Square planar bis(imino)pyridine iron halide and alkyl complexes.

Supporting Information

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Experimental Section

General Considerations. All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk and cannula techniques or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. The MBraun drybox was equipped with a cold well designed for freezing samples in liquid nitrogen. Solvents for air- and moisture-sensitive manipulations were initially dried and deoxygenated using literature procedures.[1] Argon and hydrogen gas were purchased from Airgas Incorporated and passed through a column containing manganese oxide supported on vermiculite and 4 Å molecular sieves before admission to the high vacuum line. Benzene-d_6 was purchased from Cambridge Isotope Laboratories and distilled from sodium metal under an atmosphere of argon and stored over 4 Å molecular sieves or sodium metal. Sodium triethylborohydride and $LiCH_2SiMe_3$ were purchased as 1.0 M solutions in toluene and pentane, respectively, from Aldrich. For the $LiCH_2SiMe_3$, the solvent was removed in vacuo and the resulting solid recrystallized from pentane at –35 ºC. The iron(II) dichloride complexes, **1-Cl$_2$**[2] **2-Cl** $_2$,[3] and **3-Cl$_2$**[4] were prepared according to literature procedures. Methyllithium was purchased as a 1.6 M solution in diethyl ether from Acros and was used as received. $LiCH_2SiMe_3$ was purchased from Aldrich as a 1.0 M solution in pentane.

^{1}H NMR spectra were recorded on Varian Mercury 300, Inova 400 and 500 spectrometers operating at 299.763, 399.780 and 500.62 MHz, respectively. All chemical shifts are reported relative to $SiMe_4$ using ^{1}H (residual) chemical shifts of the solvent as a secondary standard. For paramagnetic molecules, the ^{1}H NMR data are reported with the

chemical shift followed by the peak width at half height in Hertz or multiplicity, followed by integration value and where possible, peak assignment.

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and were quickly transferred to the goniometer head of a Siemens SMART CCD Area detector system equipped with a molybdenum X-ray tube (λ = 0.71073 Å). Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified and the data were processed using the Bruker SAINT program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures.

Modified Preparation of (^{Mes}PDIFeCl$_2$) (3-Cl$_2$). A 100 mL round bottomed flask was charged with 0.510 g (1.39 mmol) of (2,4,6-Me$_3$-C$_6$H$_3$N=CMe)$_2$C$_5$H$_3$N and 0.177 g (1.39 mmol) of FeCl$_2$ and a 180° needle valve was attached. On the vacuum line, approximately 50 mL of THF was added by vacuum transfer. The resulting reaction mixture was stirred at ambient temperature for 6 hours forming a blue slurry. The solvent was removed *in vacuo* and the flask assembly was transferred into the dry box where the desired product was washed with three portions of diethyl ether yielding 0.590 g (86 %) of a gray-blue solid. The product was identified as **3-Cl$_2$** by comparison of ^{1}H NMR spectral data to a previous report.[4]

Preparation of (^{iPr}PDI)FeCl (1-Cl). A 20 mL scintillation vial was charged with 0.100 g (0.165 mmol) of **1-Cl$_2$** and diethyl ether was added forming a slurry. The solution was

cooled in a –35 ºC freezer for approximately 10 minutes after which time 0.145 g (0.165 mmoles) of $NaBEt_3H$ (1M solution in toluene) was dissolved in additional diethyl ether and dripped into the cold solution. The blue slurry immediately turned to a soluble dark green solution. After stirring for approximately one hour, the solution was filtered through Celite and the solvent removed *in vacuo* to yield 0.078 g (83%) of **1-Cl**. Analysis for $C_{33}H_{43}N_3FeCl$: Calc. C, 69.17; H, 7.56; N, 7.33. Found C, 69.39; H, 8.10; N, 6.88. Magnetic susceptibility (benzene-d_6) μ_{eff}= 3.7 μ_B. ^{1}H NMR (benzene-d_6): δ = –212.9 (162, 6H, C(*Me*)), -109.2 (434.3, 4H), -33.4 (139.5, 12H, CH*Me*$_2$), -21.4 (28.5, 12H, CH*Me*$_2$), -13.3 (22.8, 2H), -6.0 (26.3, 4H), 68.1 (267.4, 2H), 385.6 (195.4, 1H, *p*-py).

Preparation of (^{iPr}PDI)FeBr (1-Br). This molecule was prepared in a similar manner to **1-Cl** with 0.100 g (0.144 mmol) of **1-Br$_2$** and 0.124 g (0.144) g of a 1 M $NaBEt_3H$ solution in toluene to yield 0.077 g (97 %) of a green solid identified as **1-Br**. Analysis for $C_{33}H_{43}N_3FeBr$: Calc. C, 64.19; H, 7.03; N, 6.80. Found C, 63.92; H, 7.36; N, 6.51. Magnetic susceptibility (benzene-d_6) μ_{eff}= 3.9 μ_B. ^{1}H NMR (benzene-d_6): δ = –210.4 (159, 6H, C(*Me*)), -107.0 (209.7, 4H), -32.3 (126.7, 12H, CH*Me*$_2$), -20.3 (30.6, 12H, CH*Me*$_2$). 4 signals not located.

Preparation of (^{Et}PDI)FeCl (2-Cl). A 250 mL round-bottom flask was charged with 0.500 g (0.906 mmol) of **2-Cl$_2$** and approximately 100 mL of diethyl ether. The resulting solution was cooled to –35 ºC over the course of 20 minutes. A second solution containing 0.11 g (0.906 mmol) of sodium triethylborohydride (from 1.0 M solution in toluene) in 25 mL of ether was added dropwise to the cold solution. The resulting

reaction mixture turned dark green in color immediately after the addition. After stirring for 3 hours, the solution was filtered through Celite. The solvent was removed *in vacuo* to afford 0.352 g (75%) of a dark green solid identified as **2-Cl**. Analysis for $C_{29}H_{35}N_3FeCl$: Calc. C, 67.38; H, 6.83; N, 8.13. Found C, 67.00; H, 6.50; N, 7.87. Magnetic susceptibility (benzene-d_6) μ_{eff} = 4.0 μ_B. ^{1}H NMR (benzene-d_6): δ = -214 (168, 12H, C(*Me*)), -61.5 (236, 4H, C*H*$_2$CH$_3$), -52.1 (196.56, 4H, C*H*$_2$CH$_3$), -31.9 (86.6, 12H, CH$_2$*CH*$_3$), -15.3 (24.4, 2H, *p-aryl*), -6.5 (31.8, 4H, *m-aryl*), 68.1 (85.0, 2H, *m-py*), 369.27 (238.18, 1H, *p-pyridine*).

Preparation of (^{Mes}PDI)FeCl (3-Cl). A 100 mL round bottomed flask was charged with 0.415 g (0.791 mmol) of **3-Cl$_2$** and 50 mL of ether. The resulting blue slurry was chilled to –35 °C in the glove box freezer. In a separate 20 mL scintillation vial, a solution containing 0.680 g (0.791 mmol) of NaBEt$_3$H (1 M in toluene, d = 0.866 g/mL) and 10 mL of ether was prepared. The NaBEt$_3$H solution was then added dropwise to the slurry containing the iron complex. The resulting reaction mixture was stirred for 3 hours forming a green solution. After this time, the sodium chloride precipitate was removed by filtration through Celite and the filtrate collected. The solvent was removed *in vacuo* and the resulting brown oil was washed with three portions of pentane to afford 0.302 g (77 %) of a green solid identified as **3-Cl**. Analysis for $C_{27}H_{31}N_3FeCl$: Calc. C, 66.34; H, 6.39; N, 8.60. Found C, 65.97; H, 6.29; N, 8.49. Magnetic Susceptibility (benzene-d_6) μ_{eff} = 4.0 μ_B. ^{1}H NMR (benzene-d_6): δ = -209.1 (381, 6H, N=CC*H*$_3$), -42.8 (406, 12H, *o*-C*H*$_3$), -7.6 (186, 4H, *m*-C*H*), 18.7 (32.5, 6H, *p*-C*H*$_3$), 63.9 (266.57, 2H, *m*-pyr), 357.1 (402, 1H, *p*-pyr).

Preparation of (^{iPr}PDI)FeCH$_3$ (1-Me). A 50 mL round bottom flask was charged with 0.706 g (1.23 mmol) of **1-Cl** and approximately 15 mL of diethyl ether. The resulting solution was chilled to -35 °C in the glovebox freezer for approximately 15 min. With stirring, 0.539 g (1.23 mmol) of MeLi (1.6 M in diethyl ether) was added to the ethereal solution containing **1-Cl**. The reaction was allowed to warm to 25 ºC and stirred for 5 h. The solution was filtered through Celite and the solvent removed in vacuo to yield 0.358 g (53 %) of a green solid identified as **1-Me**. Anal. Calcd for $C_{34}H_{46}FeN_3$: C, 73.90; H, 8.39; N, 7.60. Found: C, 73.78; H, 8.06; N, 7.33. Magnetic Susceptibility (benzene-d_6): $\mu_{eff} = 3.5\ \mu_B$. ^{1}H NMR (benzene-d_6): δ = -163.8 (142.0, 6H, C(*Me*)), -72.6 (242.1, 4H), -21.3 (70.8, 12H, CH*Me*$_2$), -11.8 (18.7, 12H CH*Me*$_2$), -2.3 (20.0, 4H), 58.9 (46.0, 2H), 216.5 (113.2, 1H, *p*-C_5H_3N), *two peaks not located*.

Preparation of 1-Me from 1-Cl$_2$ and MeLi. To a THF solution containing 0.154 g (0.25 mmol) of **1-Cl$_2$** in approximately 10 mL was added 0.3 mL (0.48 mmol) of a 1.6 M solution of MeLi diluted to approximately 5 mL of total volume. The resulting brownish red reaction mixture was stirred for approximately 90 minutes and the THF removed *in vacuo*. The resulting solid was triturated with pentane to remove any residual THF. The product was then extracted with diethyl ether to afford 0.104 g (74 %) of a green solid identified as **1-Me**.

Preparation of (^{Et}PDIFeMe) (2-Me). A 100 mL round bottomed flask was charged with 0.500 g (0.971 mmol) of **2-Cl** and 50 mL of diethyl ether. The resulting brown

solution was chilled to –35 ºC in the dry box freezer. With stirring, 0.606 mL (0.971 mmol) MeLi (1.6 M in diethyl ether) was added forming a dark reddish-brown reaction mixture. The slurry was stirred for 30 minutes and then filtered through Celite. The filtrate was collected and the solvent removed in vacuo leaving a reddish-purple solid. The product was washed twice with pentane to afford 0.374 g (78 %) of **2-Me**. Analysis for $C_{30}H_{33}N_3Fe$: Calc. C, 72.57; H, 7.71; N, 8.46. Found C, 72.43; H, 7.46; N, 8.63. Magnetic Susceptibility (benzene-d_6) μ_{eff} = 4.1 μ_B. ^{1}H NMR (benzene-d_6): δ = -167.8 (132, 6H, N=CCH_3), -57.2 (198, 4H, CH_2CH$_3$), -48.1 (142, 4H, CH_2CH$_3$), -32.6 (78, 2H, *p-aryl*), -24.6 (52, 12H, CH$_2$CH_3), -5.2 (19.2, 4H, *m-aryl*), 63.2 (57.7, 2H, *m-pyr*), 264.7 (123, 1H, *p-pyr*). Fe-*Me not located.*

Preparation of (^{Et}PDI)Fe(CH$_2$SiMe$_3$) (2-CH$_2$SiMe$_3$). A 20 mL scintillation vial was charged with 0.035 g (0.068 mmol) of **2-Cl** and approximately 5 mL of diethyl ether. After cooling to –35 ºC for 25 minutes, 0.006 g (0.068 mmol) of LiCH$_2$SiMe$_3$ dissolved in a minimal amount of diethyl ether was added dropwise. The resulting dark green solution was stirred for 5 hours after which time it was filtered through Celite. Removal of the solvent *in vacuo* yielded 0.028 g (72 %) of a lipophilic green solid identified as **2-CH$_2$SiMe$_3$**. Analysis for $C_{33}H_{46}N_3SiFe$: Calc. C, 69.21; H, 8.10; N, 7.34. Found C, 68.92 H, 7.67 N, 7.06. Magnetic susceptibility (benzene-d_6) μ_{eff} = 4.0 μ_B. ^{1}H NMR (benzene-d_6): δ = -194.0 (189, 6H, C(*Me*)), -75.4 (315, 4H, CH_2Me), -61.9 (249, 4H, CH_2Me), -23.9 (83.3, 12H, CH$_2$*Me*), -16.9 (49.5, 2H, *p-aryl*), -10.88 (56.9, 4H, *m-aryl*), 42.3 (219, 9H, SiMe_3), 67.9 (115, 2H, *m-pyridine*), 341.5 (187, 1H, p-pyridine), FeCH_2 not located.

Preparation of (^{Mes}PDIFeMe) (3-Me). This molecule was prepared in a similar manner to **1-Me** with 0.160 g (0.25 mmol) of **3-Cl$_2$** and 0.3 mL (0.48 mmol) of 1.6 M MeLi affording 0.032 (27 %) of a green solid identified as **3-Me**. Analysis for $C_{28}H_{29}N_3Fe$: Calc. C, 71.79; H, 7.32; N, 8.97. Found C, 71.32; H, 6.98; N, 8.52. Magnetic Susceptibility (benzene-d_6) μ_{eff} = 3.9 μ_B. ^{1}H NMR (400MHz, benzene-d_6): δ = -161.5 (142, 6H, N=CC*H$_3$*), -41.7 (119, 12H, o-C*H$_3$*), -6.2 (22.1, 4H, m-C*H*), 12.6 (10.4, 6H, p-C*H$_3$*), 61.5 (53.7, 2H, m-pyr), 264.5 (150, 1H, p-pyr). Fe-*Me not located.*

Preparation of 1-Cl from addition of LiCH$_2$SiMe$_3$. A scintillation vial was charged with 0.181 g (0.30 mmol) of **1-Cl$_2$** and the solid dissolved in THF. To the vial, a solution containing 0.028 mg (0.29 mmol) of LiCH$_2$SiMe$_3$ dissolved in approximately 2 mL of THF was added. The resulting reaction mixture was stirred for 20 hours and the volatiles removed in vacuo. The resulting solid was triturated with pentane to remove residual quantities of THF. The desired product was extracted into ether (2 x 10 mL) and exhibited spectral features consistent with **1-Cl**. This compound can also be prepared in diethyl ether.

Preparation of (^{iPr}PDI)Fe(CH$_2$SiMe$_3$)$_2$ (1-(CH$_2$SiMe$_3$)$_2$). A 20 mL scintillation vial was charged with 0.320 g (0.53 mmol) of **1-Cl$_2$** and the solid was dissolved in THF. A solution containing 0.095 g (1.0 mmol) of LiCH$_2$SiMe$_3$ dissolved in approximately 3 mL of THF was added to the vial. After stirring for 18 hours, the volatiles were removed in vacuo and pentane was added and removed to dry the solid of THF. The resulting solid

was washed with pentane (2 x 3 mL) and extracted into Et_2O (5 x 10 mL). The Et_2O extracts were combined and the solvent removed to afford 0.160 g (45 %) of **1-$(CH_2SiMe_3)_2$** as a purple, crystalline solid. This molecule can also be prepared in diethyl ether. Analysis for $C_{41}H_{65}FeN_3Si_2$: Calcd. C, 69.16; H, 9.20; N, 5.90. Found C, 69.05; H, 9.02; N, 5.9. Magnetic susceptibility (benzene, 23 ºC): $\mu_{eff} = 4.8\ \mu_B$. ^{1}H NMR (400MHz, benzene-d_6): δ -150.8 (574, 6H, N=CCH_3), -16.39 (75.9, 4H, m-C*H*), -2.84 (289.0, 12H, CHMe_2), 10.1-17.6 (3 br s overlapping, 30H, CHMe_2 and SiMe_3), 64.5 (238.2, 4H, C*H*Me_2), 281.9 (948.9, 1H, p-py). *Two signals not located.*

Reaction of (^{Et}PDI)$FeCl_2$ with $LiCH_2SiMe_3$. A solution of 0.168 g (1.78 mmol) of $LiCH_2SiMe_3$ in approximately 2 mL of THF was added to a stirring solution of 0.497 g (0.90 mmol) of **2-Cl_2**. After stirring for 13 hours, the volatiles were removed in vacuo. The resulting solids were triturated with pentane to remove any residual THF. Extraction of the products into pentane produced 0.446 g of a 5:1 mixture of **2-CH_2SiMe_3** and **2-$(CH_2SiMe_3)_2$**. ^{1}H NMR (400MHz, benzene-d_6) of **2-$(CH_2SiMe_3)_2$**: δ = -150.3 (465, 6H, N=CCH_3), -16.7 (82.8, 4H, m-C*H*), 10.2-14.8 (2 br s overlapping, 30H, CH_2Me and SiMe_3), 59.9 (191.8, 4H, CH_2Me), 286.0 (948.9, 1H, p-py), four peaks not located.

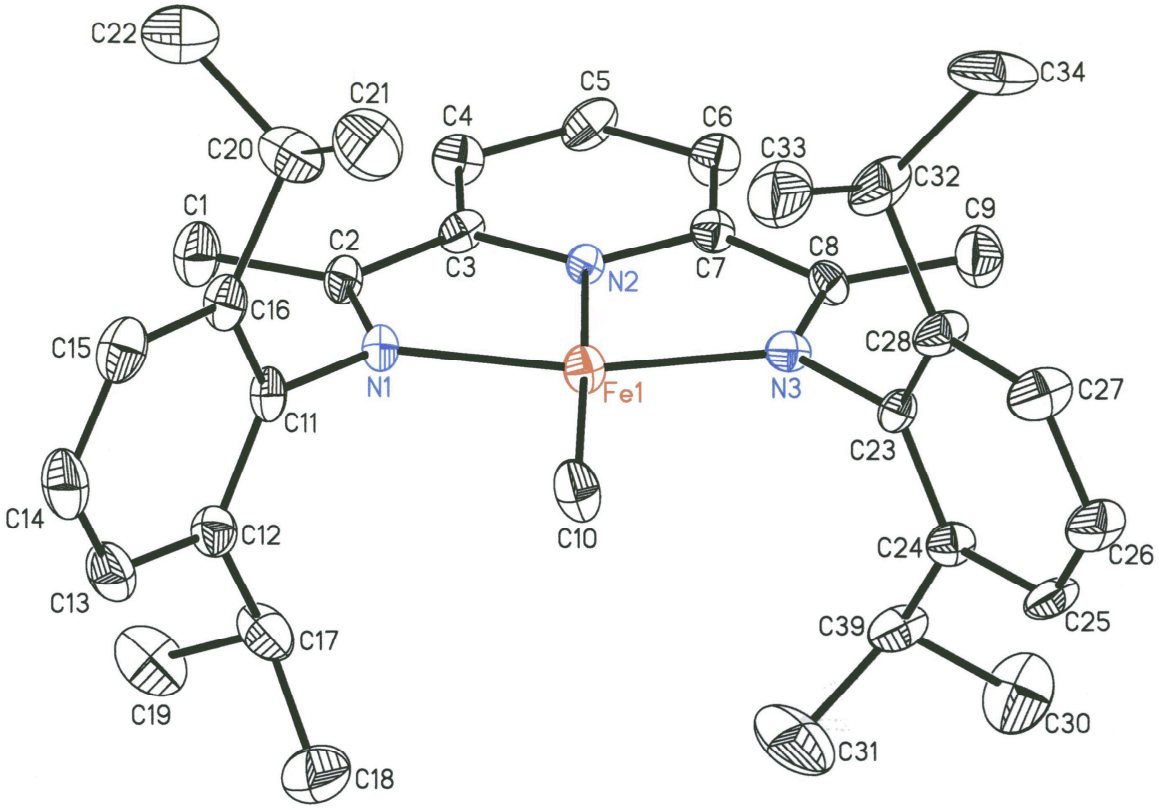

Figure S1. Fully labeled view of the molecular structure of **1-Me** at 30 % probability ellipsoids. Hydrogen atoms and diethyl ether molecules omitted for clarity.

Table S1. Crystal data and structure refinement for **1-Me**.

Identification code	**1-Me**	
Empirical formula	C34 H46 Fe N3	
Formula weight	552.59	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 16.0725(12) Å	α= 86.074(2)°.
	b = 16.2819(11) Å	β= 64.426(2)°.
	c = 17.0074(12) Å	γ = 62.003(2)°.
Volume	3494.2(4) $Å^3$	
Z	4	
Density (calculated)	1.050 Mg/m^3	
Absorption coefficient	0.454 mm^{-1}	
F(000)	1188	
Crystal size	0.40 x 0.30 x 0.10 mm^3	
Theta range for data collection	1.55 to 20.82°.	
Index ranges	-16<=h<=16, -16<=k<=16, -17<=l<=17	
Reflections collected	17737	
Independent reflections	7309 [R(int) = 0.0689]	
Completeness to theta = 20.82°	99.9 %	
Absorption correction	Semiempirical by SADABS	
Max. and min. transmission	0.9560 and 0.8392	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7309 / 0 / 685	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0674, wR2 = 0.1627	
R indices (all data)	R1 = 0.1091, wR2 = 0.1816	
Largest diff. peak and hole	0.355 and -0.363 e.$Å^{-3}$	

Table S2. Bond lengths [Å] and angles [°] for **1-Me**.

Fe(1)-N(2)	1.893(4)
Fe(1)-N(3)	1.952(5)
Fe(1)-N(1)	1.968(5)
Fe(1)-C(10)	2.001(6)
N(1)-C(2)	1.337(7)
N(1)-C(11)	1.455(7)
N(2)-C(3)	1.349(7)
N(2)-C(7)	1.368(7)
N(3)-C(8)	1.332(7)
N(3)-C(23)	1.442(7)
C(1)-C(2)	1.471(8)
C(2)-C(3)	1.432(8)
C(3)-C(4)	1.403(8)
C(4)-C(5)	1.413(9)
C(5)-C(6)	1.372(9)
C(6)-C(7)	1.398(8)
C(7)-C(8)	1.442(8)
C(8)-C(9)	1.493(8)
C(11)-C(16)	1.393(8)
C(11)-C(12)	1.397(8)
C(12)-C(13)	1.373(9)
C(12)-C(17)	1.526(9)
C(13)-C(14)	1.357(10)
C(14)-C(15)	1.375(9)
C(15)-C(16)	1.378(9)
C(16)-C(20)	1.528(9)
C(17)-C(19)	1.525(10)
C(17)-C(18)	1.558(10)
C(20)-C(21)	1.508(11)
C(20)-C(22)	1.542(10)
C(23)-C(24)	1.379(8)
C(23)-C(28)	1.393(8)
C(24)-C(25)	1.380(9)
C(24)-C(39)	1.521(8)
C(25)-C(26)	1.376(8)
C(26)-C(27)	1.367(9)
C(27)-C(28)	1.386(9)
C(28)-C(32)	1.532(9)
C(30)-C(39)	1.532(9)
C(31)-C(39)	1.525(10)
C(32)-C(34)	1.517(10)
C(32)-C(33)	1.536(10)
Fe(1')-N(2')	1.866(5)
Fe(1')-N(1')	1.935(5)
Fe(1')-N(3')	1.947(5)
Fe(1')-C(10')	1.985(6)
N(1')-C(2')	1.335(7)
N(1')-C(11')	1.446(8)
N(2')-C(3')	1.357(7)
N(2')-C(7')	1.377(7)
N(3')-C(8')	1.322(7)
N(3')-C(23')	1.440(7)
C(1')-C(2')	1.492(8)
C(2')-C(3')	1.440(9)
C(3')-C(4')	1.408(9)
C(4')-C(5')	1.402(9)
C(5')-C(6')	1.369(9)
C(6')-C(7')	1.401(9)
C(7')-C(8')	1.423(8)
C(8')-C(9')	1.507(8)
C(11')-C(12')	1.388(9)
C(11')-C(16')	1.421(9)
C(12')-C(13')	1.401(10)
C(12')-C(17')	1.486(10)
C(13')-C(14')	1.407(11)
C(14')-C(15')	1.385(10)
C(15')-C(16')	1.388(9)

C(16')-C(20')	1.512(9)	N(2)-C(3)-C(4)	121.2(6)
C(17')-C(18')	1.498(11)	N(2)-C(3)-C(2)	111.5(5)
C(17')-C(19')	1.505(12)	C(4)-C(3)-C(2)	127.2(6)
C(20')-C(21')	1.540(9)	C(3)-C(4)-C(5)	116.9(6)
C(20')-C(22')	1.542(9)	C(6)-C(5)-C(4)	121.2(6)
C(23')-C(24')	1.388(8)	C(5)-C(6)-C(7)	119.8(6)
C(23')-C(28')	1.390(8)	N(2)-C(7)-C(6)	119.0(5)
C(24')-C(25')	1.392(8)	N(2)-C(7)-C(8)	111.2(5)
C(24')-C(29')	1.509(9)	C(6)-C(7)-C(8)	129.7(6)
C(25')-C(26')	1.355(9)	N(3)-C(8)-C(7)	113.7(5)
C(26')-C(27')	1.373(9)	N(3)-C(8)-C(9)	124.7(5)
C(27')-C(28')	1.397(8)	C(7)-C(8)-C(9)	121.6(6)
C(28')-C(32')	1.523(8)	C(16)-C(11)-C(12)	121.3(6)
C(29')-C(30')	1.515(10)	C(16)-C(11)-N(1)	118.5(6)
C(29')-C(31')	1.527(10)	C(12)-C(11)-N(1)	119.9(6)
C(32')-C(34')	1.529(9)	C(13)-C(12)-C(11)	118.2(6)
C(32')-C(33')	1.542(9)	C(13)-C(12)-C(17)	120.5(6)
		C(11)-C(12)-C(17)	121.3(6)
N(2)-Fe(1)-N(3)	80.1(2)	C(14)-C(13)-C(12)	121.5(7)
N(2)-Fe(1)-N(1)	79.1(2)	C(13)-C(14)-C(15)	119.7(7)
N(3)-Fe(1)-N(1)	159.2(2)	C(14)-C(15)-C(16)	121.6(6)
N(2)-Fe(1)-C(10)	176.0(2)	C(15)-C(16)-C(11)	117.5(6)
N(3)-Fe(1)-C(10)	101.7(2)	C(15)-C(16)-C(20)	120.6(6)
N(1)-Fe(1)-C(10)	99.0(2)	C(11)-C(16)-C(20)	121.9(6)
C(2)-N(1)-C(11)	117.9(5)	C(19)-C(17)-C(12)	111.8(6)
C(2)-N(1)-Fe(1)	116.2(4)	C(19)-C(17)-C(18)	109.0(6)
C(11)-N(1)-Fe(1)	125.8(4)	C(12)-C(17)-C(18)	111.7(6)
C(3)-N(2)-C(7)	121.8(5)	C(21)-C(20)-C(16)	110.8(6)
C(3)-N(2)-Fe(1)	119.5(4)	C(21)-C(20)-C(22)	110.6(6)
C(7)-N(2)-Fe(1)	118.5(4)	C(16)-C(20)-C(22)	111.8(6)
C(8)-N(3)-C(23)	117.5(5)	C(24)-C(23)-C(28)	121.5(5)
C(8)-N(3)-Fe(1)	116.5(4)	C(24)-C(23)-N(3)	120.1(5)
C(23)-N(3)-Fe(1)	125.9(4)	C(28)-C(23)-N(3)	118.3(5)
N(1)-C(2)-C(3)	113.5(5)	C(23)-C(24)-C(25)	118.1(5)
N(1)-C(2)-C(1)	124.9(6)	C(23)-C(24)-C(39)	120.8(6)
C(3)-C(2)-C(1)	121.7(5)	C(25)-C(24)-C(39)	121.1(6)

C(26)-C(25)-C(24)	121.9(6)	N(2')-C(7')-C(6')	118.6(6)
C(27)-C(26)-C(25)	118.9(6)	N(2')-C(7')-C(8')	111.1(5)
C(26)-C(27)-C(28)	121.5(6)	C(6')-C(7')-C(8')	130.2(6)
C(27)-C(28)-C(23)	118.1(6)	N(3')-C(8')-C(7')	114.2(5)
C(27)-C(28)-C(32)	119.0(6)	N(3')-C(8')-C(9')	124.1(5)
C(23)-C(28)-C(32)	122.9(6)	C(7')-C(8')-C(9')	121.7(6)
C(34)-C(32)-C(28)	113.1(7)	C(12')-C(11')-C(16')	122.7(6)
C(34)-C(32)-C(33)	111.2(6)	C(12')-C(11')-N(1')	117.9(6)
C(28)-C(32)-C(33)	111.2(6)	C(16')-C(11')-N(1')	119.3(6)
C(24)-C(39)-C(31)	110.1(6)	C(11')-C(12')-C(13')	117.9(7)
C(24)-C(39)-C(30)	112.9(6)	C(11')-C(12')-C(17')	123.2(7)
C(31)-C(39)-C(30)	111.1(6)	C(13')-C(12')-C(17')	118.8(7)
N(2')-Fe(1')-N(1')	79.7(2)	C(12')-C(13')-C(14')	120.2(7)
N(2')-Fe(1')-N(3')	80.4(2)	C(15')-C(14')-C(13')	120.7(7)
N(1')-Fe(1')-N(3')	160.1(2)	C(14')-C(15')-C(16')	120.7(7)
N(2')-Fe(1')-C(10')	176.0(3)	C(15')-C(16')-C(11')	117.8(6)
N(1')-Fe(1')-C(10')	100.3(2)	C(15')-C(16')-C(20')	121.0(7)
N(3')-Fe(1')-C(10')	99.6(2)	C(11')-C(16')-C(20')	121.2(6)
C(2')-N(1')-C(11')	118.4(5)	C(12')-C(17')-C(18')	114.8(7)
C(2')-N(1')-Fe(1')	117.3(4)	C(12')-C(17')-C(19')	111.8(8)
C(11')-N(1')-Fe(1')	124.2(4)	C(18')-C(17')-C(19')	107.1(9)
C(3')-N(2')-C(7')	122.1(5)	C(16')-C(20')-C(21')	109.8(5)
C(3')-N(2')-Fe(1')	119.6(4)	C(16')-C(20')-C(22')	111.8(6)
C(7')-N(2')-Fe(1')	118.2(4)	C(21')-C(20')-C(22')	109.4(6)
C(8')-N(3')-C(23')	118.9(5)	C(24')-C(23')-C(28')	122.2(5)
C(8')-N(3')-Fe(1')	116.0(4)	C(24')-C(23')-N(3')	118.6(6)
C(23')-N(3')-Fe(1')	125.1(4)	C(28')-C(23')-N(3')	119.1(5)
N(1')-C(2')-C(3')	112.4(5)	C(23')-C(24')-C(25')	116.8(6)
N(1')-C(2')-C(1')	124.6(6)	C(23')-C(24')-C(29')	122.5(5)
C(3')-C(2')-C(1')	123.1(6)	C(25')-C(24')-C(29')	120.6(6)
N(2')-C(3')-C(4')	119.7(6)	C(26')-C(25')-C(24')	122.8(6)
N(2')-C(3')-C(2')	111.0(5)	C(25')-C(26')-C(27')	119.2(6)
C(4')-C(3')-C(2')	129.2(6)	C(26')-C(27')-C(28')	121.1(6)
C(5')-C(4')-C(3')	118.6(6)	C(23')-C(28')-C(27')	117.7(6)
C(6')-C(5')-C(4')	120.5(6)	C(23')-C(28')-C(32')	121.9(5)
C(5')-C(6')-C(7')	120.3(6)	C(27')-C(28')-C(32')	120.3(6)

C(24')-C(29')-C(30')	110.9(6)	C(34')-C(32')-C(33')	108.6(6)
C(24')-C(29')-C(31')	113.4(7)		
C(30')-C(29')-C(31')	110.1(7)		
C(28')-C(32')-C(34')	113.0(5)	Symmetry transformations used to generate	
C(28')-C(32')-C(33')	111.3(5)	equivalent atoms:	

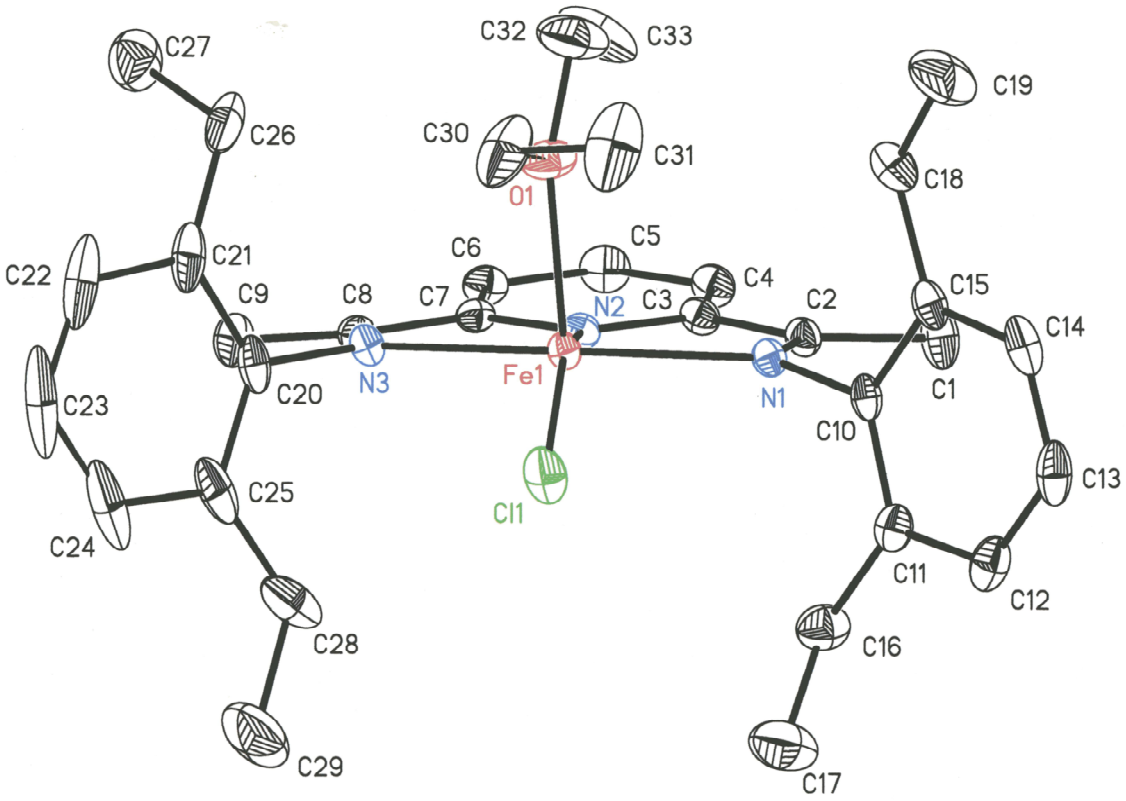

Figure S2. Fully labeled view of **2-Cl·Et$_2$O** with 30 % probability ellipsoids. Hydrogen atoms omitted for clarity.

Table S3. Crystal data and structure refinement for **2-Cl**.

Identification code	**2-Cl**	
Empirical formula	C33 H45 Cl Fe N3 O	
Formula weight	591.02	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.1161(5) Å	α= 90°.
	b = 19.2048(8) Å	β= 115.1460(10)°.
	c = 13.5204(6) Å	γ = 90°.
Volume	3082.9(2) $Å^3$	
Z	4	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	0.606 mm^{-1}	
F(000)	1260	
Crystal size	0.30 x 0.20 x 0.10 mm^3	
Theta range for data collection	1.81 to 28.28°.	
Index ranges	-17<=h<=17, -25<=k<=21, -18<=l<=18	
Reflections collected	25123	
Independent reflections	7615 [R(int) = 0.0483]	
Completeness to theta = 28.28°	99.5 %	
Absorption correction	Semiempirical by SADABS	
Max. and min. transmission	0.9419 and 0.8392	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7615 / 0 / 480	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0522, wR2 = 0.1178	
R indices (all data)	R1 = 0.0876, wR2 = 0.1326	
Largest diff. peak and hole	1.104 and -0.666 e.$Å^{-3}$	

Table S4. Bond lengths [Å] and angles [°] for **2-Cl**.

Fe(1)-N(2)	2.009(2)	C(21)-C(26)	1.506(6)
Fe(1)-N(1)	2.181(2)	C(22)-C(23)	1.354(8)
Fe(1)-N(3)	2.209(2)	C(23)-C(24)	1.374(9)
Fe(1)-O(1)	2.213(2)	C(24)-C(25)	1.385(5)
Fe(1)-Cl(1)	2.2668(8)	C(25)-C(28)	1.501(6)
O(1)-C(32)	1.415(4)	C(26)-C(27)	1.513(6)
O(1)-C(30)	1.429(5)	C(28)-C(29)	1.513(5)
N(1)-C(2)	1.313(3)	C(30)-C(31)	1.507(6)
N(1)-C(10)	1.441(3)	C(32)-C(33)	1.389(6)
N(2)-C(7)	1.371(3)		
N(2)-C(3)	1.377(3)	N(2)-Fe(1)-N(1)	75.22(8)
N(3)-C(8)	1.301(3)	N(2)-Fe(1)-N(3)	74.57(8)
N(3)-C(20)	1.438(3)	N(1)-Fe(1)-N(3)	149.56(8)
C(1)-C(2)	1.503(4)	N(2)-Fe(1)-O(1)	108.99(8)
C(2)-C(3)	1.443(4)	N(1)-Fe(1)-O(1)	100.03(8)
C(3)-C(4)	1.387(4)	N(3)-Fe(1)-O(1)	93.16(8)
C(4)-C(5)	1.398(4)	N(2)-Fe(1)-Cl(1)	150.96(6)
C(5)-C(6)	1.384(4)	N(1)-Fe(1)-Cl(1)	102.08(6)
C(6)-C(7)	1.388(4)	N(3)-Fe(1)-Cl(1)	102.46(6)
C(7)-C(8)	1.453(4)	O(1)-Fe(1)-Cl(1)	99.99(6)
C(8)-C(9)	1.499(4)	C(32)-O(1)-C(30)	109.5(3)
C(10)-C(11)	1.396(4)	C(32)-O(1)-Fe(1)	132.2(3)
C(10)-C(15)	1.405(4)	C(30)-O(1)-Fe(1)	118.3(2)
C(11)-C(12)	1.398(4)	C(2)-N(1)-C(10)	117.9(2)
C(11)-C(16)	1.507(4)	C(2)-N(1)-Fe(1)	115.20(17)
C(12)-C(13)	1.384(5)	C(10)-N(1)-Fe(1)	126.43(16)
C(13)-C(14)	1.372(5)	C(7)-N(2)-C(3)	118.8(2)
C(14)-C(15)	1.390(4)	C(7)-N(2)-Fe(1)	120.85(17)
C(15)-C(18)	1.505(4)	C(3)-N(2)-Fe(1)	119.88(17)
C(16)-C(17)	1.490(5)	C(8)-N(3)-C(20)	119.3(2)
C(19)-C(18)	1.521(5)	C(8)-N(3)-Fe(1)	115.35(17)
C(20)-C(21)	1.397(5)	C(20)-N(3)-Fe(1)	125.19(17)
C(20)-C(25)	1.406(5)	N(1)-C(2)-C(3)	115.8(2)
C(21)-C(22)	1.403(5)	N(1)-C(2)-C(1)	122.6(3)

C(3)-C(2)-C(1)	121.6(2)	C(24)-C(25)-C(20)	116.5(4)
N(2)-C(3)-C(4)	120.9(2)	C(24)-C(25)-C(28)	123.1(4)
N(2)-C(3)-C(2)	113.3(2)	C(20)-C(25)-C(28)	120.4(3)
C(4)-C(3)-C(2)	125.8(2)	C(21)-C(26)-C(27)	113.8(3)
C(3)-C(4)-C(5)	119.9(3)	C(25)-C(28)-C(29)	117.4(4)
C(6)-C(5)-C(4)	119.2(3)	O(1)-C(30)-C(31)	111.7(3)
C(5)-C(6)-C(7)	119.5(3)	C(33)-C(32)-O(1)	113.6(4)
N(2)-C(7)-C(6)	121.7(2)		
N(2)-C(7)-C(8)	113.1(2)		
C(6)-C(7)-C(8)	125.1(2)		
N(3)-C(8)-C(7)	115.6(2)		
N(3)-C(8)-C(9)	124.8(3)		
C(7)-C(8)-C(9)	119.6(2)		
C(11)-C(10)-C(15)	122.0(2)		
C(11)-C(10)-N(1)	118.7(2)		
C(15)-C(10)-N(1)	119.4(2)		
C(10)-C(11)-C(12)	117.4(3)		
C(10)-C(11)-C(16)	121.5(3)		
C(12)-C(11)-C(16)	121.1(3)		
C(13)-C(12)-C(11)	121.4(3)		
C(14)-C(13)-C(12)	119.9(3)		
C(13)-C(14)-C(15)	121.3(3)		
C(14)-C(15)-C(10)	118.0(3)		
C(14)-C(15)-C(18)	122.5(3)		
C(10)-C(15)-C(18)	119.5(3)		
C(17)-C(16)-C(11)	116.0(3)		
C(15)-C(18)-C(19)	116.3(3)		
C(21)-C(20)-C(25)	123.0(3)		
C(21)-C(20)-N(3)	119.0(3)		
C(25)-C(20)-N(3)	118.0(3)		
C(20)-C(21)-C(22)	116.2(4)		
C(20)-C(21)-C(26)	123.3(3)		
C(22)-C(21)-C(26)	120.5(4)		
C(23)-C(22)-C(21)	122.5(5)		
C(22)-C(23)-C(24)	119.6(4)		
C(23)-C(24)-C(25)	122.3(5)		

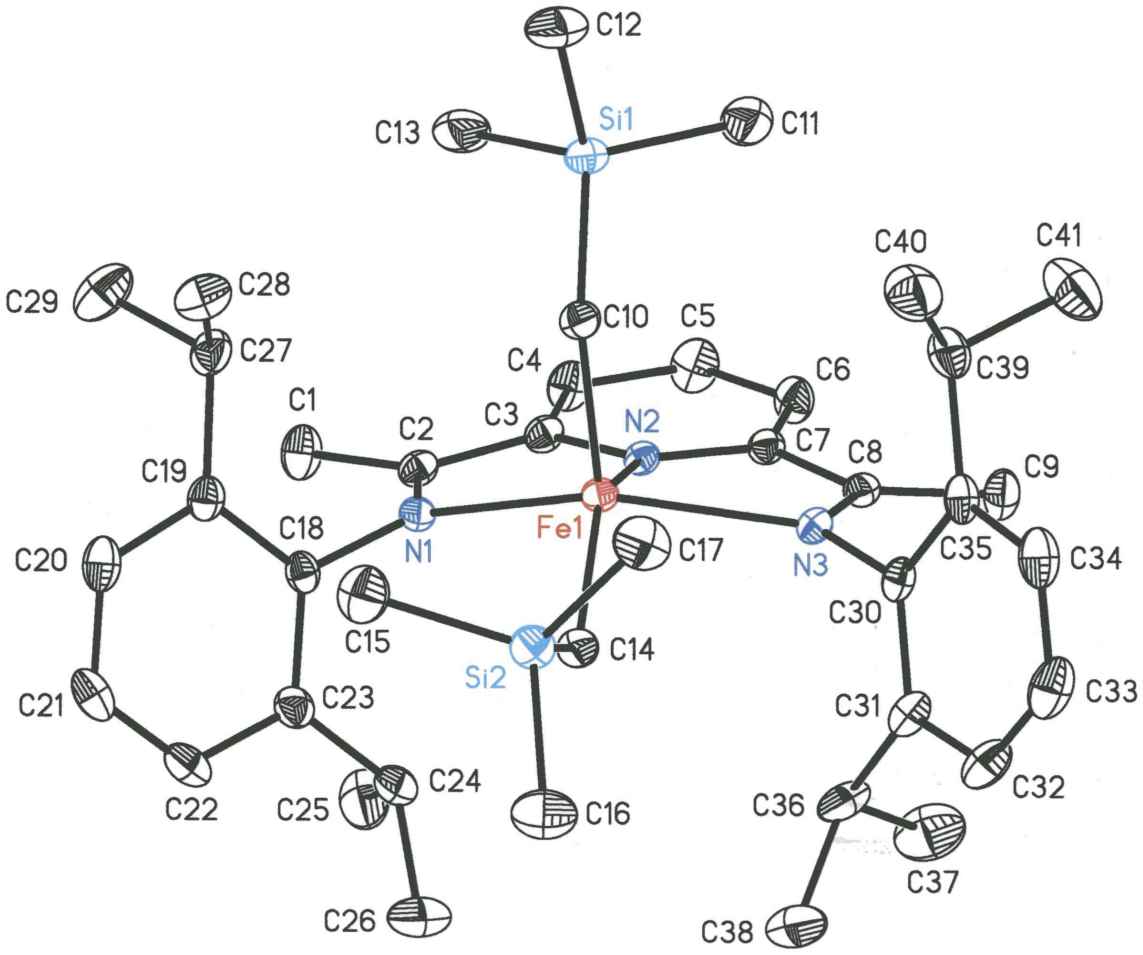

Figure S3. Fully labeled view of **1-(CH_2SiMe_3)$_2$** with 30 % probability ellipsoids. Hydrogen atoms omitted for clarity.

Table S5. Crystal data and structure refinement for **1-(CH_2SiMe_3)$_2$**.

Identification code	mwb9	
Empirical formula	C41 H65 Fe N3 Si2	
Formula weight	711.99	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 15.8771(7) Å	α= 90°.
	b = 20.0007(7) Å	β= 90°.
	c = 26.177(1) Å	γ = 90°.
Volume	8312.6(6) Å^3	
Z	8	
Density (calculated)	1.138 Mg/m^3	
Absorption coefficient	0.450 mm^{-1}	
F(000)	3088	
Crystal size	0.45 x 0.40 x 0.10 mm^3	
Theta range for data collection	1.56 to 23.29°.	
Index ranges	-16<=h<=17, -22<=k<=20, -27<=l<=29	
Reflections collected	67211	
Independent reflections	5980 [R(int) = 0.0446]	
Completeness to theta = 23.29°	99.7 %	
Absorption correction	Semiempirical by SADABS	
Max. and min. transmission	0.9563 and 0.8230	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5980 / 0 / 508	
Goodness-of-fit on F^2	0.990	
Final R indices [I>2sigma(I)]	R1 = 0.0340, wR2 = 0.0870	
R indices (all data)	R1 = 0.0532, wR2 = 0.0987	
Largest diff. peak and hole	0.762 and -0.255 e.Å^{-3}	

Table S6. Bond lengths [Å] and angles [°] for **1-(CH_2SiMe_3)$_2$**.

Fe(1)-N(2)	2.0133(19)	C(23)-C(24)	1.523(4)
Fe(1)-C(14)	2.054(3)	C(24)-C(25)	1.520(4)
Fe(1)-C(10)	2.062(3)	C(24)-C(26)	1.530(4)
Fe(1)-N(1)	2.2030(19)	C(27)-C(29)	1.528(4)
Fe(1)-N(3)	2.263(2)	C(27)-C(28)	1.533(4)
Si(1)-C(10)	1.845(3)	C(30)-C(35)	1.401(4)
Si(1)-C(11)	1.867(3)	C(30)-C(31)	1.408(4)
Si(1)-C(13)	1.871(3)	C(31)-C(32)	1.392(4)
Si(1)-C(12)	1.878(3)	C(31)-C(36)	1.516(4)
Si(2)-C(14)	1.835(3)	C(32)-C(33)	1.364(4)
Si(2)-C(15)	1.859(3)	C(33)-C(34)	1.361(4)
Si(2)-C(17)	1.869(3)	C(34)-C(35)	1.396(4)
Si(2)-C(16)	1.874(3)	C(35)-C(39)	1.516(4)
N(1)-C(2)	1.302(3)	C(36)-C(37)	1.477(4)
N(1)-C(18)	1.438(3)	C(36)-C(38)	1.531(4)
N(2)-C(3)	1.368(3)	C(39)-C(40)	1.525(4)
N(2)-C(7)	1.369(3)	C(39)-C(41)	1.527(4)
N(3)-C(8)	1.301(3)		
N(3)-C(30)	1.438(3)	N(2)-Fe(1)-C(14)	140.02(10)
C(1)-C(2)	1.499(3)	N(2)-Fe(1)-C(10)	107.93(9)
C(2)-C(3)	1.448(3)	C(14)-Fe(1)-C(10)	112.00(11)
C(3)-C(4)	1.384(3)	N(2)-Fe(1)-N(1)	74.03(7)
C(4)-C(5)	1.380(4)	C(14)-Fe(1)-N(1)	98.20(11)
C(5)-C(6)	1.385(4)	C(10)-Fe(1)-N(1)	103.37(10)
C(6)-C(7)	1.380(4)	N(2)-Fe(1)-N(3)	72.88(7)
C(7)-C(8)	1.454(3)	C(14)-Fe(1)-N(3)	94.13(10)
C(8)-C(9)	1.501(3)	C(10)-Fe(1)-N(3)	105.86(10)
C(18)-C(19)	1.405(3)	N(1)-Fe(1)-N(3)	141.07(7)
C(18)-C(23)	1.412(3)	C(10)-Si(1)-C(11)	112.09(14)
C(19)-C(20)	1.394(4)	C(10)-Si(1)-C(13)	112.58(13)
C(19)-C(27)	1.512(4)	C(11)-Si(1)-C(13)	107.31(16)
C(20)-C(21)	1.365(4)	C(10)-Si(1)-C(12)	111.00(14)
C(21)-C(22)	1.366(4)	C(11)-Si(1)-C(12)	107.34(16)
C(22)-C(23)	1.390(4)	C(13)-Si(1)-C(12)	106.18(16)

C(14)-Si(2)-C(15)	112.82(15)	C(20)-C(19)-C(18)	117.5(2)
C(14)-Si(2)-C(17)	111.75(15)	C(20)-C(19)-C(27)	120.3(2)
C(15)-Si(2)-C(17)	108.67(15)	C(18)-C(19)-C(27)	122.2(2)
C(14)-Si(2)-C(16)	108.92(14)	C(21)-C(20)-C(19)	121.8(3)
C(15)-Si(2)-C(16)	106.39(15)	C(20)-C(21)-C(22)	120.1(3)
C(17)-Si(2)-C(16)	108.05(14)	C(21)-C(22)-C(23)	121.8(3)
C(2)-N(1)-C(18)	120.8(2)	C(22)-C(23)-C(18)	117.6(2)
C(2)-N(1)-Fe(1)	115.09(15)	C(22)-C(23)-C(24)	121.4(2)
C(18)-N(1)-Fe(1)	124.14(14)	C(18)-C(23)-C(24)	121.0(2)
C(3)-N(2)-C(7)	118.2(2)	C(25)-C(24)-C(23)	111.8(2)
C(3)-N(2)-Fe(1)	119.68(15)	C(25)-C(24)-C(26)	109.4(3)
C(7)-N(2)-Fe(1)	121.93(15)	C(23)-C(24)-C(26)	113.7(2)
C(8)-N(3)-C(30)	119.9(2)	C(19)-C(27)-C(29)	111.3(2)
C(8)-N(3)-Fe(1)	115.40(16)	C(19)-C(27)-C(28)	113.2(2)
C(30)-N(3)-Fe(1)	124.66(15)	C(29)-C(27)-C(28)	108.8(2)
N(1)-C(2)-C(3)	114.9(2)	C(35)-C(30)-C(31)	121.5(2)
N(1)-C(2)-C(1)	124.9(2)	C(35)-C(30)-N(3)	120.6(2)
C(3)-C(2)-C(1)	120.2(2)	C(31)-C(30)-N(3)	117.8(2)
N(2)-C(3)-C(4)	121.3(2)	C(32)-C(31)-C(30)	117.2(3)
N(2)-C(3)-C(2)	113.5(2)	C(32)-C(31)-C(36)	120.6(3)
C(4)-C(3)-C(2)	125.1(2)	C(30)-C(31)-C(36)	122.2(2)
C(5)-C(4)-C(3)	120.0(3)	C(33)-C(32)-C(31)	122.1(3)
C(4)-C(5)-C(6)	118.7(3)	C(34)-C(33)-C(32)	119.9(3)
C(7)-C(6)-C(5)	119.9(3)	C(33)-C(34)-C(35)	121.8(3)
N(2)-C(7)-C(6)	121.5(2)	C(34)-C(35)-C(30)	117.5(3)
N(2)-C(7)-C(8)	113.5(2)	C(34)-C(35)-C(39)	120.5(3)
C(6)-C(7)-C(8)	125.0(2)	C(30)-C(35)-C(39)	121.9(2)
N(3)-C(8)-C(7)	114.8(2)	C(37)-C(36)-C(31)	111.6(3)
N(3)-C(8)-C(9)	125.5(2)	C(37)-C(36)-C(38)	107.9(3)
C(7)-C(8)-C(9)	119.7(2)	C(31)-C(36)-C(38)	114.0(3)
Si(1)-C(10)-Fe(1)	127.45(14)	C(35)-C(39)-C(40)	112.9(3)
Si(2)-C(14)-Fe(1)	128.83(16)	C(35)-C(39)-C(41)	111.9(3)
C(19)-C(18)-C(23)	121.3(2)	C(40)-C(39)-C(41)	109.1(3)
C(19)-C(18)-N(1)	121.8(2)		
C(23)-C(18)-N(1)	116.9(2)		

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