

Supporting Information for:

Diiron bridged-thiolate complexes that bind N₂ at
the Fe^{II}Fe^{II}, Fe^{II}Fe^I, and Fe^IFe^I redox states

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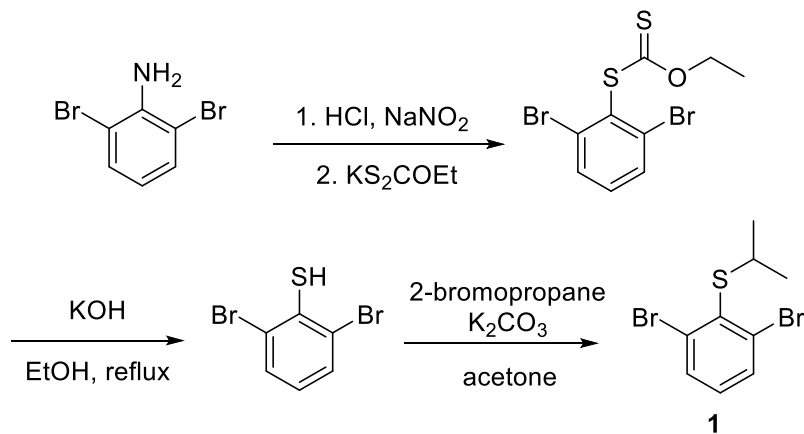
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| I. Synthesis and characterization of 1-13 | p. S2 |
| II. Reactivity studies | p. S17 |
| III. Crystallographic details and structures of 7, 9, 10, 11, and 13 | p. S18 |

I. Synthesis and characterization of **1** – **13**

General considerations. All syntheses and measurements, unless otherwise stated, were carried out under an inert atmosphere (N_2) in a glovebox or using standard Schlenk techniques, and solvents were dried and degassed by thoroughly sparging with N_2 and then passing through an activated alumina column in a solvent purification system supplied by SG Water, LLC. Combustion analyses were carried out by Midwest Microlabs (Indianapolis). Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective moisture removal. **2**,¹ $Fc[BAr^F_4]$,² $HBAr^F_4 \cdot 2Et_2O$ ($Ar^F = 3,5$ -bistrifluoromethylphenyl),³ and $\{[SiP^{iPr}_2S^{Ad}]FeN_2\}BAr^F_4$ ⁴ were prepared according to literature procedures. All other reagents were purchased from commercial vendors and used without further purification unless otherwise stated.

Physical methods. Optical spectroscopy measurements were taken on a Cary 50 UV-vis spectrophotometer using a 1-cm two-window quartz cell. Electrochemical measurements were carried out in a glovebox under a dinitrogen atmosphere in a one compartment cell using a CH Instruments 600B electrochemical analyzer. A glassy carbon electrode was used as the working electrode and a graphite rod was used as the auxiliary electrode. A silver pseudoreference electrode was used. The ferrocene couple Fc^+/Fc was used as an internal reference. Solutions (THF) of electrolyte (0.4 M tetra-*n*-butylammonium hexafluorophosphate) and analyte were also prepared under an inert atmosphere. Fourier transform infrared ATR spectra were collected on a Thermo Scientific Nicolet iS5 Spectrometer with diamond ATR crystal (utilized iD5 ATR insert). Solution phase magnetic measurements were performed by the method of Evans.⁵ Mossbauer spectra were recorded on a spectrometer from SEE Co. (Edina, MN) operating in the constant acceleration mode in a transmission geometry. The sample was kept in an SVT-400 cryostat from Janis (Wilmington, MA). The quoted isomer shifts are relative to the centroid of the spectrum of a metallic foil of α -Fe at room temperature. Solid samples were prepared by grinding polycrystalline material into a fine powder and then mounted in a Delrin cup fitted with a screw-cap as a boron nitride pellet. Data analysis was performed using the program WMOSS (www.wmoss.org) and quadrupole doublets were fit to Lorentzian lineshapes.

Scheme S1. Synthesis of **1** from 2,6-dibromoaniline



(2,6-dibromophenyl)ethyl xanthate. 2,6-dibromoaniline (24.5 g, 0.0976 mol) was slurried in 15 mL of H₂O and 16.3 mL of concentrated (35%) aqueous HCl and ~15 g of ice were added, and the resulting mixture was cooled to 0 °C in an ice-water bath. A solution of NaNO₂ (6.71 g, 0.0973 mol in 30 mL H₂O) was added slowly over 40 minutes. After the addition was complete the mixture was stirred for an additional 30 minutes at 0 °C, and was then added slowly over 20 minutes to a solution of potassium ethyl xanthate (18.77 g, 0.117 mol) in H₂O (100 mL) at 60 °C. After the addition was complete the reaction was stirred for an additional 30 minutes at 60 °C, then cooled to room temperature, extracted with dichloromethane (2 x 200 mL), dried over magnesium sulfate, filtered, and concentrated to a yellowish solid. This solid residue was recrystallized from methanol to give the desired product as a crystalline white solid (23.1 g, 0.0649 mol, 67%). ¹H NMR (CDCl₃, 300 MHz, 298 K): δ 7.67 (d, *J* = 8 Hz, 2H, 3,5-CH_{Ar}), 7.14 (t, *J* = 8 Hz, 1H, 4-CH_{Ar}), 4.61 (q, *J* = 8 Hz, 2H, -OCH₂CH₃), 1.32 (t, *J* = 8 Hz, 3H, -OCH₃CH₃) ppm. This species has been previously reported via a similar synthetic route.⁶

2,6-dibromothiophenol. (2,6-dibromophenyl)ethyl xanthate (23.1 g, .0649 mol) was dissolved in 200 mL of ethanol and KOH pellets (100g, 1.78 mol) were added. The mixture was heated to reflux while stirring overnight, then the reaction mixture was concentrated to dryness, extracted into H₂O (200 mL) and washed with diethyl ether (2 x 200 mL). The aqueous layer was then acidified with HCl and extracted with EtOAc (2 x 200 mL). The organic layers from this second extraction were combined, dried over magnesium sulfate, filtered through a silica plug, then concentrated to dryness. The resulting material (16.5 g, 0.0616 mol, 95%) was used without further purification for the subsequent step. ¹H NMR (CDCl₃, 300 MHz, 298 K): δ 7.49 (d, *J* = 8 Hz, 2H, 3,5-CH_{Ar}), 6.85 (t, *J* = 8 Hz, 1H, 4-CH_{Ar}), 5.00 (s, -SH) ppm. This species has been previously reported via a similar synthetic route.⁶

(2,6-dibromophenyl)isopropyl thioether (1). 2,6-dibromothiophenol (16.5 g, 0.0616 mol) was dissolved in acetone (200 mL) and powdered potassium carbonate (13.2 g, 0.0955 mol) was added. This mixture was heated to reflux while stirring overnight. The reaction was then cooled to room temperature and concentrated to dryness. The residue was taken up in dichloromethane (200 mL) and washed with water (2 x 100 mL). The organic layers were dried over magnesium sulfate, filtered, and concentrated to give a yellow oil. This oil was distilled at reduced pressure to give the desired product as a clear oil (16.8 g, 0.0542 mol, 88%). ¹H NMR (CDCl₃, 300 MHz, 298 K): δ 7.62 (d, *J* = 8 Hz, 2H, 3,5-CH_{Ar}), 7.00 (t, *J* = 8 Hz, 1H, 4-CH_{Ar}), 3.59 (septet, *J* = 8 Hz, 1H, -SCH(CH₃)₂), 1.28 (d, *J* = 8 Hz, 6H, -SCH(CH₃)₂) ppm.

(3-bromo-2-(isopropylthio)phenyl)(bis(2-diisopropylphenylphosphino)silane (3). **1** (1.81 g, 5.84 mmol) was dissolved in diethyl ether (50 mL) and cooled to -78 °C. *N*-butyllithium (3.84 mL, 1.6 M in hexane, 6.1 mmol) was added in one portion and the reaction mixture was stirred at low temperature for one hour and then allowed to warm to room temperature for one hour before being concentrated to dryness. The white residue was taken up in toluene (50 mL) and again cooled to -78 °C, then bis(diisopropylphenylphosphino)chlorosilane (**2**) (2.628 g, 5.95 mmol) was added dropwise as a solution in toluene (10 mL). This was stirred at low temperature for three hours and then allowed to warm to room temperature for one hour; the cloudy gray mixture was then filtered through Celite and the filtrate was concentrated to dryness and washed with pentane to give the product as a white powder (2.38 g, 3.68 mmol,

63%). ^1H NMR (C_6D_6 , 300 MHz, 298 K): δ 7.51 (d, $J = 8$ Hz, 1H, CH_{ArS}), 7.39 (d, $J = 8$ Hz, 2H, CH_{ArP}), 7.20-7.15 (m, 4H, CH_{ArP}), 7.07 (d, $J = 8$ Hz, 1H, CH_{ArS}), 6.95 (t, $J = 8$ Hz, 2H, CH_{ArP}), 6.59 (t, $J = 8$ Hz, 1H, 4- CH_{ArS}), 3.99 (septet, $J = 6$ Hz, 1H, $-\text{SCH}(\text{CH}_3)_2$), 2.02 (m, 4H, $-\text{P}[\text{CH}(\text{CH}_3)_2]_2$), 1.35 (d, $J = 6$ Hz, 6H, $-\text{SCH}(\text{CH}_3)_2$), 1.13 (dd, $J = 6, 13$ Hz, 12H, $-\text{P}[\text{CH}(\text{CH}_3)_2]_2$), 0.93 (m, 12H, $-\text{P}[\text{CH}(\text{CH}_3)_2]_2$) ppm. ^{31}P NMR (C_6D_6 , 121.4 MHz, 298 K): 1.0 (s) ppm.

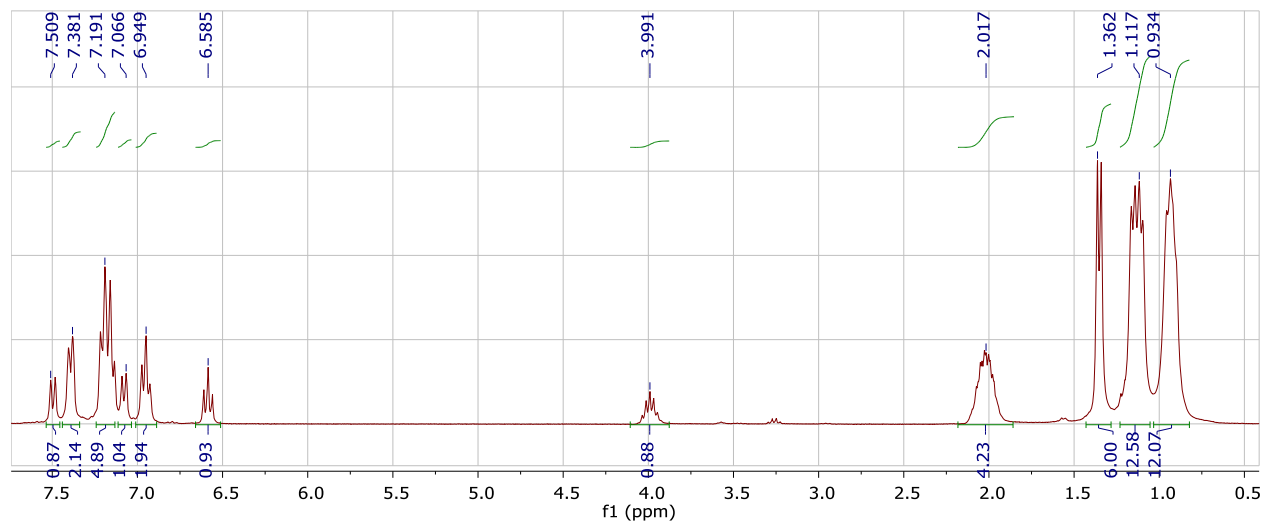


Figure S1. ^1H NMR spectrum of **3**.

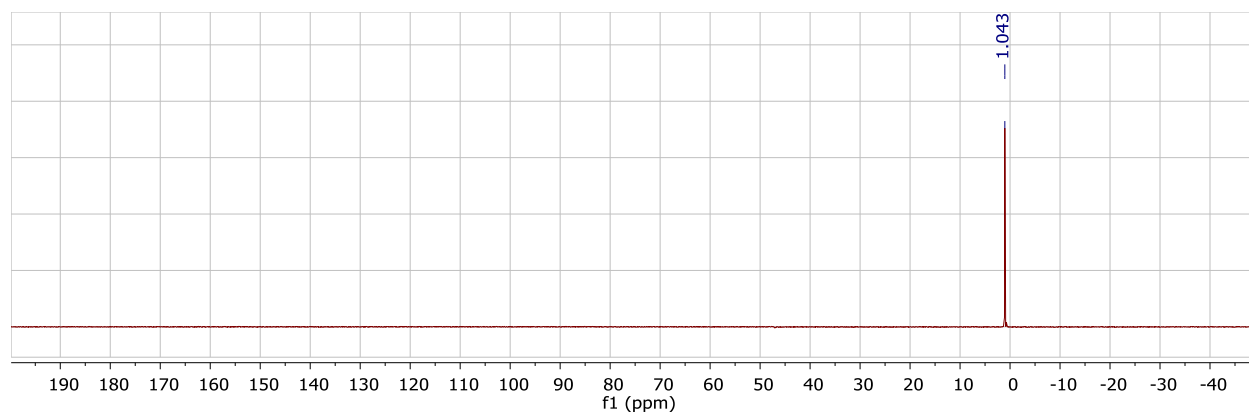


Figure S2. ^{31}P NMR spectrum of **3**.

2,6-bis[bis(2-diisopropylphenylphosphino)silyl]phenyl isopropyl thioether (4). **3** (6.70 g, 10.2 mmol) was dissolved in diethyl ether (100 mL) and cooled to -78 $^\circ\text{C}$. *N*-butyllithium (6.51 mL, 1.6 M in hexane, 10.4 mmol) was added in one portion and the mixture was allowed to stir at low temperature for one hour and then warmed to room temperature for one hour before being concentrated to dryness. The white residue was redissolved in toluene (100 mL), cooled back to -78 $^\circ\text{C}$, and then bis(diisopropylphenylphosphino)chlorosilane (**2**) (4.70 g, 10.4 mmol) was added as a solution on toluene (15 mL). The reaction was allowed to stir at low temperature overnight and slowly warmed to room temperature. The yellow suspension was then filtered through Celite and the filtrate was concentrated to dryness. The yellow residue

was washed with pentane to give the desired product as a white solid (6.4 g, 63%). ^1H NMR (C_6D_6 , 300 MHz, 298 K): δ 7.42 (d, $J = 7$ Hz, 4H, CH_{Ar}), 7.32 (d, $J = 7$ Hz, 4H, CH_{Ar}), 7.27-7.15 (m, 6H, CH_{Ar}), 7.11 (t, $J = 7$ Hz, 4H, CH_{Ar}), 6.81 (t, $J = 7$ Hz, 1H, 4- CH_{ArS}), 4.47 (br m, 1H, $-\text{SCH}(\text{CH}_3)_2$), 2.02 (m, 8H, $-\text{P}[\text{CH}(\text{CH}_3)_2]_2$), 1.57 (d, $J = 6$ Hz, 6H, $-\text{SCH}(\text{CH}_3)_2$), 1.15 (m, 24H, $-\text{P}[\text{CH}(\text{CH}_3)_2]_2$), 0.90 (m, 24 H, $-\text{P}[\text{CH}(\text{CH}_3)_2]_2$) ppm. ^{31}P NMR (C_6D_6 , 121.4 MHz, 298 K): 0.9 (s) ppm.

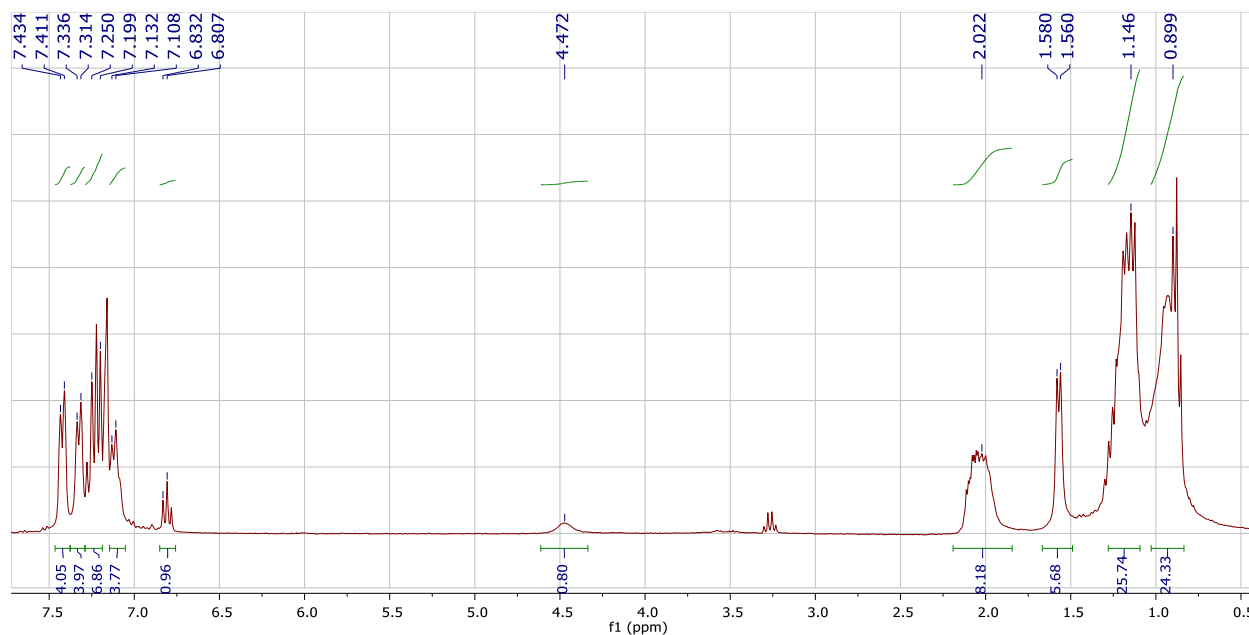


Figure S3. ^1H NMR spectrum of **4**.

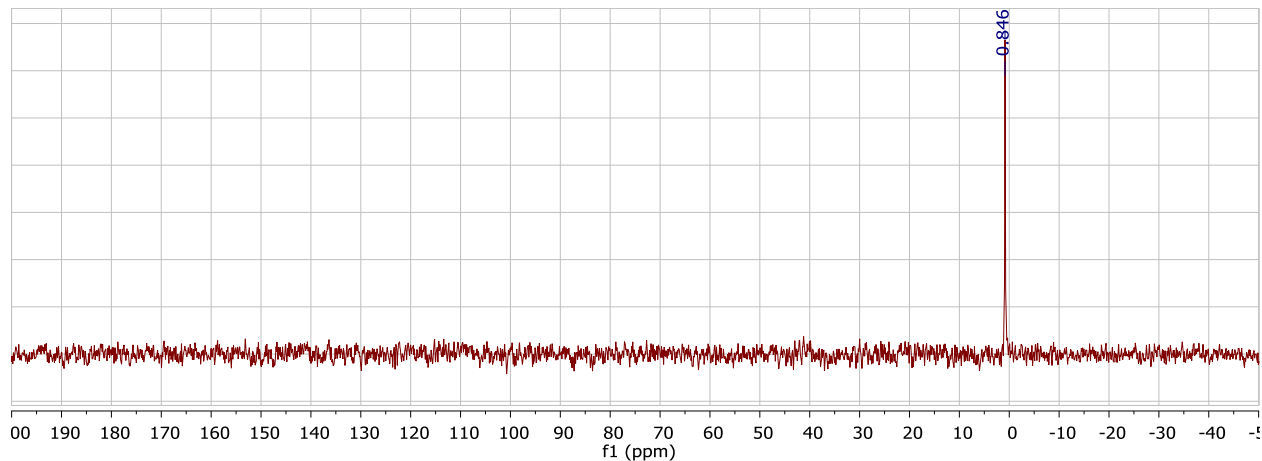


Figure S4. ^{31}P NMR spectrum of **4**.

[HSi^{*i*}Pr₂]₂Fe₂Cl₃ (6**).** Protected ligand **4** (1.0 g, 1.02 mmol) was dissolved in 15 mL of THF with naphthalene (160 mg, 1.25 mmol) and vigorously stirred over sodium (60 mg, 2.61 mmol) for two hours; the solution took on a deep orange-brown color. This step serves to cleave the S-*i*Pr bond. The solution was then decanted from the remaining sodium and quenched by stirring over excess pyridinium chloride

(300 mg) for four hours until the suspension was colorless, giving the deprotected thiol. The mixture was then concentrated to dryness *in vacuo*, extracted with benzene, filtered through Celite, and again concentrated. The residue was taken up in THF and stirred over KH (110 mg, 0.36 mmol) for one hour, resulting in the evolution of H₂, and the reaction mixture was again filtered through Celite to give a colorless solution of the potassium salt of the thiolate ligand. To this solution was added FeCl₂ (285 mg, 2.25 mmol), resulting in an immediate color change to deep blue followed by a slower color change to dark brown. This was vigorously stirred overnight, and then the reaction mixture was concentrated to dryness. The brown residue was extracted with benzene and filtered through Celite; the filtrate was concentrated to a volume of 2 mL and then layered with 15 mL of pentane and allowed to stand overnight, resulting in the precipitation of a brown microcrystalline solid; the supernatant was decanted and the solids were washed with pentane to give the desired product (770 mg, 0.67 mmol, 61%). ¹H NMR (C₆D₆, 300 MHz, 298 K): δ 116.7, 76.7, 30.0, 18.0, 15.1, 14.2, 10.0, 9.3, 8.3, 5.1, 3.9, 2.7, -1.0, -10.4, -66.8 ppm.

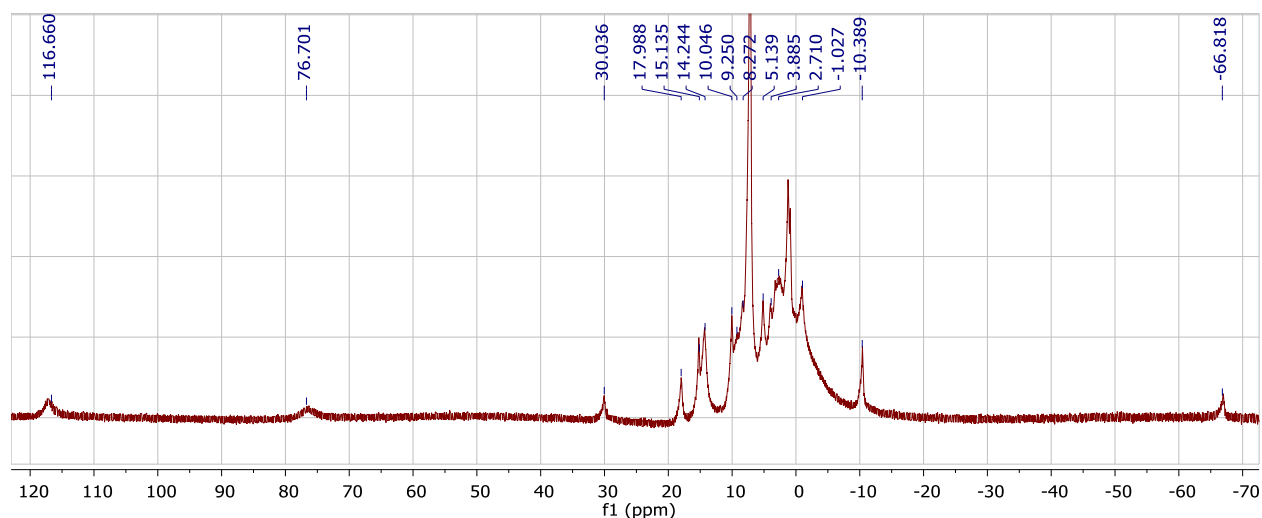


Figure S5. ¹H NMR spectrum of **6**.

{[SiP^{Pr}₂]₂Fe₂Cl₂}{PPN} (7**).** Complex **6** (1.004 g, 0.846 mmol) is dissolved in THF (30 mL) and cooled to -78 °C. A solution of methylmagnesium chloride (0.564 mL, 3.0 M in THF, 1.69 mmol) in 10 mL of THF was added dropwise over 15 minutes, and the reaction, which turned reddish-orange, was stirred at low temperature for two hours. It was then allowed to warm to room temperature for two hours, resulting in a color change to reddish brown. Then 20 mL of dioxane were added, the reaction was stirred for an additional 20 minutes, and 60 mL of pentane were added. The resulting mixture was filtered through Celite and the filtrate was concentrated to dryness. The red-brown residue was extracted with benzene and filtered through Celite again, then concentrated to dryness again. This product mixture appears to contain a mixture of dichloride and monochloride species which coordinate various donors likely including THF and bridging MgCl₂; isolation of a clean product is facilitated by treating with an additional chloride source to give the anionic dichloride. Accordingly, the red-brown solid residue is taken up in THF (40 mL) with 10 mL of dioxane and combined with [PPN]Cl (500 mg, 0.871 mmol), and the resulting suspension was stirred overnight. The resulting bright red mixture was concentrated to dryness, extracted with benzene, and filtered through Celite. The filtrate was concentrated to 10 mL, then pentane (20 mL) was added, resulting in the precipitation of dark red solids. The supernatant is

decanted and the solids are washed with pentane and then dried *in vacuo* to give the desired product as a red solid (1.2 g, 0.72 mmol, 86%). Crystals suitable for x-ray diffraction were grown by allowing a supersaturated benzene solution to sit at room temperature overnight. ^1H NMR (C_6D_6 , 300 MHz, 298 K): δ 27.6, 16.4, 12.2, 7.8, 7.7, 7.5, 4.2, 2.8, 1.9, 0.8, -0.8, -3.3, -18.9 ppm. μ_{eff} (C_6D_6 , Evans method, 298 K): 3.3 μ_{B} . Anal. Calcd. For $\text{C}_{90}\text{H}_{105}\text{Cl}_2\text{Fe}_2\text{NP}_6\text{SSi}_2$: C, 65.22; H, 6.39; N, 0.85. Found: 64.81; H, 6.58; N, 0.98. UV-vis (THF, 298 K, nm $\{\text{cm}^{-1}\text{M}^{-1}\}$): 503 {7200}.

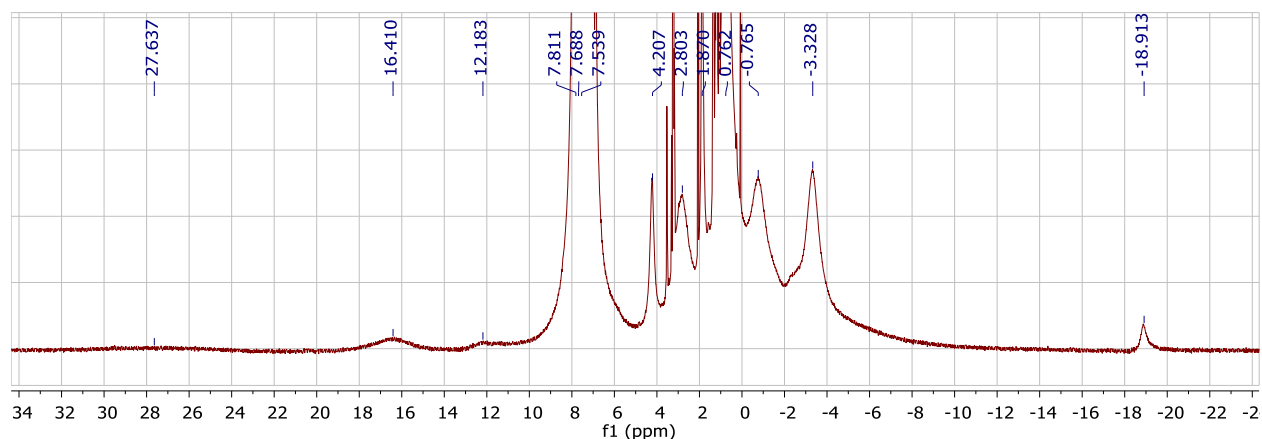


Figure S6. ^1H NMR spectrum of **7**.

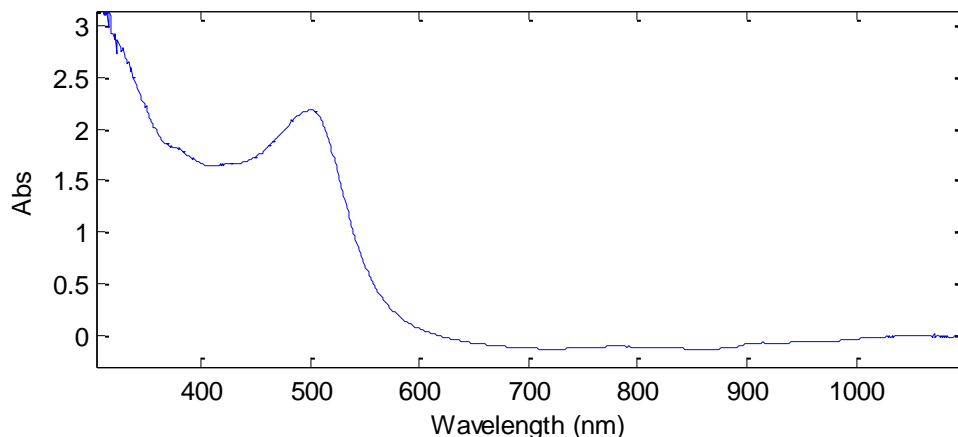


Figure S7. UV-vis spectrum of **7** (THF).

$\{[\text{Si}^{\text{iPr}}\text{Pr}_2]_2\text{Fe}_2(\text{N}_2)_2\}\{\text{Na}(\text{12-crown-4})_2\}$ (8** $\{\text{Na}(\text{12-crown-4})_2\}$).** Compound **7** (100 mg, 0.0603 mmol) is dissolved in THF and stirred with sodium tetraphenylborate (22 mg, 0.0643 mmol) overnight in order to generate a putative monochloride intermediate with precipitation of sodium chloride and $[\text{PPN}][\text{BPh}_4]$. The orange reaction mixture is concentrated to dryness and extracted with 1:2 benzene:pentane (10 mL) and filtered through Celite. The filtrate is dried to a light orange powder; NMR analysis confirms the formation of a new product. A crystal grown by slow evaporation of an Et_2O solution of this material was analyzed by X-ray crystallography, and though the resulting structure was not of sufficient quality for publication, it was consistent with a diiron complex with a single coordinated chloride disordered

over the two axial iron sites. This material is stirred over excess sodium amalgam (1% Na in Hg) in THF overnight, resulting in a color change to deep green. The solution is decanted from the remaining amalgam, concentrated to dryness, extracted with 1:1 THF:diethyl ether, and filtered through Celite. The ether filtrate is layered with a solution of two equivalents of 12-crown-4 in diethyl ether and allowed to sit overnight, resulting in the formation of dark green crystals. The supernatant is decanted and the crystals are washed with pentane and diethyl ether and then dried *in vacuo* to give the product as dark green crystals (56 mg, 0.0379 mmol, 63%). Crystals suitable for x-ray diffraction were grown by allowing pentane to diffuse into a concentrated solution of $\mathbf{8}\{\text{Na}(12\text{-crown-}4)_2\}$ in 2:1 Et₂O:THF. ¹H NMR (2:1 C₆D₆:d₈-THF, 300 MHz, 298 K): 8.40 (d, *J* = 7 Hz, 4H, CH_{Ar}), 8.05 (d, *J* = 7 Hz, 2H, CH_{Ar}), 7.27 (d, *J* = 7 Hz, 4H, CH_{Ar}), 7.10 (t, *J* = 7 Hz, 4H, CH_{Ar}), 6.97 (t, *J* = 7 Hz, 4H, CH_{Ar}), 3.26 (s, 32H, 12-crown-4), 2.42 (br s, 4H, -P[CH(CH₃)₂]₂), 2.07 (br s, 4H, -P[CH(CH₃)₂]₂), 1.07 (br s, 12 H, -P[CH(CH₃)₂]₂), 0.97-0.90 (m, 32H, -P[CH(CH₃)₂]₂) ppm. ³¹P NMR (2:1 C₆D₆:d₈-THF, 121.4 MHz, 298 K): 88.2 (br s) ppm. IR (thin film from THF): ν(N-N) = 2017, 1979 cm⁻¹. Anal. Calcd. for $\mathbf{8}\{\text{Na}(12\text{-crown-}4)_2\}3\text{THF}$, C₈₂H₁₂₈Fe₂N₄NaO₁₁P₄SSi₂: C, 58.18; H, 7.62; N, 3.31. Found: C, 58.41; H, 7.77; N, 3.49. UV-vis (THF, 298 K, nm {cm⁻¹ M⁻¹): 385 {12100}, 506 {7800}, 627 {12300}, 756 {3200}.

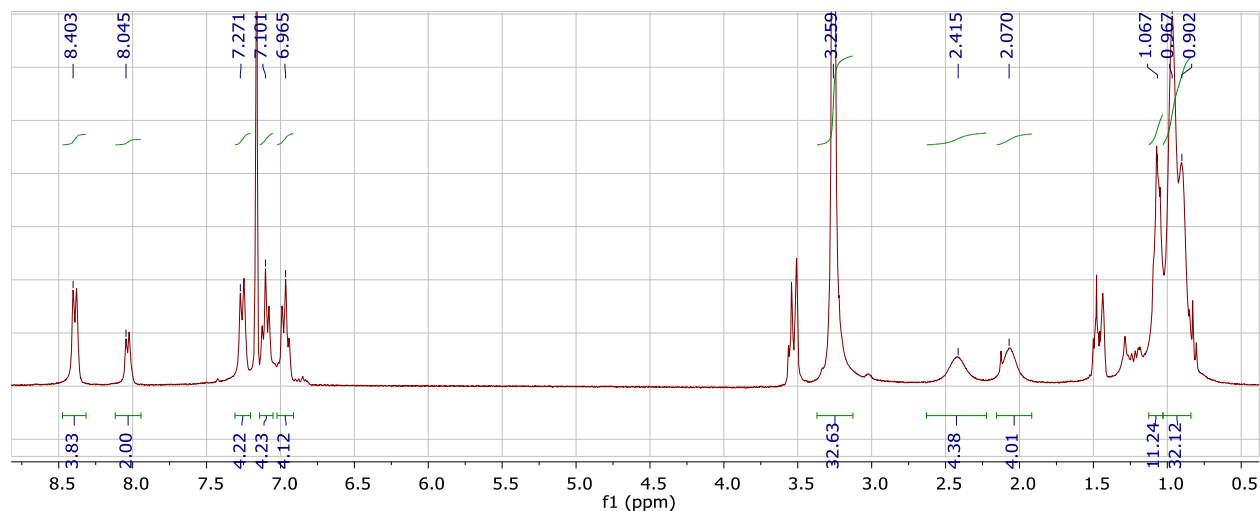


Figure S8. ¹H NMR spectrum of $\mathbf{8}\{\text{Na}(12\text{-crown-}4)_2\}$.

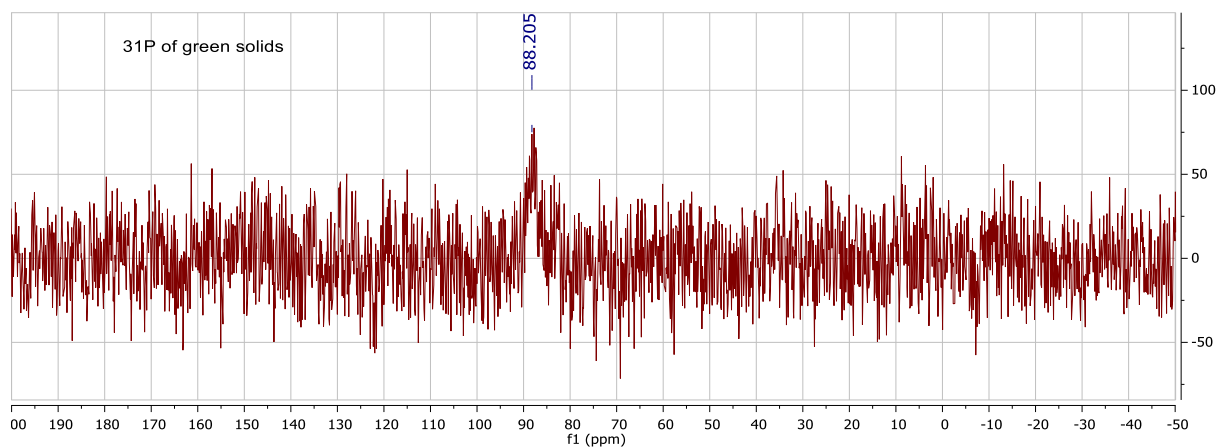


Figure S9. ³¹P NMR spectrum of $\mathbf{8}\{\text{Na}(12\text{-crown-}4)_2\}$.

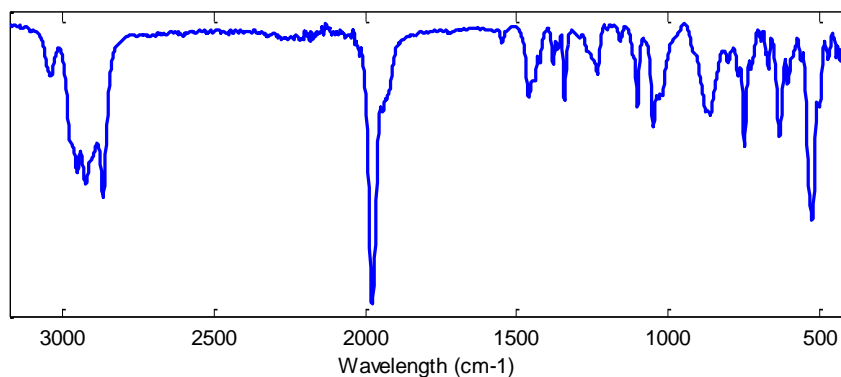


Figure S10. IR spectrum of $8\{\text{Na}(\text{THF})_x\}$ (thin film deposited from THF).

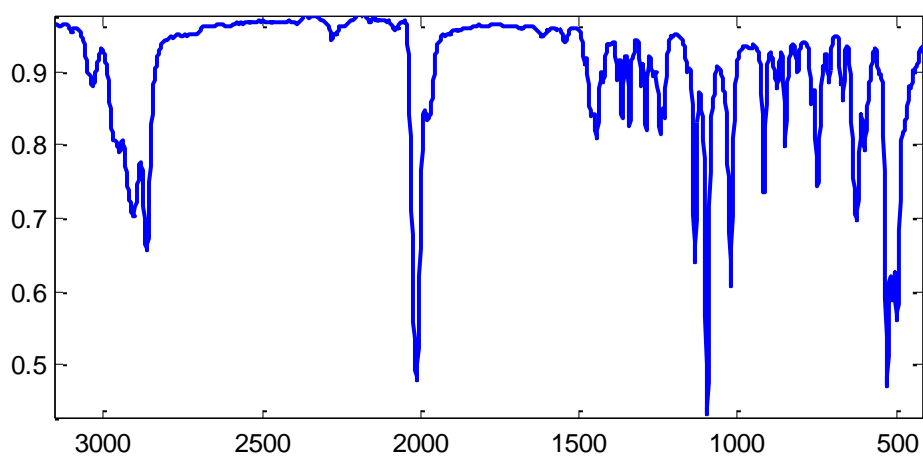


Figure S11. IR spectrum of $8\{\text{Na}(\text{12-crown-4})_2\}$ (thin film deposited from THF).

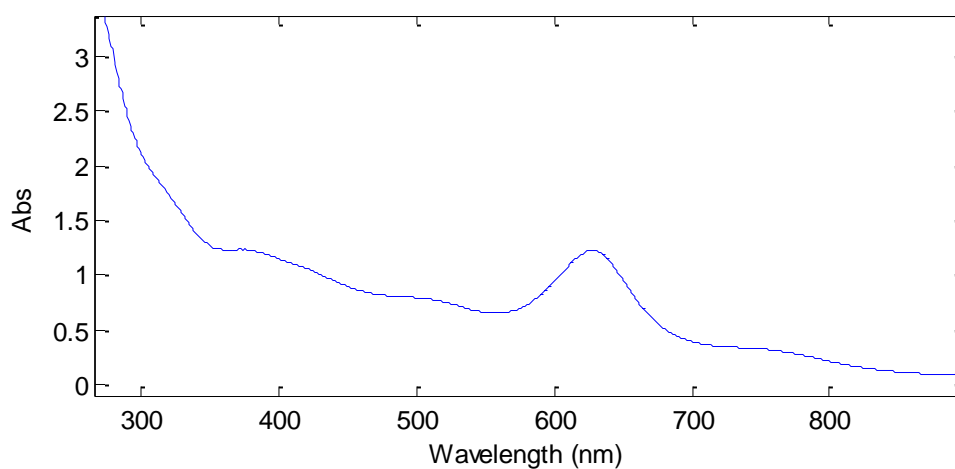


Figure S12. UV-vis spectrum of $8\{\text{Na}(\text{12-crown-4})_2\}$ (THF).

[SiP^{Pr}₂]₂Fe₂(N₂)₂ (9). Compound $8\{\text{Na}(\text{12-crown-4})_2\}$ (50 mg, 0.0338 mmol) was dissolved in THF (10 mL) and combined with ferrocenium hexafluorophosphate (12.3 mg, 0.0372 mmol) and stirred at room

temperature for 6 hours. The reaction mixture, which had turned brownish-green, was then concentrated to dryness, extracted with benzene, filtered through Celite, and concentrated. The product was recrystallized from cold diethyl ether and thoroughly washed with pentane and cold Et₂O to give **9** as a brownish-green powder (14 mg, 0.0127 mmol, 38%). Crystals suitable for X-ray diffraction were grown by evaporation of an ether solution. ¹H NMR (C₆D₆, 300 MHz, 298 K): δ 15.7, 7.8, 6.9, 6.4, 4.8, 4.0, 2.4, 1.2, -3.0, -6.7 ppm. μ_{eff} (C₆D₆, Evans method, 298 K): 2.2 μ_B. IR (thin film from benzene): ν(N-N) = 2070, 1983 cm⁻¹. UV-vis (THF, 298 K, nm {cm⁻¹ M⁻¹}): 368 {25200}, 770 {12600}, 930 {8800}. We were unable to obtain satisfactory CHN analysis on this compound, likely due to some lability of the coordinated N₂ ligand(s).

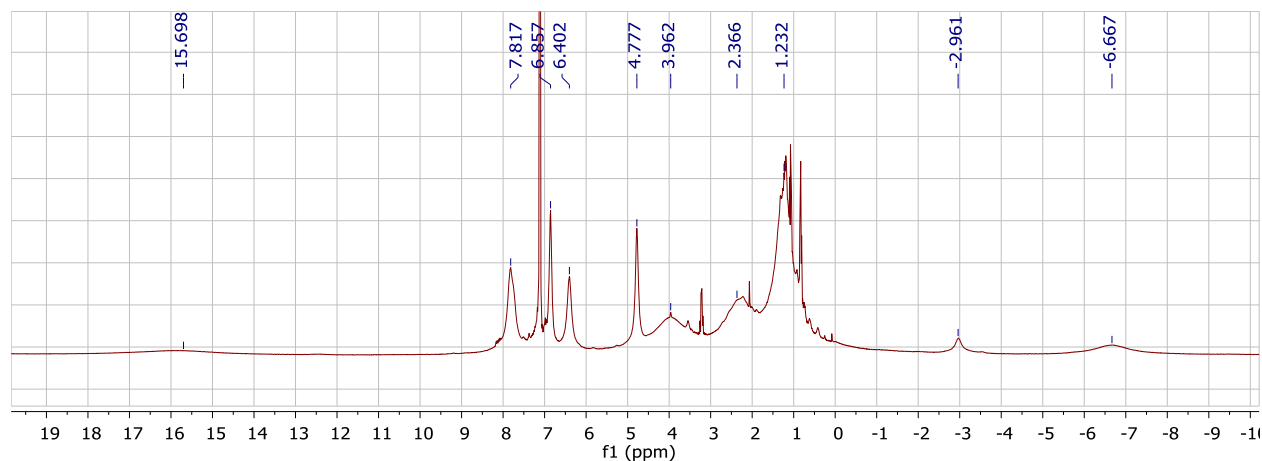


Figure S13. ¹H NMR spectrum of **9**.

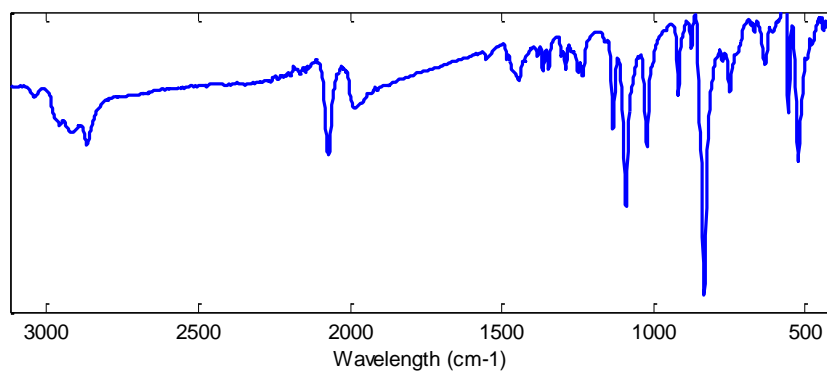


Figure S14. IR spectrum of **9** (thin film from benzene).

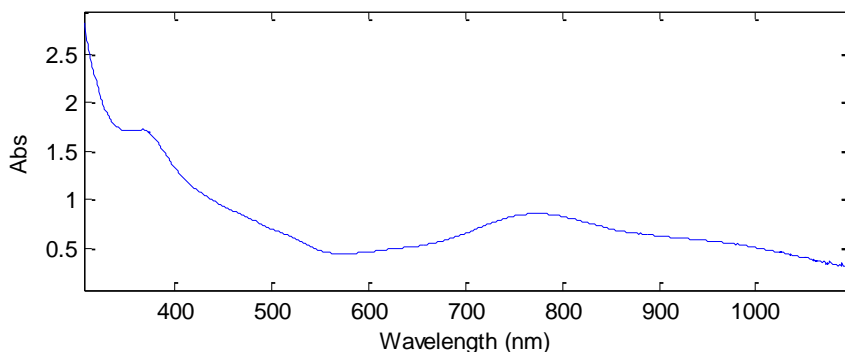


Figure S15. UV-Vis spectrum of **9** (THF).

[SiP^{Pr}]₂Fe₂(N₂)₂H (11**).** Complex **6** (334 mg, 0.288 mmol) was dissolved in benzene and stirred over excess sodium amalgam (1% Na in Hg) for four hours. The reaction is then filtered through Celite and concentrated to dryness to give **11** as an orange-brown solid residue (286 mg, 0.259 mmol, 90%). This material appeared spectroscopically pure and was used for further reactions without further purification. Single crystals suitable for x-ray diffraction were grown by evaporation of an Et₂O solution. ¹H NMR (C₆D₆, 300 MHz, 298 K): δ 8.21 (d, *J* = 7 Hz, 2H, CH_{Ar}), 8.15 (d, *J* = 7 Hz, 2H, CH_{Ar}), 8.12 (d, *J* = 7 Hz, 1H, CH_{Ar}), 7.84 (d, *J* = 7 Hz, 1H, CH_{Ar}), 7.19 (t, *J* = 8 Hz, 4H, CH_{Ar}), 7.14-6.99 (m, 8H, CH_{Ar}), 6.83 (t, *J* = 7 Hz, 1H, CH_{Ar}), 2.61 (septet, *J* = 7 Hz, 2H, -P[CH(CH₃)₂]₂), 2.26 (septet, *J* = 7 Hz, 2H, -P[CH(CH₃)₂]₂), 2.03 (m, 4H, -P[CH(CH₃)₂]₂), 1.37 (br s, 6H, -P[CH(CH₃)₂]₂), 1.15 (br s, 6H, -P[CH(CH₃)₂]₂), 0.96 (m, 18H, -P[CH(CH₃)₂]₂), 0.78 (br d, *J* = 6 Hz, 6H, -P[CH(CH₃)₂]₂), 0.66 (br s, 6H, -P[CH(CH₃)₂]₂), 0.46 (br s, 6H, -P[CH(CH₃)₂]₂) ppm. ³¹P NMR (C₆D₆, 121.4 MHz, 298 K): δ 93.7 (s), 84.2 (s) ppm. IR (thin film from benzene): ν(N-N) 2093, 2036 cm⁻¹. UV-vis (THF, 298 K, nm {cm⁻¹ M⁻¹}): 395 {13900}, 720 {2800}, 980 {15600}.

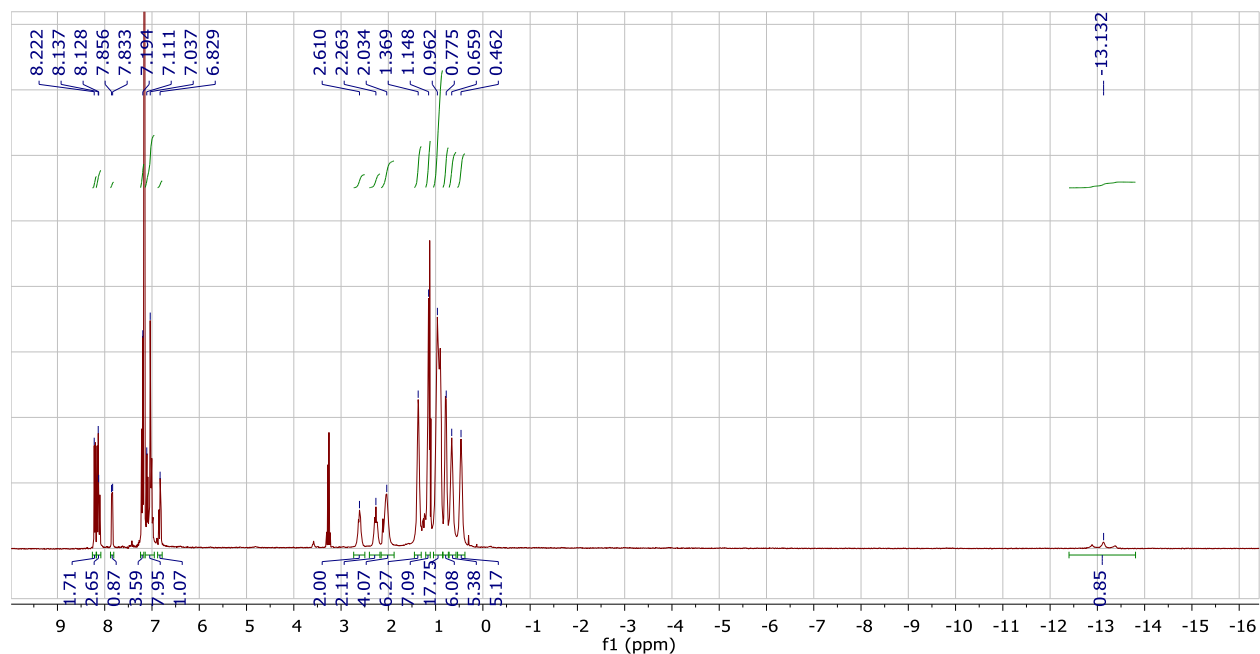


Figure S16. ¹H NMR spectrum of **11**.

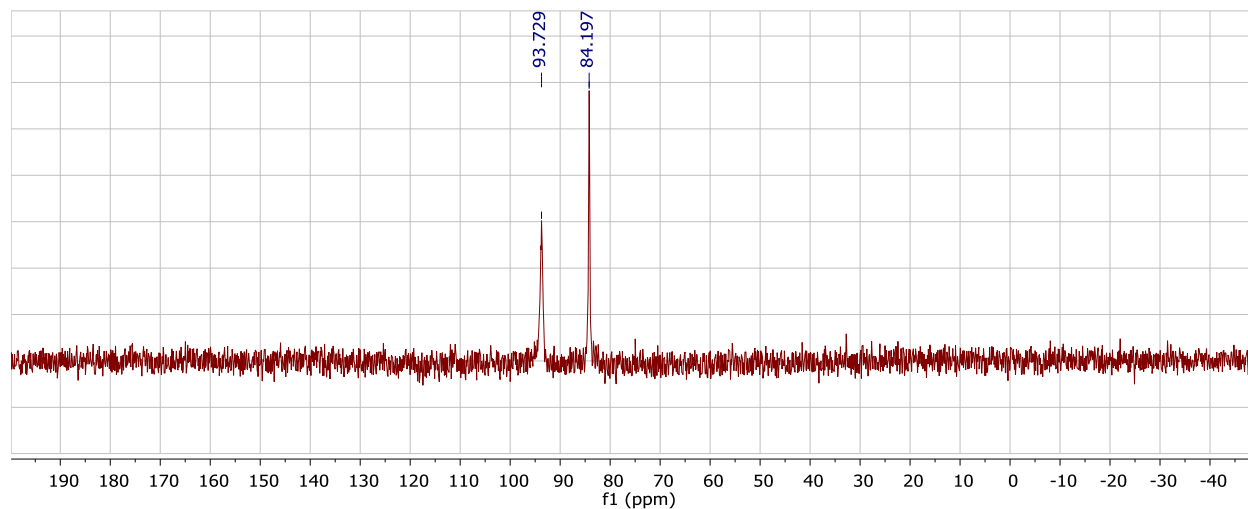


Figure S17. ^{31}P NMR spectrum of **11**.

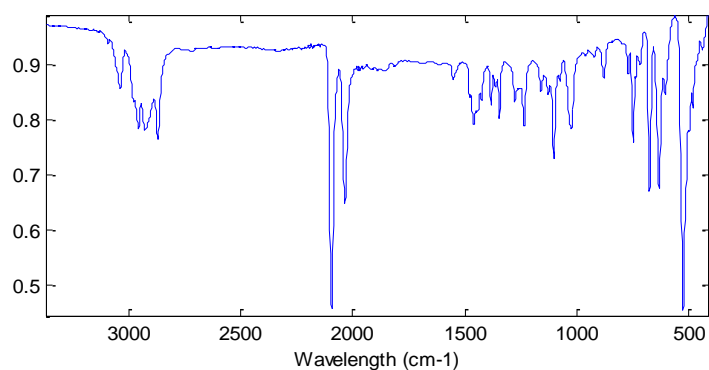


Figure S18. IR spectrum of **11** (thin film from benzene).

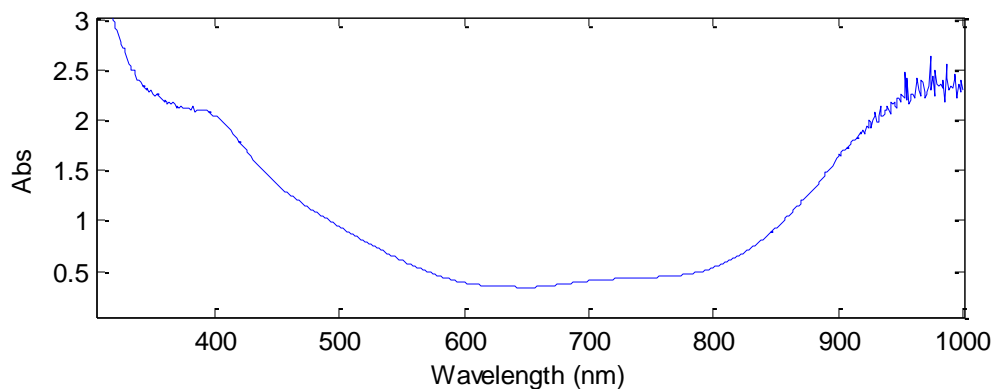


Figure S19. UV-Vis spectrum of **11** (THF).

[[SiP^{Pr}₂]₂Fe₂(N₂)₂]{BAr^F₄} (10**). **Method A:** Complex **11** (63 mg, 0.0570 mmol) was dissolved in diethyl ether (5 mL) and cooled to -35 °C. A similarly cooled solution of HBAR^F₄·2Et₂O (58 mg, 0.0572 mmol) in diethyl ether (5 mL) was then added in one portion, resulting in an immediate color change to dark blue.**

The reaction mixture was allowed to warm to room temperature, resulting in a further color change to brown. After stirring at room temperature for three hours the solution was filtered, concentrated to a volume of 2 mL, and layered with pentane (10 mL). This mixture was allowed to stand overnight resulting in the precipitation of brown solids. The supernatant was decanted and the solid residue was washed with pentane and 1:1 benzene:pentane and then dried *in vacuo*, giving **10** as a dark brown powder (82 mg, 0.0496 mmol, 87%). Single crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into an Et₂O solution. **Method B:** Complex **9** (8.9 mg, 0.0081 mmol) was dissolved in Et₂O and an ether solution of FcBAR^F₄ (8.5 mg, 0.0081 mmol) was added in one portion. After stirring for one hour at room temperature the reaction mixture was analyzed by NMR and IR, and the spectroscopic properties were consistent with those of complex **10** as synthesized by method A. ¹H NMR (5:1 C₆D₆:d₈-THF, 300 MHz, 298 K): δ 10.6, 8.8, 8.3, 8.1, 7.8, 7.6, 6.5, 6.3, 5.5, 5.1, 4.5, 2.3, 1.9, 0.6, -6.0 ppm. IR (thin film from THF): ν(N-N) 2129 cm⁻¹. UV-vis (THF, 298 K, nm {cm⁻¹ M⁻¹}): 378 {11000}, 426 {8900}, 503 {7200}, 589 {5100}. We were unable to obtain satisfactory CHN analysis on this compound, likely due to lability of the coordinated N₂ ligand(s).

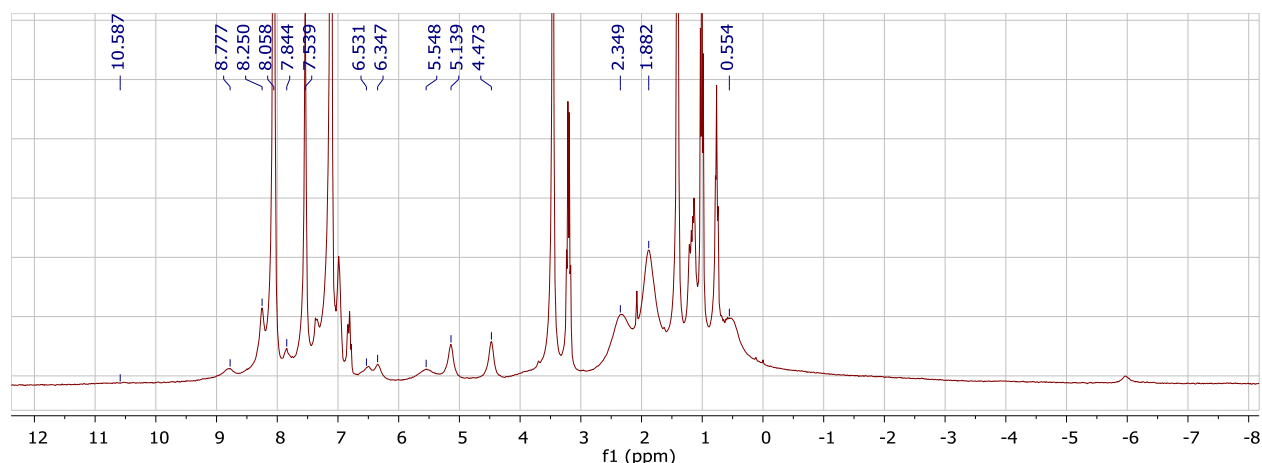


Figure S20. ¹H NMR spectrum of **10**.

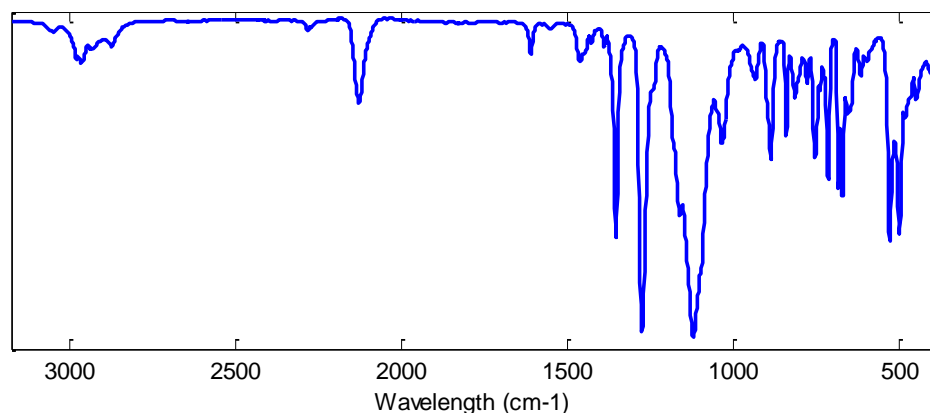


Figure S21. IR spectrum of **10** (thin film from THF).

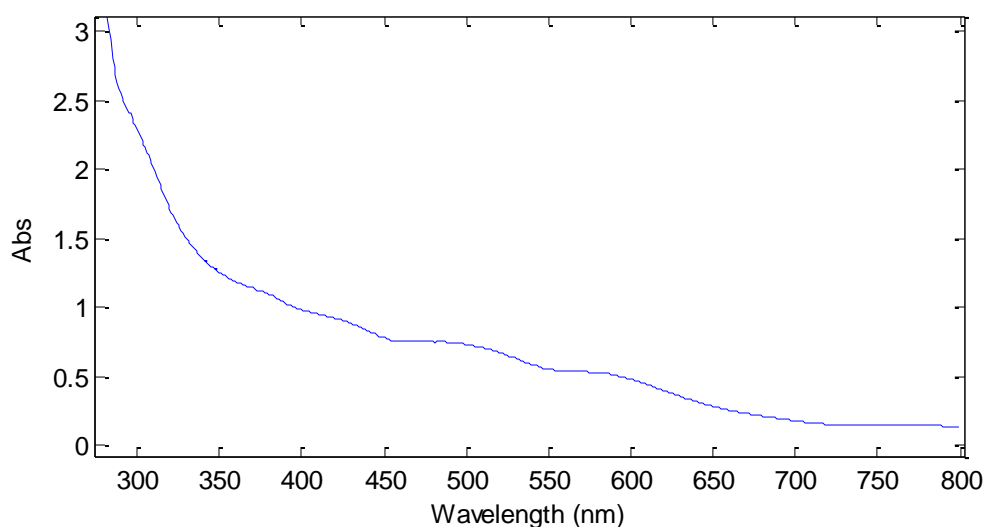


Figure S22. UV-vis spectrum of **10** (THF).

{[SiP^{Pr}₂]₂Fe₂(N₂)₂H}{Na(12-crown-4)} (12**). **Method A.** Complex **6** (120 mg, 0.104 mmol) was stirred over excess sodium amalgam (1% Na in Hg) in THF (10 mL). After stirring for 7 hours, the solution is decanted from the remaining amalgam and concentrated to dryness. The residue is extracted with diethyl ether, filtered through Celite, and concentrated to a volume of 5 mL and then layered with a solution of 12-crown-4 (39 mg, 0.22 mmol) in ether (5 mL). Brown crystals formed after sitting for several hours. The supernatant was decanted and the crystals were washed with pentane and diethyl ether and then dried *in vacuo*, giving the desired product **12** (110 mg, 0.0743, 71%). Single crystals suitable for x-ray diffraction were grown by dissolving **12** in 2:1 Et₂O:THF and allowing pentane vapors to diffuse in slowly. **Method B.** Complex **11** (50 mg, 0.0452 mmol) was stirred over excess sodium amalgam in THF (5 mL). Workup and purification were carried out as for method A and the spectroscopic parameters of the isolated product were identical. ¹H NMR (1:1 C₆D₆:d₈-THF, 300 MHz, 298 K): δ 11.2, 8.2, 7.8, 7.6, 7.1, 6.6, 4.7, 3.4, 2.8, 1.2, 0.7 ppm. μ_{eff} (d₈-THF, Evans method, 298 K): 2.2 μ_B. IR (thin film from THF): ν(N-N) 2044, 1981 cm⁻¹; ν(Fe-H) 1881 cm⁻¹. Anal. Calcd. for **12**·THF, C₇₄H₁₁₅Fe₂N₄NaO₉P₄SSi₂: C, 57.29; H, 7.47; N, 3.61. Found: C, 57.59; H, 7.56; N, 3.43. UV-vis (THF, 298 K, nm {cm⁻¹ M⁻¹): 367 {3300}, 504 {1800}, 631 {900}.**

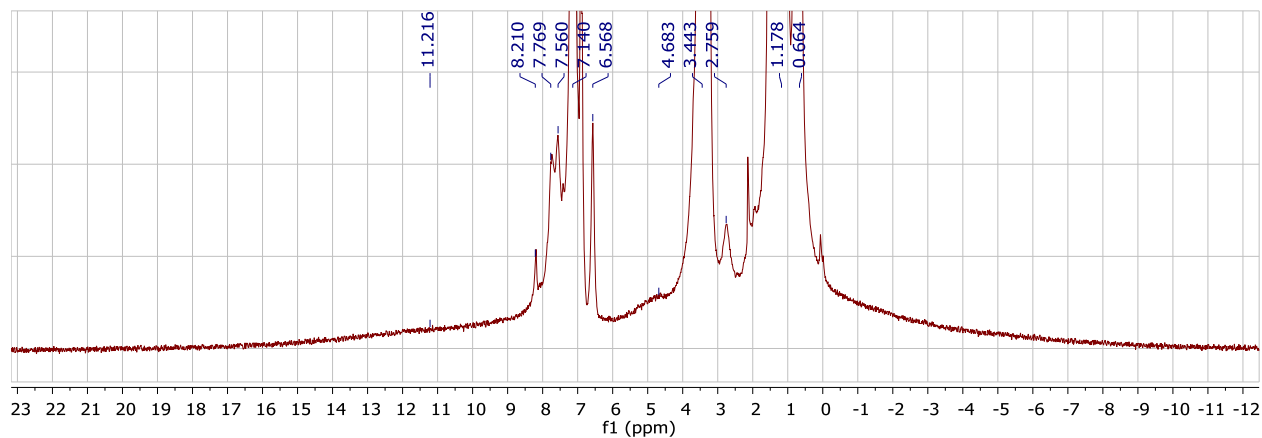


Figure S23. ^1H NMR spectrum of **12**.

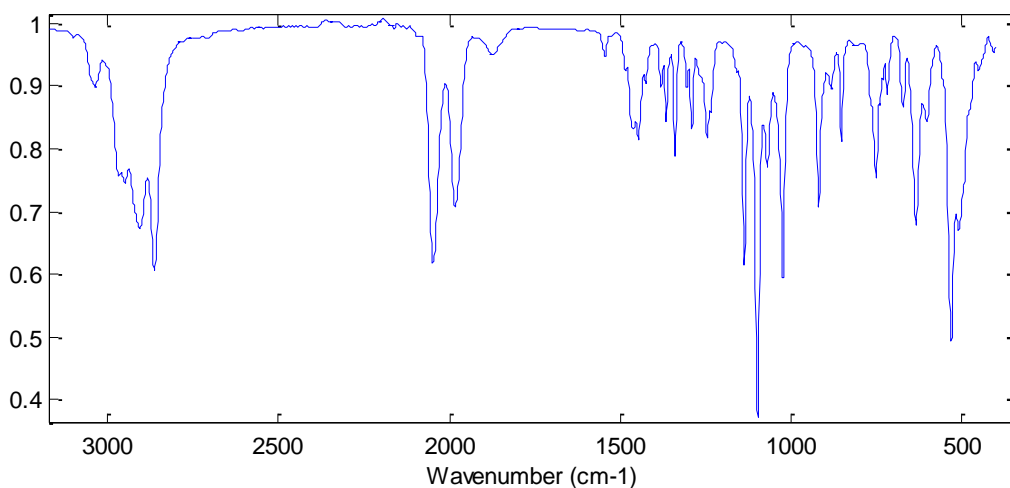


Figure S24. IR spectrum of **12** (thin film from THF).

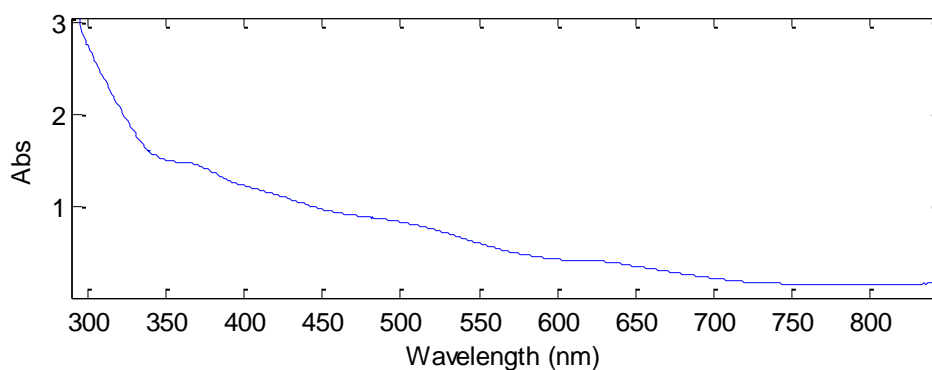


Figure S25. UV-Vis spectrum of **12** (THF).

[SiP^{Pr}₂]₂Fe₂(μ -O₂CH) (13**).** Complex **11** (32.2 mg, 0.029 mmol) was dissolved in benzene (5 mL). The orange-brown solution was freeze-pump-thawed three times and then exposed to CO₂ (1 atm). The color rapidly changed to bright red and was stirred for one hour at room temperature. The reaction

mixture was lyophilized to give the desired product as a bright red powder (31.9 mg, 0.029 mmol, quant.). Single crystals suitable for x-ray diffraction were grown by slow evaporation of a diethyl ether solution. $^1\text{H NMR}$ (C_6D_6 : d_8 , 300 MHz, 298 K): δ 36.6, 25.1, 9.9, 7.9, 7.4, 3.5, 2.4, 1.9, -0.7, -2.1, -35.3 ppm. μ_{eff} (C_6D_6 , Evans method, 298 K): $3.2 \mu_{\text{B}}$. IR (thin film from benzene): $\nu(\text{C-O})$ 1547 cm^{-1} .

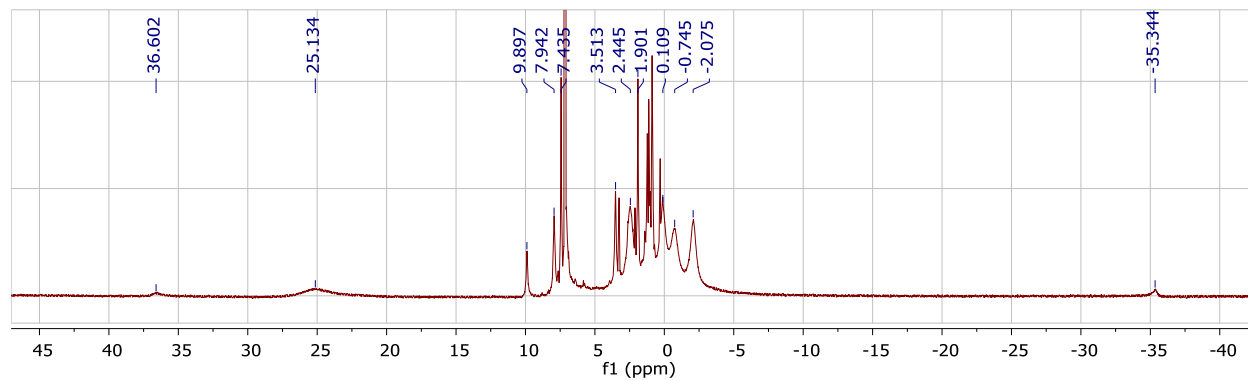


Figure S26. $^1\text{H NMR}$ spectrum of **13**.

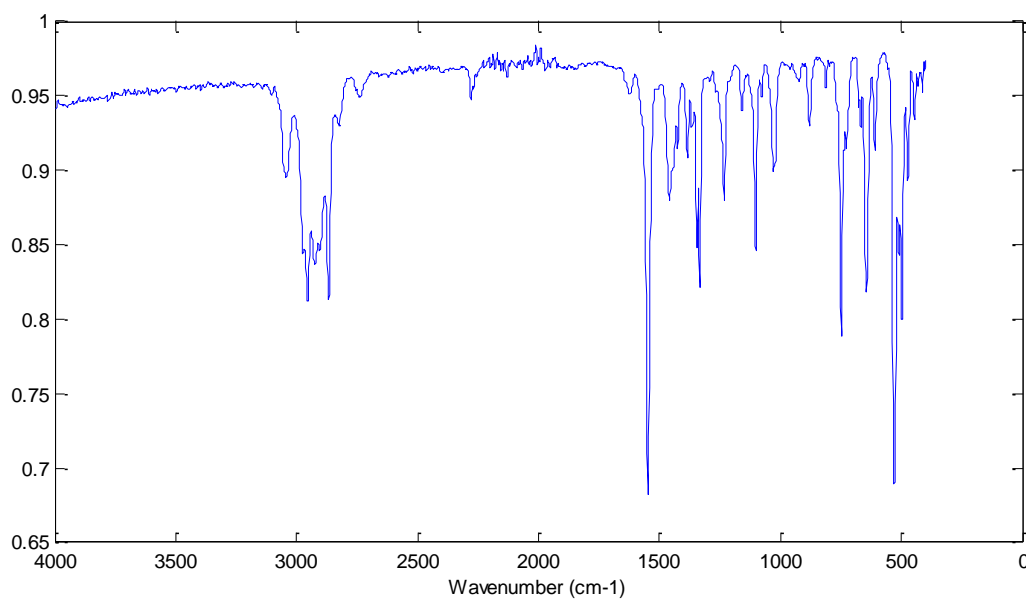


Figure S27. IR spectrum of **13** (thin film from benzene).

II. Reactivity studies

Conversion of N₂ to NH₃ by 8{Na(12-crown-4)}₂. 8{Na(12-crown-4)}₂ (1.8 mg, 0.0012 mmol) was dissolved in Et₂O (2 mL) in a Schlenk tube under an N₂ atmosphere and cooled to -78 °C. KC₈ (16 mg, 0.12 mmol) was added as a cooled suspension in Et₂O (1 mL) followed by HBAR^{F₄}·2Et₂O (100 mg, 0.10 mmol) in Et₂O. This was stirred at low temperature for two hours and then allowed to warm to room temperature for one hour. Volatiles were then vac-transferred onto an ethereal solution of HCl (4 mL, 2 M). The solid residue was treated with a solution of KO^tBu in THF and again vac transferred onto the HCl solution. The resulting ammonium chloride was analyzed by the indophenol method.⁷ This experiment was repeated twice, giving 1.5 and 2.1 equivalents of ammonia. In a separate experiment, the same conditions were used except that KC₈ was omitted from the reaction; no detectable ammonia was formed.

Conversion of N₂H₄ to NH₃ by 10. In a standard run, **10** (3.0 mg, 0.0015 mmol) was dissolved in THF (4 mL) in a Schlenk tube then a solution of N₂H₄ (2.5 mg, 0.08 mmol) and [LutH][BAR^{F₄}] (1.5 mg, 0.0015 mmol) in 4 mL THF was added and the tube was sealed and stirred at room temperature for one hour. After one hour, the volatiles were vac-transferred onto ethereal HCl (4 mL, 2M) and the resulting ammonium chloride was analyzed via the indophenol method.⁷ A table of representative conditions and results is given below; all reactions were run in THF at room temperature. While modest yields of NH₃ were sometimes achieved without added acid it was highly irreproducible. An attempted catalysis reaction was run using {[SiP^{Pr}₂S^{Ad}]FeN₂}BAR^{F₄} using the same conditions as entry **B**, and only 1.5 equivalents of NH₃ were produced.

	[10], mM	[N ₂ H ₄], mM	Equiv. N ₂ H ₄	Equiv. [LutH][BAR ^{F₄}]	Time (h)	Yield (equiv. NH ₃)
A	0.19	19	100	1	8	29
B	0.19	10	50	1	8	34
C	0.19	10	50	1	1	29
D	0	10	50	1	8	0

III. Crystallographic details

General. XRD studies were carried out at the Beckman Institute Crystallography Facility on either a Bruker Kappa Apex II diffractometer or a Bruker D8 Venture Kappa Duo Photon 100 CMOS instrument (Mo K α radiation). Structures were solved using SHELXS and refined against F² on all data by full-matrix least-squares with SHELXL.⁸ In some cases the OLEX program suites was used as well.⁹ The crystals were mounted on a wire loop or glass fiber under paratone oil. Methyl group hydrogen atoms not involved in disorder were placed at calculated positions starting from the point of maximum electron density. All other hydrogen atoms, except where otherwise noted, were placed at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of the hydrogen atoms were fixed at 1.2 (1.5 for methyl groups) times the U_{eq} of the atoms to which they are bonded. 1,2- and 1,3-rigid bond restraints were applied to all non-hydrogen atoms.

{[SiP^{Pr}₂]₂Fe₂Cl₂}{PPN} (7). The asymmetric unit of **7** contains two anions and two PPN cations in addition to nine benzene molecules. Ten reflections with large error/esd values were omitted from the refinement. A twin law (-1 0 0 0 1 0 0 0 -1) was applied (BASF = 0.00873). Three isopropyl groups were refined as disordered over two positions in 47:53, 43:57, and 27:73 ratios. Two benzene solvent molecules were refined as disordered in 47:53 and 35:65 ratios. EADP constraints and ISOR restraints were used to aid in the refinement of the disordered groups.

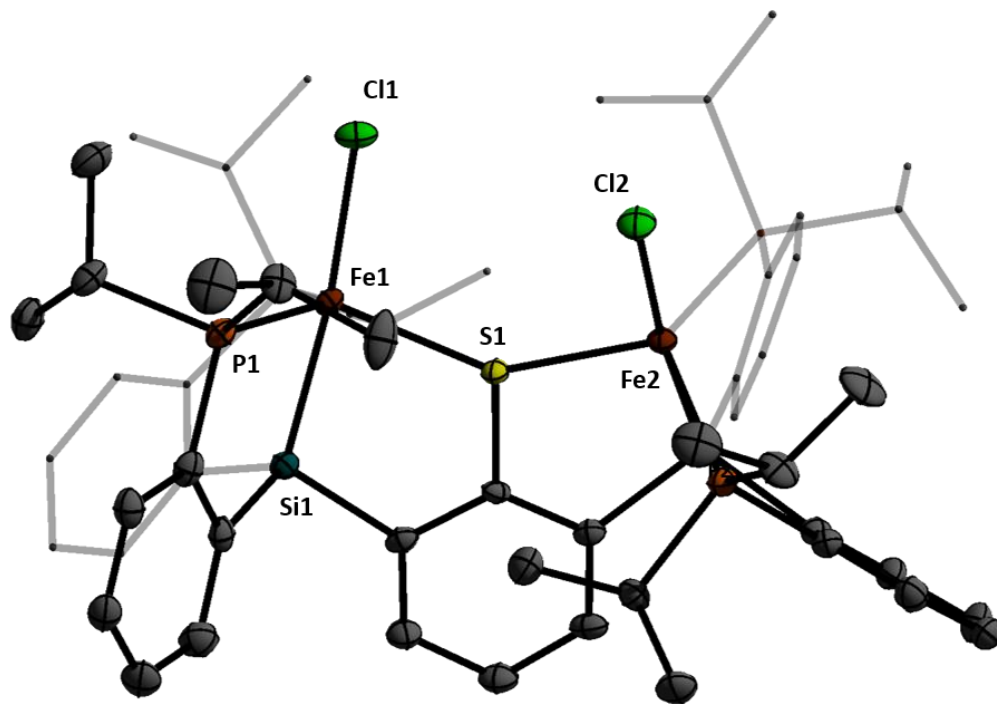


Figure S28. Structure of **7** with counteranion and solvent molecules omitted. One of two equivalent anions in the asymmetric unit shown. Ellipsoids at 50% and hydrogen atoms omitted.

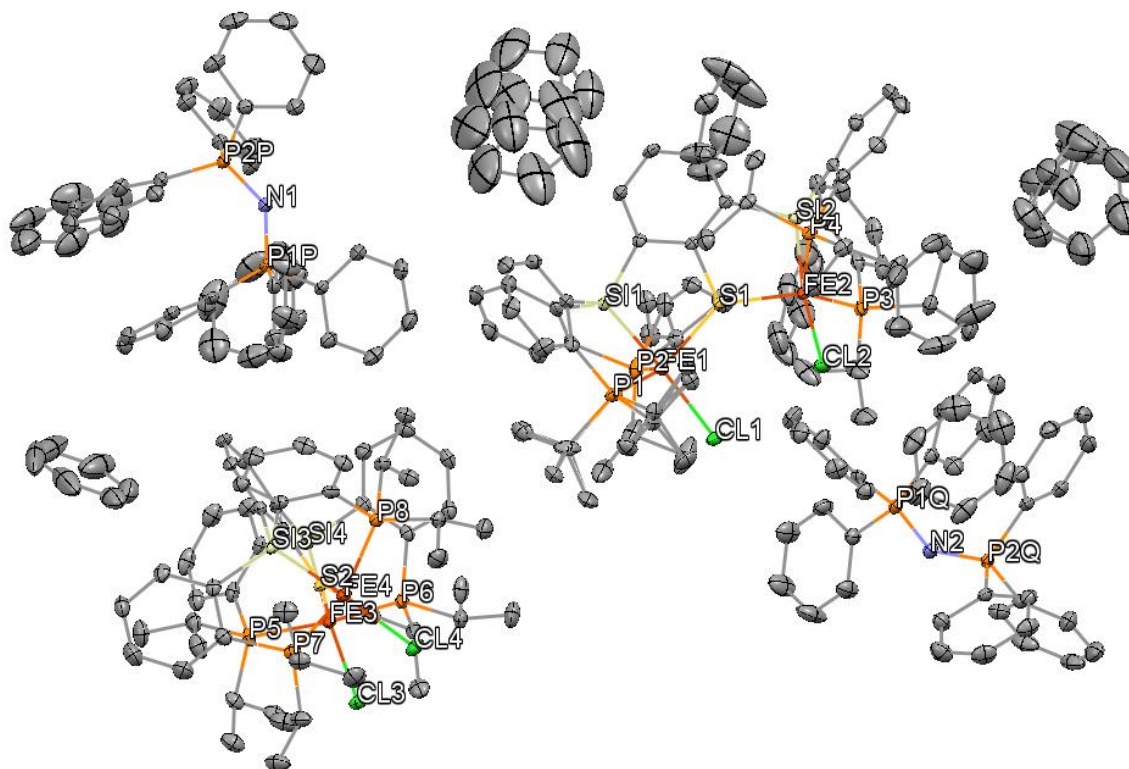


Figure S29. Full asymmetric unit of **7** including solvent and disordered components. Hydrogen atoms omitted; thermal ellipsoids at 50%.

$\{[\text{SiP}^{\text{Pr}}_2]_2\text{Fe}_2(\text{N}_2)_2\}\{\text{Na}(\text{12-crown-4})_2\} (8\{\text{Na}(\text{12-crown-4})_2\})$. One of the 12-crown-4 moieties was modeled as disordered in an 83:17 ratio. ISOR restraints and EADP constraints were used to aid in modeling the disorder. Some solvent was present which could not be modeled explicitly; the Olex program suite was used to determine the solvent-accessible voids and apply a solvent mask for refinement. One void was located with a volume of 443.3 \AA^3 containing 137.2 electrons, consistent with four solvent molecules in the unit cell (two per asymmetric unit) which could be THF, Et_2O or pentane based on the crystallization conditions.

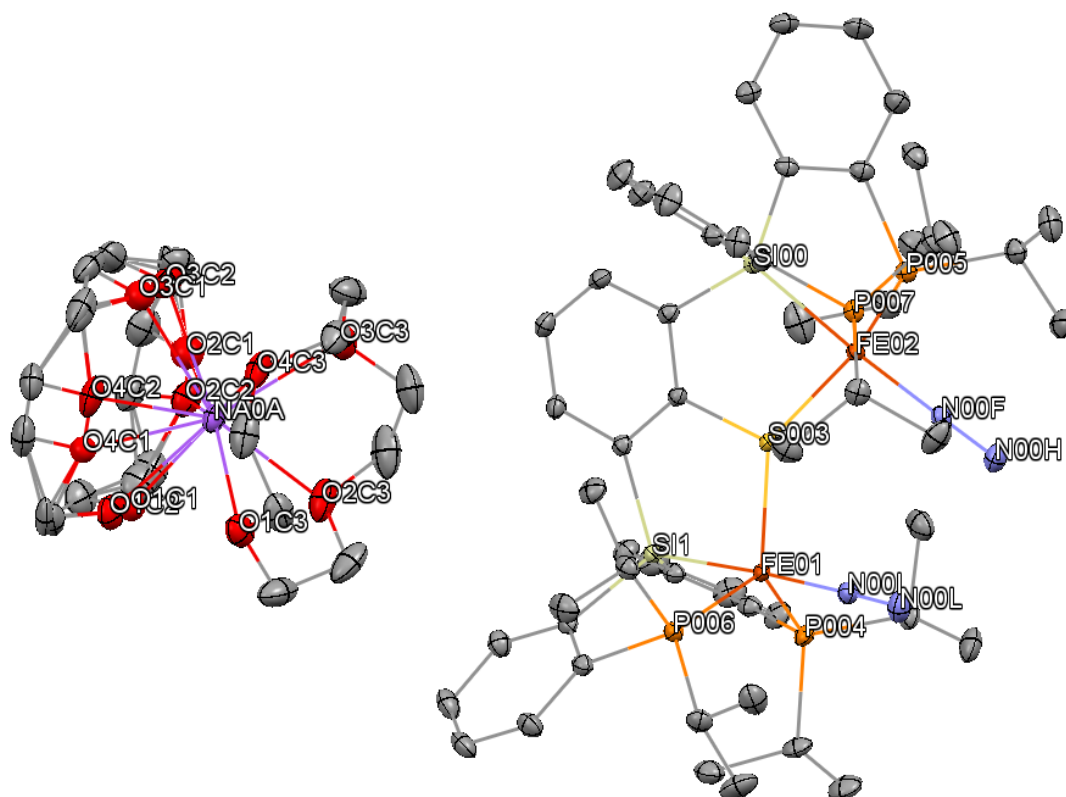


Figure S30. Full asymmetric unit of $8\{\text{Na}(12\text{-crown-}4)\}_2$ including disordered components. Hydrogen atoms omitted and thermal ellipsoids shown at 50%.

$[\text{Si}^{\text{Pr}}_2]_2\text{Fe}_2(\text{N}_2)_2$ (9). This structure was modeled with partial occupancy of chloride (15%) in lieu of N_2 in the apical sites on iron. C_2 symmetry is crystallographically enforced with half of the molecule in the asymmetric unit.

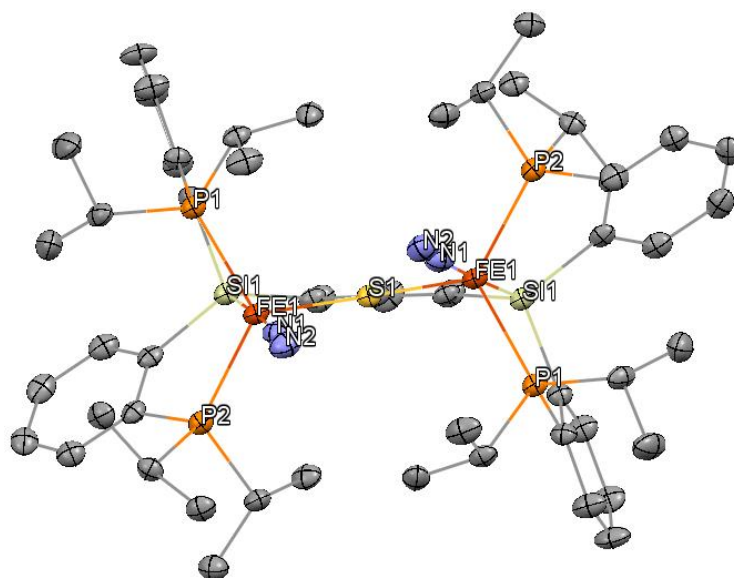


Figure S31. Structure of **9**, top view. Partial occupancy by chloride not shown. Only half the molecule (bisected along the C-C-S axis) is present in the asymmetric unit and the other half is symmetry-generated. Hydrogen atoms are omitted and thermal ellipsoids are shown at 50%.

{[SiP^{Pr}₂]₂Fe₂(N₂)₂}{BAr^F₄} (**10**). Two isopropyl groups (51:49 and 52:48 ratios) and two ligand aryl groups (51:49 and 46:54 ratios) were modeled as disordered over two positions; one of the phosphorus atoms was also modeled as disordered over two positions (51:49 ratio). In the BAr^F₄ anion, one CF₃ group was modeled as disordered over two positions (40:60 ratio), but still gives B-level cifcheck alerts due to large ADP max/min ratios. Some solvent was present which could not be modeled explicitly; the Olex program suite was used to determine the solvent-accessible voids and apply a solvent mask for refinement. One void was located with a volume of 533.8 Å³ containing 128.2 electrons, consistent with four solvent molecules in the unit cell (two per asymmetric unit) which could be Et₂O or pentane based on the crystallization conditions.

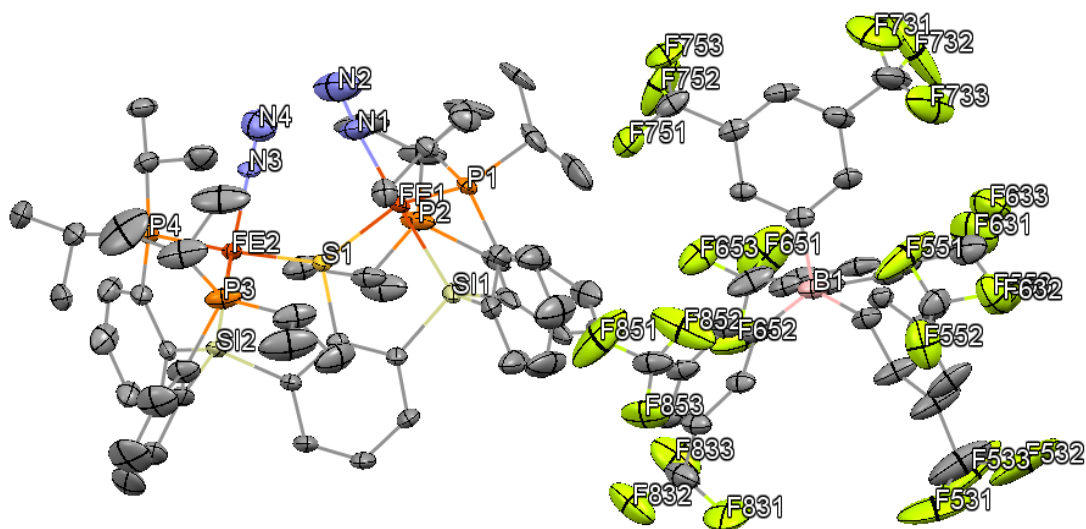


Figure S32. Structure of **10**; hydrogen atoms and minor disorder components omitted. Thermal ellipsoids at 50% probability.

Table S1. Crystal data for **7**, **8**{Na(12-crown-4)}₂, **9**, and **10**

	7	8 {Na(12-crown-4)} ₂	9	10
Formula	2[C ₅₄ H ₇₅ C ₁₂ Fe ₂ P ₄ SSi ₂] 2[C ₃₆ H ₃₀ NP ₂] 9[C ₆ H ₆]	[C ₅₄ H ₇₅ Fe ₂ N ₄ P ₄ SSi ₂] [C ₁₆ H ₃₂ NaO ₈]	C ₅₄ H ₇₅ Fe ₂ N ₄ P ₄ SSi ₂	[C ₅₄ H ₇₅ Fe ₂ N ₄ P ₄ SSi ₂] [C ₃₂ H ₁₂ BF ₂₄]
FW	4017.80	1479.46	1104.2	1920.11
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	Cc	P-1	C2/c	P-1
<i>a</i> (Å)	46.201(6)	13.3999(6)	12.2749(8)	16.5053(10)
<i>b</i> (Å)	14.4217(17)	15.4526(7)	18.9396(10)	16.6824(10)
<i>c</i> (Å)	35.447(4)	21.3794(9)	20.7859(11)	18.8438(11)
α (deg)	90	72.636(2)	90	73.269(2)
β (deg)	114.858(3)	73.491(3)	104.011(2)	77.147(2)
γ (deg)	90	77.740(3)	90	88.109(2)
Z	4	2	4	2
V (Å ³)	21430(4)	4011.4(3)	5452.5(5)	4841.8(5)
Indep. Reflections	63912	24597	7370	29598
R(int)	0.084	0.059	0.073	0.162
R1	0.0461	0.0325	0.0566	0.0789
wR2	0.0943	0.0827	0.1115	0.1942
GOF	1.01	1.05	1.06	0.99

[SiP^{Pr}₂]₂Fe₂(N₂)₂(H) (**11**). This structure lies on a crystallographic 2-fold axis of symmetry with half the molecule in the asymmetric unit. The hydride could not be located explicitly and inferring its location

based on the geometry of the iron centers is complicated by the crystallographic symmetry which convolutes the two chemically inequivalent iron centers. Indeed, this species is crystallographically isostructural to **9**. However, spectroscopic studies (IR, NMR, Mossbauer, CV) on crystalline material and crystallographic analysis of multiple crystals from multiple samples of each, as well as distinct colors, preclude them being chemically identical.

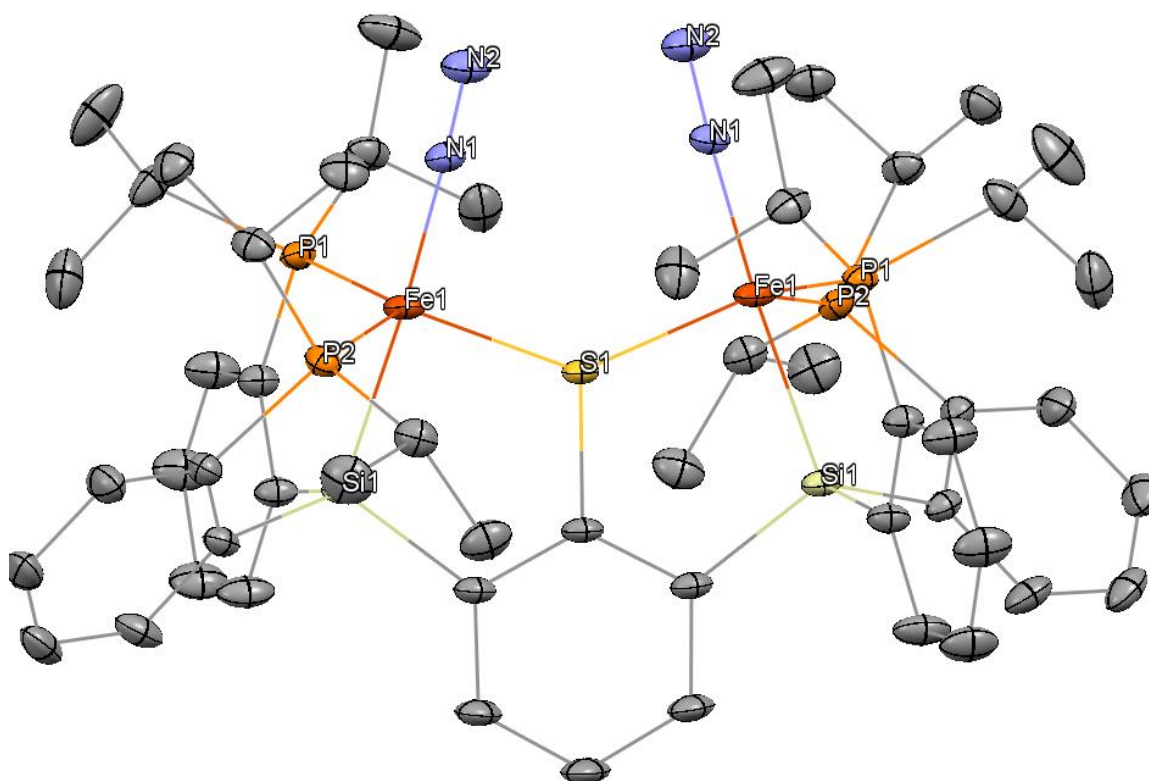


Figure S33. Structure of **11**; hydrogen atoms omitted and thermal ellipsoids shown at 50% probability.

$[\text{SiP}^{\text{Pr}}_2]_2\text{Fe}_2(\text{N}_2)_2(\text{H})\{\text{Na}(\text{12-crown-4})_2\}$ (12**).** This structure includes a $\text{Na}(\text{12-crown-4})_2$ moiety which is half on two different special positions in the unit cell (overall one per asymmetric unit). Each fragment is disordered over the special position (PART -1 refinement). All the 12-crown-4 moieties were refined only isotropically and without hydrogen atoms. Twelve reflections were omitted from the refinement due to high errors/esd. Three isopropyl groups were modeled as disordered over two positions in 70:30, 71:29, and 59:41 ratios. ISOR restraints and EADP constraints were used to aid in the refinement of disordered groups. Some solvent was present which could not be modeled explicitly; the Olex program suite was used to determine the solvent-accessible voids and apply a solvent mask for refinement. One void was located with a volume of 833.3 \AA^3 containing 21.8 electrons, consistent with one solvent molecule in the unit cell (0.5 per asymmetric unit) which could be THF, Et_2O or pentane based on the crystallization conditions.

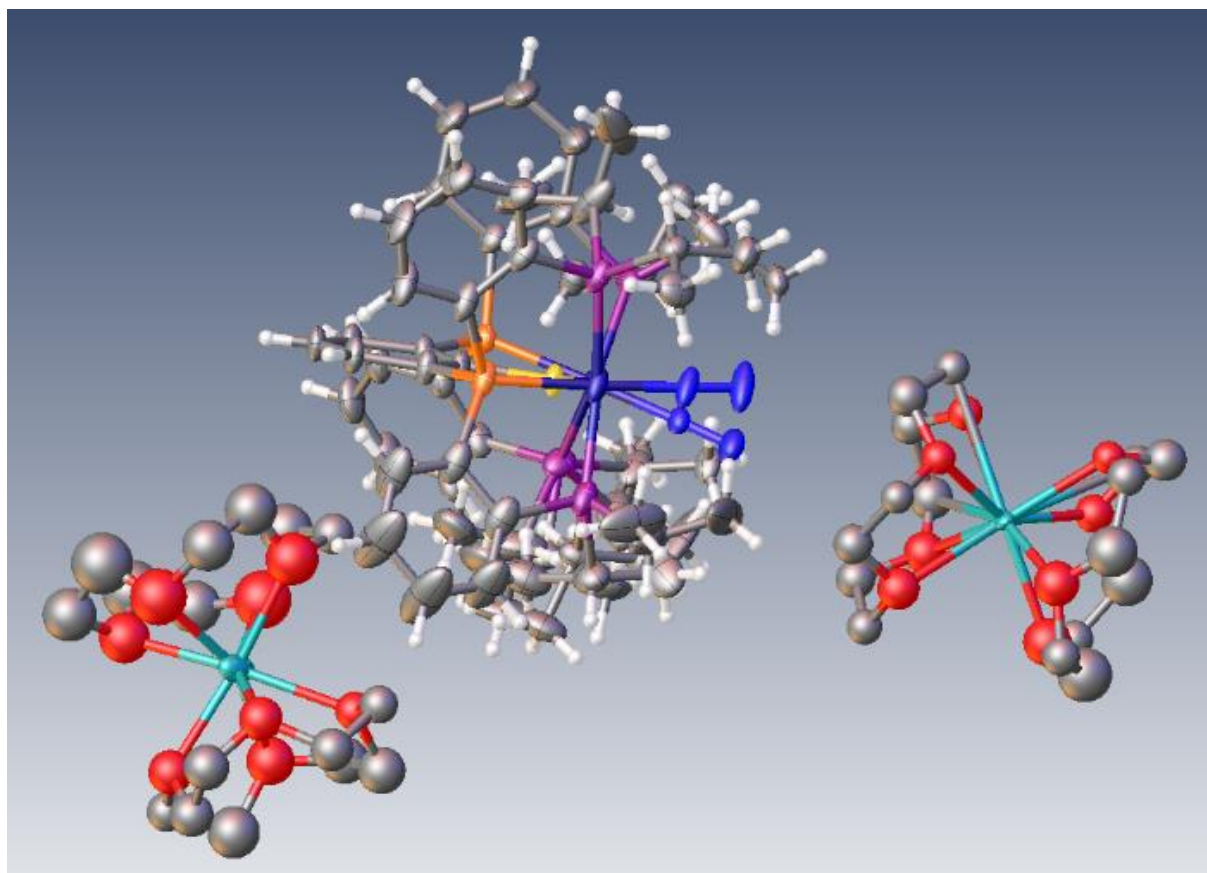


Figure S34. Structure of **12**, showing full asymmetric unit. Both half-occupied $\text{Na}(\text{12-crown-4})_2$ moieties are on special positions. Thermal ellipsoids are shown at 50%.

$[\text{Si}^{\text{Pr}}]_2\text{Fe}_2(\mu\text{-O}_2\text{CH})$ (13**).** The position of the hydrogen atom bound to the formate carbon was allowed to refine freely. Five reflections with a high error/esd (likely due to being affected by the beamstop) were omitted from the refinement. One isopropyl group was refined as disordered over two positions in a 61:39 ratio. ISOR restraints and EADP constraints were used in the refinement of this disordered group. In spite of attempts to resolve this disorder this isopropyl group remains the source of a level B cifcheck alert for large U_{eq} (C) and U_{iso} (H).

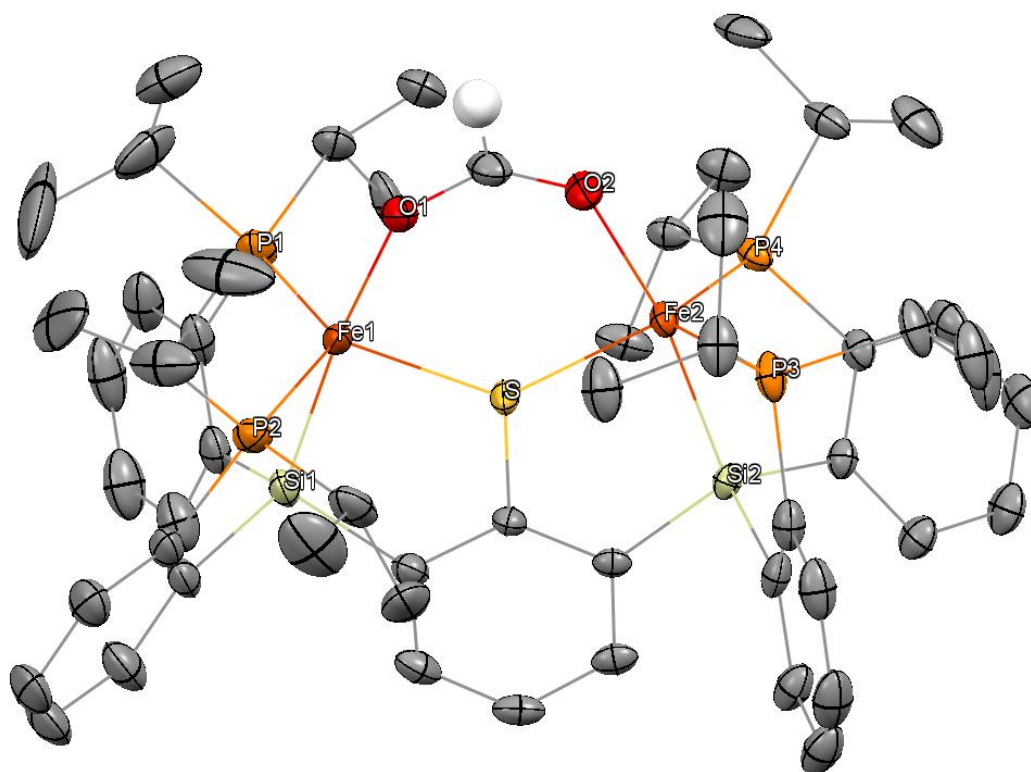


Figure S35. Crystal structure of **13** with thermal ellipsoids shown at 50% probability. The minor component of the disordered isopropyl group and hydrogen atoms other than the formate hydrogen are omitted for clarity.

Table S2. Crystal data for **11**, **12**, **13**

	11	12	13
Formula	C54H75Fe2N4P4SSi2	[C54H75Fe2N4P4SSi2] [C16NaO8]	C55H76Fe2O2P4SSi2
FW	1104.00	1479.17	1092.98
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	C2/c	P-1	P212121
<i>a</i> (Å)	14.2403(7)	14.5315(5)	13.6501(4)
<i>b</i> (Å)	18.9818(9)	14.5632(6)	19.5046(7)
<i>c</i> (Å)	20.7746(13)	23.5306(9)	20.8033(6)
α (deg)	90	80.861(1)	90
β (deg)	103.839(2)	85.585(1)	90
γ (deg)	90	61.516(1)	90
Z	4	2	4
V (Å ³)	5452.5(5)	4321.3(3)	5538.7(3)
Indep. Reflections	21626	29312	26729
R(int)	0.054	0.045	0.094
R1	0.0460	0.0806	0.0660
wR2	0.1182	0.2716	0.1368
GOF	1.08	1.15	1.01

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