Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Dinitrosyl Iron Complex as a Platform for Metal-Bound Imidazole to N-Heterocyclic Carbene Conversion

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Experimental Details

General Methods and Materials

Solvents were reagent grade, further purified and degassed by a Bruker solvent purification system, and stored over molecular sieves. Reagents, including Sodium tert-butoxide were purchased from commercial sources and used as received. Standard Schlenk-line techniques (Nitrogen atmosphere) and an Ar-filled glove box were used to maintain anaerobic conditions during preparation, isolation, and product storage. $Fe(CO)_2(NO)_2$,[1] [Na-18-crown-6-ether][$Fe(CO)_3(NO)$],[2] and 1-mesitylimidazole[3] were prepared according to published procedures.

Physical Measurements

Infrared spectra of reagents and products were recorded on a Bruker Tensor 27 FTIR spectrometer in CaF_2 solution cells of 0.1 mm path length. Elemental analyses of crystalline samples were determined by Atlantic Microlab, Inc., Norcross, GA. ^1H NMR spectra were recorded using a Mercury 300 MHz NMR spectrometer and ^{13}C NMR spectra were recorded on an Inova 500 MHz superconducting NMR instrument. All NMR samples were prepared in either CD_2Cl_2 or $CDCl_3$.

X-ray Crystallography

A Bausch and Lomb 10 x microscope was used to identify suitable crystals of the same habit. 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 F2. Anisotropic displacement parameters were determined for all nonhydrogen atoms. Hydrogen atoms were placed at idealized positions and refined with fixed isotropic displacement parameters. The following is a list of programs used: data collection and cell refinement, APEX2;[4] data reductions, SAINTPLUS Version 6.63;[5] absorption correction, SADABAS;[6] structural solutions, SHELXS-97;[7] structural refinement, SHELXL-97;[8] graphics and publication materials, Mercury Version 2.3.[9]

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(5) *SAINTPLUS*: *Program for Reduction of Area Detector Data*, version 6.63; Bruker AXS Inc.: Madison, WI, 2007.

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(7) Sheldrick, G. M. *SHELXS-97: Program for Crystal Structure Solution*; Universität Göttingen: Göttingen, Germany, 1997.

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(9) 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.

Synthesis of [Fe(NO)$_2$(Imid-mes)(CO)] (1)

In a 100 mL Schlenk flask, 0.50 g (1.10 mmol) of [Na-18-crown- 6-ether][Fe(CO)$_3$(NO)] and 0.13 g (1.11 mmol) of [NO]BF$_4$ were dissolved in 15 mL of THF and stirred for at least 10 min to produce Fe(CO)$_2$(NO)$_2$. This was vacuum-transferred to a flask previously loaded with 0.17g (0.9 mmol) of 1-mesitylimidazole (Imid-mes) and immersed in liquid N_2. The reaction mixture was stirred for 1 hour to obtain the product [Fe(NO)$_2$(Imid-mes)(CO)] **(1)** (yield >90%). IR (THF, cm^{-1}) ν(CO) : 1994, ν(NO) : 1747, 1701. Elemental Anal. calculated for FeC$_{13}$H$_{14}$N$_4$O$_3$.THF (found) : C: 50.76 (53.31), H: 5.51 (5.55), N: 13.93 (13.46). ^{1}H NMR (CD_2Cl_2): δ 7.55,7.16 (s, NCH), 7.01 (s, aromatic H on Mes), 3.45 (q, C2H), 2.34 (s, *p*-CH$_3$ on Mes), 1.99 (s, *o*-CH$_3$ on Mes).

Deprotonation of [Fe(NO)$_2$(Imid-mes)(CO)] (1)

In a separate flask, 0.16 g (1.60 mmol) of NaO^{t}Bu was dissolved in ~10 mL of THF and transferred drop wise into the flask containing the solution of 0.33 g (1.00 mmol) of **1** while stirring. An immediate color change was observed from brown to green. However, the green product **2a/2b** was extremely air sensitive, and decomposed when attempting to dry *in vacuo*.

Synthesis of [Fe(NO)$_2$(MeMes-NHC)(CO)] (3)

The solution containing the **2a/2b** was transferred via cannula into a flask containing 0.15 g (1.00 mmol) of alkylating agent, Trimethyloxonium tetrafluoroborate [(CH$_3$)$_3$O$^+$ BF$_4^-$]. A brown product was obtained (yield ~60%), and its formation could be monitored by IR spectroscopy. X-ray quality crystals were grown by cooling a saturated solution of hexanes at -35°C for three days. IR (THF, cm^{-1}) IR ν(CO) : 1988, ν(NO) : 1743, 1690. Elemental Anal. calculated for FeC$_{14}$H$_{16}$N$_4$O$_3$ (found) : C: 48.86 (49.37), H: 4.69 (4.74), N: 16.28 (16.21). ^{1}H NMR ($CDCl_3$): δ 7.23, 7.00 (s, NCH), 6.97 (s, aromatic H on Mes), 3.83 (s, NCH$_3$), 2.33 (s, *p*-CH$_3$ on Mes), 1.95 (s, *o*-CH$_3$ on Mes). ^{13}C{1H} NMR ($CDCl_3$): δ 17.55 (*o*-CH$_3$ on Mes), 21.01 (*p*-CH$_3$ on Mes), 33.75 (NCH$_3$), 123.06, 123.68 (NCH), 128.92 (C3,C5 aromatic C on Mes), 135.25 (C2,C6 aromatic C on Mes), 136.78 (C4 aromatic C on Mes), 138.80 (C1 aromatic C on Mes), 190.69 (Fe-C), 225.12 (CO).

Synthesis of $[(MeMes\text{-}NHC)_2Fe(NO)_2]$ (4)

Complex **4** can be directly synthesized in the following manner. A flask was loaded with an excess (1.31 g, 4.00 mmol) of 3-mesityl-1-methyl-imidazolium iodide and 0.39 g (4.11 mmol) of NaO^tBu, dissolved in 10 mL of THF and stirred for ~ 1 hr. The solution was then transferred via cannula to a flask containing $Fe(CO)_2(NO)_2$ freshly prepared and vacuum trapped as described above. The reaction mixture at 22 °C was stirred for 1 week, resulting in a dark brown product; the complete conversion of reactant was monitored by IR spectroscopy. The mixture was filtered through celite to remove impurities and dried in vacuo. A brown solid was obtained upon recrystallization with hexanes (yield 63%). IR (THF, cm^{-1}) IR ν(NO) : 1675, 1634. $^+$ESI-MS: Isotope bundle for the parent ion of FeC26H32N6O2 observed, centered at m/z = 516.19.

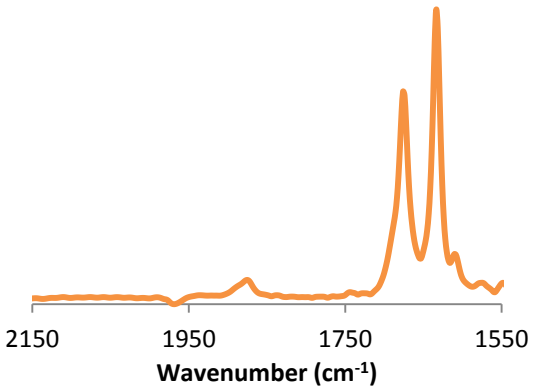

Figure S1. IR spectrum of **4** in THF. ν (NO): 1675, 1634 cm^{-1}

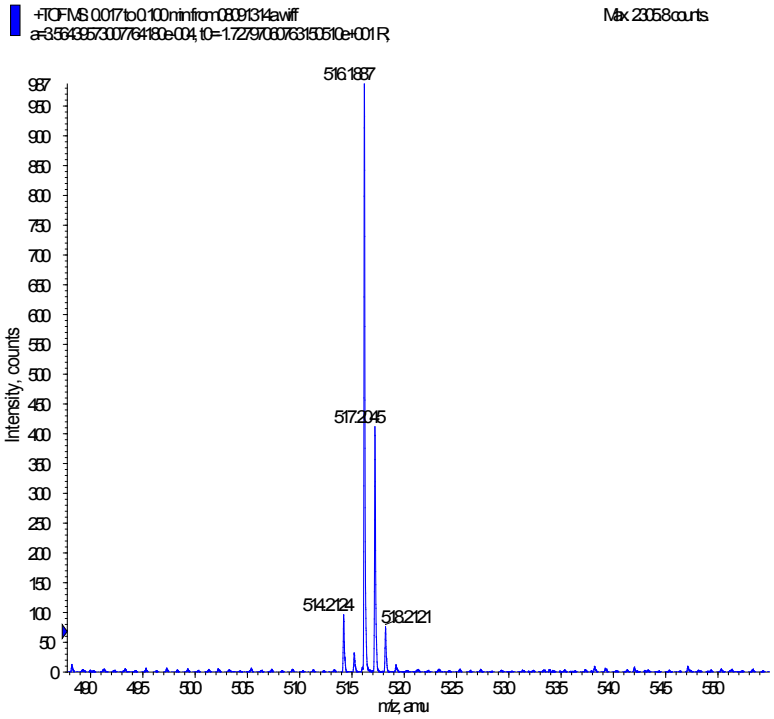

Figure S2. $^+$ESI-MS Isotope bundle for the parent ion of **4**

Synthesis of $[Fe(NO)_3(MeMes\text{-}NHC)][BF_4]$ (5)

A THF solution of complex **3** (0.34 g, 1.00 mmol), prepared as described above, was transferred by cannula to a Schlenk flask loaded with $[NO]BF_4$ (0.116 g, 1.00 mmol) at room temperature. Overnight stirring of the heterogeneous mixture gave a green precipitate. The green solid thus obtained was filtered off, and dissolved in dichloromethane. Formation of complex **5** was indicated in the IR spectrum. The green solid was washed with pentane to further remove impurities (yield: 72%). X-ray quality crystals of complex **5** were grown in dichloromethane/pentane at -35 °C. IR (CH_2Cl_2, cm^{-1}): IR ν (NO): 1991, 1814 cm^{-1}. Elemental Analysis Calculated (Found): C: 36.06 (36.15), H: 3.72 (3.81), N: 16.18 (16.40). ^1H NMR (CD_2Cl_2): δ 7.69,7.39 (s, NCH), 7.02 (s, aromatic H on Mes), 4.02 (s, NCH_3), 2.33 (s, *p*-CH_3 on Mes), 1.94 (s, *o*-CH_3 on Mes). $^{13}C\{1H\}$ NMR (CD_2Cl_2): δ 17.88 (*o*-CH_3 on Mes), 21.62 (*p*-CH_3 on Mes), 37.67 (NCH_3), 124.47, 124.94 (NCH), 130.37 (C3,C5 aromatic C on Mes), 130.51 (C2,C6 aromatic C on Mes), 135.22 (C4 aromatic C on Mes), 138.11 (C1 aromatic C on Mes), 142.34 (Fe-C).

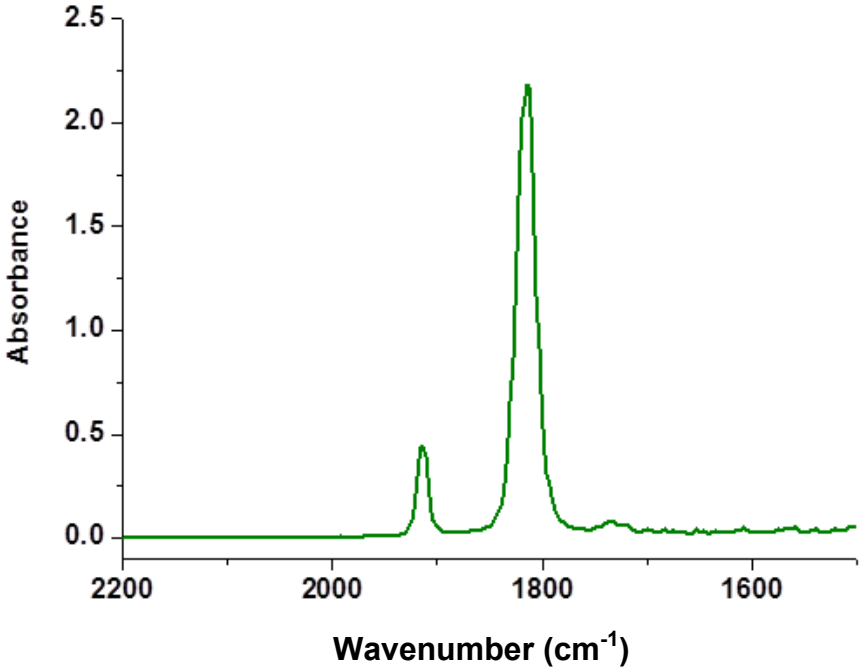

Figure S3. IR spectrum of **5** in THF. ν (NO): 1914, 1814 cm^{-1} with the typical two band (A + E) pattern indicating the C_{3v} symmetry typical for TNICs

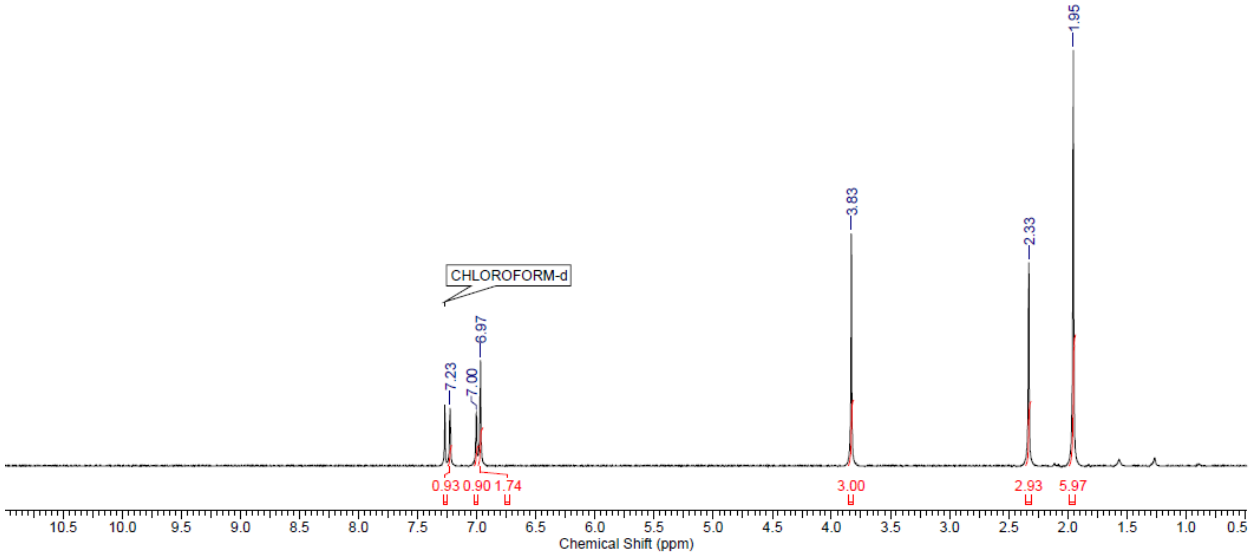

Figure S4. ^{1}H-NMR spectrum of [Fe(NO)$_2$(MeMes-NHC)(CO)] **(3)** in $CDCl_3$.

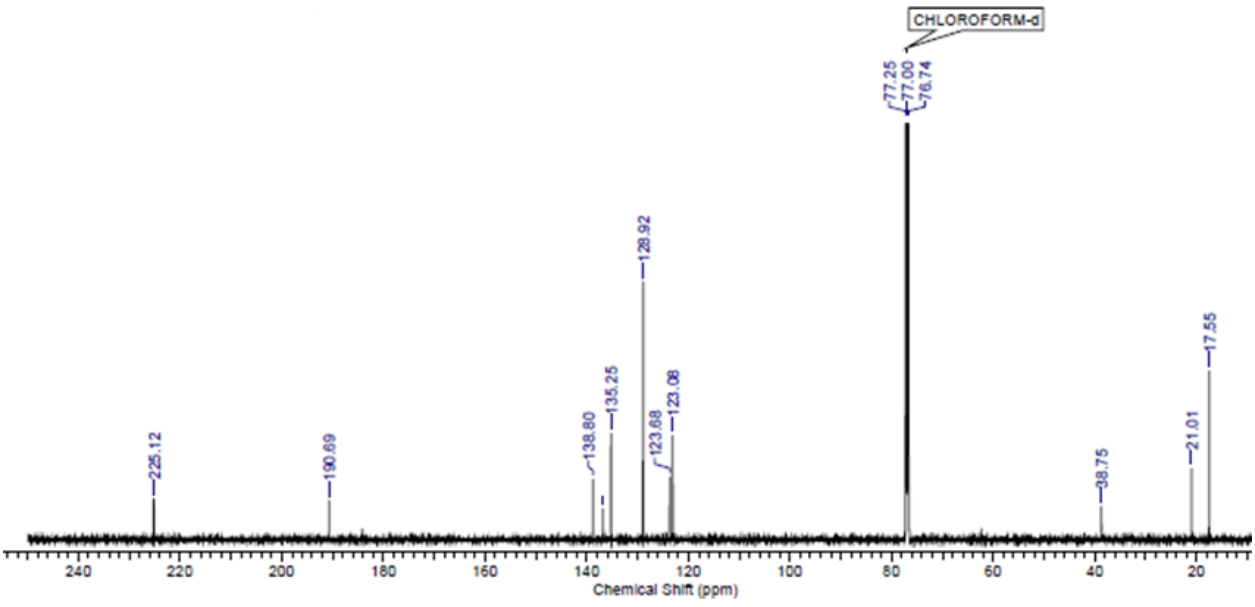

Figure S5. ^{13}C-NMR spectrum of [Fe(NO)$_2$(MeMes-NHC)(CO)] **(3)** in $CDCl_3$.

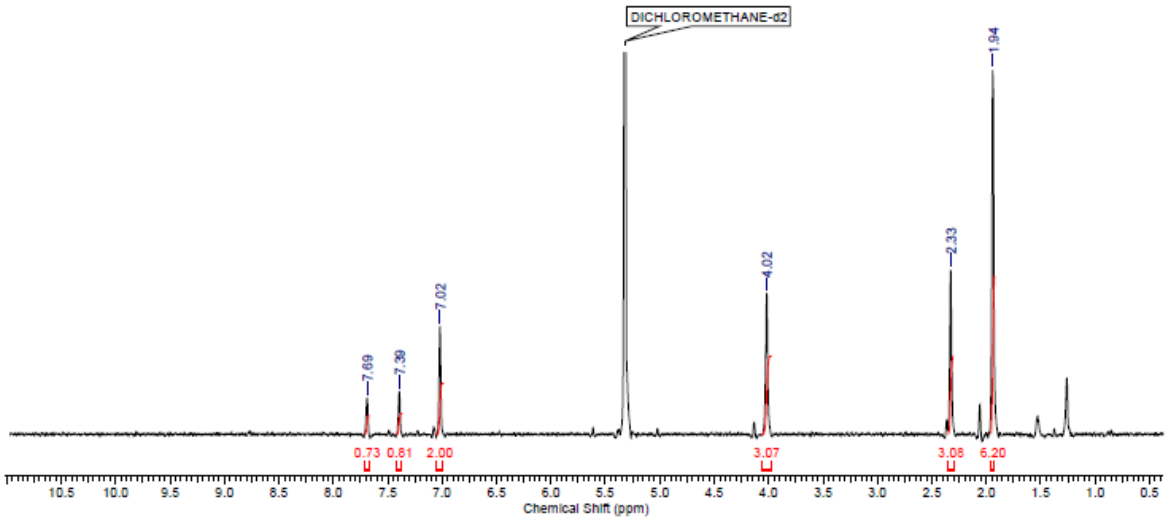

Figure S6. ^{1}H-NMR spectrum of $[Fe(NO)_3(MeMes\text{-}NHC)][BF_4]$ **(5)** in CD_2Cl_2

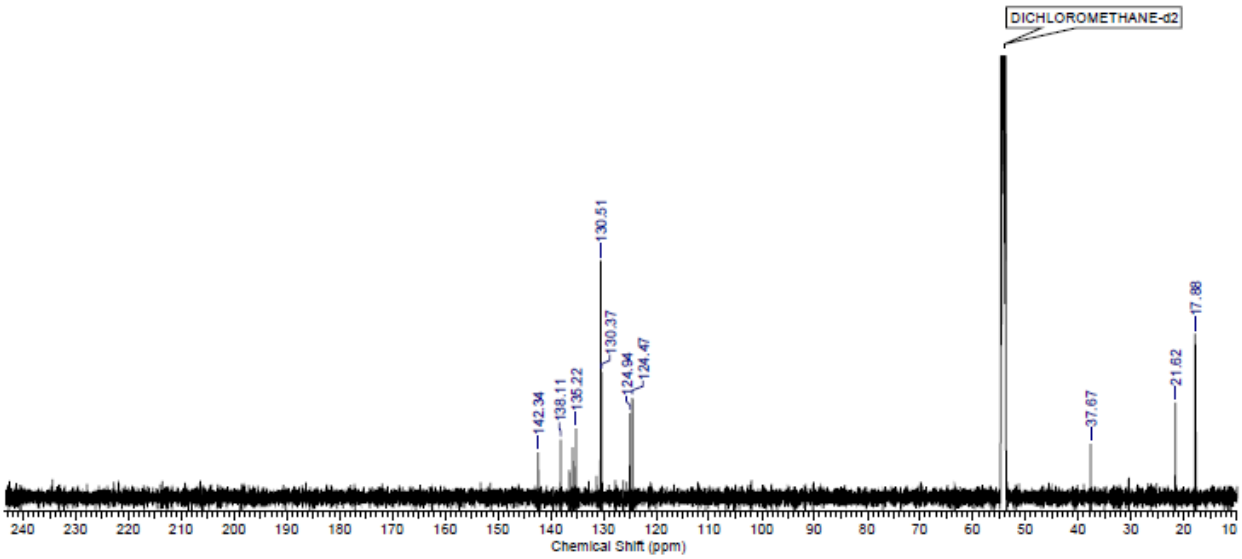

Figure S7. ^{13}C-NMR spectrum of $[Fe(NO)_3(MeMes\text{-}NHC)][BF_4]$ **(5)** in CD_2Cl_2

Table S1. Crystal data and structure refinement for $[Fe(NO)_2(MeMes\text{-}NHC)(CO)]$ **(3)**

Identification code	meimeco01_0m	
Empirical formula	C14 H16 Fe N4 O3	
Formula weight	344.16	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 10.300(2) Å	α = 90°.
	b = 10.581(2) Å	β = 103.230(2)°.
	c = 15.189(3) Å	γ = 90°.
Volume	1611.5(6) $Å^3$	
Z	4	
Density (calculated)	1.419 Mg/m^3	
Absorption coefficient	0.952 mm^{-1}	
F(000)	712	
Crystal size	0.20 x 0.10 x 0.04 mm^3	
Theta range for data collection	2.18 to 28.28°.	
Index ranges	-13<=h<=13, -14<=k<=14, -20<=l<=20	
Reflections collected	19311	
Independent reflections	3988 [R(int) = 0.0281]	
Completeness to theta = 28.28°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9629 and 0.8324	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3988 / 0 / 203	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0258, wR2 = 0.0725	
R indices (all data)	R1 = 0.0285, wR2 = 0.0746	
Largest diff. peak and hole	0.440 and -0.245 $e.Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for [Fe(NO)$_2$(MeMes-NHC)(CO)] **(3)**

Fe(1)-N(2)	1.6572(12)	O(1)-N(1)-Fe(1)	172.60(12)
Fe(1)-N(1)	1.6635(12)	O(2)-N(2)-Fe(1)	177.01(13)
Fe(1)-C(5)	1.8337(15)	C(1)-N(3)-C(3)	111.63(10)
Fe(1)-C(1)	1.9905(12)	C(1)-N(3)-C(2)	125.16(10)
N(1)-O(1)	1.1754(16)	C(3)-N(3)-C(2)	123.19(10)
N(2)-O(2)	1.1818(16)	C(1)-N(4)-C(4)	111.29(10)
N(3)-C(1)	1.3565(15)	C(1)-N(4)-C(6)	125.61(10)
N(3)-C(3)	1.3837(16)	C(4)-N(4)-C(6)	122.56(10)
N(3)-C(2)	1.4607(15)	N(3)-C(1)-N(4)	103.70(10)
N(4)-C(1)	1.3647(15)	N(3)-C(1)-Fe(1)	126.95(8)
N(4)-C(4)	1.3870(15)	N(4)-C(1)-Fe(1)	128.94(9)
N(4)-C(6)	1.4375(15)	C(4)-C(3)-N(3)	106.76(11)
O(3)-C(5)	1.1388(19)	C(3)-C(4)-N(4)	106.61(11)
C(3)-C(4)	1.3444(18)	O(3)-C(5)-Fe(1)	174.99(13)
C(6)-C(11)	1.3936(17)	C(11)-C(6)-C(7)	122.23(11)
C(6)-C(7)	1.4001(18)	C(11)-C(6)-N(4)	120.13(11)
C(7)-C(8)	1.3907(18)	C(7)-C(6)-N(4)	117.60(11)
C(7)-C(13)	1.5094(19)	C(8)-C(7)-C(6)	117.79(12)
C(8)-C(9)	1.390(2)	C(8)-C(7)-C(13)	120.92(12)
C(9)-C(10)	1.3876(19)	C(6)-C(7)-C(13)	121.29(12)
C(9)-C(14)	1.5107(18)	C(9)-C(8)-C(7)	121.77(12)
C(10)-C(11)	1.3972(17)	C(10)-C(9)-C(8)	118.73(12)
C(11)-C(12)	1.5043(19)	C(10)-C(9)-C(14)	120.77(13)
N(2)-Fe(1)-N(1)	120.30(6)	C(8)-C(9)-C(14)	120.50(13)
N(2)-Fe(1)-C(5)	113.87(6)	C(9)-C(10)-C(11)	121.79(12)
N(1)-Fe(1)-C(5)	105.74(6)	C(6)-C(11)-C(10)	117.66(12)
N(2)-Fe(1)-C(1)	103.48(5)	C(6)-C(11)-C(12)	121.62(11)
N(1)-Fe(1)-C(1)	111.62(5)	C(10)-C(11)-C(12)	120.71(12)
C(5)-Fe(1)-C(1)	100.06(6)		

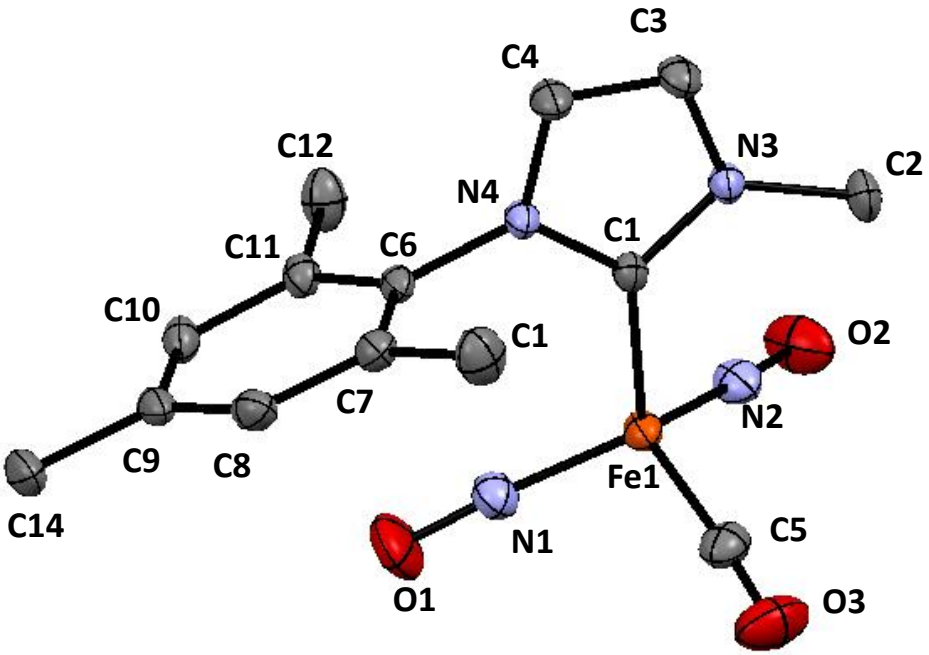

Figure S8. ORTEP drawing and labeling scheme of complex **3** with thermal ellipsoids drawn at 50% probability.

Table S3. Crystal data and structure refinement for $[(MeMes\text{-}NHC)_2Fe(NO)_2]$ **(4)**

Identification code	datax	
Empirical formula	C29 H38 Fe N6 O2	
Formula weight	558.50	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnn2	
Unit cell dimensions	a = 12.373(2) Å	α = 90°.
	b = 23.135(4) Å	β = 90°.
	c = 9.6348(18) Å	γ = 90°.
Volume	2757.8(9) $Å^3$	
Z	4	
Density (calculated)	1.345 Mg/m^3	
Absorption coefficient	0.584 mm^{-1}	
F(000)	1184	
Crystal size	0.08 x 0.05 x 0.05 mm^3	
Theta range for data collection	1.87 to 25.00°.	
Index ranges	-14<=h<=14, -27<=k<=27, -11<=l<=11	
Reflections collected	25394	
Independent reflections	4874 [R(int) = 0.0223]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9714 and 0.9547	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4874 / 1 / 351	
Goodness-of-fit on F^2	1.100	
Final R indices [I>2sigma(I)]	R1 = 0.0275, wR2 = 0.0775	
R indices (all data)	R1 = 0.0285, wR2 = 0.0783	
Absolute structure parameter	0.009(13)	
Largest diff. peak and hole	0.458 and -0.360 $e.Å^{-3}$	

Table S4. Bond lengths [Å] and angles [°] for $[(MeMes\text{-}NHC)_2Fe(NO)_2]$ **(4)**

Fe(1)-N(2)	1.6496(18)	C(13)-H(13C)	0.9600
Fe(1)-N(1)	1.6514(17)	C(14)-H(14A)	0.9600
Fe(1)-C(2)	1.984(2)	C(14)-H(14B)	0.9600
Fe(1)-C(1)	1.995(2)	C(14)-H(14C)	0.9600
N(1)-O(1)	1.202(2)	C(15)-H(15A)	0.9600
N(2)-O(2)	1.204(2)	C(15)-H(15B)	0.9600
C(1)-N(3)	1.364(3)	C(15)-H(15C)	0.9600
C(1)-N(4)	1.378(3)	C(16)-N(3)	1.464(3)
C(2)-N(6)	1.363(3)	C(16)-H(16A)	0.9600
C(2)-N(5)	1.367(3)	C(16)-H(16B)	0.9600
C(3)-C(4)	1.332(3)	C(16)-H(16C)	0.9600
C(3)-N(4)	1.395(3)	C(17)-C(18)	1.383(3)
C(3)-H(3)	0.9300	C(17)-C(22)	1.396(3)
C(4)-N(3)	1.369(3)	C(17)-N(5)	1.448(3)
C(4)-H(4)	0.9300	C(18)-C(19)	1.397(3)
C(5)-C(6)	1.339(3)	C(18)-C(24)	1.507(3)
C(5)-N(5)	1.384(3)	C(19)-C(20)	1.392(4)
C(5)-H(5)	0.9300	C(19)-H(19)	0.9300
C(6)-N(6)	1.386(3)	C(20)-C(21)	1.398(4)
C(6)-H(6)	0.9300	C(20)-C(25)	1.517(3)
C(7)-C(12)	1.391(3)	C(21)-C(22)	1.385(3)
C(7)-C(8)	1.395(3)	C(21)-H(21)	0.9300
C(7)-N(4)	1.432(3)	C(22)-C(23)	1.493(4)
C(8)-C(9)	1.401(3)	C(23)-H(23A)	0.9600
C(8)-C(14)	1.506(3)	C(23)-H(23B)	0.9600
C(9)-C(10)	1.369(3)	C(23)-H(23C)	0.9600
C(9)-H(9)	0.9300	C(24)-H(24A)	0.9600
C(10)-C(11)	1.389(3)	C(24)-H(24B)	0.9600
C(10)-C(15)	1.506(3)	C(24)-H(24C)	0.9600
C(11)-C(12)	1.392(3)	C(25)-H(25A)	0.9600
C(11)-H(11)	0.9300	C(25)-H(25B)	0.9600
C(12)-C(13)	1.513(3)	C(25)-H(25C)	0.9600
C(13)-H(13A)	0.9600	C(26)-N(6)	1.454(3)
C(13)-H(13B)	0.9600	C(26)-H(26A)	0.9600

C(26)-H(26B)	0.9600	C(5)-C(6)-N(6)	106.9(2)
C(26)-H(26C)	0.9600	C(5)-C(6)-H(6)	126.6
C(27)-C(28)	1.410(8)	N(6)-C(6)-H(6)	126.6
C(27)-C(29)	1.511(8)	C(12)-C(7)-C(8)	121.7(2)
C(27)-H(27A)	0.9700	C(12)-C(7)-N(4)	119.3(2)
C(27)-H(27B)	0.9700	C(8)-C(7)-N(4)	119.0(2)
C(28)-C(28)#1	1.321(10)	C(7)-C(8)-C(9)	117.5(2)
C(28)-H(28A)	0.9700	C(7)-C(8)-C(14)	121.4(2)
C(28)-H(28B)	0.9700	C(9)-C(8)-C(14)	121.1(2)
C(29)-C(29)#1	1.415(13)	C(10)-C(9)-C(8)	122.5(2)
C(29)-H(29A)	0.9700	C(10)-C(9)-H(9)	118.8
C(29)-H(29B)	0.9700	C(8)-C(9)-H(9)	118.8
N(2)-Fe(1)-N(1)	118.46(9)	C(9)-C(10)-C(11)	118.3(2)
N(2)-Fe(1)-C(2)	111.57(9)	C(9)-C(10)-C(15)	121.8(2)
N(1)-Fe(1)-C(2)	107.66(9)	C(11)-C(10)-C(15)	119.9(2)
N(2)-Fe(1)-C(1)	110.70(9)	C(10)-C(11)-C(12)	121.8(2)
N(1)-Fe(1)-C(1)	111.16(10)	C(10)-C(11)-H(11)	119.1
C(2)-Fe(1)-C(1)	94.70(9)	C(12)-C(11)-H(11)	119.1
O(1)-N(1)-Fe(1)	173.29(18)	C(7)-C(12)-C(11)	118.2(2)
O(2)-N(2)-Fe(1)	171.19(18)	C(7)-C(12)-C(13)	121.8(2)
N(3)-C(1)-N(4)	102.31(18)	C(11)-C(12)-C(13)	120.0(2)
N(3)-C(1)-Fe(1)	129.06(16)	C(12)-C(13)-H(13A)	109.5
N(4)-C(1)-Fe(1)	128.60(15)	C(12)-C(13)-H(13B)	109.5
N(6)-C(2)-N(5)	103.18(18)	H(13A)-C(13)-H(13B)	109.5
N(6)-C(2)-Fe(1)	128.75(16)	C(12)-C(13)-H(13C)	109.5
N(5)-C(2)-Fe(1)	128.04(16)	H(13A)-C(13)-H(13C)	109.5
C(4)-C(3)-N(4)	106.4(2)	H(13B)-C(13)-H(13C)	109.5
C(4)-C(3)-H(3)	126.8	C(8)-C(14)-H(14A)	109.5
N(4)-C(3)-H(3)	126.8	C(8)-C(14)-H(14B)	109.5
C(3)-C(4)-N(3)	107.4(2)	H(14A)-C(14)-H(14B)	109.5
C(3)-C(4)-H(4)	126.3	C(8)-C(14)-H(14C)	109.5
N(3)-C(4)-H(4)	126.3	H(14A)-C(14)-H(14C)	109.5
C(6)-C(5)-N(5)	106.7(2)	H(14B)-C(14)-H(14C)	109.5
C(6)-C(5)-H(5)	126.7	C(10)-C(15)-H(15A)	109.5
N(5)-C(5)-H(5)	126.7	C(10)-C(15)-H(15B)	109.5

H(15A)-C(15)-H(15B)	109.5	H(24A)-C(24)-H(24B)	109.5
C(10)-C(15)-H(15C)	109.5	C(18)-C(24)-H(24C)	109.5
H(15A)-C(15)-H(15C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(15B)-C(15)-H(15C)	109.5	H(24B)-C(24)-H(24C)	109.5
N(3)-C(16)-H(16A)	109.5	C(20)-C(25)-H(25A)	109.5
N(3)-C(16)-H(16B)	109.5	C(20)-C(25)-H(25B)	109.5
H(16A)-C(16)-H(16B)	109.5	H(25A)-C(25)-H(25B)	109.5
N(3)-C(16)-H(16C)	109.5	C(20)-C(25)-H(25C)	109.5
H(16A)-C(16)-H(16C)	109.5	H(25A)-C(25)-H(25C)	109.5
H(16B)-C(16)-H(16C)	109.5	H(25B)-C(25)-H(25C)	109.5
C(18)-C(17)-C(22)	122.4(2)	N(6)-C(26)-H(26A)	109.5
C(18)-C(17)-N(5)	120.1(2)	N(6)-C(26)-H(26B)	109.5
C(22)-C(17)-N(5)	117.4(2)	H(26A)-C(26)-H(26B)	109.5
C(17)-C(18)-C(19)	118.3(2)	N(6)-C(26)-H(26C)	109.5
C(17)-C(18)-C(24)	121.7(2)	H(26A)-C(26)-H(26C)	109.5
C(19)-C(18)-C(24)	120.0(2)	H(26B)-C(26)-H(26C)	109.5
C(20)-C(19)-C(18)	121.1(2)	C(28)-C(27)-C(29)	103.2(4)
C(20)-C(19)-H(19)	119.5	C(28)-C(27)-H(27A)	111.1
C(18)-C(19)-H(19)	119.5	C(29)-C(27)-H(27A)	111.1
C(19)-C(20)-C(21)	118.6(2)	C(28)-C(27)-H(27B)	111.1
C(19)-C(20)-C(25)	121.2(3)	C(29)-C(27)-H(27B)	111.1
C(21)-C(20)-C(25)	120.2(3)	H(27A)-C(27)-H(27B)	109.1
C(22)-C(21)-C(20)	121.8(2)	C(28)#1-C(28)-C(27)	116.1(6)
C(22)-C(21)-H(21)	119.1	C(28)#1-C(28)-H(28A)	108.3
C(20)-C(21)-H(21)	119.1	C(27)-C(28)-H(28A)	108.3
C(21)-C(22)-C(17)	117.7(2)	C(28)#1-C(28)-H(28B)	108.3
C(21)-C(22)-C(23)	121.1(2)	C(27)-C(28)-H(28B)	108.3
C(17)-C(22)-C(23)	121.2(2)	H(28A)-C(28)-H(28B)	107.4
C(22)-C(23)-H(23A)	109.5	C(29)#1-C(29)-C(27)	121.5(3)
C(22)-C(23)-H(23B)	109.5	C(29)#1-C(29)-H(29A)	107.0
H(23A)-C(23)-H(23B)	109.5	C(27)-C(29)-H(29A)	107.0
C(22)-C(23)-H(23C)	109.5	C(29)#1-C(29)-H(29B)	107.0
H(23A)-C(23)-H(23C)	109.5	C(27)-C(29)-H(29B)	107.0
H(23B)-C(23)-H(23C)	109.5	H(29A)-C(29)-H(29B)	106.7
C(18)-C(24)-H(24A)	109.5	C(1)-N(3)-C(4)	112.52(18)
C(18)-C(24)-H(24B)	109.5	C(1)-N(3)-C(16)	125.02(19)
C(4)-N(3)-C(16)	122.47(19)	C(2)-N(5)-C(17)	125.41(18)

C(1)-N(4)-C(3)	111.38(19)	C(5)-N(5)-C(17)	122.31(18)
C(1)-N(4)-C(7)	125.90(18)	C(2)-N(6)-C(6)	111.61(18)
C(3)-N(4)-C(7)	122.71(19)	C(2)-N(6)-C(26)	125.21(18)
C(2)-N(5)-C(5)	111.66(19)	C(6)-N(6)-C(26)	122.94(18)

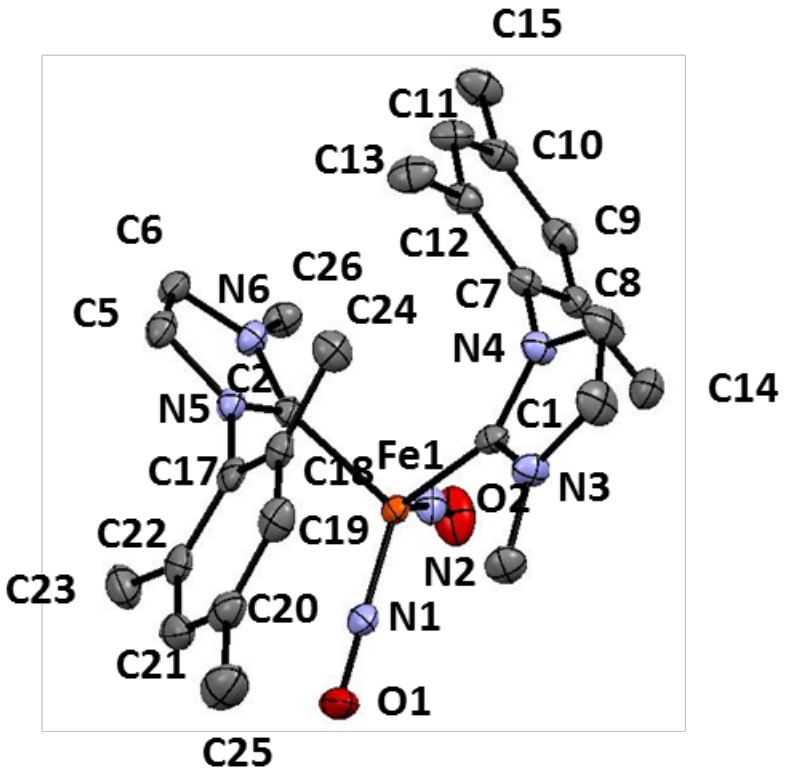

Figure S9. ORTEP drawing and labeling scheme of complex **4** with thermal ellipsoids drawn at 50% probability. (Cyclohexane packing solvent omitted for clarity)

Table S5. Crystal data and structure refinement for $[Fe(NO)_3(MeMes\text{-}NHC)][BF_4]$ **(5)**

Identification code	memestnic_0m	
Empirical formula	C13 H16 B F4 Fe N5 O3	
Formula weight	432.97	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 10.9146(13) Å	α = 90°.
	b = 15.4743(18) Å	β = 114.9070(10)°.
	c = 11.7202(14) Å	γ = 90°.
Volume	1795.4(4) $Å^3$	
Z	4	
Density (calculated)	1.602 Mg/m^3	
Absorption coefficient	0.904 mm^{-1}	
F(000)	880	
Crystal size	0.10 x 0.05 x 0.02 mm^3	
Theta range for data collection	2.14 to 28.29°.	
Index ranges	-14<=h<=14, -20<=k<=20, -15<=l<=15	
Reflections collected	21411	
Independent reflections	4451 [R(int) = 0.0245]	
Completeness to theta = 28.29°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9821 and 0.9150	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4451 / 0 / 248	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0383, wR2 = 0.0987	
R indices (all data)	R1 = 0.0432, wR2 = 0.1026	
Largest diff. peak and hole	0.906 and -0.623 $e.Å^{-3}$	

Table S6. Bond lengths [Å] and angles [°] for $[Fe(NO)_3(MeMes\text{-}NHC)][BF_4]$ **(5)**

Fe(1)-N(1)	1.6816(18)	C(12)-H(12A)	0.9600
Fe(1)-N(3)	1.7008(18)	C(12)-H(12B)	0.9600
Fe(1)-N(2)	1.7017(18)	C(12)-H(12C)	0.9600
Fe(1)-C(1)	2.0057(19)	C(13)-H(13A)	0.9600
N(1)-O(1)	1.152(2)	C(13)-H(13B)	0.9600
N(2)-O(2)	1.145(2)	C(13)-H(13C)	0.9600
N(3)-O(3)	1.148(2)	B(1)-F(1)	1.345(3)
C(1)-N(4)	1.351(2)	B(1)-F(2)	1.361(3)
C(1)-N(5)	1.356(2)	B(1)-F(3)	1.372(3)
N(4)-C(3)	1.384(3)	B(1)-F(4)	1.380(3)
N(4)-C(2)	1.466(2)	N(1)-Fe(1)-N(3)	111.76(9)
N(5)-C(4)	1.389(2)	N(1)-Fe(1)-N(2)	114.02(9)
N(5)-C(5)	1.443(2)	N(3)-Fe(1)-N(2)	113.23(9)
C(2)-H(2A)	0.9600	N(1)-Fe(1)-C(1)	103.14(8)
C(2)-H(2B)	0.9600	N(3)-Fe(1)-C(1)	107.07(8)
C(2)-H(2C)	0.9600	N(2)-Fe(1)-C(1)	106.72(8)
C(3)-C(4)	1.346(3)	O(1)-N(1)-Fe(1)	174.63(18)
C(3)-H(3)	0.9300	O(2)-N(2)-Fe(1)	172.91(18)
C(4)-H(4)	0.9300	O(3)-N(3)-Fe(1)	171.89(17)
C(5)-C(6)	1.396(3)	N(4)-C(1)-N(5)	104.92(16)
C(5)-C(10)	1.399(3)	N(4)-C(1)-Fe(1)	128.42(13)
C(6)-C(7)	1.395(3)	N(5)-C(1)-Fe(1)	126.54(14)
C(6)-C(12)	1.505(3)	C(1)-N(4)-C(3)	110.95(16)
C(7)-C(8)	1.388(3)	C(1)-N(4)-C(2)	125.59(17)
C(7)-H(7)	0.9300	C(3)-N(4)-C(2)	123.45(17)
C(8)-C(9)	1.388(3)	C(1)-N(5)-C(4)	110.56(16)
C(8)-C(13)	1.510(3)	C(1)-N(5)-C(5)	125.71(16)
C(9)-C(10)	1.392(3)	C(4)-N(5)-C(5)	123.65(15)
C(9)-H(9)	0.9300	N(4)-C(2)-H(2A)	109.5
C(10)-C(11)	1.508(3)	N(4)-C(2)-H(2B)	109.5
C(11)-H(11A)	0.9600	H(2A)-C(2)-H(2B)	109.5
C(11)-H(11B)	0.9600	N(4)-C(2)-H(2C)	109.5
C(11)-H(11C)	0.9600	H(2A)-C(2)-H(2C)	109.5

H(2B)-C(2)-H(2C)	109.5	C(10)-C(11)-H(11A)	109.5
C(4)-C(3)-N(4)	106.81(17)	C(10)-C(11)-H(11B)	109.5
C(4)-C(3)-H(3)	126.6	H(11A)-C(11)-H(11B)	109.5
N(4)-C(3)-H(3)	126.6	C(10)-C(11)-H(11C)	109.5
C(3)-C(4)-N(5)	106.76(17)	H(11A)-C(11)-H(11C)	109.5
C(3)-C(4)-H(4)	126.6	H(11B)-C(11)-H(11C)	109.5
N(5)-C(4)-H(4)	126.6	C(6)-C(12)-H(12A)	109.5
C(6)-C(5)-C(10)	122.46(18)	C(6)-C(12)-H(12B)	109.5
C(6)-C(5)-N(5)	118.36(16)	H(12A)-C(12)-H(12B)	109.5
C(10)-C(5)-N(5)	119.16(17)	C(6)-C(12)-H(12C)	109.5
C(7)-C(6)-C(5)	117.62(18)	H(12A)-C(12)-H(12C)	109.5
C(7)-C(6)-C(12)	120.45(18)	H(12B)-C(12)-H(12C)	109.5
C(5)-C(6)-C(12)	121.93(18)	C(8)-C(13)-H(13A)	109.5
C(8)-C(7)-C(6)	121.70(19)	C(8)-C(13)-H(13B)	109.5
C(8)-C(7)-H(7)	119.2	H(13A)-C(13)-H(13B)	109.5
C(6)-C(7)-H(7)	119.2	C(8)-C(13)-H(13C)	109.5
C(9)-C(8)-C(7)	118.84(18)	H(13A)-C(13)-H(13C)	109.5
C(9)-C(8)-C(13)	120.6(2)	H(13B)-C(13)-H(13C)	109.5
C(7)-C(8)-C(13)	120.5(2)	F(1)-B(1)-F(2)	108.0(3)
C(8)-C(9)-C(10)	121.94(19)	F(1)-B(1)-F(3)	109.7(2)
C(8)-C(9)-H(9)	119.0	F(2)-B(1)-F(3)	107.1(2)
C(10)-C(9)-H(9)	119.0	F(1)-B(1)-F(4)	113.0(2)
C(9)-C(10)-C(5)	117.43(18)	F(2)-B(1)-F(4)	108.1(2)
C(9)-C(10)-C(11)	120.93(18)	F(3)-B(1)-F(4)	110.7(2)
C(5)-C(10)-C(11)	121.63(18)		

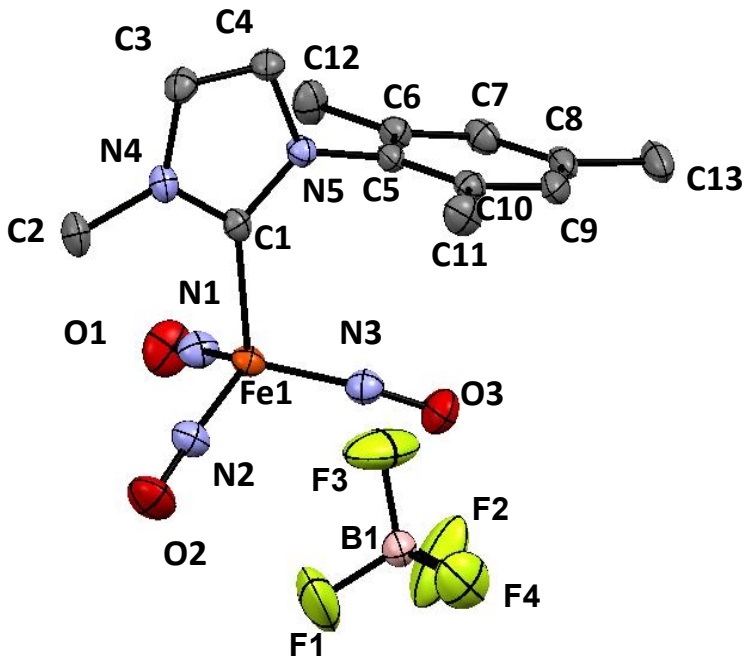

Figure S10. ORTEP drawing and labeling scheme of complex **5** with thermal ellipsoids drawn at 50% probability.