9B)-C(10)-H(10C)	108.8
H(10A)-C(10)-H(10C)	55.7
H(10B)-C(10)-H(10C)	139.6
C(11)-C(10)-H(10D)	110.7
C(9)-C(10)-H(10D)	133.9
C(9B)-C(10)-H(10D)	110.4
H(10A)-C(10)-H(10D)	58.7
H(10B)-C(10)-H(10D)	50.7
H(10C)-C(10)-H(10D)	109.5
N(3)-C(11)-C(10)	112.2(3)
N(3)-C(11)-H(11A)	109.2
C(10)-C(11)-H(11A)	109.2
N(3)-C(11)-H(11B)	109.2
C(10)-C(11)-H(11B)	109.2
H(11A)-C(11)-H(11B)	107.9
O(2)-C(12)-N(3)	125.5(4)
O(2)-C(12)-C(13)	118.9(4)

N(3)-C(12)-C(13)	115.4(3)
C(15)-C(13)-C(14)	109.0(3)
C(15)-C(13)-C(12)	109.3(3)
C(14)-C(13)-C(12)	109.9(3)
C(15)-C(13)-S(2)	110.9(3)
C(14)-C(13)-S(2)	109.0(3)
C(12)-C(13)-S(2)	108.8(3)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-N(4)	115.8(3)
C(17)-C(16)-H(16A)	108.3
N(4)-C(16)-H(16A)	108.3
C(17)-C(16)-H(16B)	108.3
N(4)-C(16)-H(16B)	108.3
H(16A)-C(16)-H(16B)	107.4
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(19)-C(18)-N(4)	115.4(3)
C(19)-C(18)-H(18A)	108.4
N(4)-C(18)-H(18A)	108.4
C(19)-C(18)-H(18B)	108.4
N(4)-C(18)-H(18B)	108.4
H(18A)-C(18)-H(18B)	107.5
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
N(4)-C(20)-C(21)	115.5(3)
N(4)-C(20)-H(20A)	108.4
C(21)-C(20)-H(20A)	108.4
N(4)-C(20)-H(20B)	108.4
C(21)-C(20)-H(20B)	108.4

H(20A)-C(20)-H(20B)	107.5
C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-N(4)	115.0(3)
C(23)-C(22)-H(22A)	108.5
N(4)-C(22)-H(22A)	108.5
C(23)-C(22)-H(22B)	108.5
N(4)-C(22)-H(22B)	108.5
H(22A)-C(22)-H(22B)	107.5
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S-10. Anisotropic displacement parameters (A^2 x 10^3) for $(Et_4N)[Fe^{III}S_2^{Me2}N^{Me}N_2^{amide}(Pr,Pr)]$ (**8**). 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)	38(1)	45(1)	35(1)	2(1)	-2(1)	-2(1)
S(1)	39(1)	42(1)	51(1)	-4(1)	0(1)	-3(1)
S(2)	58(1)	46(1)	40(1)	5(1)	6(1)	4(1)
O(1)	57(2)	50(2)	47(2)	-10(1)	7(1)	-5(1)
O(2)	48(2)	51(2)	62(2)	6(2)	14(1)	8(1)
N(2)	39(2)	63(2)	43(2)	6(2)	-4(2)	-9(2)
N(1)	53(2)	40(2)	39(2)	-3(1)	4(2)	-7(1)
N(3)	39(2)	43(2)	47(2)	9(2)	2(2)	2(1)
N(4)	42(2)	37(2)	38(2)	3(1)	6(1)	2(1)
C(1)	45(2)	50(2)	44(2)	-8(2)	-3(2)	1(2)
C(2)	55(2)	44(2)	49(2)	3(2)	6(2)	-5(2)
C(3)	42(2)	43(2)	36(2)	0(2)	0(2)	-2(2)
C(4)	51(2)	44(2)	31(2)	2(2)	-2(2)	4(2)
C(5)	60(3)	51(2)	46(2)	-3(2)	2(2)	-17(2)
C(6)	64(3)	74(3)	54(3)	-15(2)	-5(2)	-24(2)
C(7)	42(4)	78(5)	41(4)	9(3)	-14(3)	-16(4)
C(7B)	37(6)	105(11)	38(6)	5(6)	-4(5)	-30(6)
C(8)	50(4)	84(6)	37(4)	18(4)	1(3)	-14(4)
C(8B)	35(6)	113(12)	52(7)	-14(7)	-3(5)	-31(7)
C(9)	37(4)	94(6)	43(4)	-1(4)	-3(3)	-2(4)
C(9B)	42(7)	98(10)	51(7)	25(7)	-5(6)	-9(6)
C(10)	75(3)	73(3)	75(3)	18(3)	-23(3)	22(2)
C(11)	43(2)	55(2)	62(3)	15(2)	1(2)	6(2)
C(12)	36(2)	50(2)	45(2)	7(2)	1(2)	0(2)
C(13)	39(2)	48(2)	40(2)	2(2)	1(2)	4(2)
C(14)	48(2)	47(2)	62(3)	11(2)	2(2)	-2(2)
C(15)	54(2)	53(2)	43(2)	5(2)	-3(2)	-4(2)
C(16)	49(2)	42(2)	44(2)	3(2)	1(2)	7(2)
C(17)	53(2)	45(2)	55(3)	-2(2)	-2(2)	9(2)
C(18)	50(2)	49(2)	36(2)	1(2)	4(2)	1(2)
C(19)	50(2)	52(2)	44(2)	5(2)	8(2)	-1(2)
C(20)	47(2)	35(2)	45(2)	1(2)	2(2)	6(2)
C(21)	75(3)	47(2)	52(3)	-10(2)	-1(2)	1(2)
C(22)	51(2)	41(2)	42(2)	2(2)	8(2)	-5(2)
C(23)	46(2)	52(2)	55(3)	4(2)	12(2)	-3(2)

Table S-11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $(Et_4N)[Fe^{III}S_2{}^{Me2}N^{Me}N_2{}^{amide}(Pr,Pr)]$ (**8**).

	x	y	z	U(eq)
H(1A)	-1097	1952	1734	56
H(1B)	-1064	181	1454	56
H(1C)	-463	1420	1168	56
H(2A)	-1111	831	2990	59
H(2B)	-396	-54	3309	59
H(2C)	-939	-928	2745	59
H(5A)	917	4557	2571	63
H(5B)	1548	4152	1978	63
H(6A)	1526	2829	3429	77
H(6B)	2026	4309	3213	77
H(6C)	2288	3706	2894	77
H(6D)	1638	3832	3467	77
H(7A)	2651	2624	2296	64
H(7B)	2830	2131	3131	64
H(7BA)	1360	1195	3301	72
H(7BB)	2169	1443	3605	72
H(8A)	2254	-270	3568	68
H(8B)	1695	-1124	3012	68
H(8C)	1412	323	3494	68
H(8BA)	3233	1267	2782	80
H(8BB)	2840	2401	2227	80
H(8BC)	3103	745	1965	80
H(9A)	3208	-223	2769	70
H(9B)	3063	254	1927	70
H(9BA)	2547	-982	3253	76
H(9BB)	1768	-1381	2911	76
H(10A)	3137	-2527	2008	89
H(10B)	2498	-2569	2619	89
H(10C)	3093	-1467	1986	89
H(10D)	2825	-3011	2367	89
H(11A)	2272	-3088	1223	64
H(11B)	1622	-2641	1788	64
H(14A)	3222	980	-456	63
H(14B)	3335	1795	329	63
H(14C)	2910	2706	-316	63
H(15A)	1991	-99	-800	60
H(15B)	1713	1676	-770	60
H(15C)	1275	356	-320	60
H(16A)	-505	-3369	-852	54

H(16B)	-912	-3859	-106	54
H(17A)	-1028	-1229	-161	61
H(17B)	-174	-995	-386	61
H(17C)	-385	-1505	435	61
H(18A)	724	-4801	919	54
H(18B)	459	-3021	912	54
H(19A)	-248	-4514	1740	58
H(19B)	-530	-5584	1073	58
H(19C)	-767	-3784	1112	58
H(20A)	-273	-6329	-38	51
H(20B)	613	-6420	-94	51
H(21A)	83	-7302	-1190	69
H(21B)	545	-5741	-1352	69
H(21C)	-344	-5675	-1294	69
H(22A)	792	-3252	-951	53
H(22B)	933	-2300	-208	53
H(23A)	2030	-3498	-462	61
H(23B)	1631	-5135	-624	61
H(23C)	1682	-4489	201	61

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