Electronic Supplementary Information for:

Bimetallic Iron-Tin Catalyst for N_2 to NH_3 and a Silyldiazenido Model Intermediate

Michael J. Dorantes,^{a§} James T. Moore, ^{a§} Eckhard Bill, ^b Bernd Mienert,^b and Connie C. Lu^{*a}

^a Department of Chemistry, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455-0431, United States. E-mail: <u>clu@umn.edu</u>

^b Max Planck Institut für Chemische Energiekonversion, Stiftstraße 34-36, 45470 Mülheim an der Ruhr, Germany.

§ co-first authors

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Experimental Section

General Considerations. Unless otherwise stated, all manipulations were performed under an inert atmosphere in a glovebox or using standard Schlenk techniques. Standard solvents were deoxygenated by sparging with argon and dried by passing through activated alumina columns of a SG Water solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. or Sigma-Aldrich, degassed via freeze-pump-thaw cycles and stored over activated 4 Å molecular sieves. Elemental analyses were performed by Robertson Microlit Laboratories, Inc. (Ledgewood, NJ). All NMR spectra were recorded on Bruker 500 MHz, or Bruker 400 MHz spectrometers at ambient temperature unless otherwise stated. NMR referencing is perfomed in accordance with the IUPAC recommended Unified Chemical Shift Scale, with the deuterium lock acting as the primary reference, and Xi values are used to reference all other heteronuclei (¹³C, ²⁹Si, ³¹P, ¹¹⁹Sn). Cyclic voltammetry was performed using a CH instruments 600 electrochemical analyzer. The one-cell setup used a glassy carbon working electrode, Pt wirecounter electrode, and Ag reference electrode. Analyte solutions consisted of 0.4 M [nBu₄N]PF₆ or K[BAr^F₂₀] in THF and the voltammograms were referenced internally to the FeCp₂^{+/0}(abbreviated as Fc⁺/Fc) redox couple. Mössbauer data were recorded on an alternatingcurrent constant-acceleration spectrometer. The sample temperature was maintained constant at 80 K in an Oxford Instruments Variox cryostat. The ⁵⁷Co/Rh source(1.8 GBg) was positioned at room temperature inside the gap of the magnet system at a zero-field position. Isomer shifts are quoted relative to Fe metal at 300 K. Mössbauer spectra were simulated using the program MFit written by Eckhard Bill. The chemicals, N(o-(NHCH₂PⁱPr₂)C₆H₄)₃¹ and K[BAr^F₂₀],² were prepared as previously reported. The following chemicals were all purchased from Sigma-Aldrich. TMSCI was purified by distillation and degassed by freeze-pump thaw cycles prior to use. Decamethylcobaltocene (CoCp2^{*}) was sublimed prior to use. Diphenylammonium triflate ([Ph₂NH₂][OTf]) was used as received.

Synthesis of (N(o-(NCH₂PⁱPr₂)C₆H₄)₃)SnFeBr | LSnFeBr. This is a modified procedure from what was published in the literature.³ To a stirring 5 mL THF solution of $N(o-(NHCH_2P^iPr_2)C_6H_4)_3$ (300 mg, 0.443 mmol) was added *n*-BuLi (3 equiv, 1.33 mmol) dropwise at -30 °C. After warming to ambient temperature and stirring for 2 h, a 2mL THF solution of SnCl₂ (88.2 mg, 0.465 mmol) was added dropwise. The solution was allowed to stir for 12 h. All volatiles were removed under reduced pressure, the solid redissolved in ~4 mL of benzene, and the insoluble byproducts were filtered away. The filtrate was then dried under reduced pressure, and the resulting solid was washed with a 6:1 solution of hexane/Et₂O. Crystals of Li(THF)₃[LSn] were grown from a concentrated THF solution layered with pentane to yield dark-yellow crystals (321 mg, 72% yield). Then to a stirring 10 mL THF solution of Li(THF)₃[LSn] (315 mg, 0.311 mmol), a suspension of FeBr₂ (67.0 mg, 0.311 mmol) in THF (5 mL) was added dropwise at ambient temperature. The reaction solution, which immediately changed color from yellow to dark red, was stirred for 12 h. After removing all volatiles under reduced pressure, the resulting solid was dissolved in benzene and the solution was filtered through Celite. After the filtrate was concentrated under reduced pressure to ~1 mL, and 2 mL Et₂O was added. The red solution was then cooled to -30° C overnight. The solution was decanted to obtain dark red crystals of LSnFeBr (213 mg, 68% yield). The ¹H spectrum matched that reported in the literature.³

Synthesis of $(N(o-(NCH_2P^iPr_2)C_6H_4)_3)SnFeN_2 | LSnFeN_2 (1)$. To a solution of LSnFeBr (100 mg, 0.099 mmol) in THF was added a slight excess of KC₈ (14.9 mg, 0.110 mmol), and the mixture was hand-stirred periodically over the course of an hour, resulting in a color change from dark red to yellow. The solution was then filtered through Celite, the solvent removed under reduced pressure, and the crude solid was redissolved in benzene and filtered once again. After concentrating the filtrate, Et₂O was added, and then, the solution was stored at -30 °C overnight to yield yellow crystals of **1** (71 mg, 81% yield).

¹H{³¹P}s NMR (400 MHz, C₆D₆): δ 15.1, 9.36, 7.91, 7.60, 6.40, -1.5. IR (KBr pellet): ν (N₂) 2011 cm⁻¹. Anal. calcd for **1**·THF, C₃₉H₆₀N₆P₃FeSn·C₄H₁₀O (%): C, 54.11; H, 7.39; N, 8.80. Found: C 54.20; H 7.51; N 8.27.

Synthesis of $K(THF) \cdot (N(o-(NCH_2P^iPr_2)C_6H_4)_3)SnFeN_2 | K(THF) \cdot LSnFeN_2 (2)$. To a solution of LSnFeBr (200 mg, 0.199 mmol) in THF was added 2.2 equiv of KC₈ (54.1 mg, 0.437 mmol), and the reaction was stirred overnight, resulting in an intensification of the yellow color. The solution was decanted and then filtered through Celite. The filtrate was concentrated under reduced pressure to provide a crude solid. Orange crystals of **2** were grown by layering pentane onto a saturated THF solution stored at -30 °C for 2 days (168 mg, 86% yield).

¹H{³¹P} NMR (400 MHz, THF-*d*₈): δ 7.19 (br, 3H, aryl), 6.72 (br, 3H, aryl), 6.30 (br, 3H, aryl), 6.18 (br, 3H, aryl), 2.59 (6H, C*H*₂PⁱPr₂), 2.22 (6H, C*H*Me₂), 1.0 (br, 36H, C*H*₃,). ³¹P{¹H} NMR (192 MHz, THF-*d*₈): δ 88.2. ¹¹⁹Sn NMR (149 MHz, THF-*d*₈): δ 511.6 (q, *J*_{Sn-P} = 610 Hz). IR (KBr pellet): ν (N₂) 1944 cm⁻¹. Anal. calcd. for K(crypt-222)·LSnFeN₂, K(C₁₈N₂H₃₆O₆)·C₃₉H₆₀N₆P₃FeSn: C 52.83, H 7.47, N 8.65. Found: C 50.38, H 7.06, N 6.65. This complex is highly air sensitive, and elemental analysis results were consistently poor.

Synthesis of $(N(o-(NCH_2P^iPr_2)C_6H_4)_3)SnFeN_2SiMe_3 | LSnFe(N_2SiMe_3)$ (3): To a stirring solution of Na(THF)_3[LSnFeN_2] (178 mg. 0.199 mmol) in THF chilled to -78 °C, Me_3SiCl (26.5 µL, 0.205 mmol) was added dropwise. The reaction was gradually warmed to room temperature (30 min), during which the solution color changed to dark purple. After stirring for another 30 min, the reaction solution was concentrated under reduced pressure to afford a solid. The crude residue was dissolved in pentane, and then, the solution was filtered through Celite. After removing all volatiles in vacuo, a lavendar-colored solid was obtained. Dichroic maroon/purple crystals were grown from a slow evaporation of a saturated Et₂O solution of **3** (126.0 mg, 65% yield).

¹H{³¹P} NMR (400 MHz, THF-*d*₈): δ 7.28 (d, *J* = 7.7 Hz, 3H, aryl), 6.92 (t, *J* = 7.7 Hz, 3H, aryl), 6.50 (d, *J* = 7.9 Hz, 3H, aryl), 6.41 (t, *J* = 7.6 Hz, 3H, aryl), 2.94 (br, 6H, C*H*₂PiPr₂), 2.38 (br, 6H, C*H*Me₂), 1.14 (br, 36H, PCH(C*H*₃)₂), 0.29 (s, 9H, Si(C*H*₃)₃). ¹³C{¹H} NMR (101 MHz, THF-*d*₈): δ 149.4 (C_{aryl}), 135.19 (C_{aryl}), 126.61 (C_{aryl}), 125.86 (C_{aryl}), 113.14 (C_{aryl}), 109.76 (C_{aryl}), 43.04 (m, C_{methine}), 32.01 (C_{methylene}), 18.92 (C_{methyl}, PCH*Me*₂), -0.90 (C_{methyl}, Si*Me*₃). ³¹P{¹H} NMR (192 MHz, THF-*d*₈): δ 101.3 (satellites: *J*_{Sn-P} = 561 (¹¹⁹Sn) & 538 (¹¹⁷Sn) Hz). ²⁹Si NMR (79 MHz, THF-*d*₈): δ -11.0. ¹¹⁹Sn NMR (149 MHz, THF-*d*₈): δ 441.5 (q, *J*_{Sn-P} = 559 Hz). IR (KBr pellet): ν (N₂) 1756 cm⁻¹. Anal. Calcd. for **3**: C₄₂H₆₉N₆P₃FeSnSi: C, 52.90; H, 7.29; N, 8.81. Found: C 51.19, H 7.16, N 5.61; C 51.58, H 7.21, N 5.62. This complex is highly reactive, and elemental analysis results were consistently poor.

Catalytic N₂ **fixation and quantification of ammonia.** This procedure was adapted from the literature.⁴ In a nitrogen-filled glovebox, a THF solution of precatalyst (6.9 µmol) was transferred equally to three Schlenk tubes (2.3 µmol). The THF was then evaporated to provide a thin film of precatalyst at the bottom of the Schlenk tube. The tube was then charged with a stir bar; and then, the acid and reductant were added as solids. After the tubes were stored at 77 K in a LN₂ cold well, Et₂O was added to produce a final precatalyst concentration of 2.3 mM. The temperature of the system was allowed to equilibrate for 5 min, and then the tube was sealed with a Teflon screw-valve. This tube was transferred outside of the glovebox into a LN₂ bath and transported to a fume hood. The tube was then transferred to a dry ice/acetone bath where the reaction thawed at -78 °C and was stirred for 3 h. The tube was then warmed to ambient temperature and stirred for 5 min.

The reaction mixture was frozen using a LN₂ bath. To the frozen solution, excess NaO⁴Bu solution in MeOH (0.25 mM) was added dropwise over 1-2 min. While frozen, the headspace of the tube was evacuated. The sealed tube was warmed to ambient temperature and stirred for at least 10 min. The volatiles of the reaction mixture were vacuum transferred into an additional Schlenk tube that contained 3 mL of a 2.0 M HCl solution in Et₂O (6 mmol). After completion of the transfer, the Schlenk tube containing HCl was sealed and warmed to ambient temperature. After waiting several min, the solvent was removed in vacuo, and the remaining crude was dissolved in H₂O (1.0 mL). A small aliquot of this solution (10–100 μ L) was then analyzed for the presence of NH₃ (present as NH₄Cl) using the indophenol method.⁵ Quantification was performed by measuring the absorbance at 635 nm using UV–vis spectroscopy.

Computational Methods. Gas-phase geometry optimizations were performed using density functional theory (DFT) with the M06-L functional⁶, as implemented in the Gaussian 16 program⁷ package, using the following basis sets: def2-TZVPP⁸ for Fe and Sn; def2-TZVP for N, P, and Si; def2-SVP for C and H. In addition, the Stuttgart SDD pseudo potential⁷ was used for Sn. For each complex, vibrational frequency analyses were performed to confirm that each optimized structure was in fact at energetic minima. Molecular orbitals were plotted using the VMD program⁹. Finally, the density derived electrostatic and chemical (DDEC6) bond orders were calculated using the Chargemol program¹⁰ using the Gaussian-derived wavefunction (.wfx) file as input.

X-Ray Crystallography. All crystals were mounted on a 200 µm MiTeGen microloop and placed on a Bruker PHOTON-II CMOS diffractometer for data collection at 100 K. The data collection was carried out using Mo Kα radiation (graphite monochromator). The data intensity was corrected for absorption and decay (SADABS).¹¹ Final cell constants were obtained from least–squares fits of all measured reflections. The structure was solved using SHELXT–2014/5¹² and refined using refined using SHELXL-2016/7.¹³ A direct methods solution was calculated which provided most non–hydrogen atoms from the E–map. Full matrix least–squares/difference Fourier cycles were performed to locate the remaining non–hydrogen atoms. All non–hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Further refinement details can be found in the .cif file of this work.

Table S1. Crystallographic details for LSnFeN₂ (**1**), $K(THF) \cdot LSnFeN_2$ (**2**), LSnFe(N₂SiMe₃) (**3**), and Li(THF)₃·LSn.

	1	2	3	Li(THF)₃ [.] LSn
Chemical formula	C ₃₉ H ₆₀ FeN ₆ P ₃ Sn•	C ₃₉ H ₆₀ FeKN ₆ P ₃ Sn•	C ₄₀ H ₆₉ FeN ₆ P ₃ SiSn•	$C_{51}H_{72}LiN_4O_3P_3Sn\bullet$
	C ₄ H ₈ O	C ₄ H ₈ O	C ₄ H ₁₀ O	C ₄ H ₈ O
Fw	954.50	991.68	990.63	1079.8137
Crystal System	monoclinic	orthorhombic	monoclinic	hexagonal
Space group	P21/c	Pca21	P21/c	P63
a (Å)	11.8994(7)	19.5107(9)	11.4678(13)	13.6945(8)
b (Å)	16.0639(9)	10.8907(6)	21.538(2)	13.6945(8)
c (Å)	24.3083(14)	21.8866(10)	19.703(2)	18.3276(11)
α (°)	90	90	90	90
β (°)	104.102(2)	90	96.834(4)	90
γ (°)	90	90	90	120
Volume (Å ³)	4506.5(5)	4650.6 (4)	4831.8(9)	2976.7(4)
Z	4	4	4	2
Density (g/cm ³)	1.407	1.416	1.362	1.218
µ (mm⁻¹)	1.022	1.081	0.979	0.55
λ (Å)	0.71073	0.71073	0.71073	0.716
θ (°)	2.143 to 30.530	2.639 to 30.560	2.082 to 30.534	2.809 to 30.606
Total Reflections	97475	39072	119561	5996
Unique reflections	13753	14075	14762	4622
Data/restraints/ parameters	13753 / 0 / 510	14075 / 1 / 517	14762 / 0 / 538	4622 / 139 / 266
R ₁ , wR ₂ (I>2σ (I))	0.0257, 0.0538	0.0469, 0.0705	0.0444, 0.0917	0.054, 0.0133



Fig. S1. ¹H{³¹P} NMR (400 MHz) of LSnFe(N₂) (1) in C₆D₆, * denotes residual C₆H₆



Fig. S2. ¹H{³¹P} NMR (400 MHz) of K(THF)·LSnFe(N₂) (**2**) in THF- $d_{8,*}$ denotes THF resonances.



Fig. S3. ³¹P{¹H} NMR (192 MHz) of K(THF)·LSnFe(N₂) (**2**) in THF- d_8 . Inset is a zoom of the baseline that shows the average of the ¹¹⁹Sn and ¹¹⁷Sn satellites.





Fig. S5. ¹H{³¹P} NMR (400 MHz) of LSnFe(N₂SiMe₃) (3) in THF- d_{8} , * denotes THF resonances.



Fig. S6. ¹³C{¹H} NMR (101 MHz) of LSnFe(N₂SiMe₃) (3) in THF-*d*₈.



Fig. S7. ¹H-¹³C HMQC NMR of LSnFe(N₂SiMe₃) (3) in THF-d₈.



140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -2/ ppm

Fig. S8. ³¹P{¹H} NMR (192 MHz) of LSnFe(N₂SiMe₃) (**3**) in THF- d_8 . Inset is a zoom of the baseline that shows the ¹¹⁹Sn and ¹¹⁷Sn satellites.



Fig. S9. ²⁹Si NMR (79 MHz) of LSnFe(N₂SiMe₃) (**3**) in THF- d_8 . The broad peak is from siliconcontaining species in the structure of the NMR tube.

447.14 439.59 439.59



Fig. S10. ¹¹⁹Sn NMR (149 MHz) of LSnFe(N₂SiMe₃) (3) in THF-d₈.

Infrared Spectroscopy



Fig. S11. IR spectrum of LSnFe(N₂) (1) recorded as a KBr pellet.



Fig. S12. IR spectrum of [K(crypt-2.2.2)][LSnFe(N₂)] (2) recorded as a KBr pellet. The peak occurring at 2009.9 cm⁻¹ corresponds to LSnFeN₂.



Fig. S13. IR spectrum of LSnFe(N₂SiMe₃) (**3**) recorded as a KBr pellet. The peak occurring at 2011.8 cm⁻¹ corresponds to LSnFeN₂.

X-ray structure metrics and comparisons

	LSnFe(N ₂) (1)	K[LSnFe(N ₂) (2)	LSnFe(NNSiMe₃) (3)	LSnFeBr ³	Li(THF)₃[LSn]
N5-N6	1.112(2)	1.143(6)	1.182(3)	N/A	N/A
N6-Si	N/A	N/A	1.746(3)	N/A	N/A
Fe-N5	1.7933(14)	1.762(5)	1.686(2)	N/A	N/A
Fe-Sn	2.4470(3)	2.4215(8)	2.4800(5)	2.4830(6)	N/A
Fe-P1	2.3349(5)	2.2313(15)	2.2511(8)	2.3579(11)	N/A
Fe-P2	2.2883(5)	2.2370(15)	2.2744(8)	2.4031(11)	N/A
Fe-P3	2.2677(5)	2.2158(15)	2.2834(8)	2.3791(12)	N/A
Sn-N1	2.0970(13)	2.109(4)	2.094(2)	2.096(3)	2.163(5)
Sn-N2	2.0958(13)	2.107(4)	2.089(2)	2.090(3)	2.163(5)
Sn-N3	2.0936(13)	2.135(4)	2.095(2)	2.088(3)	2.163(5)
Sn-N4	2.3978(12)	2.482(4)	2.450(2)	2.410(3)	2.679(11)

Table S2. Select metrical parameters (Å) for LSnFeN₂, K[LSnFe(N₂)], LSnFe(N₂SiMe₃), LSnFeBr, and Li(THF)₃[LSn].

Compound	<u>Fe-N Bond</u> Length Å	<u>N-N Bond</u> Length Å	<u>N-N IR Vibrational</u> <u>Frequency (cm⁻¹)</u>	Ref.
LSnFeN ₂ (1)	1.7933(14)	1.112(2)	2010	This work
K[LSnFeN2] (2)	1.762(5)	1.143(6)	1943°	This work
LSnFe(N2SiMe₃) (3)	1.686(2)	1.182(3)	1756	This work
(LAIFe) ₂ (µ-N ₂)	1.843(4)	1.146(7)	2012 ^d	14
K[LAIFeN ₂]	1.783(3)	1.135(4)	1925°	14
LAIFeN2(SiMe2CH2)2	1.661(2)	1.351(3)	N/A	14
Fe(depe) ₂ N ₂	1.748(8)	1.142(7)	1956	15
[Fe(depe) ₂ N ₂ SiMe ₃][B(Ar ^F ₄) ₄]	1.732(6)	1.194(8)	1732	16
Fe(depe)(depe•SiMe ₃) (N ₂ SiMe ₃) ₂	1.642(6)	1.382(2)	N/A	17
(P ₃ ^{Si})FeN ₂	1.8191(1)	1.1245(2)	2003	18
Na[(P ₃ ^{Si})FeN ₂]	1.763(3)	1.147(4)	1891	18
(P3 ^{Si})Fe(N2SiMe3)	1.695(2)	1.195(3)	1748	18
(P ₃ ^B)FeN ₂ ^a	1.881	1.097	2009	19
Na[(P ₃ ^B)FeN ₂]	1.776(2)	1.149(2)	1879	19
(P ₃ ^B)Fe(N ₂ SiMe ₃)	1.6960(8)	1.225 ^b	1741	20
(P ₃ ^C)FeN ₂	1.797(2)	1.134(4)	1992*	21
K[(P ₃ ^C)FeN ₂]	1.7397(16)	1.153(2)	1870*	21
(P ₃ ^C)Fe(N ₂ SiMe ₃)	N/A	N/A	1736*	21

Table S3. Comparison of geometrical parameters of relevant Fe-N₂ derived complexes.

^aComputationally derived parameters, ^bAverage of two molecules. All IR were taken using KBr pellets, ^cCountercation encapsulated in [2,2,2]-cryptand, ^dAssumed to be a monomer, ^{*}thin-film deposit exceptions

Cyclic Voltammetry



Fig. S14. Cyclic voltammetry study of LSnFeN₂ (**1**) in 0.4 M [$^{n}Bu_{4}N$][PF₆] in THF at varying scan rates, scanned cathodically.



Fig. S15. Cyclic voltammetry study of K(THF)·LSnFeN₂ (**2**) in 0.4 M [ⁿBu₄N][PF₆] in THF at varying scan rates, scanned anodically.



Fig. S16. Cyclic voltammetry study of $LSnFe(N_2SiMe_3)$ (3) in 0.4 M K[B(Ar^{F20})₄] in THF at 200 mV/s scanned cathodically.

Mössbauer Spectroscopy



Fig. S17. Zero-field Mössbauer spectra. All spectra were recorded at 80 K. Experimental data is indicated by the dotted points. Components: $LSnFeN_2$ in red, $K[LSnFeN_2]$ in yellow, and $LSnFe(N_2SiMe_3)$ in blue.

⁵⁷ Fe Mössbauer Parameters* (mm/s)								
Compound	δ	ΔΕα	Width					
1	0.47	0.52	0.54					
2	0.35	1.62	0.27					
3	0.26	1.76	0.28					
LAIFeN ₂	0.54	0.91	—					
[LAIFeN ₂] ⁻	0.38	1.24	-					
(P ₃ ^{Si})FeN ₂	0.38	0.71	-					
[(P₃ ^{Si})FeN₂] [−]	0.22	0.98	-					
(P₃ ^{si})FeN₂SiMe₃	0.19	1.26	-					
^a (P₃ ^B)FeN₂	0.56	3.34	_					
^a [(P₃ ^B)FeN₂] [−]	0.40	1.01	_					
*All spectra recorded at 80K with r	no external magnetic field applied, ^a wi	th 50 mT applied field						

Table	S4.	Compiled	Mössbauer	parameters	for	LSnFe(N ₂)	(1),	K[LSnFe(N ₂)]	(2),
LSnFe(NNSil	Me₃) (3), and	d other releva	nt compounds	from	the literature	e. ^{14, 18-}	19, 22	

Density Functional Theory

	LSnFe	N ₂ , 1	K[LSnF	K[LSnFeN₂], 2		SiMe₃), 3
Metric	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
Sn-M	2.4470(3)	2.4806	2.4215(8)	2.43206	2.4800(5)	2.5125
FSR	0.95	0.96	0.94	0.94	0.96	0.97
Fe-Pavg	2.2970(8)	2.3137	2.2280(23)	2.2160	2.2696(14)	2.2578
Fe-P ₃ Plane	0.3206(3)	0.386	0.3197(2)	0.352	0.3672(1)	0.427
Fe-N5	1.7933(14)	1.8044	1.762(5)	1.787	1.686(2)	1.668
N5-N6	1.112(2)	1.12698	1.143(6)	1.13421	1.183(3)	1.186
Si-N	N/A	N/A	N/A	N/A	1.745(3)	1.716
Sn-Navg	2.0954(22)	2.1053	2.117(2)	2.1098	2.0927(22)	2.0898
Sn-N₃ Plane	0.5875(7)	0.596	0.6485(6)	0.677	0.6367(4)	0.633
Sn-N4	2.3978(12)	2.4211	2.482(4)	2.521	2.450(2)	2.475
P1-Fe-P2	116.881(18)	112.91	119.22(6)	117.54	117.35(3)	116.73
P2-Fe-P3	107.295(18)	104.89	118.65(6)	117.49	120.43(3)	116.36
P3-Fe-P1	129.923(18)	133.60	116.52(6)	117.53	114.51(3)	116.45
N4-Sn-Fe	178.96(3)	177.77	179.86(11)	179.98	179.76(6)	179.93
N1-Sn-N2	111.26(5)	110.38	110.82(16)	110.17	110.93(8)	111.24
N2-Sn-N3	112.26(5)	113.16	113.74(16)	110.25	110.47(9)	111.21
N3-Sn-N1	113.86(5)	113.38	106.30(16)	110.23	112.11(8)	111.26

Table S5. Comparison of experimental (X-ray) and calculated geometrical parameters for complexes 1, 2, and 3.



Fig. S18. Selected Kohn-Sham orbitals of LSnFeN₂ (1) plotted with an isovalue of 0.05. ^{*a*}Contributions from the Sn-Fe σ -bond and Fe d_{x2-y2} are both split between two molecular orbitals, respectively.



Fig. S19. Selected Kohn-Sham orbitals of $[LSnFeN_2]^-$ (2) plotted with an isovalue of 0.05. "Contributions from the Sn–Fe σ^* bond are split between two molecular orbitals.



Fig. S20. Selected Kohn-Sham orbitals of LSnFeN₂SiMe₃ (**3**) plotted with an isovalue of 0.05. ^{*a*}Contributions from the Sn–Fe σ -bond are split among two molecular orbitals.

Orbital	Label	Energy (eV)	% Fe 3d	% Sn 5s	% Sn 5p	% N5 2p	% N6 2p
Sn-Fe σ ^a	SOMO8,7	-5.63, -5.28	10.2, 21.4	4.9, 8.6	9.2, 9.3	< 3	< 3
Fe d _{xz}	SOMO-6	-5.06	78.5	< 3	< 3	< 3	6.7
Fe d _{yz}	SOMO-5	-5.00	76.7	< 3	< 3	< 3	5.6
Fe d _{xy}	SOMO-2	-4.35	58	< 3	< 3	< 3	3.4
Fe d _{x2-y2} ^a	SOMO-1,0	-4.27, -4.22	22.3, 32.3	<3	< 3	< 3	< 3
Sn-Fe σ*	LUMO	-1.12	35.5	16	< 3	< 3	< 3

Table S6. Molecular orbital composition analysis for LSnFeN₂, (1).

^a Contributions from these bonds were split among two molecular orbitals

Table S7. Molecular orbital composition analysis for [LSnFeN2]⁻, (2).

Orbital	Label	Energy (eV)	% Fe 3d	% Sn 5s	% Sn 5p	% N5 2p	% N6 2p
Sn-Fe σ	HOMO–7	-2.34	21.2	15.8	15.5	< 3	< 3
Fe d _{xz}	HOMO–3	1 20	71.6		< 2	< 3	9.1
Fe d _{yz}	HOMO-2	-1.39	71.0	< 3	< 3		
Fe d _{xy}	HOMO–1	0.46	-0.46 59.2	- 0	3 < 3	< 3	ΕĴ
Fe d _{x2-y2}	НОМО	-0.40		< 3			5.3
Sn-Fe σ* ª	LUMO+6,+7	2.42, 2.58	21.2, 17.7	7.7, 9.9	< 3	< 3	< 3

^a Contributions from these bonds were split among two molecular orbitals

Table S8. Molecular orbital composition analysis for $LSnFeN_2SiMe_3$, (3)).
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Orbital	Label	Energy (eV)	% Fe 3d	% Sn 5s	% Sn 5p	% N5 2p	% N6 2p
Sn-Fe σ ^a	HOMO8,7	-5.47, -5.14	10.4, 17.0	6.3, 8.8	11.1, 8.9	< 3	< 3
Fe d _{xz}	HOMO–6	4.05	60	~ 2	~ 2	~ 2	4.2
Fe d _{yz}	HOMO–5	-4.95 60	< 3	< 3	< 3	4.2	
Fe d _{xy}	HOMO-1	2 70	50.0	< 0	< 2	F 0	2.0
Fe d _{x2-y2}	НОМО	-3.70	-3.70 30.3	< 3	< 3	5.2	3.9
Fe-N ₂ π*	LUMO	1.00	00.0	- 0	<i>.</i> 0	20.0	17.0
Fe-N ₂ π*	LUMO+1	-1.30	-1.36 29.3	< 3	< 3	30.9	17.0
Sn-Fe σ*	LUMO+3	-0.68	33.5	17	< 3	< 3	< 3

^a Contributions from these bonds were split among two molecular orbitals

Selected Atoms	LSnFeN ₂ , 1	[LSnFeN₂]⁻, 2	LSnFe(N₂SiMe₃), 3
Sn–Fe	0.7339	0.7999	0.6831
Fe–N5	1.1317	1.1972	1.5033
N5–N6	2.5806	2.5604	2.1777
Avg. Fe–P	0.8211	1.0297	0.9219
Fe	-0.6106	-0.8134	-0.7060
Sn	0.9833	0.9949	1.0105
N5	0.0678	0.0978	0.0854
N6	-0.1539	-0.2418	-0.3743
Δ(N5-N6)	0.2217	0.3395	0.4598

Table S9. DDEC6-derived bond order and partial charges between selected atoms in complexes **1**, **2**, and **3**. Here, N5 refers to the proximal N, while N6 refers to the distal N.



Figure S21. Plot of the DDEC6-derived N-N bond order vs. the Fe-N bond order, for complexes **1**, **2**, and **3**.





l	Linear Fit	
N	V5 Charge = -0.483168	+ 0.5689319*Sn Charge

Summary of Fit	
RSquare	0.265597
RSquare Adj	-0.46881
Root Mean Square Error	0.018267
Mean of Response	0.083651
Observations (or Sum Wgts)	3

Analysis of Variance									
Source	DF	S S	oum of quares	м	ean Squa	re	F Rat	tio	
Model	1	0.00	012067		0.0001	21	0.36	17	
Error	Error 1 0.00033367 0.000334		34	Prob >	• F				
C. Total 2 0.0004		045434				0.655	3		
Parame	Parameter Estimates								
Term	Esti	mate	Std Er	ror	t Ratio	Pr	ob> t		
Intercept	-0.48	33168	0.942	598	-0.51	C	.6985		
Sn Charge	0.56	89319	0.946	053	0.60	C	.6553		



Linear Fit

N5 Charge = 0.0667315 - 0.0659159*N6 Charge

Summary of Fit				
RSquare	0.235649			
RSquare Adj	-0.5287			
Root Mean Square Error	0.018635			
Mean of Response	0.083651			
Observations (or Sum Wgts)	3			

Analysis of Variance Sum of Source DF Squares Mean Square F Ratio

			Contraction of the American State of the Ame	
Model	1	0.00010706	0.000107	0.3083
Error	1	0.00034727	0.000347	Prob > F
C. Total	2	0.00045434		0.6773

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.0667315	0.032315	2.07	0.2871
N6 Charge	-0.065916	0.118715	-0.56	0.6773

Figure S22. Plot of the DDEC6 derived Sn charge versus the charges of N6, N5, and Fe, respectively, for complexes 1, 2, and 3.



Figure S23. Plots of the DDEC6-derived Fe charge versus the charges of N5 and N6, respectively.



Figure S24. Plot of the DDEC6-derived charges of Sn and Fe versus the charge difference of N5 and N6, Δ (N5–N6), which serves as a measure of the polarization of the N₂ unit.

Catalytic Data

Table S10. Comparison of the catalytic N_2 reduction mediated by the LSnFeN₂ complexes and other Fe-based complexes.

		N ₂ + 66	e⁻ + 6H⁺ →	Ph_2NH_2 , $CoCp_2^*$ Fe compound Et ₂ O, -78 °C, 3 h	2 NH ₃	
Entry	Catalyst	Cp* ₂ Co (eq)	[Ph ₂ NH ₂][O]	[f] (eq) NH ₃ (eq)	yield	ref.
1	LSnFeN ₂	54	108	<u>5.9(5)</u> 6.5 5.8	33%	this work
2 ,c	LSnFeN ₂ +Hg(s)	54	108	5.4 <u>5.2(8)</u> 5.8 5.6 4 1	29%	this work
3	[LSnFeN ₂] ⁻	54	108	<u>0.9(3)</u> 1.2 0.8 0.6	5%	this work
4	LSnFe(N₂SiMe₃)	54	108	<u>4.6(2)</u> 4.7 4.7 4.3	26%	this work
5	P₃ ^B Fe⁺	54	108	12.8(5)	72%	22
6 ^b	P ₃ ^B Fe ⁺	162 x 3	322 x 3	84(8)	52%	22
7	P₃ ^{Si} Fe	54	108	1.2(1)	7%	22
8	Fe(depe) ₂	54	108	1.1(2)	6%	23

The catalyst, acid, $Cp_{2}^{*}Co$, and $Et_{2}O$ were sealed in a vessel at -196 °C under an N₂ atmosphere followed by warming to -78 °C and stirring for 3 hours. Catalytic conditions were adapted from previous work by Peters, et al.⁸ ^bThis experiment the reaction was allowed to proceed for 3 h at -78 °C before cooling to -196 °C and replenishing additional substrate and solvent. ^c200 equivalents of Hg (with respect to **1**) were added to the reaction vessel before the start of catalysis.

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