Supporting Information

For

Oxidative group transfer to a triiron complex to form a nucleophillic μ^3-nitride, $[Fe_3(\mu^3\text{-}N)]^-$

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Materials and Methods. All manipulations involving metal complexes were carried out using standard Schlenk line or glove-box techniques under a dinitrogen atmosphere. All glassware was oven-dried for a minimum of 10 h and cooled in an evacuated antechamber prior to use in the dry box. Benzene, diethyl ether, hexanes and tetrahydrofuran (THF) were dried and deoxygenated on a Glass Contour System (SG Water USA, Nashua, NH) and stored over 4 Å molecular sieves (Strem) prior to use. Benzene-d_6 was purchased from Cambridge Isotope Labs and was degassed and stored over 4 Å molecular sieves prior to use. Non-halogenated solvents were typically tested with a standard purple solution of sodium benzophenone ketyl in THF in order to confirm effective oxygen and moisture removal. Fe_2Mes_4 (Mes = 2,4,6-$Me_3C_6H_2$) and α-α-α-1,3,5-$NH_2C_6H_9 \cdot 3HBr$ were prepared following published methods.[1,2] 1-Fluoro-2-nitrobenzene and Cs_2CO_3 were used as received from Aldrich. (1α,3α,5α)-1,3,5-cyclohexane-tricarboxylic acid was purchased from TCI America and used without further purification. Tetrabutylammonium azide was recrystallized from diethyl ether/THF solution at -33 °C prior to use. All other reagents were purchased from commercial vendors and used without further purification unless explicitly stated.

Physical Measurements. All of the measurements for the metal complexes were made under anaerobic conditions. Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, New Jersey or Robertson Microlit Laboratories, Madison, S2 New Jersey. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity/Inova 500B NMR spectrometer with chemical shifts (δ ppm) referenced to residual NMR solvent. High-resolution mass spectrometry was performed on an Agilent 6210 TOF LC/MS with a dual nebulizer ESI source at the Harvard University FAS Center for Systems Biology Mass Spectrometry and Proteomics Resource Laboratory. UV/Visible spectra were recorded on a Varian Cary 50 UV/Visible spectrometer using quartz cuvettes. Solution magnetic susceptibilities were determined by Evans′ method using trifluoromethylbenzene as an internal reference. Zero-field, ^{57}Fe Mössbauer spectra were measured with a constant acceleration spectrometer (SEE Co, Minneapolis, MN). Isomer shifts are quoted relative to Fe metal at room temperature. Data was processed, simulated, and analyzed using an in-house package for IGOR Pro 6 (Wavemetrics, Lake Oswego, OR).

Experimental

$C_6H_9(NHPh\text{-}o\text{-}NO_2)_3$. A mixture of α-α-α-1,3,5-$NH_2C_6H_9\cdot 3HBr$ (10.0 g, 22.9 mmol), 1-fluoro-2-nitrobenzene (19.3 g, 137 mmol) and Cs_2CO_3 (44.6 g, 114 mmol) in 400 mL CH_3CN was stirred and heated in an evacuated, sealed bomb reactor at 120 °C for 72 hours. The resulting orange reaction mixture was then cooled to room temperature. The orange suspension was filtered through a fritted glass funnel. The resulting orange solid was washed with water (150 mL) to remove the Cs_2CO_3. The orange solid was then rinsed with a minimal amount of acetone (~50 mL) on a porous glass fritted funnel to remove excess fluoronitrobenzene. The orange solid was dried *in vacuo* overnight. Yield: 10.4 g (92%). HRMS (ESI^+) *m/z* calcd $C_{24}H_{24}N_6NaO_6^+$ $[M+Na]^+$: 515.16549, found 515.1692.

$C_6H_9(NHPh\text{-}o\text{-}NH_2)_3$ (LH_6). Solid $C_6H_9(NHPh\text{-}o\text{-}NO_2)_3$ (5.00 g, 10.2 mmol) and Zn dust (9.95g, 152 mmol) were combined in a 500 mL round bottom. To this a 50:50 mixture of *saturated* NH_4Cl:THF (total 300 mL) was added. The reaction was stirred vigorously until the orange color was no longer present. The suspension is filtered through celite and washed with EtOAc (100 mL). Next the filtrate is extracted with EtOAc and H_2O. The organic layer is collected and dried with Na_2SO_4 and filtered again through celite. Removal of the filtrate gave a brown oil. The brown oil, under inert atmosphere and with the use of anhydrous solvents, was purified by dissolving in a benzene (100 mL) and THF (20 mL) mixture. The white solid crashed out from addition of hexanes (75 mL) to the brown solution. Filtration of the suspension through a fritted glass funnel gave the product as an off-white solid. Isolated yield: 3.29 g (80%). *Note:* More Zn may be added if the orange color is not fading. Also the hexa-amine oxidizes noticeably with exposure to air, thus care must be taken to expedite the work-up until placed under an inert atmosphere. ^1H NMR ($CDCl_3$, 500 MHz, δ, ppm): 6.83 (br, 3H, aromatic C-*H*), 6.76-7.71 (m, 9H, aromatic C-*H*), 3.51 (m, 3H, C_6H_9), 3.45 (br s, 9H, N*H*), 2.59 (br d, 3H, C_6H_9), 1.13 (m, 3H, C_6H_9); ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 136.09, 134.60, 120.69, 118.99, 117.02, 113.06, 49.25, 40.28; HRMS (ESI^+) *m/z* calcd $C_{24}H_{30}N_6Na^+$ $[M+Na]^+$: 425.24242, found: 425.23881.

$C_6H_9(NHPh\text{-}o\text{-}NH(SiMe_2(t\text{-}Bu))_3$ ($^{tbs}LH_6$). A 2.5*M* solution of n-butyllithium (3.07 g, 11.6 mmol) in hexanes was added cold (-33 °C) to LH_6 (1.50 g, 3.73 mmol) dissolved in 20 mL of THF. The mixture was stirred for 2 hours at room temperature. To the reaction, tertbutyldimethylsilyl chloride (1.74 g, 11.6 mmol) in 5 mL of THF was added cold (-33 °C) and allowed to stir at room temperature for 18 hours. The volatiles were removed *in vacuo*. Hexanes was added to the resulting green-brown solid and the precipitate was collected on a fritted glass funnel via cold filtration. The solid was then re-dissolved in benzene and filtered through celite to remove the lithium chloride. The benzene solution was dried to afford clean $^{TBS}LH_6$ as an off-white solid. Yield: 1.25 g (45%) ^{1}H NMR (benzene-d$_6$, 500 MHz, δ, ppm): 6.98 (d, 3H, aromatic C-*H*, *J* = 8.00 Hz), 6.93-6.86 (m, 6H, aromatic C-*H*), 6.71 (d, 3H, aromatic C-*H*, *J* = 7.50 Hz), 3.53 (s, 3H, -Si-N*H*-C), 3.03-3.01 (m, 3H, C_6H_9), 2.81 (d, 3H, CH-N*H*-C, *J* = 7.50 Hz), 2.43 (br d, 3H, C_6H_9), 0.966 (s, 9H, $-C(CH_3)_3$), 0.938-0.891 (m, 3H, C_6H_9), 0.180 (s, 6H, $–Si(CH_3)_2$); ^{13}C NMR (benzene-d$_6$, 125 MHz, δ, ppm): -4.09, 17.82, 26.43, 41.08, 51.04, 118.37, 119.34, 120.10, 121.60, 137.72, 138.46; Anal. Calcd for $C_{42}H_{72}N_6Si_3$: C 67.68, H 9.74, N 11.28. Found: C 67.65, H 9.84, N 11.21.

(^{tbs}L)Fe$_3$(thf) (1). ^{tbs}LH$_6$ (0.300 g, 0.403 mmol) was dissolved in 30 mL of THF. The solution was added to solid Fe_2Mes_4 (0.355 g, 1.21 mmol) at room temperature. The reaction was heated in a sealed bomb at 75 °C for 12 hrs. The reaction was dried *in vacuo* to afford a brown oil. The flask containing the oil was placed in a liquid nitrogen cooled cold well in the dry box. Hexanes (40 mL), also cooled in the cold well, was added to the oil with stirring in order to remove the mesitylene biproduct. The hexane layer was decanted and the remaining solid was dried in vacuum. The solid was re-dissolved in THF and the volatiles were removed to afford a black solid. Purity of the compound was established by the absence of (^{tbs}L)Fe$_2$ product in the ^{1}H NMR.[3] Isolated yield: 315 mg, (80%). X-ray quality crystals were grown in hexanes at -33 °C. Anal. Calcd for $C_{46}H_{74}N_6OFe_3Si_3$: C 56.44, H 7.62, N 8.59. Found: C 56.62, H 7.68, N 8.59; Zero-field ^{57}Fe Mössbauer (110 K) δ, $|\Delta E_Q|$ ($^{mm}/_{s}$) component 1 (27%): 0.89, *1.68* (γ = 0.25 $^{mm}/_{s}$); component 2 (35%): 0.49, *1.57* (γ = 0.33 $^{mm}/_{s}$); component 3 (38%): 0.50, *1.92* (γ = 0.22 $^{mm}/_{s}$). UV-Vis Spectroscopy (THF): 550 nm (ε = 145 M^{-1}cm^{-1}).

[(^{tbs}L)Fe$_3$(μ^3-N)]NBu$_4$ (2). Complex **2** was synthesized *in situ* from the reaction of crude (^{tbs}L)Fe$_3$(thf) (**1**) and tetrabutylammonium azide ([N$_3$]NBu$_4$). ^{tbs}LH$_6$ (0.500 g, 0.671 mmol) was dissolved in 30 mL of THF. The solution was added to solid Fe_2Mes_4 (0.612 g, 2.08 mmol) at room temperature. The reaction was heated in a sealed bomb at 75 °C for 12 hrs. Solid [N$_3$]NBu$_4$ (210 mg, 0.738 mmol) was added to the reaction mixture cold (-33 °C). Once the reaction reached room temperature, the solution was stirred for an additional 4 hours. The volatiles were removed in vacuum resulting in a brown oil. The brown oil was triturated with hexanes (20 mL 2x) and dried. The oil was subsequently washed with cold diethyl ether (4 x 25 mL). Stirring in cold diethyl ether caused the product to crash out of solution as a brown solid. The solution was filtered through Celite and washed with cold diethyl ether; the solid was subsequently re-dissolved in benzene. Removal of the volatiles resulted in a brown solid. Isolated yield: 412 mg, (55%). Dark brown, X-ray quality crystals were grown from diethyl ether at -33 °C. ^{1}H NMR (benzene-d$_6$, 500 MHz, δ, ppm): 55.92, 44.82, 27.68, 16.41, 12.24, 7.50, 7.23, 6.36, 3.82, 3.69, 2.05, 1.57, 1.31, -1.48, -3.21; Anal. Calcd for $C_{58}H_{102}N_8Fe_3Si_3$: C 59.88, H 8.84, N 9.63. Found: C

59.74, H 8.78, N 9.49. Zero-field ^{57}Fe Mössbauer (δ, $|\Delta E_Q|$ ($^{mm}/_{s}$)): (120 K) component 1 0.37, *1.78* (49%), component 2 0.39, *1.23* (51%); (180 K) component 1 0.34, *1.72* (53%) component 2 0.37, *1.15* (47%). UV-Vis Spectroscopy (THF): 460 nm (ε = 4.34 × 10^4 $M^{-1}cm^{-1}$).

(^{tbs}L)Fe$_3$(μ^3-NMe). To a THF (3 mL) solution of **2** (100 mg, 0.09 mmol), 2 mL of a 0.045 mM solution of MeI in THF was added cold (-33 °C). The reaction was stirred at room temperature for 1 hour. The volatiles were removed *in vacuo* resulting in a black oil. The product was extracted into hexanes (15 mL) and dried to afford a black solid. Black, X-ray quality crystals were grown in hexanes at -33 °C. Isolated yield: 30 mg (35%). ^{1}H NMR (benzene-d$_6$, 500 MHz, δ, ppm): 180.8, 90.23, 76.90, 10.83, 7.46, 4.24, 3.40, 2.74, 1.95, 1.50, 1.27, 1.25, 0.49, -3.4, -4.49; Anal. Calcd for $C_{43}H_{69}N_7Fe_3Si_3$: C 55.19, H 7.43, N 10.48. Found: C 55.13, H 7.39, N 10.42. Zero-field ^{57}Fe Mössbauer (δ, $|\Delta E_Q|$ ($^{mm}/_{s}$)): (110 K) component 1 0.37, *0.94* (35%), component 2 0.36, *1.67* (65%); (180 K) 0.34, *1.44* (100%). UV-vis Spectroscopy (THF): 690 nm (ε = 4.07 × 10^4 $M^{-1}cm^{-1}$); 575 nm (ε = 5.18 × 10^4 $M^{-1}cm^{-1}$); 430 nm (ε = 6.73 × 10^4 $M^{-1}cm^{-1}$).

Figure S1. Zero-field Mössbauer spectrum of $(^{tbs}L)Fe_3(thf)$ (**1**) obtained at 110 K. Simulation yields the following parameters: δ, $|\Delta E_Q|$ ($^{mm}/_s$) component 1 (27%): 0.89, *1.68* (γ = 0.25 $^{mm}/_s$); component 2 (35%): 0.49, *1.57* (γ = 0.33 $^{mm}/_s$); component 3 (38%): 0.50, *1.92* (γ = 0.22 $^{mm}/_s$).

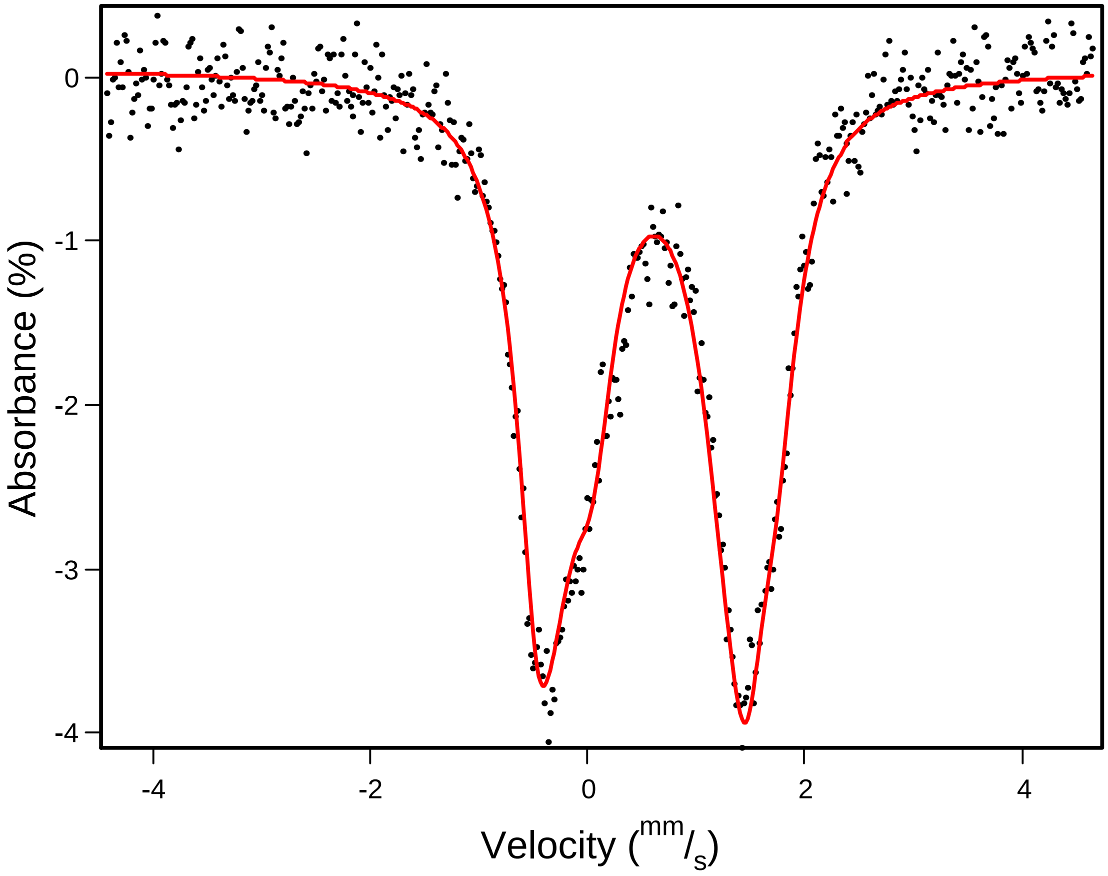


Figure S2. Zero-field Mössbauer spectrum of $[(^{tbs}L)Fe_3(\mu^3\text{-}N)]NBu_4$ (**2**) obtained at 120 K. Simulation yields the following parameters: δ, $|\Delta E_Q|$ ($^{mm}/_{s}$) component 1 (48%): 0.37, *1.78* (γ = 0.12 $^{mm}/_{s}$); component 2 (51%): 0.39, *1.23* (γ = 0.30 $^{mm}/_{s}$).

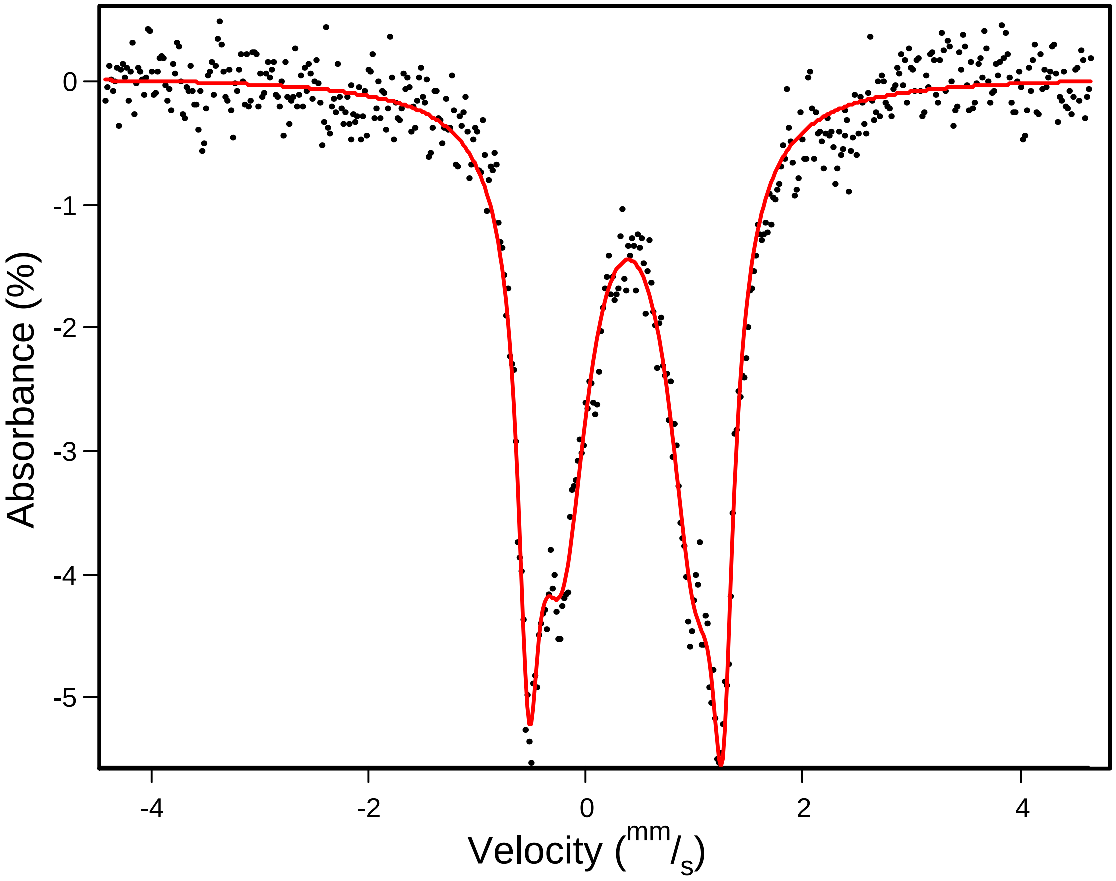


Figure S3. Zero-field Mössbauer spectrum of [(^{tbs}L)Fe$_3$(μ^3-N)]NBu$_4$ (**2**) obtained at 180 K. Simulation yields the following parameters: δ, |*ΔE$_Q$*| ($^{mm}/_{s}$) component 1 (53%): 0.34, *1.72* (γ = 0.12 $^{mm}/_{s}$); component 2 (47%): 0.37, *1.15* (γ = 0.30 $^{mm}/_{s}$).

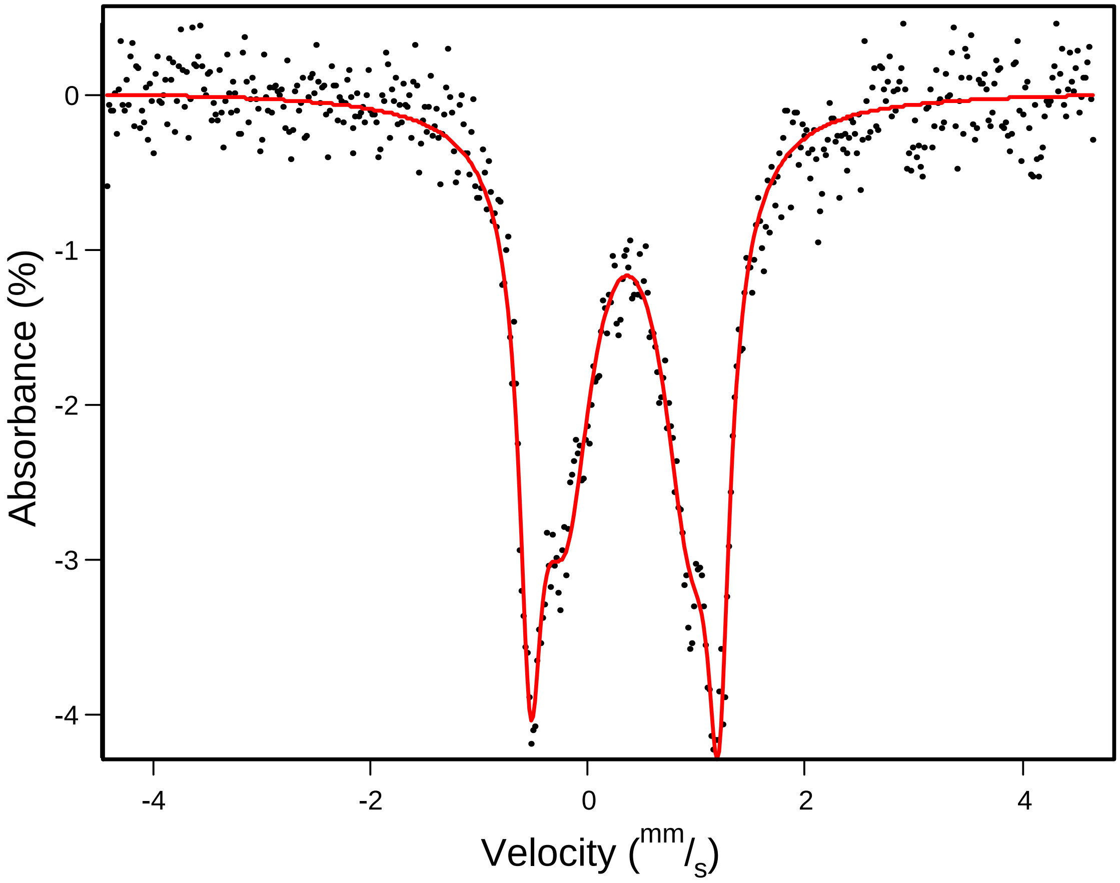


Figure S4. Zero-field Mössbauer spectrum of $(^{tbs}L)Fe_3(\mu^3\text{-}NCH_3)$ (**3**) obtained at 110 K. Simulation yields the following parameters: δ, $|\Delta E_Q|$ ($^{mm}/_s$) component 1 (35%): 0.37, *0.94* (γ = 0.16 $^{mm}/_s$); component 2 (65%): 0.36, *1.67* (γ = 0.22 $^{mm}/_s$).

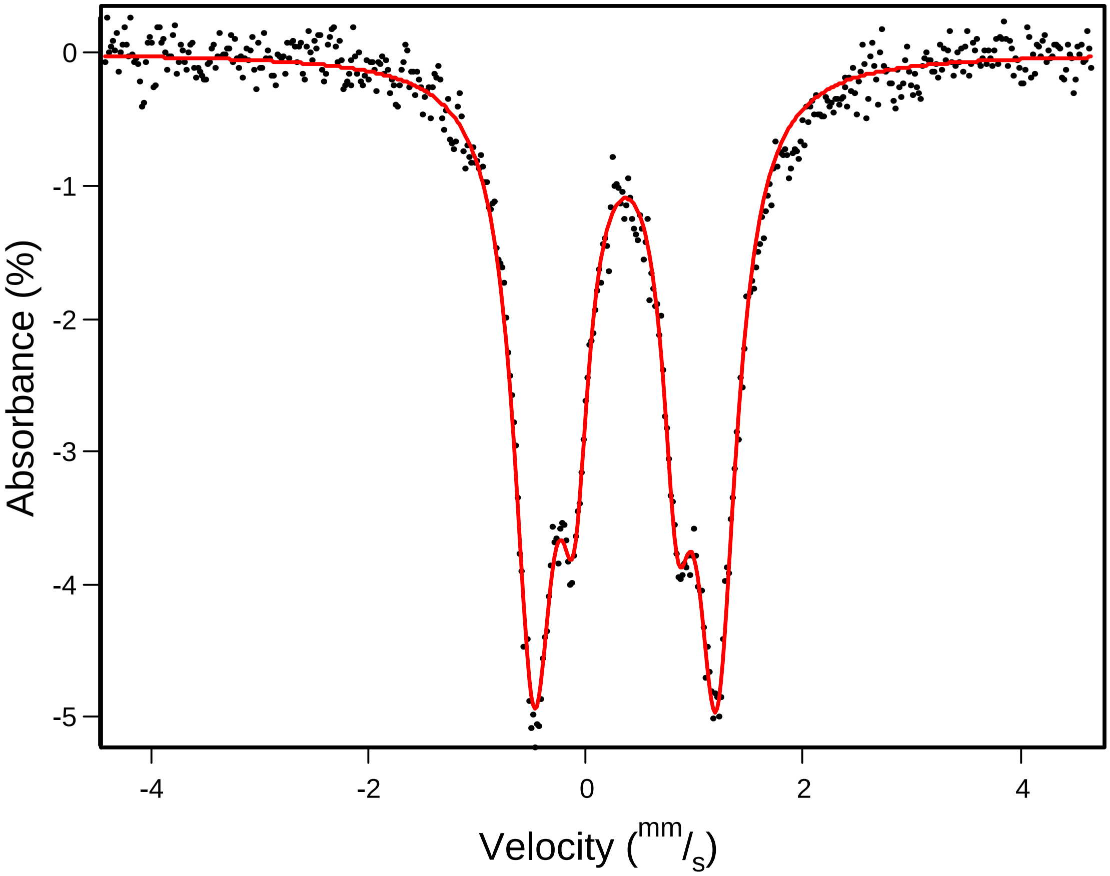
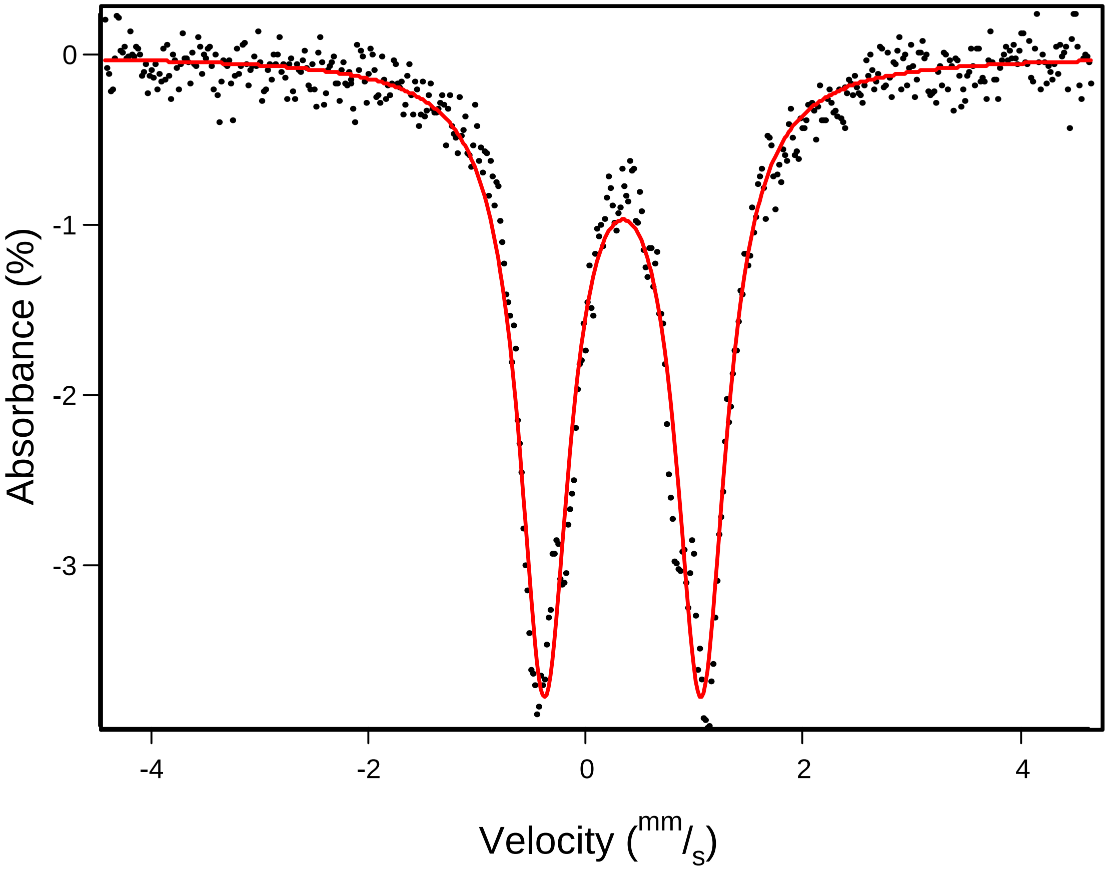


Figure S5. Zero-field Mössbauer spectrum of $(^{tbs}L)Fe_3(\mu^3\text{-}NCH_3)$ (**3**) obtained at 180 K. Simulation yields the following parameters: δ, $|\Delta E_Q|$ ($^{mm}/_s$): 0.34, *1.44* (γ = 0.28 $^{mm}/_s$).



X-Ray Diffraction Techniques. All structures were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo Kα (0.71073 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone N oil. Structures were collected at 100 K. Data was collected as a series of φ and/or ω scans. Data was integrated using SAINT (*S*[1]) and scaled with either a numerical or multi-scan absorption correction using SADABS (*S9*). The structures were solved by direct methods or Patterson maps using SHELXS-97 (*S*[2]) and refined against F^2 on all data by full matrix least squares with SHELXL-97 (*S2*). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the atoms they are linked to (1.5 times for methyl groups). Further details on particular structures are noted below.

$(^{tbs}L)Fe_3(thf)$ (**1**). The structure was solved in the triclinic space group $P\,\bar{1}$ with 2 molecules per unit cell. The asymmetric unit was found to contain one molecule of $^{TBS}LFe_3(THF)$ and half of a solvent n-hexane molecule unit. The solvent n-hexane molecule exhibited positional disorder and was refined using similarity restraints.

$[(^{tbs}L)Fe_3(\mu^3\text{-}N)]NBu_4$ (**2**). The structure was solved in the monoclinic space group *Cc* with 2 molecules per unit cell. The asymmetric unit contains one molecules of $[^{TBS}LFe_3(\mu_3\text{-}N)]N(n\text{-}Bu)_4$ and one diethyl ether solvent molecules. One of the ligand arms exhibited positional disorder and one of the dimethyl-*tert*-butyl silyl groups exhibited positional disorder. Similarity restraints were used to refine the model. No electron density peak could be found above the N, which would suggest the presence of a hydrogen atom bound to the μ^3-N. Reactivity of the molecule indicates that there is no hydrogen on N7.

$(^{tbs}L)Fe_3(\mu^3\text{-}NCH_3)$ (**3**). The structure was solved in the monoclinic space group $P\,\bar{1}$ with 2 molecules per unit cell. The asymmetric unit contains one $^{TBS}LFe_3(\mu^3\text{-}NMe)$ molecule. The crystal was twinned and weakly diffracting resulting in a higher than usual R-value. However, the high R-value does not seriously affect the chemically significant features of the structures.

S[1]. Bruker AXS (2009). Apex II. Bruker AXS, Madison, Wisconsin.
S[2]. G. M. Sheldrick, *Acta Cryst.* **A64**, 112 (2008).

Table S1. X-ray Crystallographic Data for All Compounds

Chemical formula	$C_{46}H_{74}N_6OFe_3Si_3\cdot 0.5(C_6H_{14})$	$C_{58}H_{102}N_8Fe_3Si_3\cdot(Et_2O)$	$C_{43}H_{69}N_7Fe_3Si_3$
fw	1022.02	1237.42	935.87
Space group	$P\bar{1}$	*Cc*	$P\bar{1}$
a (Å)	10.6174(10)	26.559(3)	10.057(2)
b (Å)	10.850(1)	11.6673(11)	11.562(3)
c (Å)	23.503(2)	23.123(2)	20.327(4)
α (deg)	84.540(2)		82.832(4)
β (deg)	83.122(2)	108.849(2)	89.866(4)
γ (deg)	75.734(2)		89.039(4)
V (Å^3)	2599.1(4)	6781.1(11)	2345.0(9)
Z	2	2	2
d_{calcd} (g·cm^{-3})	1.306	1.212	1.325
μ (mm^{-1})	0.94	0.73	1.03
T (K)	100(1)	100(1)	100(1)
R1^a (wR2^b)	0.0375 (0.0920)	0.0489 (0.1042)	0.1196 (0.3115)

^{a} $\mathrm{R1} = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$

^{b} $\mathrm{wR2} = [\sum [w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2(F_c^2)]/3$

Table S2. Selected Iron Core Bond Distances (Å) and Angles (degrees) for **1**, **2**, and **3**.

Compound	**1**	**2**	**3**
Fe(1)–Fe(2)	2.6129(5)	2.4212(7)	2.449(3)
Fe(1)–Fe(3)	2.5061(5)	2.5444(7)	2.487(2)
Fe(1)–O(1)	2.1162(18)	--	--
Fe(1)–N(1)	2.126(2)	2.065(3)	1.987(10)
Fe(1)–N(3)	2.016(2)	1.991(3)	1.973(9)
Fe(1)–N(4)	2.081(2)	1.953(3)	1.910(9)
Fe(1)–N(7)	--	1.883(3)	1.875(9)
Fe(2)–Fe(3)	2.6118(5)	2.4737(7)	2.513(2)
Fe(2)–N(1)	2.047(2)	1.993(3)	1.982(9)
Fe(2)–N(2)	2.091(2)	2.058(3)	2.022(9)
Fe(2)–N(4)	2.149(2)	--	--
Fe(2)–N(5)	1.950(2)	1.941(3)	1.887(10)
Fe(2)–N(7)	--	1.847(3)	1.926(11)
Fe(3)–N(2)	1.955(2)	1.997(3)	1.963(10)
Fe(3)–N(3)	2.053(2)	2.074(3)	2.051(9)
Fe(3)–N(6)	1.938(2)	1.956(3)	1.915(10)
Fe(3)–N(7)	--	1.884(3)	1.936(9)
Fe(1)–N(7)–Fe(2)	--	80.94(12)	80.2(4)
Fe(2)–N(7)–Fe(3)	--	83.04(13)	81.2(4)
Fe(1)–N(7)–Fe(3)	--	84.96(12)	81.5(4)
N(1)–Fe(1)–N(3)	--	98.80(12)	97.5(4)
N(1)–Fe(1)–N(4)	--	86.76(13)	87.8(4)
N(1)–Fe(1)–N(7)	--	100.53(13)	102.1(4)
N(1)–Fe(2)–N(2)	--	98.93(12)	97.3(4)
N(1)–Fe(2)–N(5)	--	138.61(13)	144.5(4)
N(1)–Fe(2)–N(7)	--	104.54(13)	100.5(4)
N(2)–Fe(2)–N(5)	--	86.90(13)	88.2(4)
N(2)–Fe(2)–N(7)	--	99.75(13)	98.8(4)
N(2)–Fe(3)–N(3)	--	99.30(12)	98.5(4)
N(2)–Fe(3)–N(6)	--	138.44(13)	146.1(4)
N(2)–Fe(3)–N(7)	--	100.67(14)	100.5(4)
N(3)–Fe(1)–N(4)	--	140.75(13)	145.0(4)
N(3)–Fe(1)–N(7)	--	99.38(13)	102.7(4)
N(3)–Fe(3)–N(6)	--	87.00(12)	87.0(4)
N(3)–Fe(3)–N(7)	--	96.46(13)	97.8(4)
N(4)–Fe(1)–N(7)	--	117.87(14)	110.1(4)
N(5)–Fe(2)–N(7)	--	114.85(13)	113.3(4)
N(6)–Fe(3)–N(7)	--	119.52(14)	111.9(4)
Fe(1)–Fe(2)–Fe(3)	--	62.63(2)	60.14(7)
Fe(2)–Fe(1)–Fe(3)	--	59.70(2)	61.20(7)
Fe(2)–Fe(3)–Fe(1)	--	57.68(2)	58.66(7)

Table S3. Selected Ligand Bond Distances (Å) **1**, **2**, and **3**.

Compound	**1**	**2**	**3**
N(1)–C(7)	1.410(3)	1.434(5)	1.481(14)
N(2)–C(13)	1.430(3)	1.448(5)	1.453(15)
N(3)–C(19)	1.426(3)	1.431(4)	1.400(15)
N(4)–C(12)	1.443(3)	1.393(5)	1.433(15)
N(5)–C(18)	1.402(3)	1.376(5)	1.383(15)
N(6)–C(24)	1.410(3)	1.387(5)	1.378(15)
N–C$_{\text{average}}$	**1.420(4)**	**1.412(6)**	**1.421(16)**
C(7)–C(8)	1.391(4)	1.386(5)	1.367(16)
C(7)–C(12)	1.428(4)	1.430(6)	1.374(16)
C(8)–C(9)	1.392(4)	1.389(6)	1.406(15)
C(9)–C(10)	1.378(4)	1.387(7)	1.410(16)
C(10)–C(11)	1.396(4)	1.390(6)	1.306(15)
C(11)–C(12)	1.388(4)	1.415(6)	1.438(15)
C(13)–C(14)	1.397(4)	1.386(6)	1.384(16)
C(13)–C(18)	1.420(4)	1.431(5)	1.454(16)
C(14)–C(15)	1.390(4)	1.390(6)	1.346(16)
C(15)–C(16)	1.388(4)	1.390(6)	1.415(16)
C(16)–C(17)	1.384(4)	1.385(6)	1.352(16)
C(17)–C(18)	1.405(4)	1.395(6)	1.396(16)
C(19)–C(20)	1.395(3)	1.383(5)	1.376(16)
C(19)–C(24)	1.428(4)	1.432(5)	1.445(17)
C(20)–C(21)	1.392(4)	1.398(6)	1.366(16)
C(21)–C(22)	1.383(4)	1.382(7)	1.360(17)
C(22)–C(23)	1.389(4)	1.374(6)	1.401(16)
C(23)–C(24)	1.402(3)	1.408(5)	1.409(17)
C–C$_{\text{average}}$	**1.397(5)**	**1.397(8)**	**1.389(18)**

References

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[1] Klose, A.; Solari, E.; Ferguson, R.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 2414-2416.

[2] Bowen, T.; Planalp, R. P.; Brechbiel, M. W. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 807-810.

[3] In the absence of coordinating solvent, formation of the diiron cluster $(^{tbs}L)Fe_2$ is favored over formation of the triiron cluster. $(^{tbs}L)Fe_2$ was synthesized from the reaction of Fe_2Mes_4 (41 mg, 0.139 mmol) and $^{tbs}LH_6$ (50 mg, 0.067 mmol) in benzene at 75 °C for 18 hours. ^1H NMR (benzene-d_6, 500 MHz, δ, ppm): 82.9, 52.3, 39.2, 37.7, 32.8, 25.0, 24.4, 23.2, 22.2, 20.1, 19.5, 14.5, 14.2, 12.9, 11.9, -2.31, -5.70, -15.2, -24.7, -32.2, -32.9, -34.0, -40.7. Full characterization of this compound will be provided in a future publication.