SUPPLEMENTARY INFORMATION

General Considerations

Unless otherwise noted, all compounds were purchased from commercial sources and used without further purification.[(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$],[14] [(TPB)Fe][BAr$^F_4$],[15] (TPB)(μ-H)Fe(H)(N$_2$),[29] [Lutidinium][BAr$^F_4$],[31] HBAr$^F_4$ · 2 Et$_2$O,[32] [(SiP$^{iPr}_3$)Fe(N$_2$)][Na(12-crown-4)$_2$],[26] FeCl$_2$ · 1.5 THF,[33] KC$_8$,[34] [(TPB)Fe(NH$_3$)][BAr$^F_4$],[15] [(TPB)Fe(N$_2$H$_4$)][BAr$^F_4$],[15] (TPB)Fe$\equiv$N(p-C$_6$H$_4$OMe),[14] and Fe(depe)$_2$N$_2$[35] were prepared according to literature procedures ([Lutidinium] = 2,6-dimethylpyridinium, [BAr$^F_4$] = [B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$B]$^-$). All manipulations were carried out under an N$_2$ atmosphere utilizing standard glovebox or Schlenk techniques. Solvents were dried and de-oxygenated by an argon sparge followed by passage through an activated alumina column purchased from S.G. Waters Company. Labeled ^{15}N$_2$ (98% purity) was obtained from Cambridge Isotope Laboratories. Solvents for catalytic runs were additionally stirred for more than 2 hours over Na/K alloy then filtered prior to use.

IR Spectroscopy

IR spectra were obtained *via* KBr pellets on a Bio-Rad Excalibur FTS 3000 spectrometer using Varian Resolutions Pro software set at 4 cm^{-1} resolution.

NMR Spectroscopy

NMR measurements were obtained on Varian 300 MHz or 500 MHz spectrometers. Deuterated solvents for these measurements were obtained from Cambridge Isotope Laboratories and were dried and degassed prior to use. All ^{1}H NMR spectra were referenced to residual solvent peaks.

EPR Spectroscopy

EPR X-band spectra were obtained on a Bruker EMX spectrometer with the aid of Bruker Win-EPR software suite version 3.0. The spectrometer was equipped with a rectangular cavity which operated in the TE$_{102}$ mode. Temperature control was achieved with a liquid N$_2$ filled quartz dewar in which the sample was submerged during data collection.

UV-Visible Spectroscopy

UV-Visible spectra were taken on a Cary 50 spectrometer from 1100 nm to 200 nm in the fast scan mode. Samples were prepared in a 1 cm path length quartz cuvette. All samples had a blank sample background subtraction applied.

Standard Catalytic Protocol

[(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$] (2 mg, 0.002 mmol) was suspended in Et$_2$O (0.5 mL) in a 20 mL scintillation vial equipped with a stir bar. This suspension was vigorously stirred and cooled to -78 °C in a cold well inside of the glove box. A similarly cooled solution of HBAr$^F_4$ · 2 Et$_2$O (93 mg, 0.092 mmol) in Et$_2$O (1.5 mL) was added to the suspension in one portion with rapid stirring. Any remaining acid was dissolved in cold Et$_2$O (0.25 mL) and added subsequently. The reaction mixture turned light yellow-orange and homogeneous upon addition of acid and the

resulting solution was allowed to stir for 5 minutes before being transferred into a pre-cooled Schlenk tube equipped with a stir bar. The original reaction vial was washed with cold Et_2O (0.25 mL) which was subsequently transferred to the Schlenk tube. Solid KC_8 (15 mg, 0.100 mmol) was suspended in cold Et_2O (0.75 mL) and added dropwise to the rapidly stirred solution in the Schlenk tube which was then tightly sealed. The reaction was allowed to stir for 40 minutes at -78 °C before being warmed to room temperature and stirred for 15 minutes.

Ammonia Quantification

A Schlenk tube was charged with HCl (3 mL of a 2.0 M solution in Et_2O, 6 mmol). Reaction mixtures were vacuum transferred into this collection flask. Residual solid in the reaction vessel was treated with a solution of [Na][O-*t*-Bu] (40 mg, 0.4 mmol) in 1,2-dimethoxyethane (1 mL) and sealed. The resulting suspension was allowed to stir for 10 minutes before all volatiles were again vacuum transferred into the collection flask. After completion of the vacuum transfer, the flask was sealed and warmed to room temperature. Solvent was removed *in vacuo* and the remaining residue was dissolved in H_2O (1 mL). An aliquot of this solution (20 or 40 µL) was then analyzed for the presence of NH_3 (trapped as $[NH_4][Cl]$) *via* the indophenol method.[36] Quantification was performed with UV-Visible spectroscopy by analyzing the absorbance at 635 nm. The tables shown below list the raw data for the runs. Runs with small absorbance levels (< 0.02 absorbance units) suffer from a large degree of error due to a small signal-to-noise ratio. Catalytic runs that used a 40 µL aliquot are denoted with an asterisk, accounting for larger relative absorbances.

Table S1. N_2 reduction catalysis absorption data using $[(TPB)Fe(N_2)][Na(12-crown-4)_2]$.

Run	Absorbance	Equiv NH_3/Fe	% Yield based on H^+
A*	1.095	6.52	40.7
B*	1.150	6.84	42.7
C*	0.724	4.30	26.9
D*	1.105	6.58	41.1
E*	1.165	6.93	43.3
F*	1.339	7.97	49.8
G*	1.050	6.25	39.1
H*	1.428	8.49	53.1
I*	1.418	8.44	52.7
J*	1.008	6.00	37.5
L	0.608	7.24	45.2
M	0.579	6.89	43.1
N	0.640	7.62	47.6
O	0.592	7.05	44.1
P	0.616	7.33	45.8

Catalytic protocol under $^{15}N_2$

[(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$] (4 mg, 0.004 mmol) was suspended in Et$_2$O (3 mL) in a 25 mL three neck flask (ground-glass, 14/20) equipped with a stir bar. The flask was then equipped with a stopcock adaptor in the central opening, a solid addition arm containing HBAr$^F_4$ · 2 Et$_2$O (188 mg, 0.186 mmol) in one of the side openings, and an additional solid addition arm containing KC$_8$ (37 mg, 0.274 mmol) in the final opening. The apparatus was sealed, brought out of the glovebox, and connected to a high-vacuum manifold. The solution was degassed *via* four freeze-pump-thaw cycles and then allowed to thaw to -78 °C with stirring. The flask was backfilled with 1 atm $^{15}N_2$. At this point the acid was added to the solution in one portion *via* the solid addition arm. The resulting solution was allowed to stir for 5 minutes before KC$_8$ was added *via* the other solid addition arm resulting in a dark suspension. This suspension was allowed to stir for 40 minutes at -78 °C and then an additional 10 minutes at room temperature prior to the standard work-up. The presence of [^{15}NH$_4$][Cl] was verified by ^{1}H NMR spectroscopy (Figure 4 in the SI). The yield of NH$_3$ was 3.64 equiv NH$_3$/Fe as measured using the indophenol method. The NH$_3$ yield, while still showing catalysis, was lower than the average obtained by the standard protocol, presumably due to differences associated with adding the HBAr$^F_4$ · 2 Et$_2$O and KC$_8$ solids *via* the solid addition arms.

Runs with [(TPB)Fe][BAr$^F_4$] as precursor

The procedure was identical to that of the standard catalytic protocol with the changes noted. The precursor used was [(TPB)Fe][BAr$^F_4$] (2.3 mg, 0.002 mmol) which is a dark orange solid. Note that [(TPB)Fe][BAr$^F_4$] was soluble in Et$_2$O and formed a yellow solution. No substantial color change was observed upon addition of acid.

Table S2. N$_2$ reduction catalysis absorption data using [(TPB)Fe][BAr$^F_4$].

Run	Absorbance	Equiv NH$_3$/Fe	% Yield based on H$^+$
A*	1.169	6.96	43.5
B*	1.000	5.95	37.2
C*	0.911	5.42	33.9
D*	1.117	6.65	41.6

Runs with [(SiP$^{iPr}_3$)Fe(N$_2$)][Na(12-crown-4)$_2$] as precursor

The procedure was identical to that of the standard catalytic protocol with the changes noted. The precursor used was [(SiP$^{iPr}_3$)Fe(N$_2$)][Na(12-crown-4)$_2$] (2 mg, 0.002 mmol) which is a dark purple solid.

Table S3. Attempted N$_2$ reduction catalysis absorption data using [(SiP$^{iPr}_3$)Fe(N$_2$)][Na(12-crown-4)$_2$].

Run	Absorbance	Equiv NH$_3$/Fe	% Yield based on H$^+$
A*	0.203	1.21	7.5
B*	0.059	0.35	2.1
C*	0.064	0.38	2.3
D*	0.183	1.09	6.8

Runs with (TPB)(μ-H)Fe(H)(N₂) as precursor

The procedure was identical to that of the standard catalytic protocol with the changes noted. The precursor used was $(TPB)(\mu\text{-}H)Fe(H)(N_2)$ (1.3 mg, 0.002 mmol) which is a yellow solid. Note that $(TPB)(\mu\text{-}H)Fe(H)(N_2)$ was insoluble in Et_2O and did not dissolve upon addition of acid. As such, the resulting mixture was a suspension through the remaining manipulations.

Table S4. Attempted N_2 reduction catalysis absorption data using $(TPB)(\mu\text{-}H)Fe(H)(N_2)$.

Run	Absorbance	Equiv NH_3/Fe	% Yield based on H^+
A*	0.084	0.50	3.1
B*	0.072	0.43	2.7
C	0.035	0.42	2.6
D	0.055	0.65	4.1

Runs with FeCl₂ · 1.5 THF as precursor

The procedure was identical to that of the standard catalytic protocol with the changes noted. The precursor used was $FeCl_2 \cdot 1.5$ THF (0.5 mg, 0.002 mmol) which is an off white powder. Note that $FeCl_2 \cdot 1.5$ THF did not dissolve upon addition of acid. As such, the resulting mixture was a suspension through the remaining manipulations.

Table S5. Attempted N_2 reduction catalysis absorption data using $FeCl_2 \cdot 1.5$ THF.

Run	Absorbance	Equiv NH_3/Fe	% Yield based on H^+
A	0.002	0.02	0.1
B	0.011	0.13	0.8
C	0.005	0.06	0.4
D	0.007	0.08	0.5

Runs with FeCl₃ as precursor

The procedure was identical to that of the standard catalytic protocol with the changes noted. The precursor used was $FeCl_3$ (0.3 mg, 0.002 mmol) which is a dark solid. Note that $FeCl_3$ was soluble in Et_2O and formed a yellow solution. No substantial color change was observed upon addition of acid.

Table S6. Attempted N_2 reduction catalysis absorption data using $FeCl_3$.

Run	Absorbance	Equiv NH_3/Fe	% Yield based on H^+
A	-0.0021	0	0
B	-0.0002	0	0
C	0.0002	0.002	0.01
D	0.0010	0.01	0.06

Runs with Fe(CO)$_5$ as precursor

The procedure was identical to that of the standard catalytic protocol with the changes noted. The precursor used was Fe(CO)$_5$ (0.35 mg, 0.002 mmol) which is a pale yellow liquid. Note that Fe(CO)$_5$ was soluble in Et$_2$O and formed a colorless solution. No substantial color change was observed upon addition of acid.

Table S7. Attempted N$_2$ reduction catalysis absorption data using Fe(CO)$_5$.

Run	Absorbance	Equiv NH$_3$/Fe	% Yield based on H$^+$
A	0.016	0.19	1.2
B	0.003	0.04	0.2
C	0.004	0.05	0.3
D	0.006	0.07	0.4

Runs with FeCp$_2$ as precursor

The procedure was identical to that of the standard catalytic protocol with the changes noted. The precursor used was FeCp$_2$ (0.35 mg, 0.002 mmol) which is an orange solid. Note that FeCp$_2$ was soluble in Et$_2$O and formed a yellow solution. No substantial color change was observed upon addition of acid.

Table S8. Attempted N$_2$ reduction catalysis absorption data using FeCp$_2$.

Run	Absorbance	Equiv NH$_3$/Fe	% Yield based on H$^+$
A	0.007	0.08	0.5
B	0.018	0.21	1.3
C	0.027	0.32	2.0
D	0.015	0.18	1.1

Runs without an Fe precursor

The procedure was identical to that of the standard catalytic protocol with the changes noted. A 2 mL Et$_2$O solution of HBAr$^F_4$ · 2 Et$_2$O (93 mg, 0.092 mmol) was added directly into a Schlenk tube equipped with a stir bar and cooled to -78 °C. Addition of KC$_8$ and subsequent work-up was identical to the standard catalytic protocol.

Table S9. Attempted N$_2$ reduction catalysis absorption data in the absence of an Fe precursor.

Run	Absorbance	Equiv NH$_3$/Fe	% Yield based on H$^+$
A	0.015	0.18	1.1
B	0.005	0.06	0.4
C	0.006	0.07	0.4
D	0.008	0.09	0.6

Runs with [Lutidinium][BArF4] as acid

The procedure was identical to that of the standard catalytic protocol with the changes noted. The acid used was [Lutidinium][BArF4] (0.090 g, 0.092 mmol).

Table S10. Attempted N_2 reduction catalysis absorption data using [Lutidinium][BArF4] as the acid.

Run	Absorbance	Equiv NH3/Fe	% Yield based on H+
A	0.026	0.31	1.9
B	0.004	0.05	0.3
C*	0.013	0.08	0.5
D*	0.018	0.11	0.7

Runs with HCl as acid

The procedure was identical to that of the standard catalytic protocol with the changes noted. The acid used was anhydrous HCl (46 μL of a 2.0 M solution in Et2O, 0.092 mmol) which was added without further dilution. The red suspension turned light yellow upon addition of acid, and subsequently precipitated a fine yellow solid. All subsequent manipulations were carried out with this suspension.

Table S11. Attempted N_2 reduction catalysis absorption data using anhydrous HCl.

Run	Absorbance	Equiv NH3/Fe	% Yield based on H+
A	0.007	0.08	0.5
B	0.005	0.06	0.4
C	0.010	0.12	0.8
D	0.004	0.05	0.3

Runs with trifluoromethanesulfonic acid as acid

The procedure was identical to that of the standard catalytic protocol with the changes noted. The acid used was trifluoromethanesulfonic acid (131 μL of a 0.7 M solution in Et2O, 0.092 mmol) which was added without further dilution. The red suspension turned light yellow-green and homogenized upon addition of acid.

Table S12. Attempted N_2 reduction catalysis absorption data using trifluoromethanesulfonic acid.

Run	Absorbance	Equiv NH3/Fe	% Yield based on H+
A*	0.101	0.60	3.7
B*	0.069	0.41	2.6
C*	0.081	0.48	3.0
D*	0.067	0.40	2.5

Runs with K as reductant

The procedure was identical to that of the standard catalytic protocol with the changes noted. The reductant used was K metal (4 mg, 0.1 mmol) which was added as a solid. The reaction mixture was allowed to stir at -78 °C for 40 minutes and was then warmed slowly to RT overnight. After this time, a pale red-orange solution was present. Longer reaction times were employed to ameliorate the effect of the small surface area of the K metal.

Table S13. Attempted N_2 reduction catalysis absorption data using K as the reductant.

Run	Absorbance	Equiv NH_3/Fe	% Yield based on H^+
A	0.060	0.71	4.4
B	0.049	0.58	3.6
C	0.025	0.30	1.9
D	0.019	0.23	1.4

Runs with CoCp*$_2$ as reductant

The procedure was identical to that of the standard catalytic protocol with the changes noted. The reductant used was decamethylcobaltocene, CoCp*$_2$, (19 mg, 0.058 mmol) which was added as a solid. A heterogeneous mixture resulted at -78 °C that homogenized at room temperature, producing a yellow solution.

Table S14. Attempted N_2 reduction catalysis absorption data using CoCp*$_2$.

Run	Absorbance	Equiv NH_3/Fe	% Yield based on H^+
A	0.103	1.23	7.7
B	0.062	0.74	4.6
C	0.045	0.27	1.7
D	0.069	0.41	2.6

Runs with CrCp*$_2$ as reductant

The procedure was identical to that of the standard catalytic protocol with the changes noted. The reductant used was decamethylchromocene, CrCp*$_2$, (20 mg, 0.062 mmol) which was added as a solid. The resulting suspension darkened before gradually returning to a yellow color.

Table S15. Attempted N_2 reduction catalysis absorption data using CrCp*$_2$.

Run	Absorbance	Equiv NH_3/Fe	% Yield based on H^+
A	0.012	0.14	0.9
B	0.016	0.19	1.2
C*	0.022	0.13	0.8
D*	0.007	0.04	0.2

Supplemental Discussion

In addition to the standard precatalyst [(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$] and the cationic complex [(TPB)Fe][BAr$^F_4$], we examined the related TPB-containing complexes [(TPB)Fe(NH$_3$)][BAr$^F_4$][15] and [(TPB)Fe(N$_2$H$_4$)][BAr$^F_4$][15] as precatalysts for NH$_3$ production using the standard catalytic conditions. The modest attenuation in NH$_3$ yields (see below) relative to the yields when [(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$] is used as the precatalyst may reflect less than quantitative cycling of the cationic derivatives to the Fe-bound N$_2$ species.

Runs with [(TPB)Fe(NH$_3$)][BAr$^F_4$] as precursor

The procedure was identical to that of the standard catalytic protocol with the changes noted. The precursor used was [(TPB)Fe(NH$_3$)][BAr$^F_4$] (2.9 mg, 0.002 mmol) which is an orange solid . Note that the solution became homogeneous with no significant color change upon addition of acid.

Table S16. Attempted N$_2$ reduction catalysis absorption data using [(TPB)Fe(NH$_3$)][BAr$^F_4$].

Run	Absorbance	Equiv NH$_3$/Fe	% Yield based on H$^+$
A	0.475	5.65	35.3
B	0.487	5.80	36.2
C	0.493	5.87	36.7
D	0.472	5.62	35.1

Runs with [(TPB)Fe(N$_2$H$_4$)][BAr$^F_4$] as precursor

The procedure was identical to that of the standard catalytic protocol with the changes noted. The precursor used was [(TPB)Fe(N$_2$H$_4$)][BAr$^F_4$] (2.9 mg, 0.002 mmol) which is an orange solid. Note that the solution became homogeneous with no significant color change upon addition of acid.

Table S17. Attempted N$_2$ reduction catalysis absorption data using [(TPB)Fe(N$_2$H$_4$)][BAr$^F_4$].

Run	Absorbance	Equiv NH$_3$/Fe	% Yield based on H$^+$
A	0.531	6.32	39.5
B	0.417	4.96	31.0
C	0.580	6.90	43.1
D	0.441	5.25	32.8

Runs with Fe(depe)$_2$N$_2$ as precursor

The procedure was identical to that of the standard catalytic protocol with the changes noted. The precursor used was Fe(depe)$_2$N$_2$ (1 mg, 0.002 mmol), which is a dark red solid. Note that the solution became homogeneous with no significant color change upon addition of acid.

Table S18. Attempted N$_2$ reduction catalysis absorption data using Fe(depe)$_2$N$_2$.

Run	Absorbance	Equiv NH$_3$/Fe	% Yield based on H$^+$
A	0.028	0.33	2.1

B	0.057	0.67	4.2
C	0.033	0.39	2.4
D	0.021	0.25	1.6

Runs at room temperature

The procedure was identical to that of the standard catalytic protocol with the changes noted. All manipulations were performed analogously to the standard conditions at room temperature.

Table S19. Attempted N_2 reduction catalysis at room temperature absorption data.

Run	Absorbance	Equiv NH_3/Fe	% Yield based on H^+
A	0.158	1.88	11.7
B	0.130	1.55	9.7
C	0.114	1.36	8.5
D	0.045	0.54	3.4

Supplemental Discussion

Hydrazine (N_2H_4) is a possible product of the N_2 reduction catalysis described but is not detected under the standard catalytic protocol using $[(TPB)Fe(N_2)][Na(12\text{-crown-}4)_2]$ as the precatalyst. As the experiment below establishes, even if N_2H_4 is produced as an intermediate en route to NH_3 formation, it would be likely be consumed and converted to NH_3 under the standard catalysis conditions employed.

Inclusion of hydrazine in a catalytic run with [(TPB)Fe(N₂)][Na(12-crown-4)₂]

The procedure was identical to that of the standard catalytic protocol with the following changes noted. Hydrazine (0.12 µL, 0.004 mmol) was added directly to the suspension of $[(TPB)Fe(N_2)][Na(12\text{-crown-}4)_2]$ prior to subjecting the mixture to the standard catalytic protocol. No color change was observed upon addition of N_2H_4. After workup the aqueous solution was analyzed for NH_3 as described above, and also for N_2H_4 *via* a literature protocol.[37] The results obtained show most all of the N_2H_4 had been consumed, indicating that if it is produced in some amount under the standard catalytic protocol it is unlikely to be detectable. As a control experiment it was shown that N_2H_4 was not degraded to NH_3 under the standard catalytic conditions in the absence of $[(TPB)Fe(N_2)][Na(12\text{-crown-}4)_2]$.

Table S20. Absorption data for a standard catalytic run in which N_2H_4 was added prior to $[(TPB)Fe(N_2)][Na(12\text{-crown-}4)_2]$ acid and reductant.

Run	Abs. for N_2H_4	Equiv N_2H_4/Fe	Abs. for NH_3	Equiv NH_3/Fe
A	0.085	0.16	0.771	9.18
B	0.116	0.22	0.424	5.05

IR spectral analysis of addition of 2 equiv $HBAr^F_4 \cdot 2\ Et_2O$ to $[(TPB)Fe(N_2)][Na(12\text{-}crown\text{-}4)_2]$, followed by 3 equiv KC_8

A 20 mL scintillation vial was charged with a stir bar and $[(TPB)Fe(N_2)][Na(12\text{-}crown\text{-}4)_2]$ (8 mg, 0.0074 mmol). In a separate vial, $HBAr^F_4 \cdot 2\ Et_2O$ (15 mg, 0.015 mmol) was dissolved in Et_2O (1 mL). Finally, a third vial was prepared containing a suspension of potassium graphite (3 mg, 0.023 mmol) in Et_2O (1 mL). All three vials were chilled in the cold well to -70 +/- 5 °C for 30 minutes. The solution of $HBAr^F_4 \cdot 2\ Et_2O$ was quickly added to the stirring suspension of $[(TPB)Fe(N_2)][Na(12\text{-}crown\text{-}4)_2]$ with a glass pipette pre-cooled to -70 °C. Any residue of the acid was washed with pre-chilled Et_2O (0.5 mL) and transferred to the stirring solution. The resulting solution turned homogeneous. After stirring for 5 minutes, the suspension of KC_8 was added rapidly to the stirring solution. Any additional KC_8 was washed with pre-chilled Et_2O (0.5 mL) and the resulting suspension was transferred to the stirring mixture. After addition of KC_8 the solution adopted a red color. This mixture was capped and stirred at -70 °C for 40 minutes and then brought to room temperature and stirred for 10 minutes. The red color persisted upon thawing to room temperature. Graphite was removed by filtration through glass filter paper. To the red solution was added 12-crown-4 (13.1 mg, 74.3 µmol) in Et_2O (1 mL) and the resulting solution was stirred for 10 minutes. The solution was then cooled to -70 °C for 30 minutes and stirred vigorously, leading to a red precipitate. The precipitate was collected on a filter pad and the light orange filtrate was concentrated to dryness *in vacuo*. IR analysis of the precipitate (KBr pellet) showed an intense band at $\nu_{NN} = 1904\ cm^{-1}$, identical to that of authentic $[(TPB)Fe(N_2)][Na(12\text{-}crown\text{-}4)_2]$ ($\nu_{NN} = 1905\ cm^{-1}$, KBr pellet). No assignable ν_{NN} IR bands were observed for the filtrate in the window of $1700 - 2300\ cm^{-1}$. See Figure S6 of the SI.

IR and ^{31}P NMR spectral analysis of addition of 10 equiv $HBAr^F_4 \cdot 2\ Et_2O$ to $[(TPB)Fe(N_2)][Na(12\text{-}crown\text{-}4)_2]$, followed by 12 equiv KC_8

A 20 mL scintillation vial was charged with a stir bar and $[(TPB)Fe(N_2)][Na(12\text{-}crown\text{-}4)_2]$ (10.4 mg, 10.2 µmol). In a separate vial, $HBAr^F_4 \cdot 2\ Et_2O$ (103 mg, 102 µmol) was dissolved in Et_2O (1 mL). Finally, a third vial was prepared containing a suspension of potassium graphite (16.5 mg, 122 µmol) in Et_2O (1 mL). All three vials were chilled in the cold well to -70 +/- 5 °C for 30 minutes. The solution of $HBAr^F_4 \cdot 2\ Et_2O$ was quickly added to the stirring suspension of $[(TPB)Fe(N_2)][Na(12\text{-}crown\text{-}4)_2]$ with a glass pipette pre-cooled to -70 °C. Any residue of the acid was washed with pre-chilled Et_2O (0.5 mL) and transferred to the stirring solution. The resulting solution turned homogeneous. After stirring for 5 minutes, the suspension of KC_8 was added rapidly to the stirring solution. Any additional KC_8 was washed with pre-chilled Et_2O (0.5 mL) and the resulting suspension was transferred to the stirring mixture. The large amount of graphite present in the vial prevented the color of the resulting solution to be accurately discerned. This mixture was capped and stirred at -70 °C for 40 minutes and then brought to RT and stirred for 10 minutes. Graphite was removed by filtration through glass filter paper. To the resulting orange solution was added 12-crown-4 (60 mg, 340 µmol) in Et_2O (1 mL) and and a ^{31}P NMR integration standard of triphenylphosphine (11.9 mg, 45.4 µmol) in toluene (1 mL) followed by stirring for 10 minutes. The solution was then cooled to -70 °C for 30 minutes and stirred vigorously. No precipitate formed and volatiles were removed *in vacuo*. The orange powder was dissolved in THF and integration of ^{31}P NMR resonances suggest the formation of $(TPB)(\mu\text{-}H)Fe(N_2)(H)$ (3.4 µmol) in 30% yield. Solid-state IR analysis of the orange solid (KBr pellet) showed a strong, sharp band at $\nu_{NN} = 2073\ cm^{-1}$ (s), identical to that of authentic $(TPB)(\mu\text{-}$

H)Fe(N$_2$)(H). Additional broad, weak bands were observed at 1942, 1875, 1802, 1734 cm^{-1} that could not be assigned. ^{31}P{^{1}H} NMR (400 MHz, THF): 72.6, 63.1 ppm. See Figures S6 and S7 of the SI.

Reactivity of (TPB)(μ-H)Fe(N$_2$)(H) with KC$_8$

A 20 mL scintillation vial was charged with a stir bar and (TPB)(μ-H)Fe(N$_2$)(H) (11 mg, 0.016 mmol) suspended in Et$_2$O (2 mL). A separate vial was charged with KC$_8$ (2.6 mg, 0.019 mmol) suspended in Et$_2$O (2 mL). Both vials were cooled to -70 +/- 5 ^{o}C and the Fe-containing vial was stirred vigorously. The suspension of KC$_8$ was quickly transferred to the vial containing (TPB)(μ-H)Fe(N$_2$)(H) and stirred for 10 minutes at low temperature. The vial was then brought to room temperature and the brown color of KC$_8$ slowly turned to black over 1 hour. Graphite was filtered through a glass filter pad and the orange filtrate was transferred to a vial containing 12-crown-4 (21.0 mg, 119.17 μmol, 7.25 equivalents) and stirred vigorously at -70 ^{o}C for 10 minutes. No precipitate formed and the resulting orange solution was brought to room temperature and concentrated to dryness *in vacuo*. IR analysis of the residue (KBr pellet) showed a strong stretch at ν_{NN} = 2073 cm^{-1}, consistent with authentic (TPB)(μ-H)Fe(N$_2$)(H) (2073 cm^{-1}, KBr pellet). ^{1}H NMR analysis was consistent with the presence of predominately (TPB)(μ-H)Fe(N$_2$)(H) and minor amounts of unidentified paramagnetic species.

Reactivity of (TPB)(μ-H)Fe(N$_2$)(H) with HBAr$^F_4$ · 2 Et$_2$O

A 20 mL scintillation vial was charged with a stir bar and (TPB)(μ-H)Fe(N$_2$)(H) (9 mg, 0.014 mmol) suspended in Et$_2$O (2 mL). A separate vial was charged with HBAr$^F_4$ · 2 Et$_2$O (15 mg, 0.015 mmol, 1.08) suspended in Et$_2$O (2 mL). Both vials were cooled to -70 +/- 5°C and the Fe-containing vial was stirred vigorously. The solution of HBAr$^F_4$ · 2 Et$_2$O was quickly transferred to the vial containing (TPB)(μ-H)Fe(N$_2$)(H) and stirred for 10 minutes at low temperature. The vial was then brought to room temperature and no noticeable color change was observed over 1 hour. The solution was concentrated to dryness *in vacuo* and the remaining residue was analyzed with IR spectroscopy (KBr pellet) which showed a strong stretch at ν_{NN} = 2073 cm^{-1}, consistent with authentic (TPB)(μ-H)Fe(N$_2$)(H) (2073 cm^{-1}, KBr pellet). The residue was then re-dissolved in C$_6$D$_6$ and analyzed by ^{1}H NMR spectroscopy which showed (TPB)(μ-H)Fe(N$_2$)(H) with minor amounts of unidentified paramagnetic species and resonances from the BAr$^F_4$ anion. Complete consumption of (TPB)(μ-H)Fe(N$_2$)(H) to unidentified paramagnetic species was observed after 12 hours at room temperature.

Identification of [(TPB)Fe(NH$_3$)][BAr$^F_4$] from protonation of [(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$]

[(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$] (5 mg, 0.005 mmol) was dissolved in 2 mL of THF and cooled to -78 °C. This dark red solution was added dropwise to a similarly cooled 2 mL THF solution of HBAr$^F_4$ · 2 Et$_2$O (29 mg, 0.029 mmol) with stirring. The resulting yellow-orange solution was allowed to stir for 10 minutes at low temperature before being warmed to room temperature and stirred for an additional 40 minutes. 1,8-Bis(dimethylamino)naphthalene (6 mg, 0.029 mmol) was added and the solution was allowed to stir for 15 minutes with no noticeable color change. Volatiles were removed from the solution and the resulting yellow residue was taken up in THF-d_8. The presence of [(TPB)Fe(NH$_3$)][BAr$^F_4$][15] was determined by comparison of the ^{1}H NMR spectrum with that of an authentic sample prepared as recently reported.

Addtionally, a capillary insert of the previously reported (TPB)FeMe[15] in THF-d_8 was added to the NMR sample which allowed for crude measurements of the yield of [(TPB)Fe(NH$_3$)][BAr$^F_4$], a species tentatively assigned as [(TPB)Fe][BAr$^F_4$][15] and the total amount of $S = 3/2$ TPB species as roughly 30%, 50%, and 100% respectively. Note that there is likely a significant degree of error on these measurements due to the broad paramagnetic peaks used for integration. See Figure S1of the SI.

Identification of H$_2$ in standard catalytic runs

The catalytic runs were performed according to the standard procedure. Prior to the vacuum transfer of volatiles, the solutions inside of the Schlenk tubes were frozen. The ground glass joint of the Schlenk tube was then sealed with a rubber septum and the head space between the Teflon stopcock of the Schlenk tube and the septum was evacuated. This head space was left under static vacuum and the Teflon stopcock of the reaction vessel was opened after which a 10 mL aliquot of the headspace was sampled through the septa *via* a gas-tight syringe. This sample was then analyzed for hydrogen with an Agilent 7890A gas chromatograph using a thermal conductivity detector. After H$_2$ analysis, the reaction vessel was sealed and subjected to the standard analysis for NH$_3$. As some H$_2$ leakage is unavoidable by the procedure used, these values represent lower limits of the H$_2$ yield.

Table S21. Absorption and gas chromatograph integration data for standard catalytic runs.

Run	Absorbance	Equiv NH$_3$/Fe	% Yield based on H$^+$	% Yield of H$_2$
A	0.500	5.95	37.2	30
B	0.365	4.34	27.1	40

Identification of H$_2$ in runs without an Fe precursor

A Schlenk tube was charged with a stir bar and a suspension of KC$_8$ (14 mg, 0.100 mmol) in Et$_2$O (0.5 mL). The Schlenk tube was then fitted with a Teflon stopcock, but not sealed. The ground glass joint on the Schlenk tube was sealed with a rubber septum. This reaction vessel was then cooled to -78 °C. A pre-cooled solution of HBAr$^F_4$ · 2 Et$_2$O (92 mg, 0.092 mmol) in Et$_2$O (2 mL) was then syringed directly into the reaction vessel with stirring after which the vessel was rapidly sealed with its Teflon stopcock. The reaction was allowed to stir for 40 minutes at low temperature before the headspace between the Teflon valve and the septa was evacuated. After evacuation, the Teflon stopcock was opened and a 10 mL aliquot of the headspace was sampled *via* a gas tight syringe. This sample was then analyzed for hydrogen with an Agilent 7890A gas chromatograph using a thermal conductivity detector. The yield of hydrogen observed, based on proton-equivalents was 66% and 88% for each of two runs, respectively. As some H$_2$ leakage is unavoidable by the procedure used, these values represent lower limits of the H$_2$ yield.

Figure S1: ^{1}H NMR spectrum of the reaction mixture following protonation of [(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$] compared with an authentic sample of [(TPB)Fe(NH$_3$)][BAr$^F_4$]
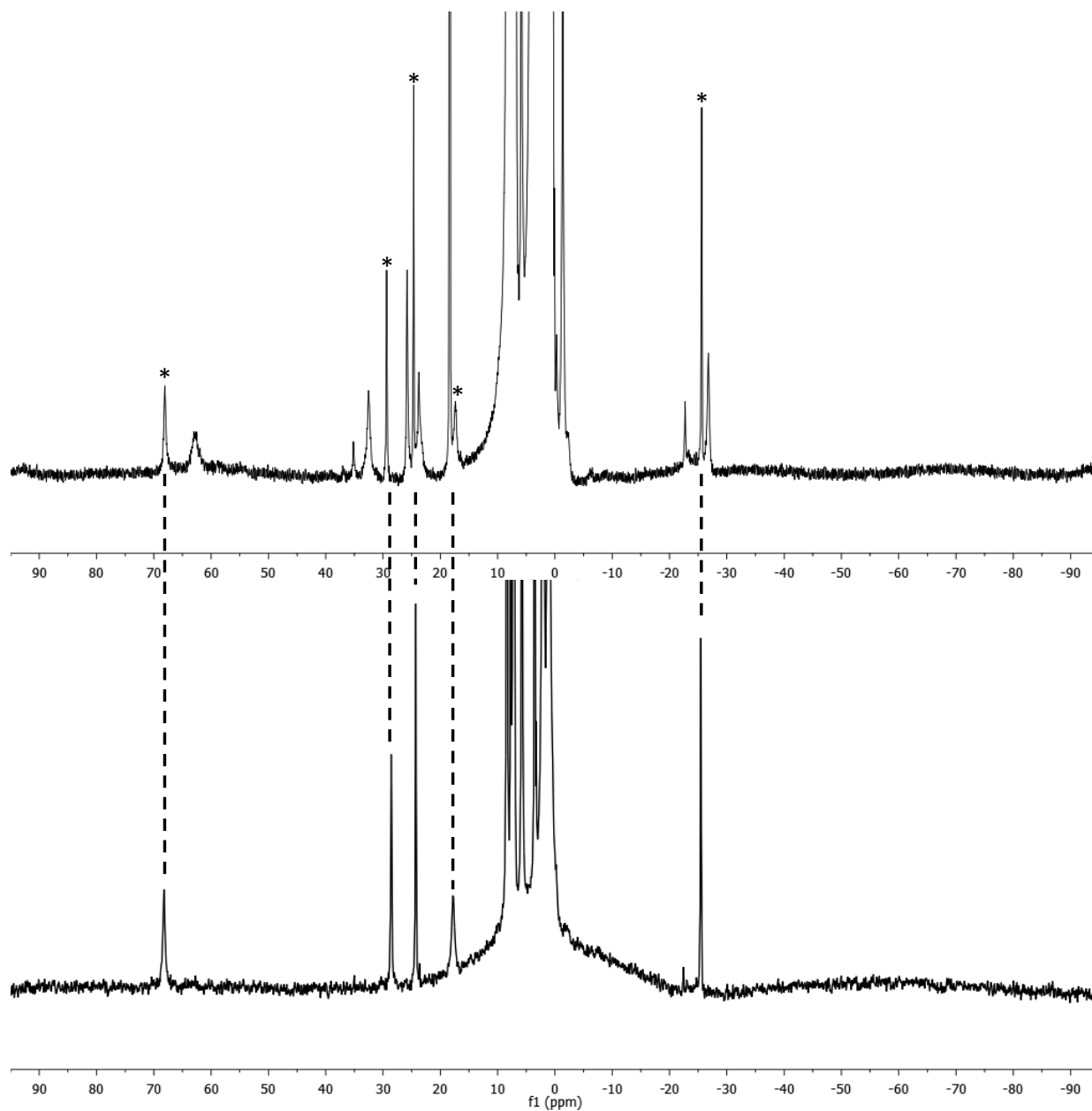
Top: reaction mixture

Bottom: authentic [(TPB)Fe(NH$_3$)][BAr$^F_4$]

Conditions: THF-d_8, 300 MHz

Figure S2: Stacked EPR at 77 K spectra of [(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$], the yellow species generated upon addition of acid to [(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$], and the green-yellow species generated from (TPB)Fe≡N(p-C$_6$H$_4$OMe) and [Fc][BAr$^F_4$]
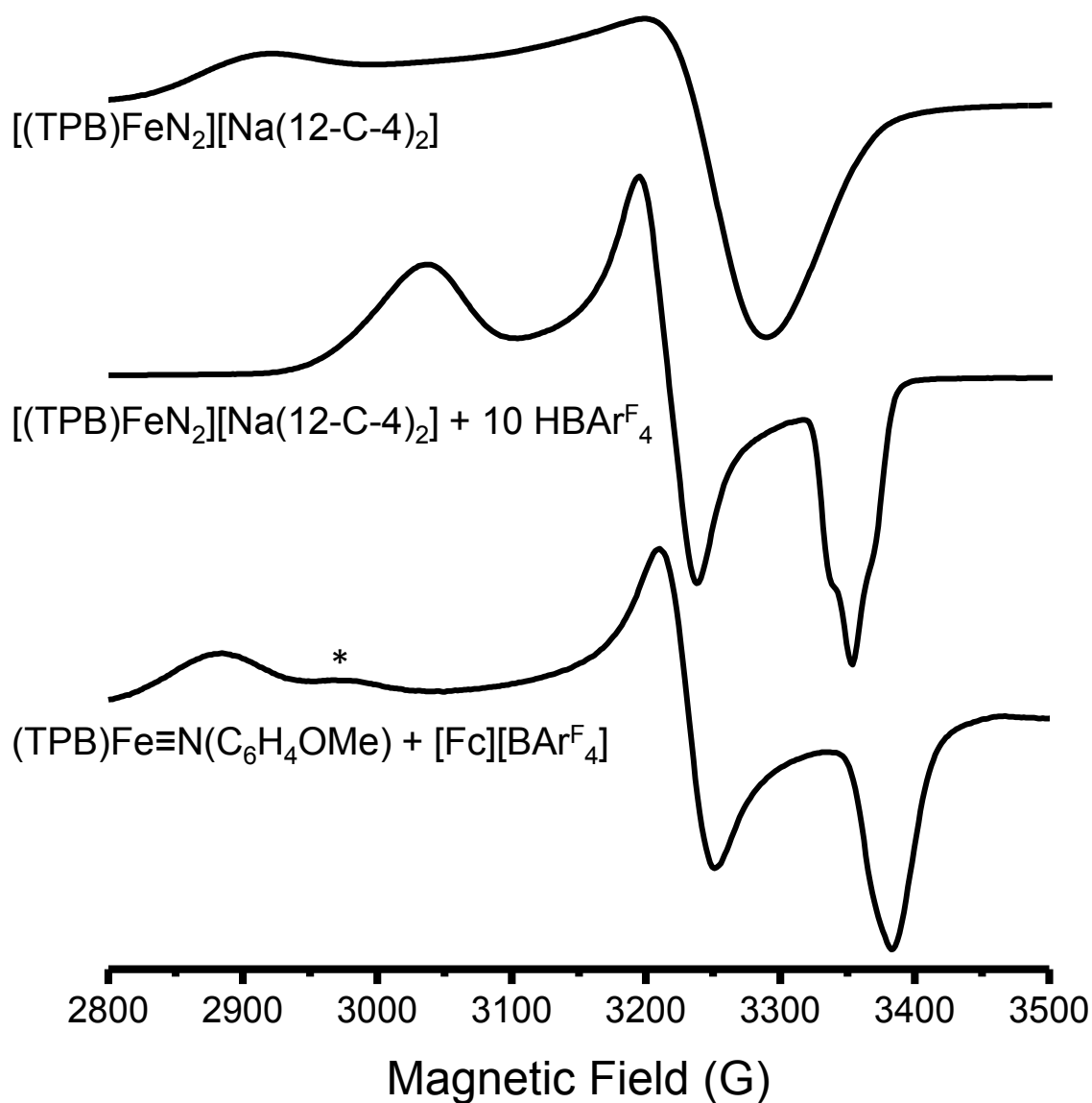
Conditions: 77 K, 2-MeTHF, Freq = 9.4 GHz, Power = 2.05 mW

The middle spectrum was generated by dissolving [(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$] (4 mg, 0.004 mmol) in 250 μL of 2-MeTHF to generate a deep red solution. This solution was then transferred to an EPR tube and frozen within a liquid N$_2$ cooled cold well. Another 250 μL 2-MeTHF solution of HBAr$^F_4$ · 2 Et$_2$O (38 mg, 0.037 mmol) was prepared and carefully layered onto the frozen solution of [(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$] in the EPR tube. The layered solutions were then frozen. At this time, the solutions were warmed until barely thawing (-140 °C) and mechanically mixed with a long needle. Upon mixing, the red color of [(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$] disappeared and a yellow solution was obtained. The solution was frozen and the EPR spectrum shown was obtained at 77 K. Immediately prior to obtaining this spectrum, a spectrum of a sample of [(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$] (4 mg, 0.004 mmol) in 500 μL of 2-MeTHF was obtained under identical conditions. Both spectra were then doubly integrated and compared to obtain an integrated yield for the formation of the new $S = 1/2$ species shown in the figure. Repetition of this experiment in triplicate provided an average yield of ~90%.

The bottom spectrum was generated by dissolving (TPB)Fe≡N(p-C$_6$H$_4$OMe)[14] (3 mg, 0.004 mmol) in 250 μL of 2-MeTHF. This solution was then cooled to -78 °C and then mixed with a similarly cooled 250 μL solution of [Fc][BAr$^F_4$] (Fc = ferrocenium) (4 mg, 0.004 mmol) with rapid stirring. Upon mixing the dark blue color of [Fc][BAr$^F_4$] disappeared and the dark green color of (TPB)Fe≡N(p-C$_6$H$_4$OMe) lightened slightly to green-yellow. The solution was allowed to stir for an additional 10 minutes then transferred to a quartz EPR tube and frozen. The EPR spectrum shown was obtained at 77 K. Note that the asterisk denotes a signal of an unknown $S = 1/2$ component of the product mixture.
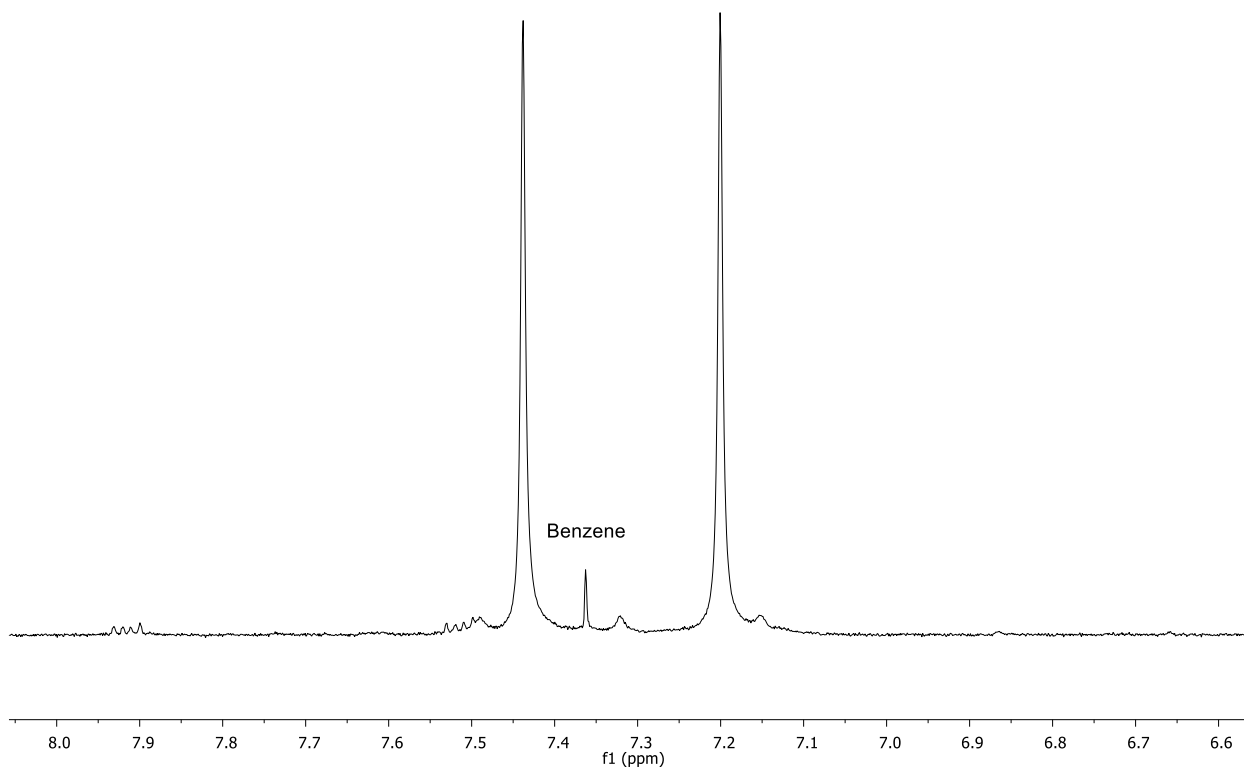
Figure S3: ^{1}H NMR spectrum of [^{14}NH$_4$][Cl] produced from [(TPB)Fe(N$_2$)][Na(12-crown-4)$_2$], HBAr$^F_4$ · 2 Et$_2$O, and KC$_8$ under ^{14}N$_2$
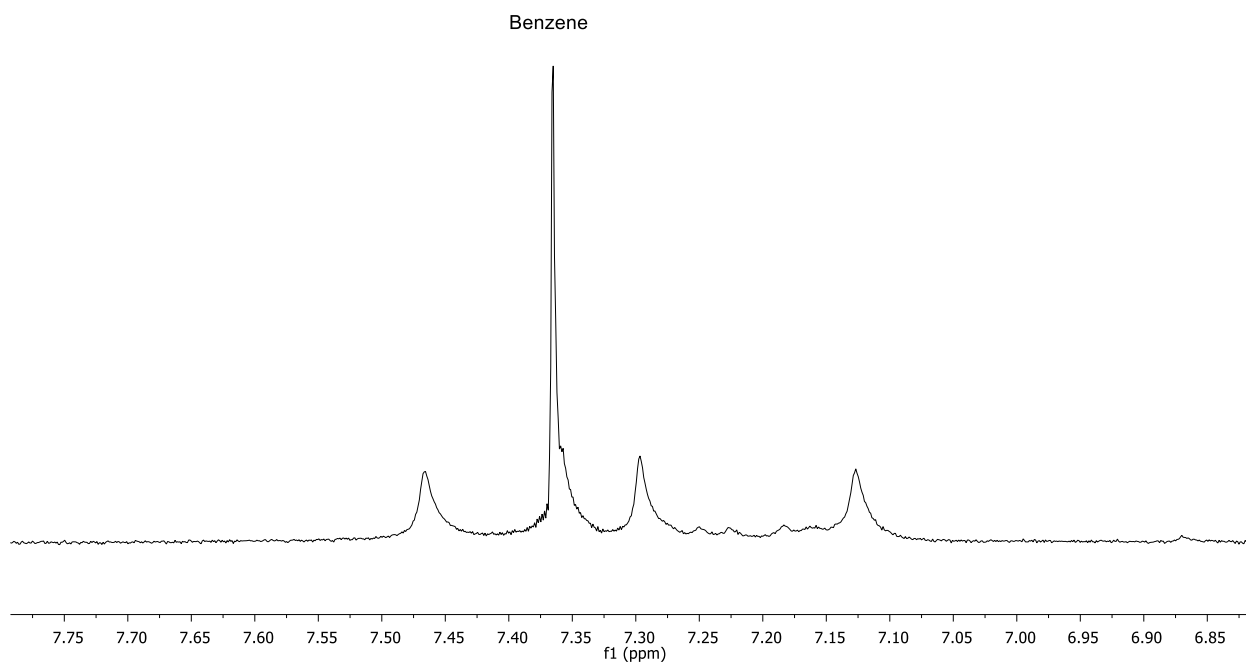
Conditions: DMSO-d$_6$, 300 MHz.

$^1J_{N-H}$ = 51 Hz.

Figure S4: ^{1}H NMR spectrum of $[^{15}NH_4][Cl]$ produced from $[(TPB)Fe(N_2)][Na(12\text{-crown-}4)_2]$, $HBAr^F_4 \cdot 2\ Et_2O$, and KC_8 under $^{15}N_2$

Benzene

Conditions: DMSO-d_6, 300 MHz

Note that a small amount of $[^{14}NH_4][Cl]$ is observed as the small triplet centered at the same chemical shift as that of $[^{15}NH_4][Cl]$. $^1J_{N\text{-}H}$ = 71 Hz.

Figure S5: Calibration Curves for NH_3 and N_2H_4 UV-Vis quantification
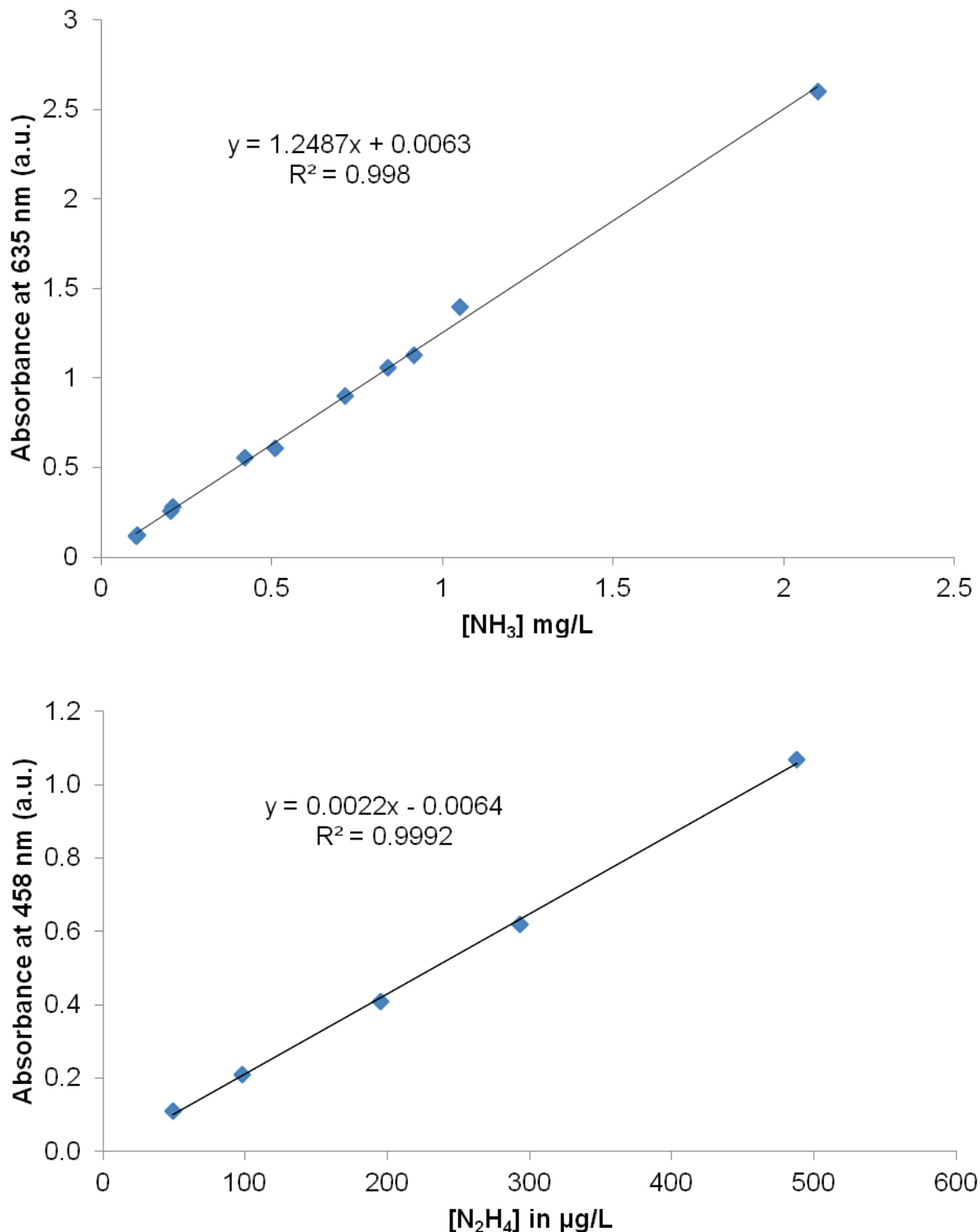
Curves were generated by creating solutions of $[NH_4][Cl]$ and $[N_2H_5][HSO_4]$ of known concentrations and then analyzing by the aforementioned literature procedures by UV-Vis spectroscopy.[36]

Figure S6: IR spectra of addition of 10 equiv $HBAr^F_4 \cdot 2\ Et_2O$ to $[(TPB)Fe(N_2)][Na(12\text{-crown-}4)_2]$, followed by 12 equiv KC_8
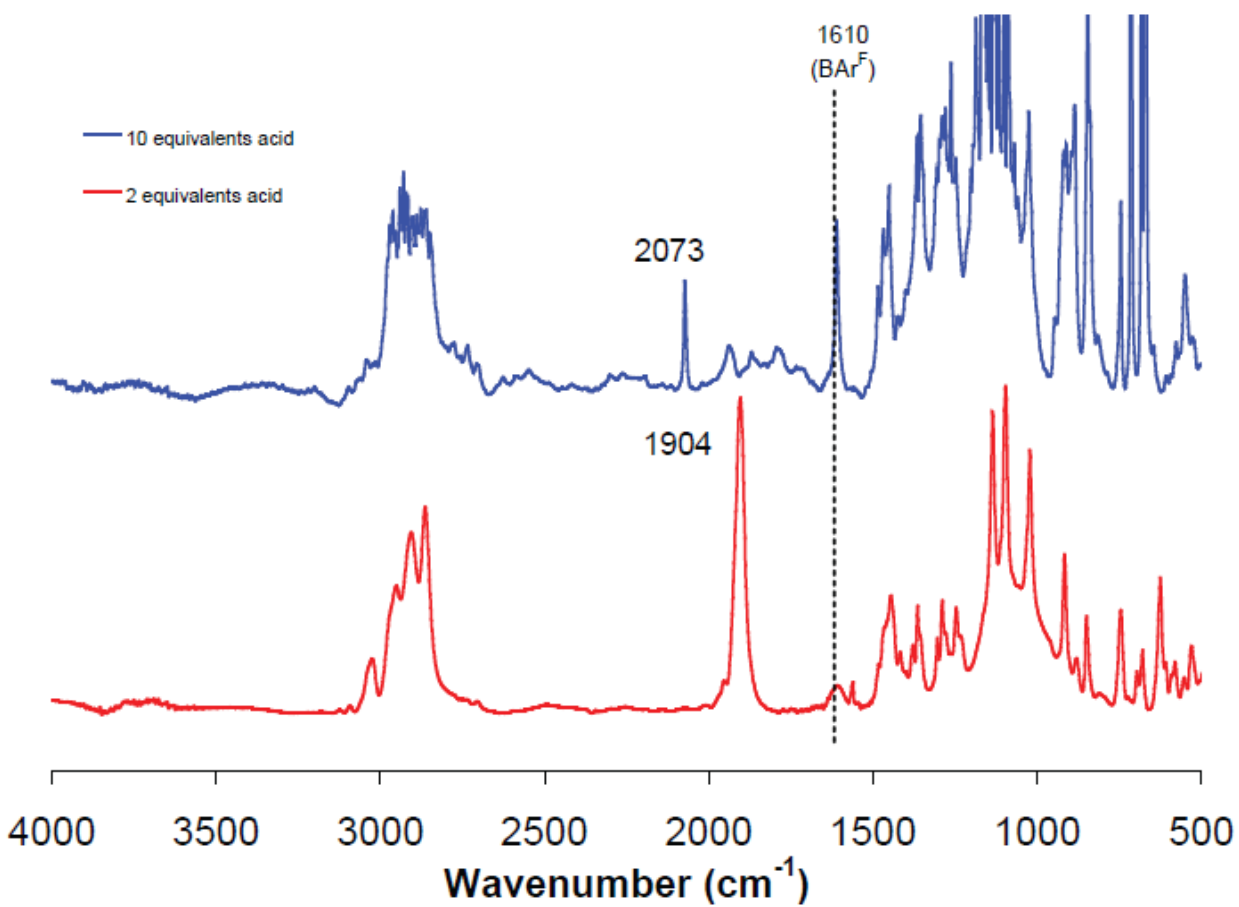
Figure S7: $^{31}P\{^{1}H\}$ NMR spectra of addition of 10 equiv $HBAr^{F}_{4} \cdot 2\ Et_{2}O$ to $[(TPB)Fe(N_2)][Na(12-crown-4)_2]$, followed by 12 equiv KC_8
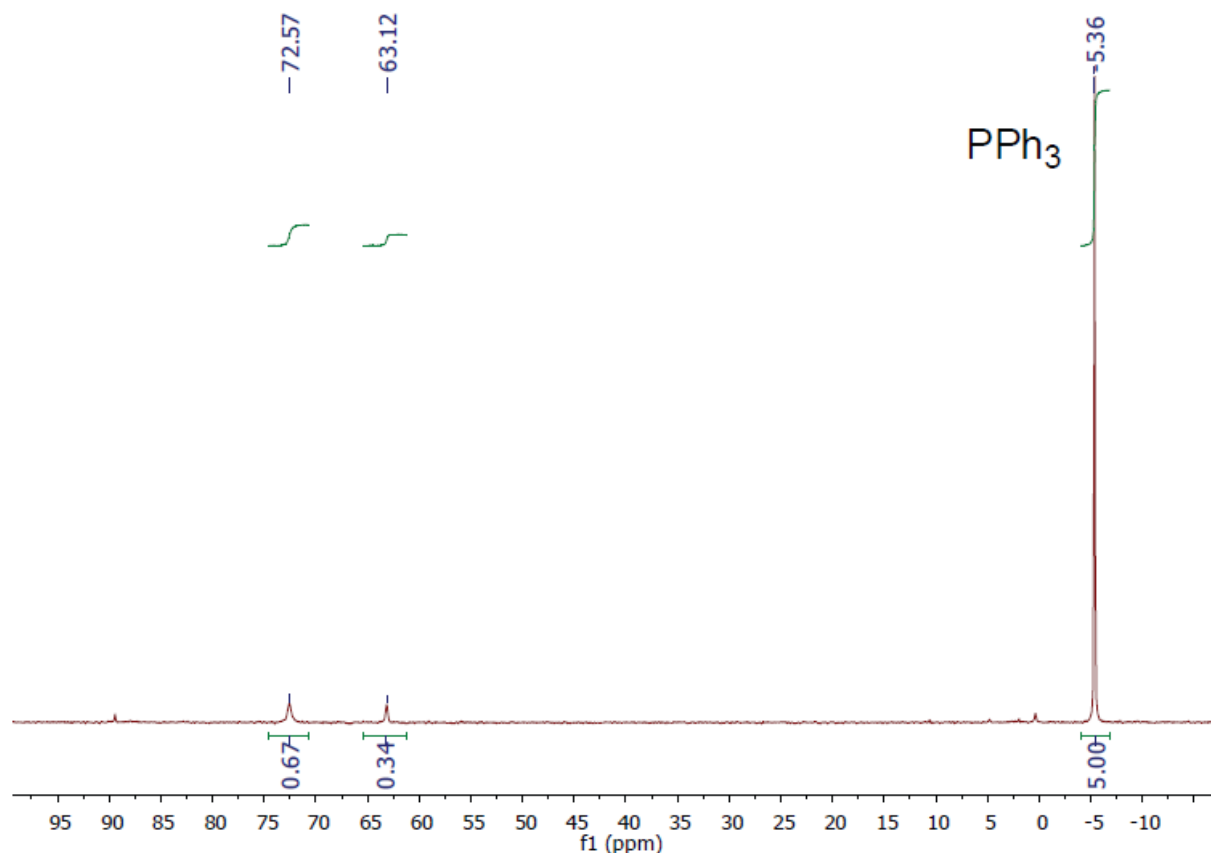
Cited References

(31) Yandulov, D. V. & Schrock, R. R. Reduction of Dinitrogen to Ammonia at a Well-Protected Reaction Site in a Molybdenum Triamidoamine Complex. *J. Am. Chem. Soc.* **124**, 6252-6253 (2002).

(32) Brookhart, M., Grant, B. & Volpe Jr., A. F. $[(3,5-(CF_3)_2C_6H_3)_4B]^{-}[H(OEt_2)_2]^{+}$: a convenient reagent for generation and stabilization of cationic, highly electrophilic organometallic complexes. *Organometallics* **11**, 3920-3922 (1992).

(33) Kern, R. J. Tetrahydrofuran complexes of transition metal chlorides. *J. Inorg. Nucl. Chem.* **24**, 1105-1109 (1962).

(34) Wietz, I. S. & Rabinovitz, M. The application of C8K for organic synthesis: reduction of substituted naphthalenes. *J. Chem. Soc., Perkin Trans.* **1**, 117-120 (1993).

(35) Komiya, S. *et al.*, Isolation of a zerovalent iron dinitrogen complex with 1,2-bis(diethylphosphino)ethane ligands. *J. Chem. Soc., Chem. Commun.* **1993**, 787-788.

(36) Weatherburn, M. W. Phenol-hypochlorite reaction for determination of ammonia. *Anal. Chem.* **39**, 971 (1967).

(37) Watt, G. W. & Chrisp, J. D. A Spectrophotometric Method for the Determination of Hydrazine. *Anal. Chem.* **24**, 2006 (1952).