Supporting Information

Light Alters the NH$_3$ vs N$_2$H$_4$ Product Profile in Iron-catalyzed Nitrogen Reduction via Dual Reactivity from an Iron Hydrazido (Fe=NNH$_2$) Intermediate

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SUPPORTING INFORMATION

S1. Methods:

S1.1. General methods

All manipulations were carried out using standard Schlenk or glovebox techniques under an N$_2$. Solvents were deoxygenated and dried by thoroughly sparging with N$_2$ followed by passage through an activated alumina column in a solvent purification system by SG Water, USA LLC. Subsequently, the solvents were further dried and stored under N$_2$ atmosphere inside a glove box with molecular sieves obtained from Sigma Aldrich that were activated at 200ºC overnight under vacuum. Non-halogenated solvents were tested with sodium benzophenone ketyl in tetrahydrofuran (THF) in order to confirm the absence of oxygen and water. The diethyl ether (Et$_2$O) employed for catalytic and mechanistic investigations was further dried using Na/K overnight and filter over celite prior use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., and use as received.

N$_2$ gas in a MB-Unilab Pro SP (2500/780) Glovebox System (MBraun Company) was purified by passing through two filter beds: molecular sieve and copper catalyst. The purity of N$_2$ gas was assessed via colorimetric, gas chromatography and NMR methods, with regard to NH$_3$, N$_2$O, NO$_2^-$ and NO$_3^-$ impurities.

Cp*$_2$Co, $^1$[P$_3$BFe][BAR$_4^-$], $^2$[H(OEt)$_2$][BAR$_4^-$] (HBAR$_4^-$; BAR$_4^-$ = tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate),$^3$ and sodium BAR$_4^-$ (NaBAR$_4^-$),$^3$ were prepared according to literature procedures. All other reagents were purchased from commercial vendors and used without further purification unless otherwise stated. Whenever water was specified as solvent, deionized water OmniSolv (Supelco, Sigma Aldrich) was used to prepare the solutions.

S1.3. UV-vis spectroscopy

UV-vis measurements were taken on a Cary 50 UV-visible spectrophotometer using a 1 cm quartz cell sealed with a Teflon stopcock. The temperature was controlled by using a Unisoke probe equipped with magnetic stir plate.

S1.4. Gas chromatography

Gas chromatography coupled to a thermal conductivity detector (GC-TCD) was performed in the Environmental Analysis Center (Caltech) using a HP 5890 Series II instrument with N$_2$ as the carrier gas for H$_2$ detection. A calibration curve was determined by direct injection of known volumes of H$_2$.

S1.5. Electrochemistry

A CHI 600B potentiostat was used for all electrochemical data collection.

Cyclic voltammetry (CV) experiments were carried out in a one-compartment three-electrode cell using a glassy carbon (GC) disk as the working electrode (3 mm diameter), a Pt disk as the counter electrode, and a Ag/AgOTf (5 mM) reference electrode. Details for the CVs are noted as they appear. For all measurements IR compensation was applied accounting for 85% of the total resistance. All the reported potentials are referenced to the ferrocenium/ferrocene couple (Fc$^{+}$/0) used as an external standard.

S1.6. Mössbauer spectroscopy

Mössbauer 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 form 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 (RT). Solution samples were transferred to a sample cup and freeze-quenched with liquid nitrogen inside of the glovebox and then immersed in liquid N2 until mounted in the cryostat. Data analysis was performed using version 4 of the program WMoss (www.wmoss.org) and quadrupole doublets were fit to Lorentzian lineshapes. See discussion below for detailed notes on the fitting procedure.
All single point energy, frequency and localized orbital analysis were performed with the ORCA 4.0 package\(^4\)\(^,\)\(^5\) using DFT-D3 ( Grimmes D3 dispersion correction)\(^6\) with an BP86 functional,\(^7\) with the zeroth order regular approximation (ZORA) to account for relativistic effects,\(^8\) in combination with the scalar relativistically recontracted versions of the def2-TZVP basis set on transition metals and a def2- SVP basis set on all other atoms.\(^9\)\(^,\)\(^10\) This methodology is based on previous reported results showing that the ZORA-BP86 method produces the most accurate geometry, as well as a singlet-triplet $\Delta H$ that agrees well with the experimental value.\(^11\) The localized orbitals have been calculated based on the Pipek-Mezey (PM) localization method as implemented in ORCA.\(^12\) NBO single-point calculations\(^13\) to attain natural population analyses were performed in Gaussian09.\(^14\) The BP86 functional and def2-TZVP basis set on transition metals and a def2-SVP basis set on all other atoms.
S2. Catalytic set-up and N-fixed products quantification

S2.1. Standard procedure for the catalytic runs

All manipulations were done in a nitrogen-filled glovebox unless otherwise mentioned. Before use, Et₂O solvent was stirred over Na/K for more than 1 hour and filtered through alumina plug prior to use. The \([P(\text{P}3)\text{Fe}][\text{BARF}_4]\) precatalyst (ca. 2.3 μmol) was weighed into a vial, dissolved in THF and transferred quantitatively into an oven-dried Schlenk tube as a solution. The solvent was then evaporated resulting in a solid layer of precatalyst at the bottom of the Schlenk tube. The acid and reductant were then added as solids and the tube was equipped with a stir bar previously oven-dried. The tube was cooled down to 77 K in the Coldwell using liquid nitrogen and 2.0 mL of Et₂O were subsequently added through the walls of the tube to allow for fast freezing before contact with the reagents. The temperature of the system was allowed to equilibrate for 5 minutes and then the tube was sealed with a Teflon screw-valve. This tube was brought out of the glovebox into a liquid nitrogen bath and transported to a fume hood. The tube was then transferred to a dry ice/acetone bath (–78 °C) where it thawed and was allowed to stir at –78 °C. For runs under light irradiation, LED was turned on as the tube was in the ice/acetone bath and constant flow of nitrogen was employed to prevent water condensation on the tube interfering with the light irradiation. For runs utilizing HBArF₄, reactions were stirred at –78 °C for 1 hour, followed by stirring at room temperature for 45 minutes. For all other runs, reactions were allowed to stir and gradually warm to room temperature overnight. To ensure reproducibility, all experiments were conducted in 200 mL Schlenk tubes (51 mm OD) using 25 mm stir bars, and stirring was conducted at ~900 rpm.

S2.2. Quantification of H₂

After the reaction time, the headspace of the reaction vessel was sampled using a 10 ml Hamilton syringe and subsequently injected in a Agilent 7890A gas chromatograph (HP-PLOT U, 30 m, 0.32 mm ID; 30 °C isothermal; nitrogen carrier gas) using a thermal conductivity detector. Integration area was converted to percent H₂ composition by use of a calibration obtained from injection of H₂ solutions in N₂ of known concentration and correcting for the vapor pressure of Et₂O and the removed H₂ from previous samplings as previously reported.

S2.3. Quantification of NH₃ and N₂H₄

After the reaction time, the catalytic reaction mixture was cooled to 77 K and allowed to freeze. The reaction vessel was then opened to atmosphere and to the frozen solution was added dropwise 3 mL of 2M HCl in Et₂O over 1-2 mins through the wall of the tube. The tube was allowed to equilibrate for 5 mins and then the headspace of the tube was evacuated to a constant pressure and subsequently sealed. The tube was allowed to warm up to room temperature and stir for 10 mins. The resulting solution was then evaporated to dryness under vacuum. The tube with the remaining solids was cooled down in a dry ice/acetone bath for 10 mins. A 1 M aqueous HCl solution (4 ml) was delivered through the wall of the tube, allowed to freeze and the tube was subsequently sealed and allowed to warm up to room temperature. After 10 mins of stirring, the resulting suspension was filtered through celite into a 10 ml volumetric flask. The tube was further extracted twice with 2 mL of 1 M aqueous HCl solution, followed by filtration through celite into the same 10 mL volumetric flask. More HCl solution was added up to 10 mL total volume and 5 mL of this solution were transferred to a 5 mL volumetric flask, where it was extracted 5x with 1 mL of n-butanol to remove remaining metal containing impurities. After extraction, the 5 mL flask was refilled to the mark and 100 μL aliquots were used for the colorimetric detection methods to analyze for the presence of NH₃ (present as [NH₄][Cl]) by the indophenol method, or N₂H₄ (present as [N₂H₅][Cl]) by a standard colorimetric method. Quantification was performed with UV-visible spectroscopy by analyzing the absorbance at 635 nm (NH₃) and 458 nm (N₂H₄) in a quartz cuvette. Calibration curves for ammonia and hydrazine (see below) were constructed.
Figure S1. UV-vis absorption spectra for standard solutions containing different concentration of \( \text{N}_2\text{H}_4 \) after color development using the previously described method. The absorption at 458 nm was measured and plotted versus the concentration of hydrazine in the analyte to build a calibration curve for hydrazine quantification.

Figure S2. Calibration curve for the detection of hydrazine using the colorimetric method previously described. The plot was built using different \( \text{N}_2\text{H}_4 \) solutions in aqueous HCl (1M) obtained by dilution of a standard \( \text{N}_2\text{H}_4 \) solution. The absorption at 435 nm was measured and plotted versus the concentration of hydrazine in the analyte.
**Figure S3.** Calibration curve for the quantification of H₂ in the reaction headspace using GC-TCD using 10 ml sample manual injection.
S3. Catalytic runs under light/dark conditions

For catalytic runs performed under illumination, a 440 nm LED lamp (Kessil PR160-440 nm lamp, 45 W) or a Hg lamp (HBO 100 Mercury Arc lamp, 100 W) were employed as the light source and placed close to the wall of the reaction tube above the dry ice/acetone bath, with a separation no longer than 10 cm. Continuous flow of nitrogen over the tube external wall was employed during the experiment to prevent condensation of water affecting the illumination.

Table S1. Catalytic runs under light irradiation

<table>
<thead>
<tr>
<th>Entry</th>
<th>Light source</th>
<th>Acid</th>
<th>Reductant</th>
<th>NH₄Cl equiv. (%)</th>
<th>N₂H₄Cl equiv. (%)</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>LED 440 nm</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp⁺₂Co</td>
<td>7.4 (56)</td>
<td>4.4 (44)</td>
<td>73.8</td>
</tr>
<tr>
<td>B</td>
<td>LED 440 nm</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp⁺₂Co</td>
<td>8.0 (69)</td>
<td>2.7 (31)</td>
<td>63.8</td>
</tr>
<tr>
<td>C</td>
<td>LED 440 nm</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp⁺₂Co</td>
<td>6.6 (66)</td>
<td>2.5 (34)</td>
<td>54.9</td>
</tr>
<tr>
<td>D</td>
<td>LED 440 nm</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp⁺₂Co</td>
<td>6.4 (62)</td>
<td>2.9 (38)</td>
<td>56.8</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>LED 440 nm</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp⁺₂Co</td>
<td>7.1 ± 0.7 (63 ± 6)</td>
<td>3.1 ± 0.8 (37 ± 6)</td>
</tr>
<tr>
<td>E</td>
<td>Hg Lamp</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp⁺₂Co</td>
<td>8.6 (68)</td>
<td>3.1 (32)</td>
<td>70.7</td>
</tr>
<tr>
<td>F</td>
<td>Hg Lamp</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp⁺₂Co</td>
<td>8.2 (68)</td>
<td>2.9 (32)</td>
<td>67.0</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>Hg Lamp</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp⁺₂Co</td>
<td>8.4 ± 0.3 (68 ± 0.3)</td>
<td>3.0 ± 0.1 (32 ± 0.3)</td>
</tr>
<tr>
<td>G</td>
<td>LED 440 nm</td>
<td>[2,6-ClPhNH₃][OTf]</td>
<td>Cp⁺₂Co</td>
<td>3.6 (46)</td>
<td>3.2 (54)</td>
<td>44.7</td>
</tr>
<tr>
<td>H</td>
<td>LED 440 nm</td>
<td>[2,6-ClPhNH₃][OTf]</td>
<td>Cp⁺₂Co</td>
<td>3.0 (49)</td>
<td>2.3 (51)</td>
<td>33.8</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>LED 440 nm</td>
<td>[2,6-ClPhNH₃][OTf]</td>
<td>Cp⁺₂Co</td>
<td>3.3 ± 0.4 (48 ± 3)</td>
<td>2.7 ± 0.6 (52 ± 3)</td>
</tr>
<tr>
<td>I</td>
<td>LED 440 nm</td>
<td>[2,4,6-ClPhNH₃][OTf]</td>
<td>Cp⁺₂Co</td>
<td>6.8 (69)</td>
<td>2.2 (30)</td>
<td>54.1</td>
</tr>
<tr>
<td>J</td>
<td>LED 440 nm</td>
<td>[2,4,6-ClPhNH₃][OTf]</td>
<td>Cp⁺₂Co</td>
<td>6.2 (61)</td>
<td>2.9 (38)</td>
<td>55.92</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>LED 440 nm</td>
<td>[2,4,6-ClPhNH₃][OTf]</td>
<td>Cp⁺₂Co</td>
<td>6.5 ± 0.4 (66 ± 6)</td>
<td>2.5 ± 0.5 (34 ± 6)</td>
</tr>
<tr>
<td>K</td>
<td>Hg Lamp</td>
<td>HBAr⁴⁺</td>
<td>KC₈</td>
<td>4.5 (40)</td>
<td>5.0 (60)</td>
<td>22.3</td>
</tr>
<tr>
<td>L</td>
<td>Hg Lamp</td>
<td>HBAr⁴⁺</td>
<td>KC₈</td>
<td>4.0 (41)</td>
<td>4.3 (59)</td>
<td>19.5</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>Hg Lamp</td>
<td>HBAr⁴⁺</td>
<td>KC₈</td>
<td>4.2 ± 0.3 (41 ± 1)</td>
<td>4.7 ± 0.5 (59 ± 1)</td>
</tr>
<tr>
<td>M</td>
<td>LED 440 nm</td>
<td>HBAr⁴⁺</td>
<td>KC₈</td>
<td>2.3 (24)</td>
<td>5.4 (75)</td>
<td>18.4</td>
</tr>
</tbody>
</table>
Table S2. Catalytic runs under dark conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Acid</th>
<th>Reductant</th>
<th>NH₃Cl equiv. (%)</th>
<th>N₂H₅Cl equiv. (%)</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp²Co</td>
<td>11.7 (96)</td>
<td>0.35 (4)</td>
<td>67.6</td>
</tr>
<tr>
<td>D</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp²Co</td>
<td>11.5 (95)</td>
<td>0.46 (5)</td>
<td>67.2</td>
</tr>
</tbody>
</table>

| Average | [H₂NPh₂][OTf] | Cp²Co     | 11.6 ± 0.1 (96 ± 1) | 0.4 ± 0.1 (4 ± 1) | 67.4 ± 0.3 |

| C     | [²,⁶-Me₂PhNH₃][OTf] | Cp²Co     | 8.6 (98)          | 0.1 (2)          | 47.8    |
| D     | [²,⁴,⁶-Cl₃PhNH₃][OTf] | Cp²Co     | 12.3 (98)         | 0.2 (2)          | 68.7    |

Figure S4. Representative UV-vis spectra of the colorimetric methods for detection of NH₃ and N₂H₄ after a catalytic run under light irradiation using Cp²Co and [H₂NPh₂][OTf] as reactant cocktail.
Figure S5. Representative UV-vis spectra of the colorimetric methods for detection of NH$_3$ and N$_2$H$_4$ after a catalytic run under light irradiation using KC$_8$ and HBArF$_4$ as reactant cocktail, leading to the highest selectivity for hydrazine.

Figure S6. Representative UV-vis spectra of the colorimetric methods for detection of NH$_3$ and N$_2$H$_4$ after a catalytic run under dark conditions using Cp$^\ast$Co and [H$_2$NPh$_2$][OTf] as reactant cocktail.
S4. Control experiments

S4.1. Compatibility of acids with the colorimetric methods for detection of NH₃ and N₂H₄

To test for potential interferences of the three acids employed in this work with the colorimetric detection methods, a control experiment in the absence of catalyst was run following similar procedure as for the catalytic runs in the dark. The acid was added to a Na/K died Et₂O solution in the presence or absence of a known amount of NH₃ or N₂H₄ (12 µmol corresponding to 5 equiv in a catalytic run) in a Schlenk tube. This mixture was brought out of the glove box and the solution was subjected to quantification methods previously described. Results confirmed that the acid employed do not show any absorbance in these methods and that their presence did not affect the quantification of the known amounts of added N₂H₄ and NH₃.

Figure S7. Representative UV-vis spectra for the hydrazine test to evaluate the interference of the acid ([H₂NPh₂][OTf]) in the quantification. The hydrazine detected corresponded to 0.88 of the total hydrazine initially added, similar to the detection in the absence of acid.
Figure S8. Representative UV-vis spectra for the ammonia test to evaluate the interference of the acid ([H₂NPh₂][OTf]) in the quantification. The ammonia detected corresponded to 0.9 of the total ammonia initially added, similar to the detection in the absence of acid.

S4.2. Control experiments for the generation of NH₃ and N₂H₄ under catalytically relevant conditions

Table S3. Summary of the control experiments.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Acid</th>
<th>Reductant</th>
<th>N₂H₅Cl (mM)</th>
<th>NH₄Cl (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>LED 450 nm No catalyst, N₂H₄ (0.023 mmol)</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp*₂Co</td>
<td>0.02</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>LED 450 nm P₃Fe⁺ (2.3 mM) N₂H₄ (0.023 mmol) Ar atmosphere</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp*₂Co</td>
<td>0.018</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>LED 450 nm No catalyst</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp*₂Co</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
**Figure S9.** Representative UV-vis spectra of the colorimetric methods for detection of NH$_3$ and N$_2$H$_4$ after a control experiment using Cp$^\ast$:Co and [H$_2$NPh$_2$][OTf] as reactant cocktail in the presence of the (P$_3$)$_2$Fe$^+$ precatalyst and 10 equiv of N$_2$H$_4$ under Ar atmosphere, showing that N$_2$H$_4$ is not further reduced to NH$_3$.
S5. Variable-temperature catalytic runs

For catalytic runs performed at different temperatures, the reaction tubes were wrapped into aluminum foil to maintain strict dark conditions and placed into either acetonitrile/dry ice or aqueous NaCl solution/ice to provide the specific temperatures, -45 °C or -10 °C respectively.

Table S4. Catalytic runs under light irradiation

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature</th>
<th>Acid</th>
<th>Reductant</th>
<th>NH₄Cl</th>
<th>N₂H₅Cl</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-45 °C</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp*₂Co</td>
<td>8.5</td>
<td>1.3</td>
<td>57.1</td>
</tr>
<tr>
<td>B</td>
<td>-45 °C</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp*₂Co</td>
<td>9.0</td>
<td>0.8</td>
<td>55.8</td>
</tr>
<tr>
<td>Average</td>
<td>-45 °C</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp*₂Co</td>
<td>8.8</td>
<td>1</td>
<td>56.4</td>
</tr>
<tr>
<td>E</td>
<td>-10 °C</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp*₂Co</td>
<td>3.4</td>
<td>0.8</td>
<td>34.8</td>
</tr>
<tr>
<td>F</td>
<td>-10 °C</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp*₂Co</td>
<td>5.8</td>
<td>0.6</td>
<td>36.7</td>
</tr>
<tr>
<td>Average</td>
<td>-10 °C</td>
<td>[H₂NPh₂][OTf]</td>
<td>Cp*₂Co</td>
<td>4.6</td>
<td>0.7</td>
<td>30.7</td>
</tr>
</tbody>
</table>

Figure S10. Representative UV-vis spectra of the N₂H₅ colorimetric test after a catalytic run under dark conditions, using Cp*₂Co and [H₂NPh₂][OTf] as reactant cocktail, at different temperatures.
**Figure S11.** Representative UV-vis spectra of the NH₃ colorimetric test after a catalytic run under dark conditions, using Cp*₂Co and [H₂NPh₂][OTf] as reactant cocktail, at different temperatures.
S6. Freeze-quench Mössbauer

General procedure:

Et₂O and THF were stirred with Na/K overnight and filtered over alumina prior to use. In a nitrogen filled glovebox, [(P₃B)₅Fe][BArF₄] (0.0023 mmol) was quantitatively transferred using THF to a Schlenk tube and then evaporated to yield a thin film. The tube is charged with a oven-dried stir bar and the other reagents as solids. The tube is then cooled down to 77 K in a liquid nitrogen bath inside the glove box and allowed to equilibrate for five minutes. To the tube is added 1 mL of Et₂O over the tube wall and this allowed to equilibrate for another five minutes. The tube is then transferred to a cold well that has been precooled for at least fifteen minutes to −78 °C with a dry ice/acetone bath. After 30 mins from the beginning of the stirring, the reaction mixture was sampled using a prechilled pipette and subsequently transferred in one portion to a prechilled Mössbauer cup sitting in a vial. The vial is then placed in a liquid nitrogen bath causing the reaction mixture to freeze in approximately twenty seconds. The Mössbauer cup is then submerged in the liquid nitrogen and then removed from the glovebox and standard procedure is used to mount the sample on the Mössbauer spectrometer.

P₃BFe⁺ + 54 eq Cp*₂Co + 108 eq [Ph₂NH₂][OTf] −78 °C, Et₂O
Blue LED
30 minutes

Figure S12. Mössbauer spectrum collected from a reaction freeze quenched after stirring for 30 minutes at −78 °C in 1 mL of Et₂O between [(P₃B)₅Fe][BArF₄] and excess Cp*₂Co (54 equiv.) and [H₂NPh₂][OTf] (108 equiv.) as reactant cocktail. Raw data shown as black points, simulation as a solid red line, with components in green, purple, blue, and yellow (see Table S5 for parameters). The spectrum was collected at 80 K with a parallel applied magnetic field of 50 mT in Et₂O.

Table S5. Fe speciation based on simulation parameters extracted from Mössbauer spectroscopy.
Species | Simulation color | δ (mm sec\(^{-1}\)) | | \(\Delta_{\text{eq}}\) (mm sec\(^{-1}\)) | Weight (%) |
---|---|---|---|---|---|
P\(_3^B\)Fe–N\(_2\) | green | 0.56 | 3.24 | 29 |
P\(_3^B\)Fe\(^+\) | purple | 0.72 | 2.62 | 12 |
h.s. Fe\(_{\text{II}}\) | blue | 1.29 | 2.88 | 39 |
unknown | orange | 0.17 | 1.51 | 20 |

Comments on the Mössbauer spectrum:

Freeze-quench Mössbauer spectroscopy was performed after 30 minutes of turnover during light irradiation to determine the speciation of \(^{57}\)Fe labeled-catalyst (Figure S12). Four main species with well-resolved sets of quadrupole doublets can be identified by deconvolution of the 80 K spectrum; these correspond to the neutral (P\(_3^B\)Fe(N\(_2\)) complex (δ = 0.56 mm/s, \(\Delta E_Q = 3.24\) mm/s, 29%),\(^{17}\) the precatalyst [(P\(_3^B\)Fe)]\(^+\) (δ = 0.72 mm/s, \(\Delta E_Q = 2.62\) mm/s, 12%)\(^{18}\) a high spin Fe\(_{\text{II}}\) species (δ = 1.29 mm/s, \(\Delta E_Q = 2.88\) mm/s, 39%) previously associated with off-path or decomposition species, and an unidentified, likely P\(_3^B\)-metalated Fe species (δ = 0.17 mm/s, \(\Delta E_Q = 1.51\) mm/s, 20%). This speciation closely resembles that obtained in the absence of light irradiation using the same reductant and acid combination.\(^{17}\)
S7. Rotating ring disk electrode experiment

A rotating ring disk electrode (RRDE) was employed for the detection of hydrazine during electrochemical N₂R by P₃BFe⁺. To confirm the viability of the RRDE experiment a series of linear sweep voltammograms (LSVs) were performed (Figure S14). LSVs of the electrolyte containing 0.1 M NaBAR₄ and 10 mM [Ph₂NH₂][OTf] with the Pt ring electrode in the presence of added N₂H₄ (5 mM) show an oxidative feature starting at -0.5 V vs Fc⁺/⁻ compared to a LSV of the blank electrolyte, demonstrating that N₂H₄ and its protonated forms can be oxidized at this (or higher) potentials. P₃BFe⁺ and its more reduced analogues are reduced at potentials below -1 V. Therefore, at potentials below -1 V, only Fe- based intermediates will be oxidized at the Pt ring, and at potentials above -0.5 V hydrazine will also be oxidized. In the RRDE experiment a LSV is performed at the glassy carbon (GC) disk electrode that is surrounded by the Pt ring electrode. By scanning reductively at the GC disk and monitoring the current at the Pt electrode either at -0.5 V or at -1.0 V, we can detect if N₂H₄ is formed on the LSV time scale. In LSV experiments at slow scan rate (10 mV·s⁻¹), increased current is observed at the Pt electrode when it is held at -0.5 V vs -1.0V starting from a potential of -2.0 V at the GC disk where P₃BFe⁺ is reduced to P₃BFeN₂ and enters the N₂R catalytic cycle. This is consistent with N₂H₄ formation at the electrode on the LSV time scale mediated by Fe.

![Schematic representation of the RRDE experiment for the detection of hydrazine as product of electrocatalytic N₂R by (P₃B)Fe⁺.](image)

**Figure S13.** Schematic representation of the RRDE experiment for the detection of hydrazine as product of electrocatalytic N₂R by (P₃B)Fe⁺.
**Figure S14.** Linear sweep voltammograms (LSVs) performed at the Pt ring electrode of Et₂O solution containing 0.1 M [Na][Barf₄] and 10 mM [Ph₂NH₂][OTf] (red trace) and with addition of 10 mM of N₂H₄ (green trace). A Pt counter electrode and a Ag/AgOTf (5 mM) reference electrode were used and the scan rate was set to 100 mV s⁻¹.
Figure S15. Rotating ring disk electrode experiment for hydrazine detection in a 0.1 M [Na][BArF₄] solution in Et₂O at RT with (blue trace) and without (black trace) P₃BFe⁺ (1 mM). The top graph shows the current collected at the glassy carbon disk electrode during a linear sweep voltammetry at 20 mV·s⁻¹. The bottom graph shows the current simultaneously collected in the Pt ring electrode upon applying a constant potential of −1 V vs Fc⁺/₀ where hydrazine is not oxidized, so only oxidation of Fe-based products is detected. A Pt-wire counter electrode, a 5 mM Ag/AgOTf reference electrode and a rotation speed of 1600 rpm were employed.
**S8. UV-vis spectroscopy**

**Figure S16.** UV-vis spectra of $P_3B^{8}\text{Fe}*(1\, \text{mM})$ formed via addition of 10 equiv of $N_2H_4$ in $\text{Et}_2\text{O}$ solution at $-78\, \text{°C}$ before (red trace) and after (blue trace) irradiation with a LED (450 nm) to test for the stability of the complex.

**Figure S17.** UV-vis spectra of $P_3B^{8}\text{Fe}*$ (1 mM, dashed black trace) and $P_3B^{8}\text{Fe}(N_2H_4)^*$ formed via addition of 10 equiv of $N_2H_4$ in $\text{Et}_2\text{O}$ solution at either 25 °C (red trace) or −78 °C (blue trace).
Figure S18. UV-vis spectra of P$_3$BFe$^+$ (1 mM, black trace), P$_3$BFeOTf formed via addition of 10 equiv of [Ph$_2$NH$_2$][OTf] (red trace), P$_3$BFe(N$_2$H$_4$)$^+$ formed via addition of 10 equiv of N$_2$H$_4$ (green trace), and the consumption of P$_3$BFe(N$_2$H$_4$)$^+$ upon addition of 10 equiv of [Ph$_2$NH$_2$][OTf] (blue trace) to form P$_3$BFeOTf. The spectra were taken in Et$_2$O solution at $-78$ °C.
Figure S19. Representative UV-vis spectra of the colorimetric methods for detection of NH₃ and N₂H₄ after the reaction of P₃βFe⁺ in the presence of 10 equiv of N₂H₄ with 10 equiv of [Ph₂NH₂][OTf] at -78 °C in Et₂O (Figure S18). 9.8 equiv of hydrazine were recovered with no evidence for ammonia generation.

Figure S20. UV-vis spectra under Ar atmosphere of P₃βFe⁺ after reduction with one equiv of Cp*:Co to P₃βFe (1 mM, red trace), and similar experiments in the presence of N₂H₄ adding Cp*:Co before (green trance) or after (blue trace) 10 equiv of N₂H₄. The spectra were taken in Et₂O solution at -78 °C.
Figure S22. Representative UV-vis spectra of the colorimetric methods for detection of NH$_3$ and N$_2$H$_4$ after the reaction of P$_3$B$^6$Fe$^*$ in the presence of 10 equiv of N$_2$H$_4$ with one equivalent of Cp$^*$$_2$Co at -78 $^\circ$C in Et$_2$O (Figure S21). 9.7 equiv of hydrazine were recovered with no evidence for ammonia generation.
S9. Electrochemistry

Mechanistic analysis from cyclic voltammetry:

\[ \text{P}_3^{\text{B}}\text{Fe(N}_2\text{H}_4)^+ \] displays a typical square mechanism where an electron transfer step (E) consisting on the one electron reduction to \( \text{P}_3^{\text{B}}\text{Fe(N}_2\text{H}_4) \) is followed by a chemical step (C) that involves substitution of \( \text{N}_2\text{H}_4 \) by \( \text{N}_2 \) to form \( \text{P}_3^{\text{B}}\text{Fe(N}_2 \) . In the reverse oxidative scan, an analogous CE mechanism is observed where substitution of \( \text{N}_2 \) by \( \text{N}_2\text{H}_4 \) precedes the oxidation to initial \( \text{P}_3^{\text{B}}\text{Fe(N}_2\text{H}_4)^+ \), resulting in a broader and less intense oxidation peak.

\[
\begin{align*}
\text{Reductive EC pathway} & \\
\text{Oxidative CE pathway} & \\
\end{align*}
\]

\[ \begin{align*}
\text{P}_3^{\text{B}}\text{Fe(N}_2\text{H}_4)^+ & \xrightleftharpoons[-e^-]{+e^-} \text{P}_3^{\text{B}}\text{Fe(N}_2\text{H}_4) \\
\text{P}_3^{\text{B}}\text{Fe(N}_2\text{H}_4) & \xrightarrow{\text{N}_2} \text{P}_3^{\text{B}}\text{Fe(N}_2 \\
\text{P}_3^{\text{B}}\text{Fe(N}_2) & \xleftarrow{\text{N}_2\text{H}_4} \text{P}_3^{\text{B}}\text{Fe(N}_2\text{H}_4) \\
\text{P}_3^{\text{B}}\text{Fe(N}_2\text{H}_4) & \xrightarrow{+e^-} \text{P}_3^{\text{B}}\text{Fe(N}_2\text{H}_4)^+ \\
\end{align*}
\]

Figure S22. Schematic representation of the square mechanism involved in the first redox event at around -1.4 V vs Fc\(^{+/-0}\).

The shape of the redox wave with a broader oxidation peak suggests a KE regimen under our conditions. This regime is characterized by relatively large reaction kinetics and equilibrium constants for the chemical step, and leads to partial reversibility. The reductive EC step of this square mechanism follows Eq. S1, where \( E \) is the potential of the redox event under operating conditions, \( E^0 \) is the standard redox potential for the \( \text{P}_3^{\text{B}}\text{Fe(N}_2\text{H}_4)^+/-0 \) couple. \( F \) is Faraday’s constant, \( R \) is the ideal gas constant, \( T \) is the temperature, \( K \) is the pseudo first order equilibrium constant for the C step. To confirm so, a variable scan rate experiment was performed (Fig. S23) and the potential of the reduction peak was plotted versus the \( \ln[\text{N}_2\text{H}_4] \). The linear regression of that plot shows a slope of -0.022, very similar to the theoretical -0.025 expected according to Eq. S2, confirming the KE regime.

\[ E = E^0 - \frac{RT}{F} \ln(K) \quad \text{(Eq. S1)} \]

\[ K = K_{eq} \frac{[\text{N}_2]}{[\text{N}_2\text{H}_4]} \quad \text{(Eq. S2)} \]
Figure S23. Cyclic voltammetry of $P_3BFe^+$ (1 mM) in the presence of different concentrations of $N_2H_4$ in a 0.1 M $[\text{Na}]\text{[BAr}_4\text{F}_4]$ solution in Et$_2$O at RT. Set-up used a glassy carbon working electrode, a Pt-wire counter electrode, and 5 mM Ag/AgOTf reference electrode; the scan rate was 100 mV·s$^{-1}$.

Figure S24. Plot of the redox potential for the first reductive event vs the natural logarithm of the hydrazine concentration with the corresponding linear fit. The slope of the fit support a KE regime for this overall EC process as its value is close to the theoretical slope of $-0.025$. 

$$
y = -0.0226x - 1.6491 \\
R^2 = 0.9988 
$$
Figure S25. Cyclic voltammetry of P₃⁸Fe⁺ (1 mM) in the presence of 10 equivalent of N₂H₄ in a 0.1 M [Na][BAr⁷F₄] solution in Et₂O at RT and at different scan rates. At high scan rates, the oxidation event at the first wave outcompetes the N₂/N₂H₄ substitution process allowing for the detection of the peak associated to P₃⁸Fe(N₂)⁰⁺ (blue arrow) anodic of the one associated to P₃⁸Fe(N₂H₄)⁰⁺. Set-up used a glassy carbon working electrode, a Pt-wire counter electrode, and 5 mM Ag/AgOTf reference electrode.
Figure S26. Cyclic voltammetry at different scan rates of the first redox event of $P_3B$Fe$^+$ (1 mM) in the presence of 10 equivalent of $N_2H_4$ in a 0.1 M $[Na][BArF_4]$ solution in Et$_2$O at RT. Set-up used a glassy carbon working electrode, a Pt-wire counter electrode, and 5 mM Ag/AgOTf reference electrode.

Figure S27. Scan-rate normalized current of the first redox event from cyclic voltammetry of $P_3B$Fe$^+$ (1 mM) in the presence of 10 equivalent of $N_2H_4$ in a 0.1 M $[Na][BArF_4]$ solution in Et$_2$O at RT. Set-up used a glassy carbon working electrode, a Pt-wire counter electrode, and 5 mM Ag/AgOTf reference electrode.
**Figure S28.** Cyclic voltammetry of P₃BF⁺ (1 mM) in the presence of N₂H₄ in a 0.1 M [Na][BARF₄] solution in Et₂O at RT at 100 mV·s⁻¹ showing one (orange) or two (blue) redox processes. Set-up used a glassy carbon working electrode, a Pt-wire counter electrode, and 5 mM Ag/AgOTf reference electrode.

**Calculation of the equilibrium constant for the N₂/N₂H₄ binding to the P₃BF intermediate:**

Since the reduction potential of P₃BF(N₂H₄)⁺/0 remains unknown due to the fast kinetics of N₂H₄ release that affect the position of the reduction peak even at high scan rates and concentrations of N₂H₄, we analyzed the CE oxidation event instead that follows Eq. S3. In this case, the oxidation potential for P₃BF⁺/0 is determined in the absence of N₂H₄ (−1.4 V), and the concentration of N₂ is estimated from the literature values for the solubility of N₂ in Et₂O solutions (0.0116 M). Therefore, for CVs collected in the presence of 10 equiv. of N₂H₄, the oxidation peak potential is around −1.5 V (Figure S4). Applying Eq. X, a value for K is obtained to be 5.5·10⁻⁴.

\[
E = E^0(Fe/Fe^+) - \frac{RT}{F} \ln \left( \frac{K}{1+K} \right) \quad \text{(Eq. S3)}
\]

\[
K = K_{eq} \frac{[N₂H₄]}{[N₂]} \quad \text{(Eq. S4)}
\]
S10. DFT calculations

**Figure S29.** Spin density of the low-lying $S=1$ excited state evidencing the population of an antibonding Fe-N molecular orbital involving overlap between $d_{xz}$ and $\pi^*$ N-N orbitals.

**TD-DFT calculation**

![Calculated Absorption Spectrum](image)

**Figure S30.** Absorption spectrum simulated via TD-DFT for the neutral $P_3^8Fe(NNH_2)$ intermediate.
Figure S31. HOMO (left) and LUMO (right) from the TD-DFT calculation. Although these are recalculated for each natural transition orbital (NTO) their character Fe-based non-bonding orbital and Fe-Nπ* orbitals is intrinsically the same throughout, as can be seen in the example difference densities in Figure S32.
**Figure S32.** Difference densities for selected transitions relevant to irradiation with blue LED or Hg lamp. Green correspond to positive spin density while purple refers to negative spin density, thus showing the electronic transition involved in the excitation.

**Table S6.** Natural population analyses determined in an NBO calculation for relevant atoms of $P_3^8Fe(NNH_2)$ in the singlet, triplet, and singlet state arising at 435 nm.

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*Optimized XYZ coordinates used for single point calculations, TD-DFT and localized orbital analysis:*

$P_3^8Fe(NNH_2)$ (S = 0)

Fe -0.01048639641004 -0.08031349586972 -1.14003339411490
### SUPPORTING INFORMATION

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S11. References