Supporting Information

Hammett Correlations as Test of Mechanism of CO-Induced Disulfide Elimination from Dinitrosyl Iron Complexes

Randara Pulukkody, Samuel J. Kyran, Michael J. Drummond,

Chung-Hung Hsieh, Donald J. Darensbourg, and Marcetta Y. Darensbourg*

Department of Chemistry, Texas A & M University, College Station, TX 77843

E-mail: marcetta@mail.chem.tamu.edu

SI Table of Contents **Page**

Experimental Section

General Methods and Materials

Reagent grade solvents were used, further purified and degassed by a Bruker solvent purification system, and stored over molecular sieves. All reagents, including 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride ($sIMesH^+Cl^-$) and sodium *tert*-butoxide, NaOtBu, were purchased from Sigma-Aldrich Chemical Co. and were used as received. Air-free conditions were maintained during synthesis, isolation, and storage of products through the use of standard Schlenk-line techniques (N_2 atmosphere) and an Ar-filled glove box. Roussin's Red esters (**RRE(a-e)**) $(\mu\text{-}(S\text{-}C_6H_4X))_2[Fe(NO)_2]_2$ were prepared according to published procedures.[1]

Physical Measurements

A Bruker Tensor 37 FTIR spectrometer and CaF_2 solution cells of 0.1 mm pathlength were used to record infrared spectra. EPR spectra were recorded in THF using a Bruker ESP 300 equipped with an Oxford ER910 cryostat operating at 298 K. Elemental analyses of crystalline samples was determined by Atlantic Microlab, Inc., Norcross, GA.

A Bioanalytical Systems 100 electrochemical workstation with a glassy carbon working electrode and a platinum wire auxiliary electrode was used to conduct the electrochemical analysis of all compounds. A standard three electrode cell under an Ar atmosphere at room temperature was used to obtain all voltammograms. Cyclic voltammograms of complexes **1a-1e**, the unsubstituted analogue (sIMes)(SPh)$Fe(NO)_2$ or **1**, and bis(4-nitrophenyl)disulfide were recorded in 2 mM THF solutions with 100 mM $[n\text{-}Bu_4N][PF_6]$ as the supporting electrolyte. The potentials were measured relative to a $Ag^0/AgNO_3$ electrode using a glassy carbon working electrode, and are referenced to $Cp_2Fe/\ Cp_2Fe^+$ ($E_{1/2}$ = 0.00 V vs $Ag/AgNO_3$ in THF).

X-ray Crystallography

Suitable crystals of the same habit were identified using a Bausch and Lomb 10x microscope. Each crystal was coated in paratone, affixed to a Nylon loop and placed under streaming nitrogen (110K) in a SMART Apex CCD diffractometer (See details in .cif files). The space groups were determined on the basis of systematic absences and intensity statistics. The structures were solved by direct methods and refined by full-matrix least squares on F^2. Anisotropic displacement parameters were determined for all nonhydrogen atoms. Hydrogen atoms were placed at idealized positions and refined with fixed isotropic displacement parameters. A list of programs used is as follows: data collection and cell refinement, APEX2;[2] data reductions, SAINTPLUS Version 6.63;[3] absorption correction, SADABAS;[4] structural solutions, SHELXS-97;[5] structural refinement, SHELXL-97;[6] graphics and publication materials, Mercury Version 2.3.[7]

Synthesis of compounds 1a- 1e [(sIMes)(S-C_6H_4X)Fe$(NO)_2$]

The Roussin's Red Esters (μ-(S-C_6H_4X))$_2$[Fe$(NO)_2$]$_2$, represented as **RRE(a, b, c** and **e)**, were synthesized by the room temperature reaction of 0.5 mmol of the corresponding 4,4'-XArSSArX disulfide with 1 mmol of freshly prepared Fe$(CO)_2(NO)_2$ (isolated by vacuum transfer to a flask immersed in liquid N_2) [8] in THF solution. (The –CF_3 derivative (**RRE d**) was synthesized using similar procedures, but with 1 mmol of 4-(trifluoromethyl)thiophenol in place of the disulfide.) In a separate degassed flask, a 0.34 g (1.0 mmol) sample of 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride and 0.12 g (1.2 mmol) of NaOtBu were dissolved in 20 mL of THF and stirred for 30 minutes. This carbene solution was then transferred via cannula into the flask containing the THF solution of the respective RRE. The solution was stirred for 1

h, resulting in a color change from brown to blue/purple. Formation of the product DNIC (**1a-1e**) was confirmed by IR spectroscopy, and the solution was then dried in vacuo. The resulting residue (> 85% crude yield) was dissolved in 10 mL of ether, filtered through celite, and recrystallized in cold hexanes. The solids were handled under inert gas as a precaution against degradation by moisture and air. X-ray quality crystals of **1b** and **1c** were obtained by slow evaporation of concentrated ether solutions, while those of **1a** and **1e** were obtained from solutions of THF/hexanes. Note that complex **1b** co-crystallized with one molecule of cyclohexane, found in low abundance in the hexanes used in the recrystallization process. IR (THF, cm^{-1}) **1a:** *ν*(NO) 1759(s), 1713(vs). Elemental Analysis, Found: C, 60.1; H, 6.3; N, 9.4. Calc. for $FeC_{28}H_{33}N_4O_3S$: C, 59.9; H, 5.9; N, 9.9 %. IR (THF, cm^{-1}) **1b**: *ν*(NO) 1761(s), 1714(vs). Elemental Analysis, Found: C, 64.1; H, 7.1; N, 8.7. Calc. for $FeC_{28}H_{33}N_4O_2S$• c-C_6H_{12}: C, 64.85; H, 7.2; N, 8.9 %. IR (THF, cm^{-1}) **1c:** *ν*(NO) 1767(s), 1717(vs). Elemental Analysis, Found: C, 57.4; H, 5.5; N, 9.7. Calc. for $FeC_{27}H_{30}N_4O_2SCl$: 57.3; H, 5.3; N, 9.9 %. IR (THF, cm^{-1}) **1d:** *ν*(NO) 1769(s), 1718(vs). Elemental Analysis, Found: C, 56.4; H, 5.1; N, 9.0. Calc. for $FeC_{28}H_{30}N_4O_2F_3S$: C, 56.1; H, 5.0; N, 9.35 %. IR (THF, cm^{-1}) **1e:** *ν*(NO) 1772(s), 1720(vs). Elemental Analysis, Found: C, 56.6; H, 5.5; N, 11.4. Calc. for $FeC_{27}H_{30}N_5O_4S$: C, 56.3; H, 5.25; N, 12.15 %.

Kinetic Measurements

In situ infrared monitoring was carried out using a Mettler Toledo iC10 ReactIR with an AgX fiber conduit probe having a SiComp ATR crystal. In a typical experiment, a 0.0100 M solution of *para* substituted (sIMes)(S-C_6H_4X)$Fe(NO)_2$ (**1a-1e**) was prepared in a 250 mL 3-neck round bottom flask fitted with the probe by dissolving the compound with 5 mL of CO-saturated toluene under an atmosphere of CO. Once completely dissolved (within 30 s of stirring), the

FTIR monitoring was started and the reactions were followed until completion (with exception of **1e**, see text). All reactions were conducted at 333 K; the solubility data of CO was obtained from extrapolation of data in literature.[9,10] The temperature of 333 K was chosen as being a for this study based on the convenient reaction rates of complex **1** previously investigated. At this temperature, with a $t_{1/2}$ of 3.2 hrs, complex **1** takes close to 20 hrs for complete conversion to complex **2**. Temperatures below 333 K extended the reaction time to more than a day.

References

1. Rauchfuss, T. B.; Weatherill, T. D. *Inorg. Chem.* 1982, **21**, 827.
2. APEX2, version 2009.7-0; Bruker AXS Inc.: Madison, WI, 2007.
3. SAINTPLUS: Program for Reduction of Area Detector Data, version 6.63; Bruker AXS Inc.: Madison, WI, 2007.
4. Sheldrick, G. M. SADABS: Program for Absorption Correction of Area Detector Frames; Bruker AXS Inc.: Madison, WI, 2001.
5. Sheldrick, G. M. SHELXS-97: Program for Crystal Structure Solution; Universität Göttingen: Göttingen, Germany, 1997.
6. Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; Universität Göttingen: Göttingen, Germany, 1997.
7. Mercury: Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van de Streek, J. J. Appl. Crystallogr. 2006, 39, 453–457.
8. Hess, J. L.; Hsieh, C. H.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* 2011, **50**, 8541.
9. Field, L. R.; Wilhelm, E.; Battino, R. J. Chem. Thermodyn. 1974, 6, 237-243.
10. Park, J.; Yi, X.; Gasem, K. A. M.; Robinson, R. L., Jr. J. Chem. Eng. Data 1995, 40, 245-247.

Table S1. Crystal data and structure refinement for [(sIMes)(S-C_6H_4-OCH_3)Fe$(NO)_2$] **(1a)**.

Identification code	simesfeno2sphome_0m	
Empirical formula	C28 H33 Fe N4 O3 S	
Formula weight	561.49	
Temperature	110.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 27.927(4) Å	α= 90°.
	b = 8.0895(12) Å	β= 98.822(2)°.
	c = 38.227(5) Å	γ = 90°.
Volume	8534(2) $Å^3$	
Z	12	
Density (calculated)	1.311 Mg/m^3	
Absorption coefficient	0.638 mm^{-1}	
F(000)	3540	
Crystal size	0.3 x 0.1 x 0.05 mm^3	
Theta range for data collection	1.957 to 28.403°.	
Index ranges	-37<=h<=37, -10<=k<=10, -51<=l<=51	
Reflections collected	102754	
Independent reflections	21306 [R(int) = 0.0700]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6572	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21306 / 0 / 1021	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.0996	
R indices (all data)	R1 = 0.0854, wR2 = 0.1135	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.594 and -0.346 $e.Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for [(sIMes)(S-C_6H_4-OCH_3)Fe$(NO)_2$] **(1a)**.

Fe(1)-N(1)	1.6734(19)	C(5)-C(32)	1.513(4)
Fe(1)-N(2)	1.671(2)	C(6)-H(6A)	0.9800
Fe(1)-S(1)	2.2431(7)	C(6)-H(6B)	0.9800
Fe(1)-C(1)	2.052(2)	C(6)-H(6C)	0.9800
Fe(2)-N(3)	1.671(2)	C(6)-O(9)	1.424(3)
Fe(2)-N(4)	1.672(2)	C(7)-C(12)	1.393(3)
Fe(2)-S(2)	2.2409(8)	C(7)-C(19)	1.383(3)
Fe(2)-C(2)	2.050(2)	C(7)-C(28)	1.506(4)
Fe(3)-N(5)	1.668(2)	C(8)-C(14)	1.391(4)
Fe(3)-N(6)	1.671(2)	C(8)-C(15)	1.391(3)
Fe(3)-S(3)	2.2367(8)	C(8)-N(9)	1.439(3)
Fe(3)-C(3)	2.049(2)	C(9)-C(10)	1.393(3)
N(1)-O(1)	1.177(2)	C(9)-C(13)	1.397(3)
N(2)-O(2)	1.178(2)	C(10)-H(10)	0.9500
N(3)-O(3)	1.178(2)	C(10)-C(17)	1.390(3)
N(4)-O(4)	1.183(2)	C(11)-C(16)	1.388(3)
N(5)-O(5)	1.182(3)	C(11)-C(17)	1.386(3)
N(6)-O(6)	1.178(3)	C(11)-O(8)	1.371(3)
S(1)-C(63)	1.766(3)	C(12)-C(21)	1.391(4)
S(2)-C(9)	1.770(3)	C(12)-N(10)	1.436(3)
S(3)-C(35)	1.766(3)	C(13)-H(13)	0.9500
C(1)-N(7)	1.343(3)	C(13)-C(16)	1.383(3)
C(1)-N(8)	1.336(3)	C(14)-C(25)	1.502(4)
C(2)-N(9)	1.329(3)	C(14)-C(26)	1.395(4)
C(2)-N(10)	1.333(3)	C(15)-C(20)	1.389(4)
C(3)-N(11)	1.338(3)	C(15)-C(24)	1.508(4)
C(3)-N(12)	1.340(3)	C(16)-H(16)	0.9500
C(4)-H(4A)	0.9800	C(17)-H(17)	0.9500
C(4)-H(4B)	0.9800	C(18)-C(19)	1.382(4)
C(4)-H(4C)	0.9800	C(18)-C(22)	1.388(4)
C(4)-O(7)	1.419(4)	C(18)-C(30)	1.503(4)
C(5)-H(5A)	0.9800	C(19)-H(19)	0.9500
C(5)-H(5B)	0.9800	C(20)-H(20)	0.9500
C(5)-H(5C)	0.9800	C(20)-C(32)	1.390(4)

C(21)-C(22)	1.386(4)	C(34)-C(46)	1.391(3)
C(21)-C(31)	1.510(4)	C(34)-N(12)	1.434(3)
C(22)-H(22)	0.9500	C(35)-C(51)	1.396(3)
C(23)-H(23A)	0.9800	C(35)-C(54)	1.393(4)
C(23)-H(23B)	0.9800	C(36)-C(38)	1.386(3)
C(23)-H(23C)	0.9800	C(36)-C(47)	1.385(3)
C(23)-O(8)	1.427(3)	C(36)-C(48)	1.509(3)
C(24)-H(24A)	0.9800	C(37)-C(44)	1.390(3)
C(24)-H(24B)	0.9800	C(37)-C(53)	1.509(4)
C(24)-H(24C)	0.9800	C(38)-H(38)	0.9500
C(25)-H(25A)	0.9800	C(38)-C(39)	1.393(3)
C(25)-H(25B)	0.9800	C(39)-C(52)	1.502(3)
C(25)-H(25C)	0.9800	C(40)-C(47)	1.391(3)
C(26)-H(26)	0.9500	C(40)-C(55)	1.503(3)
C(26)-C(32)	1.385(4)	C(41)-H(41A)	0.9900
C(27)-H(27A)	0.9900	C(41)-H(41B)	0.9900
C(27)-H(27B)	0.9900	C(41)-C(42)	1.523(3)
C(27)-C(29)	1.523(4)	C(41)-N(11)	1.477(3)
C(27)-N(9)	1.485(3)	C(42)-H(42A)	0.9900
C(28)-H(28A)	0.9800	C(42)-H(42B)	0.9900
C(28)-H(28B)	0.9800	C(42)-N(12)	1.470(3)
C(28)-H(28C)	0.9800	C(43)-C(44)	1.381(4)
C(29)-H(29A)	0.9900	C(43)-C(45)	1.384(4)
C(29)-H(29B)	0.9900	C(43)-C(58)	1.511(3)
C(29)-N(10)	1.476(3)	C(44)-H(44)	0.9500
C(30)-H(30A)	0.9800	C(45)-H(45)	0.9500
C(30)-H(30B)	0.9800	C(45)-C(46)	1.393(3)
C(30)-H(30C)	0.9800	C(46)-C(57)	1.498(4)
C(31)-H(31A)	0.9800	C(47)-H(47)	0.9500
C(31)-H(31B)	0.9800	C(48)-H(48A)	0.9800
C(31)-H(31C)	0.9800	C(48)-H(48B)	0.9800
C(33)-C(39)	1.392(3)	C(48)-H(48C)	0.9800
C(33)-C(40)	1.395(3)	C(49)-C(50)	1.386(4)
C(33)-N(11)	1.437(3)	C(49)-C(56)	1.385(4)
C(34)-C(37)	1.388(3)	C(49)-O(9)	1.367(3)

C(50)-H(50)	0.9500	C(65)-H(65)	0.9500
C(50)-C(51)	1.399(4)	C(65)-C(67)	1.397(3)
C(51)-H(51)	0.9500	C(65)-C(71)	1.391(3)
C(52)-H(52A)	0.9800	C(66)-H(66)	0.9500
C(52)-H(52B)	0.9800	C(66)-C(71)	1.379(4)
C(52)-H(52C)	0.9800	C(67)-C(78)	1.501(3)
C(53)-H(53A)	0.9800	C(68)-H(68)	0.9500
C(53)-H(53B)	0.9800	C(68)-C(70)	1.377(3)
C(53)-H(53C)	0.9800	C(68)-C(73)	1.384(4)
C(54)-H(54)	0.9500	C(69)-H(69)	0.9500
C(54)-C(56)	1.373(4)	C(69)-C(75)	1.388(4)
C(55)-H(55A)	0.9800	C(70)-H(70)	0.9500
C(55)-H(55B)	0.9800	C(71)-C(79)	1.510(3)
C(55)-H(55C)	0.9800	C(72)-H(72A)	0.9900
C(56)-H(56)	0.9500	C(72)-H(72B)	0.9900
C(57)-H(57A)	0.9800	C(72)-C(77)	1.526(3)
C(57)-H(57B)	0.9800	C(72)-N(7)	1.478(3)
C(57)-H(57C)	0.9800	C(73)-C(75)	1.376(4)
C(58)-H(58A)	0.9800	C(73)-O(7)	1.380(3)
C(58)-H(58B)	0.9800	C(74)-H(74)	0.9500
C(58)-H(58C)	0.9800	C(74)-C(80)	1.376(4)
C(59)-C(62)	1.387(3)	C(75)-H(75)	0.9500
C(59)-C(64)	1.392(3)	C(76)-H(76)	0.9500
C(59)-N(7)	1.429(3)	C(76)-C(80)	1.368(4)
C(60)-C(61)	1.391(3)	C(77)-H(77A)	0.9900
C(60)-C(67)	1.396(3)	C(77)-H(77B)	0.9900
C(60)-N(8)	1.441(3)	C(77)-N(8)	1.475(3)
C(61)-C(66)	1.391(3)	C(78)-H(78A)	0.9800
C(61)-C(81)	1.503(4)	C(78)-H(78B)	0.9800
C(62)-C(74)	1.394(4)	C(78)-H(78C)	0.9800
C(62)-C(82)	1.496(4)	C(79)-H(79A)	0.9800
C(63)-C(69)	1.390(3)	C(79)-H(79B)	0.9800
C(63)-C(70)	1.402(3)	C(79)-H(79C)	0.9800
C(64)-C(76)	1.395(4)	C(80)-C(83)	1.518(4)
C(64)-C(84)	1.498(4)	C(81)-H(81A)	0.9800

C(81)-H(81B)	0.9800	O(6)-N(6)-Fe(3)	169.14(19)
C(81)-H(81C)	0.9800	C(63)-S(1)-Fe(1)	113.18(8)
C(82)-H(82A)	0.9800	C(9)-S(2)-Fe(2)	112.63(8)
C(82)-H(82B)	0.9800	C(35)-S(3)-Fe(3)	111.79(9)
C(82)-H(82C)	0.9800	N(7)-C(1)-Fe(1)	126.88(15)
C(83)-H(83A)	0.9800	N(8)-C(1)-Fe(1)	125.13(16)
C(83)-H(83B)	0.9800	N(8)-C(1)-N(7)	107.93(19)
C(83)-H(83C)	0.9800	N(9)-C(2)-Fe(2)	126.49(18)
C(84)-H(84A)	0.9800	N(9)-C(2)-N(10)	108.4(2)
C(84)-H(84B)	0.9800	N(10)-C(2)-Fe(2)	125.02(18)
C(84)-H(84C)	0.9800	N(11)-C(3)-Fe(3)	128.33(16)
		N(11)-C(3)-N(12)	107.60(19)
N(1)-Fe(1)-S(1)	114.25(7)	N(12)-C(3)-Fe(3)	124.06(16)
N(1)-Fe(1)-C(1)	106.38(9)	H(4A)-C(4)-H(4B)	109.5
N(2)-Fe(1)-N(1)	115.49(9)	H(4A)-C(4)-H(4C)	109.5
N(2)-Fe(1)-S(1)	102.84(7)	H(4B)-C(4)-H(4C)	109.5
N(2)-Fe(1)-C(1)	105.71(9)	O(7)-C(4)-H(4A)	109.5
C(1)-Fe(1)-S(1)	111.97(6)	O(7)-C(4)-H(4B)	109.5
N(3)-Fe(2)-N(4)	113.38(10)	O(7)-C(4)-H(4C)	109.5
N(3)-Fe(2)-S(2)	114.54(7)	H(5A)-C(5)-H(5B)	109.5
N(3)-Fe(2)-C(2)	106.57(9)	H(5A)-C(5)-H(5C)	109.5
N(4)-Fe(2)-S(2)	106.25(8)	H(5B)-C(5)-H(5C)	109.5
N(4)-Fe(2)-C(2)	105.82(10)	C(32)-C(5)-H(5A)	109.5
C(2)-Fe(2)-S(2)	109.95(7)	C(32)-C(5)-H(5B)	109.5
N(5)-Fe(3)-N(6)	114.39(10)	C(32)-C(5)-H(5C)	109.5
N(5)-Fe(3)-S(3)	114.37(7)	H(6A)-C(6)-H(6B)	109.5
N(5)-Fe(3)-C(3)	106.61(9)	H(6A)-C(6)-H(6C)	109.5
N(6)-Fe(3)-S(3)	104.06(8)	H(6B)-C(6)-H(6C)	109.5
N(6)-Fe(3)-C(3)	107.36(9)	O(9)-C(6)-H(6A)	109.5
C(3)-Fe(3)-S(3)	109.85(7)	O(9)-C(6)-H(6B)	109.5
O(1)-N(1)-Fe(1)	167.35(18)	O(9)-C(6)-H(6C)	109.5
O(2)-N(2)-Fe(1)	168.95(18)	C(12)-C(7)-C(28)	121.5(2)
O(3)-N(3)-Fe(2)	166.32(19)	C(19)-C(7)-C(12)	118.2(2)
O(4)-N(4)-Fe(2)	166.3(2)	C(19)-C(7)-C(28)	120.3(2)
O(5)-N(5)-Fe(3)	165.1(2)	C(14)-C(8)-N(9)	118.9(2)

C(15)-C(8)-C(14)	121.8(2)	C(15)-C(20)-H(20)	119.1
C(15)-C(8)-N(9)	119.3(2)	C(15)-C(20)-C(32)	121.9(2)
C(10)-C(9)-S(2)	118.11(18)	C(32)-C(20)-H(20)	119.1
C(10)-C(9)-C(13)	117.6(2)	C(12)-C(21)-C(31)	121.8(3)
C(13)-C(9)-S(2)	124.29(19)	C(22)-C(21)-C(12)	117.3(2)
C(9)-C(10)-H(10)	119.2	C(22)-C(21)-C(31)	120.9(3)
C(17)-C(10)-C(9)	121.7(2)	C(18)-C(22)-H(22)	118.8
C(17)-C(10)-H(10)	119.2	C(21)-C(22)-C(18)	122.3(2)
C(17)-C(11)-C(16)	119.5(2)	C(21)-C(22)-H(22)	118.8
O(8)-C(11)-C(16)	116.0(2)	H(23A)-C(23)-H(23B)	109.5
O(8)-C(11)-C(17)	124.5(2)	H(23A)-C(23)-H(23C)	109.5
C(7)-C(12)-N(10)	119.2(2)	H(23B)-C(23)-H(23C)	109.5
C(21)-C(12)-C(7)	122.1(2)	O(8)-C(23)-H(23A)	109.5
C(21)-C(12)-N(10)	118.7(2)	O(8)-C(23)-H(23B)	109.5
C(9)-C(13)-H(13)	119.4	O(8)-C(23)-H(23C)	109.5
C(16)-C(13)-C(9)	121.1(2)	C(15)-C(24)-H(24A)	109.5
C(16)-C(13)-H(13)	119.4	C(15)-C(24)-H(24B)	109.5
C(8)-C(14)-C(25)	121.2(2)	C(15)-C(24)-H(24C)	109.5
C(8)-C(14)-C(26)	118.2(2)	H(24A)-C(24)-H(24B)	109.5
C(26)-C(14)-C(25)	120.6(3)	H(24A)-C(24)-H(24C)	109.5
C(8)-C(15)-C(24)	121.1(2)	H(24B)-C(24)-H(24C)	109.5
C(20)-C(15)-C(8)	118.1(2)	C(14)-C(25)-H(25A)	109.5
C(20)-C(15)-C(24)	120.8(2)	C(14)-C(25)-H(25B)	109.5
C(11)-C(16)-H(16)	119.8	C(14)-C(25)-H(25C)	109.5
C(13)-C(16)-C(11)	120.4(2)	H(25A)-C(25)-H(25B)	109.5
C(13)-C(16)-H(16)	119.8	H(25A)-C(25)-H(25C)	109.5
C(10)-C(17)-H(17)	120.2	H(25B)-C(25)-H(25C)	109.5
C(11)-C(17)-C(10)	119.6(2)	C(14)-C(26)-H(26)	119.2
C(11)-C(17)-H(17)	120.2	C(32)-C(26)-C(14)	121.6(3)
C(19)-C(18)-C(22)	118.4(2)	C(32)-C(26)-H(26)	119.2
C(19)-C(18)-C(30)	121.0(2)	H(27A)-C(27)-H(27B)	109.2
C(22)-C(18)-C(30)	120.6(2)	C(29)-C(27)-H(27A)	111.3
C(7)-C(19)-H(19)	119.2	C(29)-C(27)-H(27B)	111.3
C(18)-C(19)-C(7)	121.6(2)	N(9)-C(27)-H(27A)	111.3
C(18)-C(19)-H(19)	119.2	N(9)-C(27)-H(27B)	111.3

N(9)-C(27)-C(29)	102.2(2)	C(54)-C(35)-S(3)	124.9(2)
C(7)-C(28)-H(28A)	109.5	C(54)-C(35)-C(51)	117.0(2)
C(7)-C(28)-H(28B)	109.5	C(38)-C(36)-C(48)	120.4(2)
C(7)-C(28)-H(28C)	109.5	C(47)-C(36)-C(38)	118.2(2)
H(28A)-C(28)-H(28B)	109.5	C(47)-C(36)-C(48)	121.4(2)
H(28A)-C(28)-H(28C)	109.5	C(34)-C(37)-C(44)	117.6(2)
H(28B)-C(28)-H(28C)	109.5	C(34)-C(37)-C(53)	121.8(2)
C(27)-C(29)-H(29A)	111.2	C(44)-C(37)-C(53)	120.5(2)
C(27)-C(29)-H(29B)	111.2	C(36)-C(38)-H(38)	118.9
H(29A)-C(29)-H(29B)	109.2	C(36)-C(38)-C(39)	122.3(2)
N(10)-C(29)-C(27)	102.6(2)	C(39)-C(38)-H(38)	118.9
N(10)-C(29)-H(29A)	111.2	C(33)-C(39)-C(38)	117.7(2)
N(10)-C(29)-H(29B)	111.2	C(33)-C(39)-C(52)	121.9(2)
C(18)-C(30)-H(30A)	109.5	C(38)-C(39)-C(52)	120.4(2)
C(18)-C(30)-H(30B)	109.5	C(33)-C(40)-C(55)	121.6(2)
C(18)-C(30)-H(30C)	109.5	C(47)-C(40)-C(33)	118.1(2)
H(30A)-C(30)-H(30B)	109.5	C(47)-C(40)-C(55)	120.3(2)
H(30A)-C(30)-H(30C)	109.5	H(41A)-C(41)-H(41B)	109.2
H(30B)-C(30)-H(30C)	109.5	C(42)-C(41)-H(41A)	111.3
C(21)-C(31)-H(31A)	109.5	C(42)-C(41)-H(41B)	111.3
C(21)-C(31)-H(31B)	109.5	N(11)-C(41)-H(41A)	111.3
C(21)-C(31)-H(31C)	109.5	N(11)-C(41)-H(41B)	111.3
H(31A)-C(31)-H(31B)	109.5	N(11)-C(41)-C(42)	102.51(18)
H(31A)-C(31)-H(31C)	109.5	C(41)-C(42)-H(42A)	111.3
H(31B)-C(31)-H(31C)	109.5	C(41)-C(42)-H(42B)	111.3
C(20)-C(32)-C(5)	121.0(3)	H(42A)-C(42)-H(42B)	109.2
C(26)-C(32)-C(5)	120.5(3)	N(12)-C(42)-C(41)	102.50(18)
C(26)-C(32)-C(20)	118.5(2)	N(12)-C(42)-H(42A)	111.3
C(39)-C(33)-C(40)	121.8(2)	N(12)-C(42)-H(42B)	111.3
C(39)-C(33)-N(11)	118.7(2)	C(44)-C(43)-C(45)	118.5(2)
C(40)-C(33)-N(11)	119.4(2)	C(44)-C(43)-C(58)	120.5(3)
C(37)-C(34)-C(46)	122.4(2)	C(45)-C(43)-C(58)	121.0(3)
C(37)-C(34)-N(12)	118.4(2)	C(37)-C(44)-H(44)	119.0
C(46)-C(34)-N(12)	119.2(2)	C(43)-C(44)-C(37)	122.1(2)
C(51)-C(35)-S(3)	118.0(2)	C(43)-C(44)-H(44)	119.0

C(43)-C(45)-H(45)	119.1	H(53B)-C(53)-H(53C)	109.5
C(43)-C(45)-C(46)	121.8(2)	C(35)-C(54)-H(54)	119.2
C(46)-C(45)-H(45)	119.1	C(56)-C(54)-C(35)	121.6(3)
C(34)-C(46)-C(45)	117.6(2)	C(56)-C(54)-H(54)	119.2
C(34)-C(46)-C(57)	121.4(2)	C(40)-C(55)-H(55A)	109.5
C(45)-C(46)-C(57)	121.1(2)	C(40)-C(55)-H(55B)	109.5
C(36)-C(47)-C(40)	121.9(2)	C(40)-C(55)-H(55C)	109.5
C(36)-C(47)-H(47)	119.0	H(55A)-C(55)-H(55B)	109.5
C(40)-C(47)-H(47)	119.0	H(55A)-C(55)-H(55C)	109.5
C(36)-C(48)-H(48A)	109.5	H(55B)-C(55)-H(55C)	109.5
C(36)-C(48)-H(48B)	109.5	C(49)-C(56)-H(56)	119.6
C(36)-C(48)-H(48C)	109.5	C(54)-C(56)-C(49)	120.8(3)
H(48A)-C(48)-H(48B)	109.5	C(54)-C(56)-H(56)	119.6
H(48A)-C(48)-H(48C)	109.5	C(46)-C(57)-H(57A)	109.5
H(48B)-C(48)-H(48C)	109.5	C(46)-C(57)-H(57B)	109.5
C(56)-C(49)-C(50)	119.4(3)	C(46)-C(57)-H(57C)	109.5
O(9)-C(49)-C(50)	124.5(2)	H(57A)-C(57)-H(57B)	109.5
O(9)-C(49)-C(56)	116.0(3)	H(57A)-C(57)-H(57C)	109.5
C(49)-C(50)-H(50)	120.4	H(57B)-C(57)-H(57C)	109.5
C(49)-C(50)-C(51)	119.2(2)	C(43)-C(58)-H(58A)	109.5
C(51)-C(50)-H(50)	120.4	C(43)-C(58)-H(58B)	109.5
C(35)-C(51)-C(50)	121.9(3)	C(43)-C(58)-H(58C)	109.5
C(35)-C(51)-H(51)	119.0	H(58A)-C(58)-H(58B)	109.5
C(50)-C(51)-H(51)	119.0	H(58A)-C(58)-H(58C)	109.5
C(39)-C(52)-H(52A)	109.5	H(58B)-C(58)-H(58C)	109.5
C(39)-C(52)-H(52B)	109.5	C(62)-C(59)-C(64)	121.9(2)
C(39)-C(52)-H(52C)	109.5	C(62)-C(59)-N(7)	118.5(2)
H(52A)-C(52)-H(52B)	109.5	C(64)-C(59)-N(7)	119.4(2)
H(52A)-C(52)-H(52C)	109.5	C(61)-C(60)-C(67)	122.3(2)
H(52B)-C(52)-H(52C)	109.5	C(61)-C(60)-N(8)	118.8(2)
C(37)-C(53)-H(53A)	109.5	C(67)-C(60)-N(8)	118.9(2)
C(37)-C(53)-H(53B)	109.5	C(60)-C(61)-C(66)	117.6(2)
C(37)-C(53)-H(53C)	109.5	C(60)-C(61)-C(81)	121.8(2)
H(53A)-C(53)-H(53B)	109.5	C(66)-C(61)-C(81)	120.5(2)
H(53A)-C(53)-H(53C)	109.5	C(59)-C(62)-C(74)	117.5(2)

C(59)-C(62)-C(82)	120.7(2)	C(75)-C(73)-C(68)	119.8(3)
C(74)-C(62)-C(82)	121.8(3)	C(75)-C(73)-O(7)	125.6(3)
C(69)-C(63)-S(1)	118.5(2)	O(7)-C(73)-C(68)	114.5(3)
C(69)-C(63)-C(70)	117.5(2)	C(62)-C(74)-H(74)	118.8
C(70)-C(63)-S(1)	123.95(18)	C(80)-C(74)-C(62)	122.3(3)
C(59)-C(64)-C(76)	117.4(2)	C(80)-C(74)-H(74)	118.8
C(59)-C(64)-C(84)	121.3(2)	C(69)-C(75)-H(75)	120.1
C(76)-C(64)-C(84)	121.3(3)	C(73)-C(75)-C(69)	119.7(2)
C(67)-C(65)-H(65)	119.0	C(73)-C(75)-H(75)	120.1
C(71)-C(65)-H(65)	119.0	C(64)-C(76)-H(76)	118.7
C(71)-C(65)-C(67)	122.0(2)	C(80)-C(76)-C(64)	122.5(3)
C(61)-C(66)-H(66)	118.8	C(80)-C(76)-H(76)	118.7
C(71)-C(66)-C(61)	122.5(2)	C(72)-C(77)-H(77A)	111.2
C(71)-C(66)-H(66)	118.8	C(72)-C(77)-H(77B)	111.2
C(60)-C(67)-C(65)	117.4(2)	H(77A)-C(77)-H(77B)	109.2
C(60)-C(67)-C(78)	121.5(2)	N(8)-C(77)-C(72)	102.60(19)
C(65)-C(67)-C(78)	121.1(2)	N(8)-C(77)-H(77A)	111.2
C(70)-C(68)-H(68)	119.8	N(8)-C(77)-H(77B)	111.2
C(70)-C(68)-C(73)	120.4(3)	C(67)-C(78)-H(78A)	109.5
C(73)-C(68)-H(68)	119.8	C(67)-C(78)-H(78B)	109.5
C(63)-C(69)-H(69)	119.2	C(67)-C(78)-H(78C)	109.5
C(75)-C(69)-C(63)	121.6(3)	H(78A)-C(78)-H(78B)	109.5
C(75)-C(69)-H(69)	119.2	H(78A)-C(78)-H(78C)	109.5
C(63)-C(70)-H(70)	119.5	H(78B)-C(78)-H(78C)	109.5
C(68)-C(70)-C(63)	120.9(2)	C(71)-C(79)-H(79A)	109.5
C(68)-C(70)-H(70)	119.5	C(71)-C(79)-H(79B)	109.5
C(65)-C(71)-C(79)	120.6(2)	C(71)-C(79)-H(79C)	109.5
C(66)-C(71)-C(65)	118.1(2)	H(79A)-C(79)-H(79B)	109.5
C(66)-C(71)-C(79)	121.3(2)	H(79A)-C(79)-H(79C)	109.5
H(72A)-C(72)-H(72B)	109.2	H(79B)-C(79)-H(79C)	109.5
C(77)-C(72)-H(72A)	111.3	C(74)-C(80)-C(83)	120.8(3)
C(77)-C(72)-H(72B)	111.3	C(76)-C(80)-C(74)	118.3(2)
N(7)-C(72)-H(72A)	111.3	C(76)-C(80)-C(83)	121.0(3)
N(7)-C(72)-H(72B)	111.3	C(61)-C(81)-H(81A)	109.5
N(7)-C(72)-C(77)	102.44(19)	C(61)-C(81)-H(81B)	109.5

C(61)-C(81)-H(81C)	109.5	C(8)-N(9)-C(27)	120.6(2)
H(81A)-C(81)-H(81B)	109.5	C(2)-N(10)-C(12)	126.1(2)
H(81A)-C(81)-H(81C)	109.5	C(2)-N(10)-C(29)	113.4(2)
H(81B)-C(81)-H(81C)	109.5	C(12)-N(10)-C(29)	120.3(2)
C(62)-C(82)-H(82A)	109.5	C(3)-N(11)-C(33)	126.78(18)
C(62)-C(82)-H(82B)	109.5	C(3)-N(11)-C(41)	113.52(18)
C(62)-C(82)-H(82C)	109.5	C(33)-N(11)-C(41)	119.27(18)
H(82A)-C(82)-H(82B)	109.5	C(3)-N(12)-C(34)	125.33(18)
H(82A)-C(82)-H(82C)	109.5	C(3)-N(12)-C(42)	113.84(18)
H(82B)-C(82)-H(82C)	109.5	C(34)-N(12)-C(42)	120.71(18)
C(80)-C(83)-H(83A)	109.5	C(73)-O(7)-C(4)	116.9(3)
C(80)-C(83)-H(83B)	109.5	C(11)-O(8)-C(23)	117.4(2)
C(80)-C(83)-H(83C)	109.5	C(49)-O(9)-C(6)	117.3(2)
H(83A)-C(83)-H(83B)	109.5		
H(83A)-C(83)-H(83C)	109.5		
H(83B)-C(83)-H(83C)	109.5		
C(64)-C(84)-H(84A)	109.5		
C(64)-C(84)-H(84B)	109.5		
C(64)-C(84)-H(84C)	109.5		
H(84A)-C(84)-H(84B)	109.5		
H(84A)-C(84)-H(84C)	109.5		
H(84B)-C(84)-H(84C)	109.5		
C(1)-N(7)-C(59)	126.38(18)		
C(1)-N(7)-C(72)	113.37(18)		
C(59)-N(7)-C(72)	120.23(18)		
C(1)-N(8)-C(60)	124.76(19)		
C(1)-N(8)-C(77)	113.61(19)		
C(60)-N(8)-C(77)	121.61(18)		
C(2)-N(9)-C(8)	125.8(2)		
C(2)-N(9)-C(27)	113.4(2)		

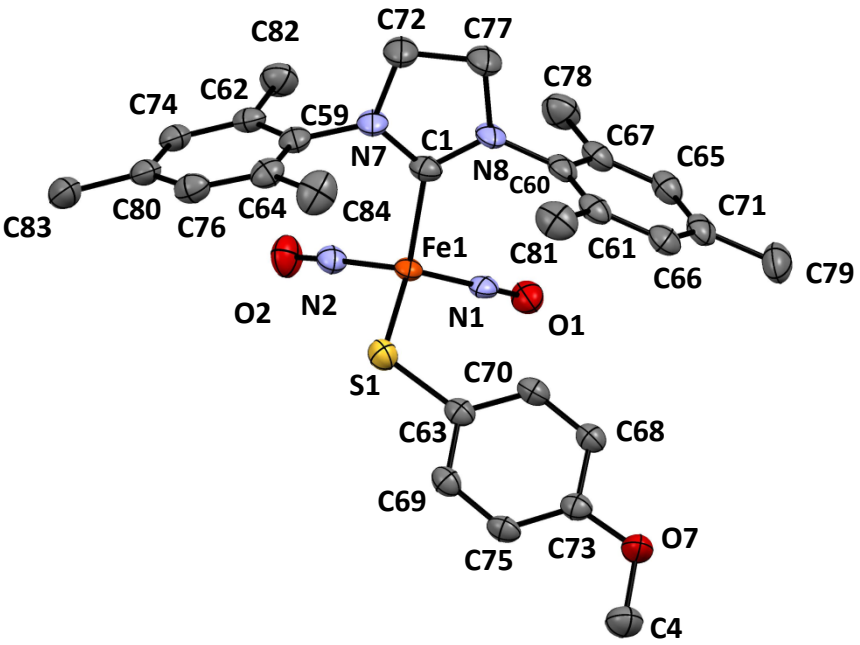

Figure S1a. ORTEP drawing and labeling scheme of complex **1a** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

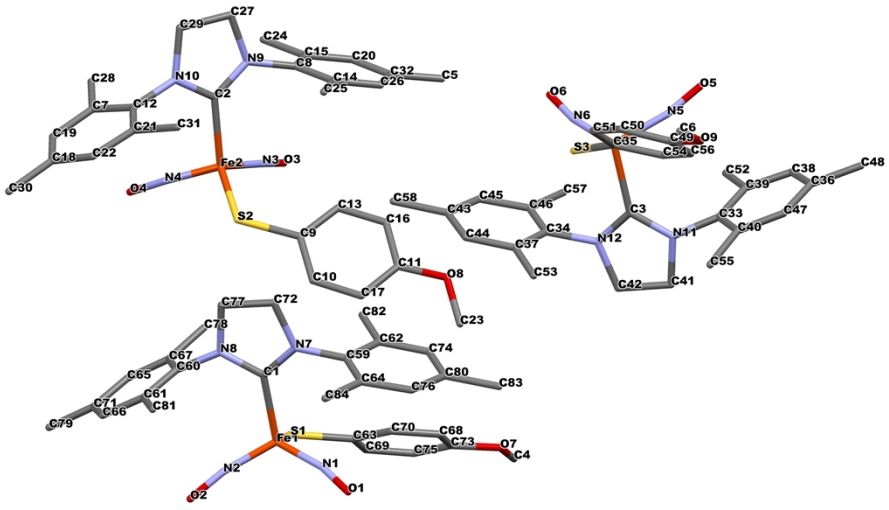

Figure S1b. Capped stick rendition of the three independent molecules in the smallest asymmetric unit of complex **1a**. Hydrogen atoms are omitted for clarity.

Table S3. Crystal data and structure refinement for [(sIMes)(S-C_6H_4-CH_3)Fe$(NO)_2$] **(1b)**.

Identification code	simesdnicsph_me_0m	
Empirical formula	C31 H39 Fe N4 O2 S	
Formula weight	587.57	
Temperature	110.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 16.745(3) Å	α= 90°.
	b = 8.1442(14) Å	β= 93.720(2)°.
	c = 22.278(4) Å	γ = 90°.
Volume	3031.7(9) $Å^3$	
Z	4	
Density (calculated)	1.287 Mg/m^3	
Absorption coefficient	0.600 mm^{-1}	
F(000)	1244	
Crystal size	0.4 x 0.2 x 0.08 mm^3	
Theta range for data collection	1.832 to 27.967°.	
Index ranges	-22<=h<=22, -10<=k<=10, -29<=l<=29	
Reflections collected	35261	
Independent reflections	7279 [R(int) = 0.0548]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6600	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7279 / 19 / 357	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0439, wR2 = 0.1268	
R indices (all data)	R1 = 0.0570, wR2 = 0.1378	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.141 and -0.616 e.$Å^{-3}$	

Table S4. Bond lengths [Å] and angles [°] for [(sIMes)(S-C_6H_4-CH_3)Fe$(NO)_2$] **(1b)**.

Fe(1)-N(1)	1.6751(17)	C(12)-C(13)	1.392(3)
Fe(1)-N(2)	1.6729(19)	C(12)-C(17)	1.507(4)
Fe(1)-S(1)	2.2391(7)	C(13)-H(13)	0.9500
Fe(1)-C(1)	2.049(2)	C(13)-C(14)	1.383(4)
N(1)-O(1)	1.172(2)	C(14)-C(15)	1.378(3)
N(2)-O(2)	1.175(2)	C(14)-C(19)	1.512(3)
S(1)-C(4)	1.758(3)	C(15)-H(15)	0.9500
C(1)-N(3)	1.333(3)	C(15)-C(16)	1.392(3)
C(1)-N(4)	1.330(2)	C(16)-C(18)	1.502(3)
C(2)-H(2A)	0.9900	C(17)-H(17A)	0.9800
C(2)-H(2B)	0.9900	C(17)-H(17B)	0.9800
C(2)-C(3)	1.524(3)	C(17)-H(17C)	0.9800
C(2)-N(4)	1.480(3)	C(18)-H(18A)	0.9800
C(3)-H(3A)	0.9900	C(18)-H(18B)	0.9800
C(3)-H(3B)	0.9900	C(18)-H(18C)	0.9800
C(3)-N(3)	1.482(3)	C(19)-H(19A)	0.9800
C(4)-C(5)	1.390(4)	C(19)-H(19B)	0.9800
C(4)-C(9)	1.401(3)	C(19)-H(19C)	0.9800
C(5)-H(5)	0.9500	C(20)-C(21)	1.392(3)
C(5)-C(6)	1.380(4)	C(20)-C(25)	1.387(3)
C(6)-H(6)	0.9500	C(20)-N(4)	1.434(3)
C(6)-C(7)	1.401(4)	C(21)-C(22)	1.392(3)
C(7)-C(8)	1.367(5)	C(21)-C(27)	1.501(3)
C(7)-C(10)	1.526(5)	C(22)-H(22)	0.9500
C(8)-H(8)	0.9500	C(22)-C(23)	1.376(4)
C(8)-C(9)	1.370(4)	C(23)-C(24)	1.392(4)
C(9)-H(9)	0.9500	C(23)-C(28)	1.505(3)
C(10)-H(10A)	0.9800	C(24)-H(24)	0.9500
C(10)-H(10B)	0.9800	C(24)-C(25)	1.388(3)
C(10)-H(10C)	0.9800	C(25)-C(26)	1.502(3)
C(11)-C(12)	1.388(3)	C(26)-H(26A)	0.9800
C(11)-C(16)	1.389(3)	C(26)-H(26B)	0.9800
C(11)-N(3)	1.437(3)	C(26)-H(26C)	0.9800

C(27)-H(27A)	0.9800	C(4)-S(1)-Fe(1)	112.50(8)
C(27)-H(27B)	0.9800	N(3)-C(1)-Fe(1)	124.66(14)
C(27)-H(27C)	0.9800	N(4)-C(1)-Fe(1)	127.04(15)
C(28)-H(28A)	0.9800	N(4)-C(1)-N(3)	108.30(17)
C(28)-H(28B)	0.9800	H(2A)-C(2)-H(2B)	109.2
C(28)-H(28C)	0.9800	C(3)-C(2)-H(2A)	111.3
C(1C)-H(1CA)	0.9900	C(3)-C(2)-H(2B)	111.3
C(1C)-H(1CB)	0.9900	N(4)-C(2)-H(2A)	111.3
C(1C)-C(2C)	1.541(5)	N(4)-C(2)-H(2B)	111.3
C(1C)-C(3C)#1	1.541(4)	N(4)-C(2)-C(3)	102.49(17)
C(2C)-H(2CA)	0.9900	C(2)-C(3)-H(3A)	111.4
C(2C)-H(2CB)	0.9900	C(2)-C(3)-H(3B)	111.4
C(2C)-C(3C)	1.533(5)	H(3A)-C(3)-H(3B)	109.3
C(3C)-C(1C)#1	1.541(4)	N(3)-C(3)-C(2)	101.77(17)
C(3C)-H(3CA)	0.9900	N(3)-C(3)-H(3A)	111.4
C(3C)-H(3CB)	0.9900	N(3)-C(3)-H(3B)	111.4
C(4C)-H(4CA)	0.9900	C(5)-C(4)-S(1)	124.36(18)
C(4C)-H(4CB)	0.9900	C(5)-C(4)-C(9)	117.2(3)
C(4C)-C(5C)	1.534(5)	C(9)-C(4)-S(1)	118.5(2)
C(4C)-C(6C)#1	1.530(4)	C(4)-C(5)-H(5)	119.5
C(5C)-H(5CA)	0.9900	C(6)-C(5)-C(4)	120.9(2)
C(5C)-H(5CB)	0.9900	C(6)-C(5)-H(5)	119.5
C(5C)-C(6C)	1.536(5)	C(5)-C(6)-H(6)	119.6
C(6C)-C(4C)#1	1.530(4)	C(5)-C(6)-C(7)	120.9(3)
C(6C)-H(6CA)	0.9900	C(7)-C(6)-H(6)	119.6
C(6C)-H(6CB)	0.9900	C(6)-C(7)-C(10)	119.5(3)
		C(8)-C(7)-C(6)	118.2(3)
N(1)-Fe(1)-S(1)	113.11(6)	C(8)-C(7)-C(10)	122.3(3)
N(1)-Fe(1)-C(1)	107.33(8)	C(7)-C(8)-H(8)	119.4
N(2)-Fe(1)-N(1)	115.39(9)	C(7)-C(8)-C(9)	121.3(3)
N(2)-Fe(1)-S(1)	105.75(7)	C(9)-C(8)-H(8)	119.4
N(2)-Fe(1)-C(1)	105.48(8)	C(4)-C(9)-H(9)	119.2
C(1)-Fe(1)-S(1)	109.43(6)	C(8)-C(9)-C(4)	121.6(3)
O(1)-N(1)-Fe(1)	168.64(16)	C(8)-C(9)-H(9)	119.2
O(2)-N(2)-Fe(1)	167.84(17)	C(7)-C(10)-H(10A)	109.5

C(7)-C(10)-H(10B)	109.5	C(14)-C(19)-H(19A)	109.5
C(7)-C(10)-H(10C)	109.5	C(14)-C(19)-H(19B)	109.5
H(10A)-C(10)-H(10B)	109.5	C(14)-C(19)-H(19C)	109.5
H(10A)-C(10)-H(10C)	109.5	H(19A)-C(19)-H(19B)	109.5
H(10B)-C(10)-H(10C)	109.5	H(19A)-C(19)-H(19C)	109.5
C(12)-C(11)-C(16)	122.2(2)	H(19B)-C(19)-H(19C)	109.5
C(12)-C(11)-N(3)	118.1(2)	C(21)-C(20)-N(4)	119.37(19)
C(16)-C(11)-N(3)	119.6(2)	C(25)-C(20)-C(21)	121.99(19)
C(11)-C(12)-C(13)	117.6(2)	C(25)-C(20)-N(4)	118.55(19)
C(11)-C(12)-C(17)	121.1(2)	C(20)-C(21)-C(22)	117.9(2)
C(13)-C(12)-C(17)	121.3(2)	C(20)-C(21)-C(27)	121.4(2)
C(12)-C(13)-H(13)	119.0	C(22)-C(21)-C(27)	120.8(2)
C(14)-C(13)-C(12)	122.0(2)	C(21)-C(22)-H(22)	119.0
C(14)-C(13)-H(13)	119.0	C(23)-C(22)-C(21)	122.1(2)
C(13)-C(14)-C(19)	120.5(2)	C(23)-C(22)-H(22)	119.0
C(15)-C(14)-C(13)	118.5(2)	C(22)-C(23)-C(24)	118.2(2)
C(15)-C(14)-C(19)	121.0(2)	C(22)-C(23)-C(28)	121.0(3)
C(14)-C(15)-H(15)	119.0	C(24)-C(23)-C(28)	120.9(3)
C(14)-C(15)-C(16)	122.0(2)	C(23)-C(24)-H(24)	119.0
C(16)-C(15)-H(15)	119.0	C(25)-C(24)-C(23)	122.0(2)
C(11)-C(16)-C(15)	117.7(2)	C(25)-C(24)-H(24)	119.0
C(11)-C(16)-C(18)	121.6(2)	C(20)-C(25)-C(24)	117.9(2)
C(15)-C(16)-C(18)	120.7(2)	C(20)-C(25)-C(26)	120.9(2)
C(12)-C(17)-H(17A)	109.5	C(24)-C(25)-C(26)	121.2(2)
C(12)-C(17)-H(17B)	109.5	C(25)-C(26)-H(26A)	109.5
C(12)-C(17)-H(17C)	109.5	C(25)-C(26)-H(26B)	109.5
H(17A)-C(17)-H(17B)	109.5	C(25)-C(26)-H(26C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(26A)-C(26)-H(26B)	109.5
H(17B)-C(17)-H(17C)	109.5	H(26A)-C(26)-H(26C)	109.5
C(16)-C(18)-H(18A)	109.5	H(26B)-C(26)-H(26C)	109.5
C(16)-C(18)-H(18B)	109.5	C(21)-C(27)-H(27A)	109.5
C(16)-C(18)-H(18C)	109.5	C(21)-C(27)-H(27B)	109.5
H(18A)-C(18)-H(18B)	109.5	C(21)-C(27)-H(27C)	109.5
H(18A)-C(18)-H(18C)	109.5	H(27A)-C(27)-H(27B)	109.5
H(18B)-C(18)-H(18C)	109.5	H(27A)-C(27)-H(27C)	109.5

H(27B)-C(27)-H(27C)	109.5	C(6C)#1-C(4C)-H(4CA)	110.4
C(23)-C(28)-H(28A)	109.5	C(6C)#1-C(4C)-H(4CB)	110.4
C(23)-C(28)-H(28B)	109.5	C(6C)#1-C(4C)-C(5C)	106.7(5)
C(23)-C(28)-H(28C)	109.5	C(4C)-C(5C)-H(5CA)	109.8
H(28A)-C(28)-H(28B)	109.5	C(4C)-C(5C)-H(5CB)	109.8
H(28A)-C(28)-H(28C)	109.5	C(4C)-C(5C)-C(6C)	109.4(6)
H(28B)-C(28)-H(28C)	109.5	H(5CA)-C(5C)-H(5CB)	108.3
C(1)-N(3)-C(3)	113.41(17)	C(6C)-C(5C)-H(5CA)	109.8
C(1)-N(3)-C(11)	126.34(17)	C(6C)-C(5C)-H(5CB)	109.8
C(11)-N(3)-C(3)	120.05(17)	C(4C)#1-C(6C)-C(5C)	107.1(5)
C(1)-N(4)-C(2)	113.06(17)	C(4C)#1-C(6C)-H(6CA)	110.3
C(1)-N(4)-C(20)	126.79(16)	C(4C)#1-C(6C)-H(6CB)	110.3
C(20)-N(4)-C(2)	119.94(17)	C(5C)-C(6C)-H(6CA)	110.3
H(1CA)-C(1C)-H(1CB)	108.4	C(5C)-C(6C)-H(6CB)	110.3
C(2C)-C(1C)-H(1CA)	110.1	H(6CA)-C(6C)-H(6CB)	108.6
C(2C)-C(1C)-H(1CB)	110.1		
C(2C)-C(1C)-C(3C)#1	108.0(4)		
C(3C)#1-C(1C)-H(1CA)	110.1		
C(3C)#1-C(1C)-H(1CB)	110.1		
C(1C)-C(2C)-H(2CA)	110.0		
C(1C)-C(2C)-H(2CB)	110.0		
H(2CA)-C(2C)-H(2CB)	108.3		
C(3C)-C(2C)-C(1C)	108.6(4)		
C(3C)-C(2C)-H(2CA)	110.0		
C(3C)-C(2C)-H(2CB)	110.0		
C(1C)#1-C(3C)-H(3CA)	110.0		
C(1C)#1-C(3C)-H(3CB)	110.0		
C(2C)-C(3C)-C(1C)#1	108.5(5)		
C(2C)-C(3C)-H(3CA)	110.0		
C(2C)-C(3C)-H(3CB)	110.0		
H(3CA)-C(3C)-H(3CB)	108.4		
H(4CA)-C(4C)-H(4CB)	108.6		
C(5C)-C(4C)-H(4CA)	110.4		
C(5C)-C(4C)-H(4CB)	110.4		

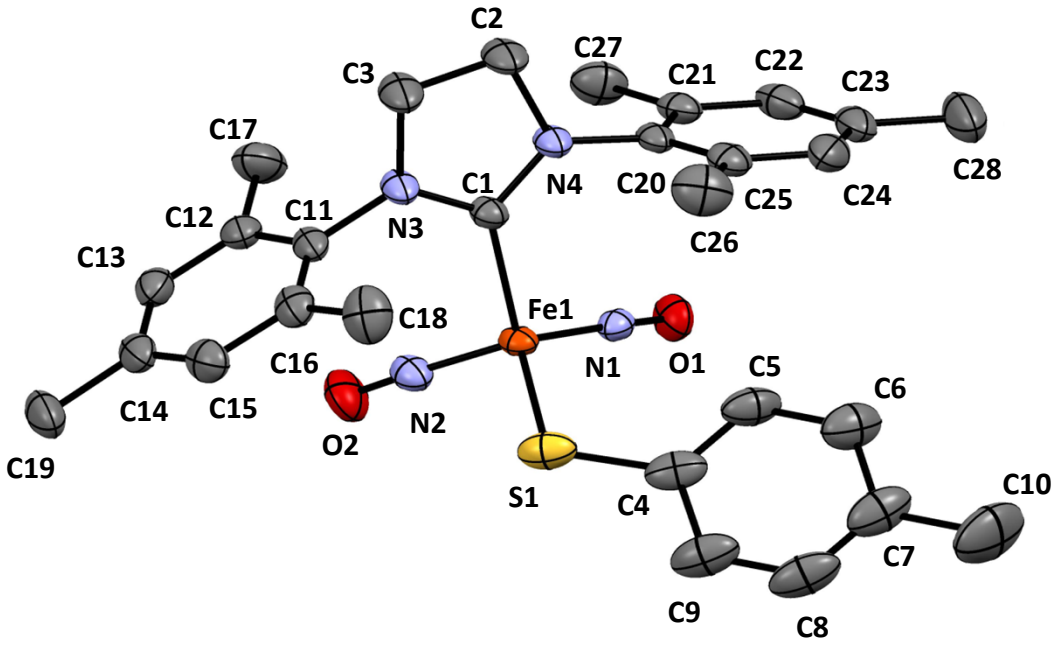

Figure S2a. ORTEP drawing and labeling scheme of complex **1b** with thermal ellipsoids drawn at 50% probability. Packing cyclohexane solvent molecule and hydrogen atoms are omitted.

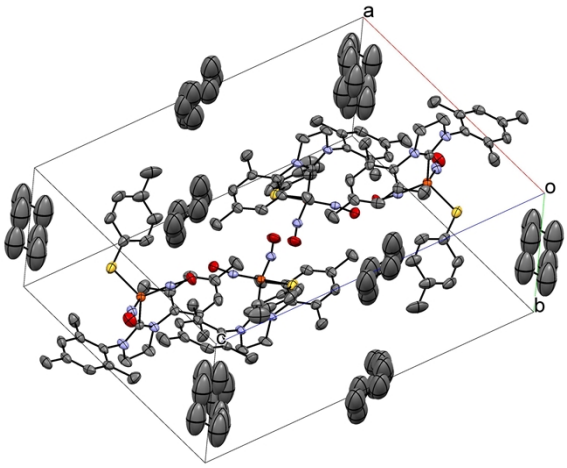

Figure S2b. Unit cell of complex **1b** complete with 4 cyclohexane molecules of crystallization.*

* The solvated cyclohexane in this structure was found disordered which we could model between two positions; several restraints and/ or constraints were added to keep the bond distances and bond angles of the disordered molecules meaningful. The residual electron densities close to the cyclohexanes indicated additional disorder; but no further modeling was attempted. Examination of the structure indicated formation of tunnels along the b axis where the cyclohexane molecules reside. The free movement of the latter during crystallization agrees well for the multiple disorder.

Table S5. Crystal data and structure refinement for [(sIMes)(S-C_6H_4-Cl)Fe$(NO)_2$] **(1c)**.

Identification code	061813dnicsph_cl_0m	
Empirical formula	C27 H30 Cl Fe N4 O2 S	
Formula weight	565.91	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 12.028(3) Å	α = 90°.
	b = 14.710(3) Å	β = 104.944(3)°.
	c = 16.167(4) Å	γ = 90°.
Volume	2763.6(11) $Å^3$	
Z	4	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	0.749 mm^{-1}	
F(000)	1180	
Crystal size	0.10 x 0.03 x 0.03 mm^3	
Theta range for data collection	1.90 to 28.37°.	
Index ranges	-16<=h<=16, -19<=k<=19, -21<=l<=21	
Reflections collected	33850	
Independent reflections	6888 [R(int) = 0.0637]	
Completeness to theta = 28.37°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9779 and 0.9289	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6888 / 0 / 331	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0942	
R indices (all data)	R1 = 0.0790, wR2 = 0.1109	
Largest diff. peak and hole	0.457 and -0.358 $e.Å^{-3}$	

Table S6. Bond lengths [Å] and angles [°] for [(sIMes)(S-C_6H_4-Cl)Fe$(NO)_2$] **(1c)**.

Fe(1)-N(1)	1.671(2)	C(21)-C(22)	1.384(4)
Fe(1)-N(2)	1.678(2)	C(22)-C(23)	1.391(4)
Fe(1)-C(1)	2.048(2)	C(22)-C(27)	1.499(3)
Fe(1)-S(1)	2.2483(8)	C(23)-C(24)	1.385(3)
N(1)-O(1)	1.176(2)	C(24)-C(25)	1.511(4)
N(2)-O(2)	1.168(2)		
S(1)-C(4)	1.768(2)	N(1)-Fe(1)-N(2)	116.77(10)
C(1)-N(4)	1.335(3)	N(1)-Fe(1)-C(1)	107.97(9)
C(1)-N(3)	1.339(3)	N(2)-Fe(1)-C(1)	104.09(9)
C(2)-N(3)	1.475(3)	N(1)-Fe(1)-S(1)	112.92(7)
C(2)-C(3)	1.517(3)	N(2)-Fe(1)-S(1)	105.51(7)
C(3)-N(4)	1.465(3)	C(1)-Fe(1)-S(1)	109.06(6)
C(4)-C(9)	1.387(3)	O(1)-N(1)-Fe(1)	169.50(18)
C(4)-C(5)	1.397(3)	O(2)-N(2)-Fe(1)	169.7(2)
C(5)-C(6)	1.378(3)	C(4)-S(1)-Fe(1)	112.53(8)
C(6)-C(7)	1.383(3)	N(4)-C(1)-N(3)	107.69(19)
C(7)-C(8)	1.375(3)	N(4)-C(1)-Fe(1)	124.75(16)
C(7)-Cl(1)	1.740(3)	N(3)-C(1)-Fe(1)	127.46(16)
C(8)-C(9)	1.378(3)	N(3)-C(2)-C(3)	102.10(19)
C(10)-C(15)	1.397(3)	N(4)-C(3)-C(2)	102.75(19)
C(10)-C(11)	1.400(3)	C(9)-C(4)-C(5)	118.1(2)
C(10)-N(3)	1.431(3)	C(9)-C(4)-S(1)	124.61(19)
C(11)-C(12)	1.385(3)	C(5)-C(4)-S(1)	117.30(18)
C(11)-C(17)	1.502(3)	C(6)-C(5)-C(4)	121.2(2)
C(12)-C(13)	1.389(4)	C(5)-C(6)-C(7)	119.2(2)
C(13)-C(14)	1.379(4)	C(8)-C(7)-C(6)	120.7(2)
C(13)-C(18)	1.510(3)	C(8)-C(7)-Cl(1)	119.5(2)
C(14)-C(15)	1.385(3)	C(6)-C(7)-Cl(1)	119.7(2)
C(15)-C(16)	1.505(3)	C(7)-C(8)-C(9)	119.7(2)
C(19)-C(24)	1.390(3)	C(8)-C(9)-C(4)	121.1(2)
C(19)-C(20)	1.394(3)	C(15)-C(10)-C(11)	121.4(2)
C(19)-N(4)	1.433(3)	C(15)-C(10)-N(3)	119.6(2)
C(20)-C(21)	1.385(3)	C(11)-C(10)-N(3)	118.8(2)
C(20)-C(26)	1.498(3)	C(12)-C(11)-C(10)	117.8(2)

C(12)-C(11)-C(17)	120.4(2)
C(10)-C(11)-C(17)	121.7(2)
C(11)-C(12)-C(13)	122.3(2)
C(14)-C(13)-C(12)	118.0(2)
C(14)-C(13)-C(18)	121.4(3)
C(12)-C(13)-C(18)	120.6(3)
C(13)-C(14)-C(15)	122.5(2)
C(14)-C(15)-C(10)	118.0(2)
C(14)-C(15)-C(16)	121.3(2)
C(10)-C(15)-C(16)	120.7(2)
C(24)-C(19)-C(20)	122.1(2)
C(24)-C(19)-N(4)	119.9(2)
C(20)-C(19)-N(4)	118.0(2)
C(21)-C(20)-C(19)	117.5(2)
C(21)-C(20)-C(26)	121.1(2)
C(19)-C(20)-C(26)	121.4(2)
C(22)-C(21)-C(20)	122.5(2)
C(21)-C(22)-C(23)	118.0(2)
C(21)-C(22)-C(27)	121.0(3)
C(23)-C(22)-C(27)	121.0(3)
C(24)-C(23)-C(22)	121.9(2)
C(23)-C(24)-C(19)	117.9(2)
C(23)-C(24)-C(25)	120.9(2)
C(19)-C(24)-C(25)	121.2(2)
C(1)-N(3)-C(10)	127.09(19)
C(1)-N(3)-C(2)	113.26(18)
C(10)-N(3)-C(2)	118.82(18)
C(1)-N(4)-C(19)	126.75(19)
C(1)-N(4)-C(3)	113.47(18)
C(19)-N(4)-C(3)	119.77(18)

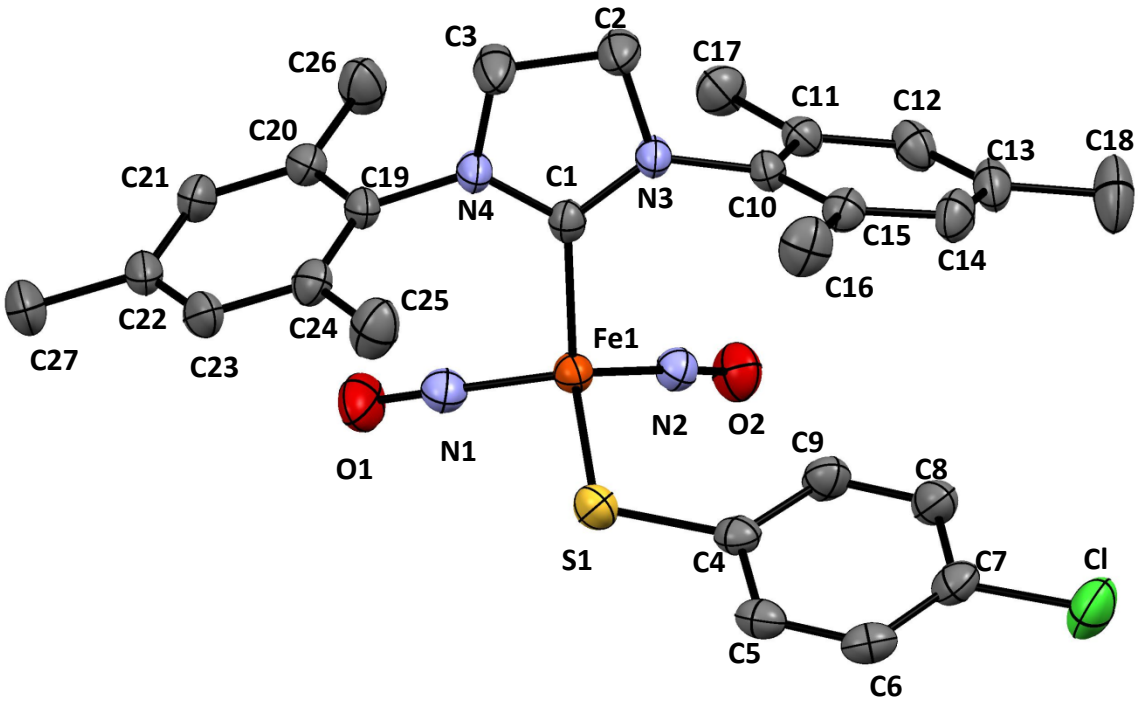

Figure S3. ORTEP drawing and labeling scheme of complex **1c** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

Table S7. Crystal data and structure refinement for [(sIMes)(S-C_6H_4-NO_2)Fe$(NO)_2$] **(1e)**.

Identification code	simesfesno2_0m	
Empirical formula	C27 H30 Fe N5 O4 S	
Formula weight	576.47	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 15.596(3) Å	α = 90°.
	b = 7.9152(17) Å	β = 107.772(3)°.
	c = 23.348(5) Å	γ = 90°.
Volume	2744.6(10) $Å^3$	
Z	4	
Density (calculated)	1.395 Mg/m^3	
Absorption coefficient	0.667 mm^{-1}	
F(000)	1204	
Crystal size	0.13 x 0.08 x 0.05 mm^3	
Theta range for data collection	1.83 to 27.95°.	
Index ranges	-20<=h<=20, -10<=k<=10, -30<=l<=30	
Reflections collected	32181	
Independent reflections	6593 [R(int) = 0.0666]	
Completeness to theta = 27.95°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9674 and 0.9183	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6593 / 0 / 349	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.0893	
R indices (all data)	R1 = 0.0664, wR2 = 0.1012	
Largest diff. peak and hole	0.407 and -0.528 e.$Å^{-3}$	

Table S8. Bond lengths [Å] and angles [°] for [(sIMes)(S-C_6H_4-NO_2)Fe$(NO)_2$] **(1e)**.

Fe(1)-N(1)	1.672(2)	C(16)-C(18)	1.397(3)
Fe(1)-N(2)	1.673(2)	C(17)-C(24)	1.508(3)
Fe(1)-C(1)	2.044(2)	C(18)-C(25)	1.506(3)
Fe(1)-S(2)	2.2594(8)	C(19)-C(22)	1.393(3)
S(2)-C(4)	1.754(2)	C(19)-C(21)	1.510(3)
N(1)-O(1)	1.172(2)	C(22)-C(23)	1.383(4)
N(2)-O(2)	1.172(3)	C(23)-C(27)	1.513(3)
N(3)-C(1)	1.330(3)		
N(3)-C(12)	1.435(3)	N(1)-Fe(1)-N(2)	110.86(10)
N(3)-C(2)	1.477(3)	N(1)-Fe(1)-C(1)	107.46(9)
N(4)-C(1)	1.339(3)	N(2)-Fe(1)-C(1)	104.63(9)
N(4)-C(16)	1.433(3)	N(1)-Fe(1)-S(2)	115.23(7)
N(4)-C(3)	1.476(3)	N(2)-Fe(1)-S(2)	110.55(8)
N(5)-O(4)	1.224(2)	C(1)-Fe(1)-S(2)	107.46(6)
N(5)-O(3)	1.234(2)	C(4)-S(2)-Fe(1)	113.23(8)
N(5)-C(7)	1.457(3)	O(1)-N(1)-Fe(1)	165.75(19)
C(2)-C(3)	1.517(3)	O(2)-N(2)-Fe(1)	163.7(2)
C(4)-C(9)	1.392(3)	C(1)-N(3)-C(12)	126.94(17)
C(4)-C(5)	1.403(3)	C(1)-N(3)-C(2)	113.32(17)
C(5)-C(6)	1.375(3)	C(12)-N(3)-C(2)	119.72(17)
C(6)-C(7)	1.379(3)	C(1)-N(4)-C(16)	126.39(17)
C(7)-C(8)	1.386(3)	C(1)-N(4)-C(3)	113.17(17)
C(8)-C(9)	1.382(3)	C(16)-N(4)-C(3)	120.18(16)
C(10)-C(17)	1.387(3)	O(4)-N(5)-O(3)	122.88(19)
C(10)-C(15)	1.393(3)	O(4)-N(5)-C(7)	118.82(19)
C(11)-C(23)	1.382(4)	O(3)-N(5)-C(7)	118.30(18)
C(11)-C(14)	1.394(3)	N(3)-C(1)-N(4)	108.19(18)
C(12)-C(19)	1.391(3)	N(3)-C(1)-Fe(1)	126.46(15)
C(12)-C(14)	1.394(3)	N(4)-C(1)-Fe(1)	125.34(15)
C(13)-C(18)	1.391(3)	N(3)-C(2)-C(3)	102.60(17)
C(13)-C(17)	1.392(3)	N(4)-C(3)-C(2)	102.48(17)
C(14)-C(26)	1.502(3)	C(9)-C(4)-C(5)	118.4(2)
C(15)-C(16)	1.394(3)	C(9)-C(4)-S(2)	124.64(17)
C(15)-C(20)	1.506(3)	C(5)-C(4)-S(2)	116.98(16)

C(6)-C(5)-C(4)	120.9(2)	C(22)-C(23)-C(27)	120.5(3)
C(5)-C(6)-C(7)	119.0(2)		
C(6)-C(7)-C(8)	121.9(2)		
C(6)-C(7)-N(5)	119.30(19)		
C(8)-C(7)-N(5)	118.82(19)		
C(9)-C(8)-C(7)	118.5(2)		
C(8)-C(9)-C(4)	121.3(2)		
C(17)-C(10)-C(15)	121.7(2)		
C(23)-C(11)-C(14)	122.1(2)		
C(19)-C(12)-C(14)	122.2(2)		
C(19)-C(12)-N(3)	118.74(19)		
C(14)-C(12)-N(3)	118.94(19)		
C(18)-C(13)-C(17)	122.0(2)		
C(12)-C(14)-C(11)	117.5(2)		
C(12)-C(14)-C(26)	120.9(2)		
C(11)-C(14)-C(26)	121.6(2)		
C(10)-C(15)-C(16)	118.32(19)		
C(10)-C(15)-C(20)	120.3(2)		
C(16)-C(15)-C(20)	121.36(19)		
C(15)-C(16)-C(18)	121.66(19)		
C(15)-C(16)-N(4)	119.67(18)		
C(18)-C(16)-N(4)	118.58(19)		
C(10)-C(17)-C(13)	118.3(2)		
C(10)-C(17)-C(24)	121.4(2)		
C(13)-C(17)-C(24)	120.2(2)		
C(13)-C(18)-C(16)	117.92(19)		
C(13)-C(18)-C(25)	120.6(2)		
C(16)-C(18)-C(25)	121.5(2)		
C(12)-C(19)-C(22)	117.7(2)		
C(12)-C(19)-C(21)	121.1(2)		
C(22)-C(19)-C(21)	121.2(2)		
C(23)-C(22)-C(19)	121.9(2)		
C(11)-C(23)-C(22)	118.5(2)		
C(11)-C(23)-C(27)	121.0(3)		

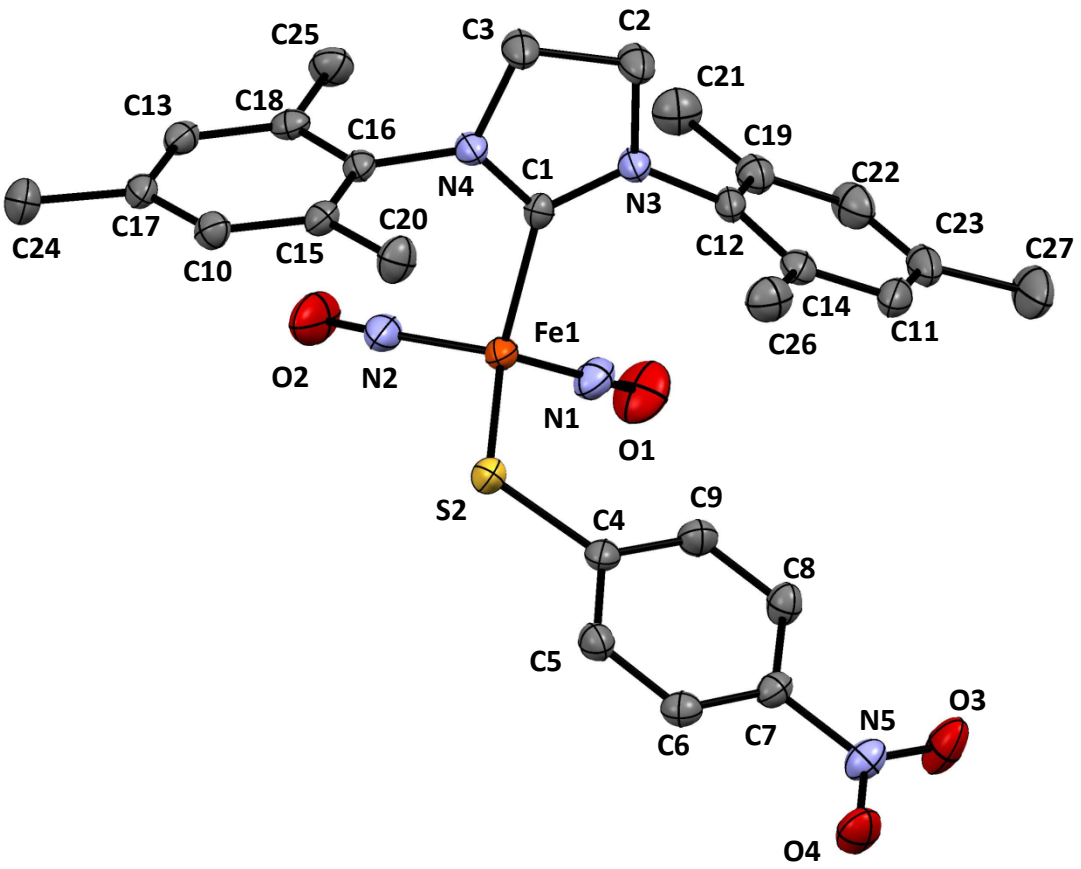

Figure S4. ORTEP drawing and labeling scheme of complex **1e** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity.

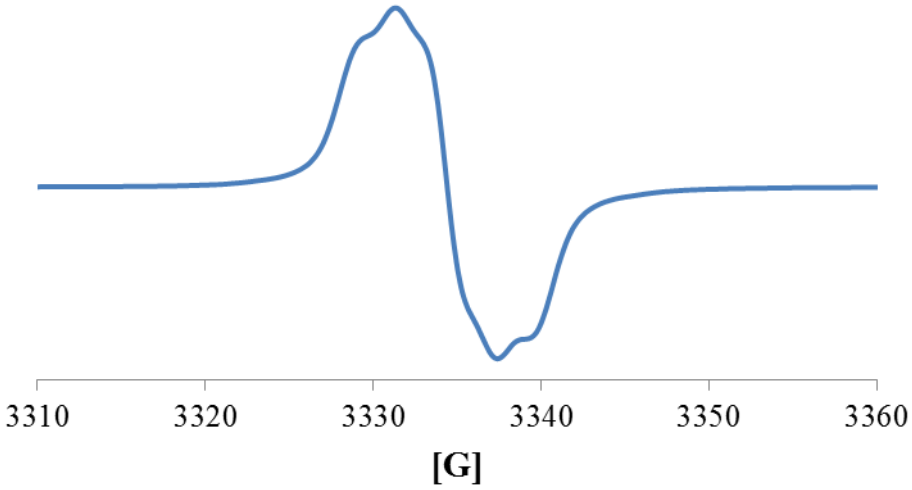

Figure S5. X-band EPR spectrum of complex **1a** in THF solution at 295 K.

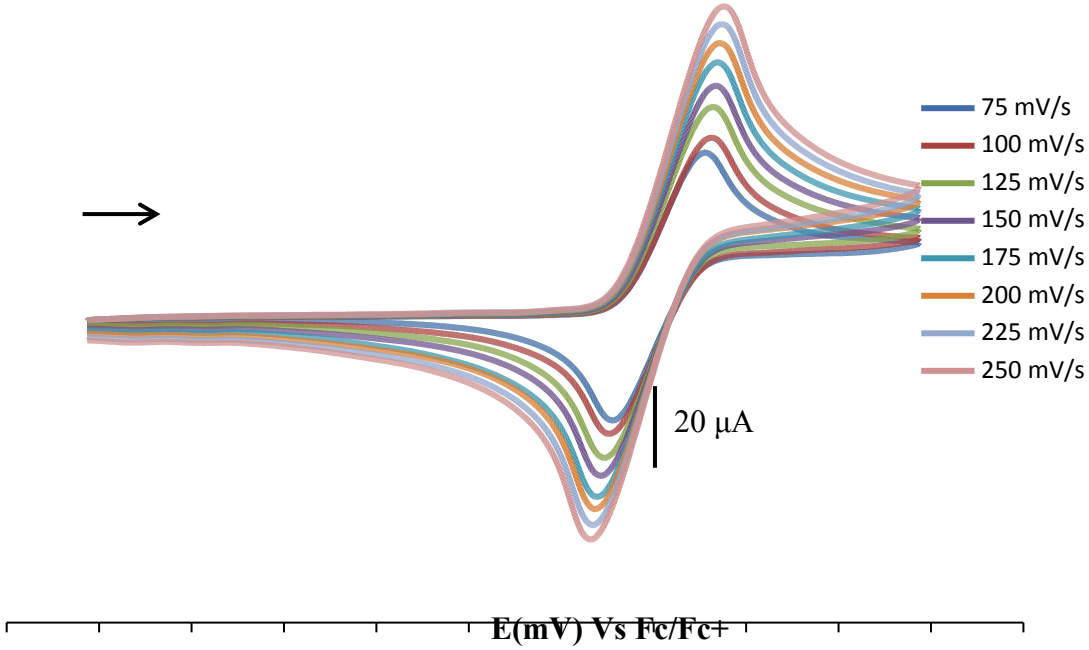

Figure S6. Scan rate – independent reversibility of **1b** (THF solution, scan rates 75-250 mV/s) as representative of DNICs **1**, **1a-1e**

Table S9. Cyclic voltammetric parameter values at a scan rate of 100 mV/s for **1a-1e** in THF solution

DNICs 1, 1a-1e	**Scan rate = 100 mV/s**			
X	**i_{pc}/i_{pa}**	**$E_{1/2}$ (V)**	**ΔE (mV)**	**ΔE for Fc/Fc^+ standard(mV)**
NO_2	0.96	-1.19	-239	-261
CF_3	0.92	-1.30	-254	-261
Cl	0.98	-1.33	-255	-246
H	1.0	-1.40	-226	-246
CH_3	1.1	-1.41	-261	-246
OCH_3	1.0	-1.44	-256	-261

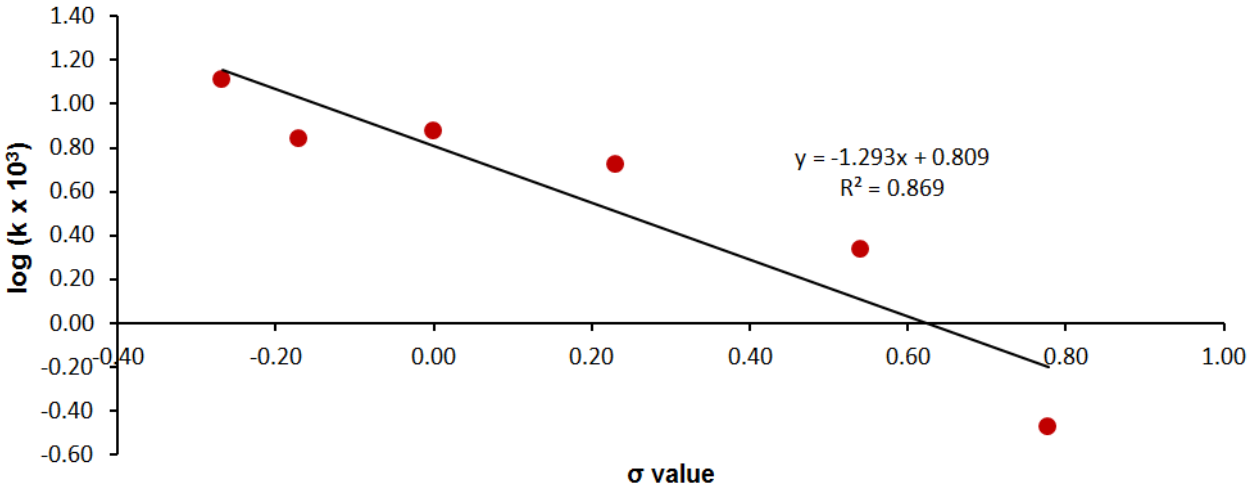

Figure S7. Hammett plot of rate constants from reactions of DNICs (**1a-1e, 1**) with CO.