

# Selective Catalytic Reduction of N<sub>2</sub> to N<sub>2</sub>H<sub>4</sub> by a Simple Fe Complex

Peter J. Hill,<sup>†</sup> Laurence R. Doyle,<sup>†</sup> Andrew D. Crawford,<sup>†</sup> William K. Myers,<sup>‡</sup> and Andrew E. Ashley<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, Imperial College London, Imperial College Road, South Kensington, London SW7 2AZ, United Kingdom

<sup>‡</sup>Centre for Advanced Electron Spin Resonance, Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, United Kingdom

## Supporting Information

**ABSTRACT:** The catalytic fixation of N<sub>2</sub> by molecular Fe compounds is a rapidly developing field, yet thus far few complexes can effect this transformation, and none are selective for N<sub>2</sub>H<sub>4</sub> production. Herein we report that the simple Fe(0) complex Fe(Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PEt<sub>2</sub>)<sub>2</sub>(N<sub>2</sub>) (**1**) is an efficient catalyst for the selective conversion of N<sub>2</sub> (>25 molecules N<sub>2</sub> fixed) into N<sub>2</sub>H<sub>4</sub>, attendant with the production of ca. one molecule of NH<sub>3</sub>. Notably, the reductant (CoCp\*<sub>2</sub>) and acid (Ph<sub>2</sub>NH<sub>2</sub>OTf) used are considerably weaker than conventional chemical H<sup>+</sup> and e<sup>-</sup> sources used in previous demonstrations of N<sub>2</sub> turnover by synthetic Fe compounds. These results show that the direct catalytic conversion of N<sub>2</sub> to the hydrazine oxidation state on molecular Fe complexes is viable and that the mechanism of NH<sub>3</sub> formation by such systems may proceed via Fe–N<sub>2</sub>H<sub>4</sub> intermediates.

The conversion of N<sub>2</sub> into NH<sub>3</sub> is an essential process for supplying fixed nitrogen in the biosphere and for industry as a vital feedstock chemical.<sup>1</sup> This process is challenging due to the inertness of N<sub>2</sub> and is carried out only by specialized organisms or under forcing conditions in industry;<sup>2</sup> both biological (nitrogenase enzymes)<sup>3</sup> and anthropogenic methods (Haber–Bosch process) employ Fe for efficient N<sub>2</sub> fixation.<sup>4</sup> Recent efforts have targeted homogeneous catalysts capable of converting N<sub>2</sub> to NH<sub>3</sub>, which are more amenable to mechanistic studies.<sup>5</sup>

Hydrazine (N<sub>2</sub>H<sub>4</sub>) is also an important chemical with an array of uses.<sup>6</sup> Unlike NH<sub>3</sub> however, the formation of N<sub>2</sub>H<sub>4</sub> is considerably endoergic ( $\Delta G_{\text{f}}^{\circ}(298) = -33.2$  and  $+158.5$  kJ mol<sup>-1</sup> respectively), rendering its direct synthesis from N<sub>2</sub> challenging; currently no practical and economical route exists. Industrial methods for producing N<sub>2</sub>H<sub>4</sub> rely on the oxidative coupling of NH<sub>3</sub><sup>7</sup> and hence ultimately depend on the Haber–Bosch process. Despite the significant amount of work conducted on NH<sub>3</sub> forming catalysts, the development of protocols for the direct formation of N<sub>2</sub>H<sub>4</sub> from N<sub>2</sub> is still underdeveloped. Shilov et al. reported the first systems capable of catalytically transforming N<sub>2</sub> into N<sub>2</sub>H<sub>4</sub> and NH<sub>3</sub> in protic media, using Mo(III) and stoichiometric reductant (Na/Hg).<sup>8</sup> Although the yields of fixed products remain the highest to date, the mechanism and active catalyst remain poorly defined, probably due to the heterogeneous nature of the system and the elevated pressures (70–100 atm) required. Considering the prevalence of Fe in anthropogenic and biological N<sub>2</sub> fixation, synthetic Fe-

based catalysts remain scarce (Figure 1); these almost exclusively produce NH<sub>3</sub> as the terminal product. Peters reported the first

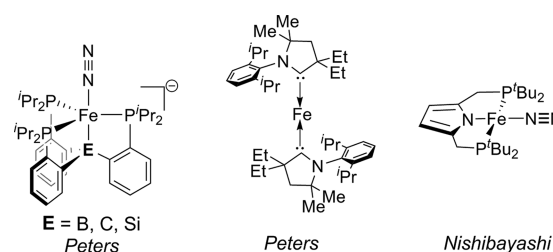


Figure 1. Current Fe-based synthetic catalysts for N<sub>2</sub> fixation.

such example of N<sub>2</sub> fixation to NH<sub>3</sub> using the [(P<sub>3</sub>B)Fe(N<sub>2</sub>)]<sup>-</sup> complex [P = *o*-(PiPr<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>], producing up to 64 equiv of NH<sub>3</sub>/Fe (32 N<sub>2</sub> molecules fixed) which represents the highest turnover to date; [(P<sub>3</sub>E)Fe(N<sub>2</sub>)]<sup>-</sup> (E = C, Si) congeners were also active, albeit displaying a more limited productivity.<sup>9</sup>

The Peters' group have also shown that the Fe(0) compound Fe(CAAC)<sub>2</sub> [CAAC = cyclic (alkyl) (amino) carbene] is capable of catalytically yielding modest amounts of NH<sub>3</sub> at very low temperatures (-95 °C).<sup>10</sup> Very recently Nishibayashi has reported the catalytic production ( $\leq 9$  N<sub>2</sub> consumed) of NH<sub>3</sub> and N<sub>2</sub>H<sub>4</sub> using Fe(I) ligated by a pyrrolide [PNP]<sup>-</sup> platform; while this is the first example of superstoichiometric N<sub>2</sub> conversion to N<sub>2</sub>H<sub>4</sub> as a product, the formation of NH<sub>3</sub> is consistently favored over N<sub>2</sub>H<sub>4</sub>, and at best, an equimolar ratio of these products was isolated.<sup>11</sup> For all of these examples, the superlative reaction protocol involved the powerful reductant KC<sub>8</sub> and strong Brønsted acid [H(OEt)<sub>2</sub>][BAR<sup>F</sup><sub>4</sub>] [BAR<sup>F</sup><sub>4</sub> = B(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>; aq. pK<sub>a</sub> (Et<sub>2</sub>O·H)<sup>+</sup> = -3.59]<sup>12</sup> to deliver H<sup>+</sup>/e<sup>-</sup> equivalents for the necessary proton-coupled electron transfer (PCET) events. Peters has shown that the limiting strength of the reductant necessary to drive catalytic N<sub>2</sub> reduction by the [(P<sub>3</sub>B)Fe(N<sub>2</sub>)]<sup>-</sup> system is determined by the reduction couple of the most reduced, active form, i.e., [(P<sub>3</sub>B)Fe(N<sub>2</sub>)]<sup>-</sup>/[(P<sub>3</sub>B)Fe(N<sub>2</sub>)]<sup>-</sup>; external e<sup>-</sup> sources with more negative potentials ought to be able to reform this species from oxidized intermediates which form concomitant with N<sub>2</sub> reduction.

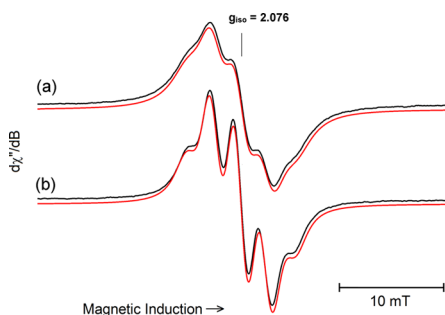
We recently reported that the simple Fe(0) complex Fe(depe)<sub>2</sub>(N<sub>2</sub>) (**1**; depe = Et<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PEt<sub>2</sub>) is remarkably

Received: August 29, 2016

Published: October 4, 2016

efficient in the stoichiometric conversion of  $N_2$  to  $N_2H_4$  and  $NH_3$  upon treatment with HOTf.<sup>13</sup> Herein we report the catalytic reduction of  $N_2$  to  $N_2H_4$  by **1**, with concomitant formation of ca. one  $NH_3$  molecule; the amount of  $N_2H_4$  produced is significantly higher ( $\sim 25$  turnovers of  $N_2$ ) than for any known molecular catalyst and utilizes milder  $H^+/e^-$  sources than previous Fe-catalyzed protocols.

Stoichiometric  $N_2$  fixation using **1**/HOTf proved to be too rapid to study mechanistically using standard spectroscopic techniques, even under cryogenic conditions ( $< -78$  °C). Accordingly we investigated a series of weaker acid salts incorporating  $[TfO]^-$ , since we have previously shown that this anion was privileged in obtaining high yields of fixed-N products (e.g., compared with  $[BAR^F_4]^-$  or  $Cl^-$  acid analogues);<sup>13</sup> this behavior is possibly due to its hemilabile nature and capacity to H-bond, which could stabilize  $Fe(N_xH_y)$  ( $x = 1, 2; y = 1-4$ )<sup>14</sup> intermediates through  $N-H\cdots[OTf]^-$  interactions. After an extensive survey, we found that  $[Ph_2NH_2][OTf]$  could promote the conversion of  $N_2$  in **1** to  $N_2H_4/NH_3$  with even greater efficiency than HOTf (based on  $e^-$  conversions, THF or  $Et_2O$ ; see SI), despite its markedly weaker protic strength (aq.  $pK_a$   $[Ph_2NH_2]^+$ , HOTf = +0.8, -12).<sup>15,16</sup> Curiously, during these acidifications, the reaction color changed from orange (**1**) to green, before ultimately becoming almost colorless; in the case of HOTf this was transient ( $\sim 10$  s), yet for  $[Ph_2NH_2][OTf]$ , this lasted for  $\sim 5$  min. The CW X-band EPR spectrum of a warming frozen THF solution of **1**/ $[Ph_2NH_2][OTf]$  (1:10; 160 K) was initially silent, thereafter a single isotropic signal (Figure 2a; 223

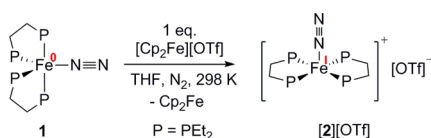


**Figure 2.** X-band CW-EPR spectra of (a) in situ reaction of **1**/ $[Ph_2NH_2][OTf]$  and (b)  $[2][OTf]$  in THF at 223 K (black traces). The microwave frequency was 9.3941 and 9.4010 GHz for (a) and (b), respectively, with 1 mW power and 0.5 mT of 100 kHz field modulation. EPR simulations (red traces) involved an isotropic  $g = 2.0762(5)$  and four  $A_{iso}(^{31}P) = 66.2(2)$  MHz, while line widths were (Gaussian, Lorentzian) parts of (a: 1, 2.07) mT and (b: 1.1, 1.34) mT.

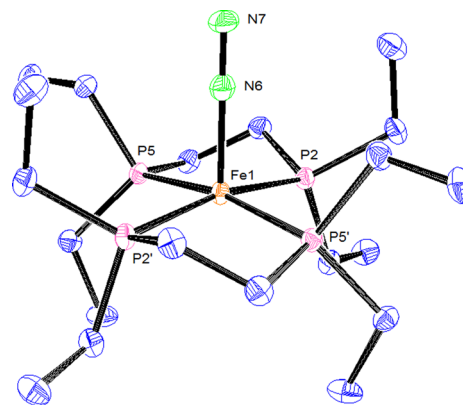
K) appeared with evidence of hyperfine coupling, which subsequently decayed rapidly upon reaching room temperature; such a resonance at  $g = 2.076$  is characteristic of a low-spin  $S = 1/2$  Fe complex.

We postulated that the identity of the paramagnetic species might be the Fe(I) counterpart of **1**;  $[Cp_2Fe][OTf]$  oxidation of **1** (1:1) afforded green solutions (Scheme 1) from which a

#### Scheme 1. Synthesis of $[Fe(depe)_2(N_2)][OTf]$ ; $[2][OTf]$



yellow-green microcrystalline solid was isolated upon workup (72% yield). Single crystals suitable for X-ray diffraction (XRD) were obtained from slow diffusion of  $Et_2O$  into a THF solution, which indeed solved as  $[Fe(depe)_2(N_2)]^+[OTf]^-$  ( $[2][OTf]$ ; Figure 3).



**Figure 3.** ORTEP diagram of the  $[Fe(depe)_2(N_2)]^+$  fragment in  $[2][OTf]$ . Thermal ellipsoids set at 50% probability. C atoms in blue, P in pink, Fe in orange, and N in green. H atoms and the  $[OTf]^-$  counterion have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe(1)–N(6) 1.857(6); N(6)–N(7) 1.121(9); Fe(1)–P(2) 2.2471(9); Fe(1)–P(5) 2.2512(9); Fe(1)–N(6)–N(7) 180.0; P(2)–Fe(1)–P(2') 168.09(8); P(5)–Fe(1)–P(5') 169.05(8); P(2)–Fe(1)–P(5') 95.03(3); P(2)–Fe(1)–P(5) 83.83(3).

$[2][OTf]$  is extremely air-sensitive, insoluble in  $Et_2O$  yet appreciably so in THF; the magnetic moment (Evans NMR, THF) of  $\mu_{eff} = 1.80 \mu_B$ , is in good agreement with the spin-only value for a low-spin  $d^7$  complex ( $S = 1/2$ ,  $1.73 \mu_B$ ). Coordination of  $N_2$  in solution was confirmed by a  $\nu_{NN}$  stretch (IR:  $2052 \text{ cm}^{-1}$ ; THF). Crucially, the CW-EPR X-band spectrum of  $[2][OTf]$  (THF, 223 K) produced an almost identical resonance to that observed for the in situ experiment of **1**/ $[Ph_2NH_2][OTf]$ , albeit with more clearly resolved hyperfine coupling to 4 equiv P nuclei (Figure 2b). Notably, the Fe(I) analogue  $[Fe(N_2)(DMeOPrPE)_2]^+$  ( $DMeOPrPE = R_2PC_2H_4PR_2R$ ;  $R = CH_2CH_2CH_2OMe$ ) has been previously described, yet its characterization was only conducted in the solution phase;<sup>17</sup> the UV-vis ( $\lambda_{max}$  (nm) = 1000, 360) spectral data for  $[2]^+$  are indeed very similar (see SI),<sup>18</sup> and conclusively our solid-state XRD data are able to structurally validate the existence of a  $[Fe(N_2)(diphosphine)_2]^+$  moiety, for which the square pyramidal geometry is unprecedented in Fe(I) dinitrogen chemistry.

Cyclic voltammetry studies on  $[2][OTf]$  ( $[nBu_4N][OTf]$  electrolyte, THF, vs  $Fc^+/Fc$ ) revealed a reversible  $1e^-$  reduction at  $-1.96$  V for the  $[2]^+/1$  couple, in addition to an irreversible Fe(I/II) oxidation at  $E_{p,ox} = \sim -1.1$  V. These potentials are comparable to the redox manifold  $[(P_3B)Fe(N_2)]/[(P_3B)Fe(N_2)]^-$  ( $E_{rev} = -2.2$  V vs  $Fc^+/Fc$ ) and  $[(P_3B)Fe(N_2)]/[(P_3B)Fe]^+$  ( $E_{irrev} = -1.5$  V vs  $Fc^+/Fc$ ) of the most productive  $N_2$ -fixing catalyst system, albeit being anodically shifted by over 200 mV.<sup>9b</sup>

Acidification of  $[2][OTf]$  with TfOH or  $[Ph_2NH_2][OTf]$  ( $Et_2O$  or THF) did not yield any  $N_2H_4$  or  $NH_3$ , paralleling the results of previous acidification experiments conducted on  $[Fe(N_2)(DMeOPrPE)_2]^+$  and  $[(P_3B)Fe(N_2)]$ .<sup>9b,17</sup> In the case of  $[2][OTf]$ ,  $H_2$  was rapidly produced attendant with protolytic degradation of the  $[Fe(depe)_2]$  core, as evidenced by formation

Table 1. Results of Catalytic N<sub>2</sub> Fixation Reactions in the Presence of External Reductants and Acids and Fe Compounds<sup>a</sup>

$$\text{N}_2 \xrightarrow[\text{Fe compound}]{\text{Acid, reductant}} \text{N}_2\text{H}_4 + \text{NH}_3$$

-78 °C to 25 °C, 3 h

entry	compd <sup>b</sup>	reductant (eq)	acid (eq)	N <sub>2</sub> H <sub>4</sub> (eq) <sup>c</sup>	NH <sub>3</sub> (eq) <sup>c</sup>	N atom yield (eq) <sup>d</sup>	e <sup>-</sup> yield (%) <sup>e</sup>
1 <sup>f</sup>	1	CoCp* <sub>2</sub> (18)	[Ph <sub>2</sub> NH <sub>2</sub> ][OTf] (24)	0.6	0.4	1.6	18
2 <sup>g</sup>	1	CoCp* <sub>2</sub> (18)	[Ph <sub>2</sub> NH <sub>2</sub> ][OTf] (24)	1.6 ± 0.1	0.9 ± 0.1	4.1 ± 0.3	46 ± 0
3 <sup>g</sup>	1	CoCp* <sub>2</sub> (36)	[Ph <sub>2</sub> NH <sub>2</sub> ][OTf] (48)	5.0 ± 0.1	0.95 ± 0.05	11 ± 0.2	60.5 ± 1.5
4 <sup>g</sup>	1	CoCp* <sub>2</sub> (54)	[Ph <sub>2</sub> NH <sub>2</sub> ][OTf] (108)	8.9 ± 0.1	1.1 ± 0.2	19 ± 0.5	70 ± 2
5 <sup>h</sup>	1	CoCp* <sub>2</sub> (270)	[Ph <sub>2</sub> NH <sub>2</sub> ][OTf] (360)	24.5 ± 0.4	0.95 ± 0.05	50 ± 0.8	37.5 ± 0.5
6	1	CoCp* <sub>2</sub> (360)	[Ph <sub>2</sub> NH <sub>2</sub> ][OTf] (480)	17.0	0.3	34	19
7	1	CoCp* <sub>2</sub> (2 × 36)	[Ph <sub>2</sub> NH <sub>2</sub> ][OTf] (2 × 48)	4.7	0.6	10	28
8	none	CoCp* <sub>2</sub> (36)	[Ph <sub>2</sub> NH <sub>2</sub> ][OTf] (48)	0	0	0	0
9	1	CoCp <sub>2</sub> (36)	[Ph <sub>2</sub> NH <sub>2</sub> ][OTf] (48)	0	0	0	0
10	1	KC <sub>8</sub> (18)	[Ph <sub>2</sub> NH <sub>2</sub> ][OTf] (24)	0.1	<0.1	0.2	3
11	[2][OTf]	CoCp* <sub>2</sub> (36)	[Ph <sub>2</sub> NH <sub>2</sub> ][OTf] (48)	2.2	0.6	5.1	29
12	1	CoCp* <sub>2</sub> (18)	[Ph <sub>2</sub> NH <sub>2</sub> ][BAR <sup>F</sup> <sub>4</sub> ] (24)	<0.1	0.2	0.2	4
13	[3][OTf] <sub>2</sub>	CoCp* <sub>2</sub> (36)	[Ph <sub>2</sub> NH <sub>2</sub> ][OTf] (48)	0.6	0.75	2.0	4

<sup>a</sup>All reactions performed at -78 °C and warmed gradually to 25 °C in Et<sub>2</sub>O solution under N<sub>2</sub>, unless otherwise indicated; eq = equivalents. N<sub>2</sub>H<sub>4</sub> and NH<sub>3</sub> yields were determined using *p*-dimethylbenzaldehyde and <sup>1</sup>H NMR spectroscopy, respectively, upon liberation via base distillation (see SI for full experimental details). <sup>b</sup>8 μmol Fe compound. <sup>c</sup>Yields per mol Fe. <sup>d</sup>N atom yield = 2[N<sub>2</sub>H<sub>4</sub> (eq)] + [NH<sub>3</sub> (eq)]. <sup>e</sup>Yield assuming (2/1/0) e<sup>-</sup> available per initial Fe(0/I/II) center + external reductant. <sup>f</sup>Performed in THF. <sup>g</sup>Average 2 runs. <sup>h</sup>Average 3 runs.

of [depe(H)<sub>2</sub>]<sup>2+</sup> (identified by <sup>1</sup>H and <sup>31</sup>P NMR). Thus, while the Fe(0) complex **1** is a potent 1e<sup>-</sup> reductant, the substantially weaker Fe(I/II) couple for [2]<sup>+</sup> cannot provide a sufficient driving force for N<sub>2</sub> reduction with these H<sup>+</sup> sources, although this is likely due to kinetic rather than thermodynamic factors.<sup>19</sup>

Since [2]<sup>+</sup> forms in the N<sub>2</sub>H<sub>4</sub> and NH<sub>3</sub>-producing stoichiometric acidification of **1**, yet it is not able to fix N<sub>2</sub> under these conditions, it is evident that regeneration of active **1** via reduction of [2]<sup>+</sup> (i.e., -1.96 V) will be necessary to engender conditions suitable for a catalytic protocol. Gratifyingly we discovered that CoCp\*<sub>2</sub> (*E* = -1.98 V vs Fc<sup>+</sup>/Fc; THF) converts an Et<sub>2</sub>O suspension (15 min) or THF solution (instant) of [2][OTf] to **1**, as ascertained by <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy, along with precipitation of [CoCp\*<sub>2</sub>][OTf]. Use of the much stronger reductant KC<sub>8</sub> was also effective in THF, whereas weaker CoCp<sub>2</sub> (*E* = -1.31 V vs Fc<sup>+</sup>/Fc; DME)<sup>20</sup> was not.

Having established that [Ph<sub>2</sub>NH<sub>2</sub>][OTf] and **1** form N<sub>2</sub>H<sub>4</sub>, NH<sub>3</sub>, and [2][OTf] and that CoCp\*<sub>2</sub> is capable of reducing the latter to **1**, our attention turned to employing this H<sup>+</sup> and e<sup>-</sup> combination in excess and testing whether **1** could effect catalytic N<sub>2</sub> reduction. Using THF as solvent (Table 1, entry 1), only substoichiometric N<sub>2</sub> conversion to N<sub>2</sub>H<sub>4</sub> and NH<sub>3</sub> was observed, which we attribute to the rapid background reaction between CoCp\*<sub>2</sub> and [Ph<sub>2</sub>NH<sub>2</sub>][OTf] in the homogeneous reaction mixture, which squanders reducing equivalents to produce H<sub>2</sub>. In order to suppress this competing side-reaction, we changed to Et<sub>2</sub>O as reaction medium, in which [Ph<sub>2</sub>NH<sub>2</sub>][OTf] is only sparingly soluble; using a heterogeneous H<sup>+</sup> or e<sup>-</sup> source is a strategy to hinder H<sub>2</sub> formation, while promoting catalytic N<sub>2</sub> fixation by synthetic complexes.<sup>9a,21</sup> As can be seen in entries 2–4, significant catalytic turnover of N<sub>2</sub> to produce N<sub>2</sub>H<sub>4</sub> and NH<sub>3</sub> is achieved using **1** under this protocol, with high efficiencies (up to 72%), based on the limiting reagent (electrons supplied; 2e<sup>-</sup>/Fe(0) and 1e<sup>-</sup>/CoCp\*<sub>2</sub>). A maximum turnover of 25.4 molecules of N<sub>2</sub> reduced (50.8 fixed-N atom equivalents, entry 5) was demonstrated for 270 and 360 equiv of CoCp\*<sub>2</sub> and [Ph<sub>2</sub>NH<sub>2</sub>][OTf], respectively, displaying one of the highest N<sub>2</sub> conversions for a molecular catalyst to date and proving impressively selective for N<sub>2</sub>H<sub>4</sub> over NH<sub>3</sub>. This set of conditions

represented the optimal conversion since mass transfer effects limit the overall yield at higher H<sup>+</sup>/e<sup>-</sup> loadings, when the reaction becomes too viscous to mix efficiently (due to formation of [CoCp\*<sub>2</sub>][OTf]<sub>(s)</sub>; entry 6).<sup>22</sup> Attempting to recharge the reaction with the same amount of H<sup>+</sup> and e<sup>-</sup> (entry 7) gave a very similar total N atom yield to the single-charge result (entry 3), showing that no catalytic activity remains postreaction. Additionally, the control reaction of CoCp\*<sub>2</sub> and [Ph<sub>2</sub>NH<sub>2</sub>][OTf], as well as isotopic labeling experiments using <sup>15</sup>N<sub>2</sub> (see SI), conclusively demonstrates that the reaction atmosphere, and not the acid salt, is the source of N<sub>2</sub>H<sub>4</sub> and NH<sub>3</sub> (entry 8). Use of the weaker (CoCp<sub>2</sub>; entry 9) or stronger (KC<sub>8</sub>; entry 10) reductants is clearly inferior; in the latter case, this can be attributed to the heterogeneous nature of both acid and reductant, which leads to inefficient PCET kinetics. [2][OTf] is also catalytically competent (entry 11), although it is not as effective as **1**; this we ascribe to its faster, nonproductive reaction with [Ph<sub>2</sub>NH<sub>2</sub>][OTf] vs reduction by CoCp\*<sub>2</sub>, when it is introduced in relatively higher concentrations at the start of the reaction. Substituting the [OTf]<sup>-</sup> counterion with [BAR<sup>F</sup><sub>4</sub>]<sup>-</sup> in the acid salt resulted in only trace N<sub>2</sub>H<sub>4</sub>/NH<sub>3</sub> (entry 13) and parallels stoichiometric acidification results using [H(OEt)<sub>2</sub>][BAR<sup>F</sup><sub>4</sub>]<sup>13</sup> suggesting that [BAR<sup>F</sup><sub>4</sub>]<sup>-</sup> (in contrast to [OTf]<sup>-</sup>) is extremely detrimental to the mechanistic steps involved for the **1**-mediated reduction of N<sub>2</sub>.

Uniquely, increased concentrations of CoCp\*<sub>2</sub> and [Ph<sub>2</sub>NH<sub>2</sub>][OTf] result in increased N<sub>2</sub>H<sub>4</sub> formation instead of NH<sub>3</sub>, demonstrating that N<sub>2</sub> reduction proceeds almost exclusively via a N<sub>2</sub>H<sub>4</sub> pathway. We believe that reduction of N<sub>2</sub> proceeds via initial N<sub>β</sub> protonation of **1**, with ensuing PCET reductions leading to an Fe(N<sub>2</sub>H<sub>4</sub>) intermediate, by analogy to the conversion steps [(P<sub>3</sub>Si)Fe(N<sub>2</sub>)]<sup>-</sup> → [(P<sub>3</sub>Si)Fe(=N-NH<sub>2</sub>)] → [(P<sub>3</sub>Si)Fe(NH<sub>2</sub>NH<sub>2</sub>)]<sup>+</sup> reported by Peters,<sup>23</sup> this is subsequently intercepted through protonation by [Ph<sub>2</sub>NH<sub>2</sub>][OTf] to form [N<sub>2</sub>H<sub>5</sub>][OTf], which is completely insoluble in Et<sub>2</sub>O. Indeed, control reactions of CoCp\*<sub>2</sub> and [N<sub>2</sub>H<sub>5</sub>][OTf] (with or without [Ph<sub>2</sub>NH<sub>2</sub>][OTf]) in Et<sub>2</sub>O led to no reaction, whereas analogous homogeneous experiments in THF instantaneously react to produce NH<sub>3</sub> and [CoCp\*<sub>2</sub>][OTf]. This



demonstrates that the inability to observe further reduction of  $[\text{N}_2\text{H}_5]^+$  is likely due to kinetic (solubility) factors. We postulated that the  $\text{N}_2\text{H}_4$ -producing pathway may involve the hitherto unknown Fe(II)  $[\text{Fe}(\text{depe})_2(\text{N}_2\text{H}_4)]^{2+}$  complex, for which the DMeOPrPE and dmpe counterparts (dmpe =  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ) have been reported.<sup>24</sup> Accordingly we synthesized *cis*- $[\text{Fe}(\text{depe})_2(\eta^2\text{-N}_2\text{H}_4)][\text{OTf}]_2$  ( $[\mathbf{3}][\text{OTf}]_2$ ) via reaction of  $[\mathbf{2}][\text{OTf}]$  and  $[\text{N}_2\text{H}_5][\text{OTf}]$ . The complex was crystallographically characterized, and the metric parameters closely resemble its congeners, apart from extensive H-bonding between  $\text{TfO}^-$  counteranions and the  $\text{N}_2\text{H}_4$  ligand (see SI). Surprisingly, subjecting  $[\mathbf{3}][\text{OTf}]_2$  to the catalytic  $\text{CoCp}^*/[\text{Ph}_2\text{NH}_2][\text{OTf}]$  protocol yielded only a stoichiometric amount of fixed-N products (Table 1, entry 13), thus demonstrating that it cannot be an on-cycle intermediate. In light of the recent report by Peters et al. which suggested a hydride resting state in their catalytic  $\text{N}_2$ -to- $\text{NH}_3$  system,<sup>9b</sup> we also assessed the catalytic competence of the Fe(II) hydride *trans*- $[\text{Fe}(\text{H})(\text{N}_2)(\text{depe})_2][\text{OTf}]$  ( $[\mathbf{4}][\text{OTf}]$ ). No fixed N-products were produced, which we believe can be attributed to the failure of  $\text{CoCp}^*$  to reduce  $[\mathbf{4}][\text{OTf}]$  to  $\mathbf{1}$ , either with or without  $[\text{Ph}_2\text{NH}_2][\text{OTf}]$ , hence we conclude that it is not a mechanistically relevant species (see SI).

<sup>31</sup>P and <sup>1</sup>H NMR spectroscopic analysis of the postcatalytic reaction mixture showed only  $[\text{depe}(\text{H})_2][\text{OTf}]_2$ ,  $[\text{N}_2\text{H}_5][\text{OTf}]$  and  $[\text{NH}_4][\text{OTf}]$  in the precipitate (which explains the nonresumption of catalytic activity upon additional loadings of  $\text{CoCp}^*/[\text{Ph}_2\text{NH}_2][\text{OTf}]$ ), whereas the  $\text{Et}_2\text{O}$  supernatant showed  $\text{Ph}_2\text{NH}$  as the only diamagnetic species present; both fractions were silent by EPR (X-band) spectroscopy. Interestingly, base distillation of the solution revealed that it is the source of the majority of the  $\text{NH}_3$  produced (80%),<sup>25</sup> indicating that it may originate from an as yet unidentified soluble Fe complex.<sup>26</sup>

In conclusion, we have demonstrated the effective catalytic, and selective, fixation of  $\text{N}_2$  to  $\text{N}_2\text{H}_4$  by  $\text{Fe}(\text{depe})(\text{N}_2)$ , using considerably milder  $\text{H}^+$  and  $\text{e}^-$  sources than previously used in Fe-catalyzed protocols. Rational development of this system has allowed the catalytic reduction of over 25 molecules of  $\text{N}_2$ , with increased loadings of  $\text{H}^+$  and  $\text{e}^-$  equivalents directly translating to greater  $\text{N}_2\text{H}_4$  yields. This represents the highest production of  $\text{N}_2\text{H}_4$  observed for any known molecular catalyst to date and is distinct from transition-metal  $\text{N}_2$  fixation catalysts which are highly selective for  $\text{NH}_3$ . The judicious choice of  $[\text{OTf}]^-$  counteranion and  $\text{Et}_2\text{O}$  solvent fortuitously exposes a  $\text{N}_2\text{H}_4$  mechanistic pathway, due to kinetic precipitation of  $[\text{N}_2\text{H}_5][\text{OTf}]$ . While the exact nature of the reactive intermediates for reduction of  $\text{N}_2$  in this system is as yet unknown, investigations into the mechanism of this important transformation are currently underway.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b08802.

Crystallographic data (TXT)

Crystallographic data (TXT)

Crystallographic data (TXT)

Experimental details and data (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

\*a.ashley@imperial.ac.uk

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We wish to thank the EPSRC (L.R.D. and P.J.H.) and an Imperial College Scholarship (A.D.C.) for Ph.D. studentship funding and the Royal Society for a University Research Fellowship (AEA/UF110061).

## ■ REFERENCES

- (1) Hinrichsen, S.; Broda, H.; Gradert, C.; Sönksen, L.; Tuczek, F. *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **2012**, *108*, 17.
- (2) Jia, H. P.; Quadrelli, E. A. *Chem. Soc. Rev.* **2014**, *43*, 547.
- (3) Hu, Y. L.; Ribbe, M. W. *JBIC, J. Biol. Inorg. Chem.* **2015**, *20*, 435.
- (4) Hazari, N. *Chem. Soc. Rev.* **2010**, *39*, 4044.
- (5) (a) Nishibayashi, Y. *Inorg. Chem.* **2015**, *54*, 9234. (b) MacLeod, K. C.; Holland, P. L. *Nat. Chem.* **2013**, *5*, 559.
- (6) Schirrmann, J.-P.; Bourdauducq, P. Hydrazine. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2001.
- (7) Maxwell, G. R. *Synthetic nitrogen products: a practical guide to the products and processes*; Kluwer Academic/Plenum Publishers: New York, 2004.
- (8) Bazhenova, T. A.; Shilov, A. E. *Coord. Chem. Rev.* **1995**, *144*, 69.
- (9) (a) Anderson, J. S.; Rittle, J.; Peters, J. C. *Nature* **2013**, *501*, 84. (b) Del Castillo, T. J.; Thompson, N. B.; Peters, J. C. *J. Am. Chem. Soc.* **2016**, *138*, 5341.
- (10) Ung, G.; Peters, J. C. *Angew. Chem., Int. Ed.* **2014**, *54*, 532.
- (11) Kuriyama, S.; Arashiba, K.; Nakajima, K.; Matsuo, Y.; Tanaka, H.; Ishii, K.; Yoshizawa, K.; Nishibayashi, Y. *Nat. Commun.* **2016**, *7*, 12181.
- (12) Arnett, E. M.; Wu, C. Y. *J. Am. Chem. Soc.* **1960**, *82*, 4999.
- (13) Doyle, L. R.; Hill, P. J.; Wildgoose, G. G.; Ashley, A. E. *Dalton Trans.* **2016**, *45*, 7550.
- (14) Köthe, C.; Limberg, C. Z. *Anorg. Allg. Chem.* **2015**, *641*, 18.
- (15) (a) Arnett, E. M.; Quirk, R. P.; Burke, J. J. *J. Am. Chem. Soc.* **1970**, *92*, 1260. (b) Raamat, E.; Kaupmees, K.; Ovsjannikov, G.; Trummal, A.; Kütt, A.; Saame, J.; Koppel, I.; Kaljurand, I.; Lipping, L.; Rodima, T.; Pihl, V.; Koppel, I. A.; Leito, I. *J. Phys. Org. Chem.* **2013**, *26*, 162.
- (16) We have previously shown that weaker acids such as 2,6-dimethylpyridinium (aq.  $\text{p}K_a = 6.8$ ) are ineffective; see ref 13.
- (17) Balesdent, C. G.; Crossland, J. L.; Regan, D. T.; López, C. T.; Tyler, D. R. *Inorg. Chem.* **2013**, *52*, 14178.
- (18)  $[\text{Fe}(\text{N}_2)(\text{DMeOPrPE})_2]^+$  (see ref 17) is proposed to equilibrate between bimetallic  $\{[\text{Fe}(\text{DMeOPrPE})_2]_2(\mu\text{-N}_2)\}^{2+}$  and  $\text{N}_2$  at elevated temperature and/or limiting  $\text{N}_2$ . While we do observe comparable changes in the UV-vis spectrum under similar conditions, the corresponding EPR spectra for  $[\mathbf{2}][\text{OTf}]$  are complicated, which may be due to competing  $\text{N}_2$  loss and/or  $[\text{OTf}]^-$  coordination. Accordingly, an unambiguous assignment of the solution-phase speciation is not possible. This is the subject of ongoing investigation and will be reported in due course.
- (19) Lindley, B. M.; Appel, A. M.; Krogh-Jespersen, K.; Mayer, J. M.; Miller, A. J. M. *ACS Energy Lett.* **2016**, *698*.
- (20) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
- (21) (a) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76. (b) Arashiba, K.; Miyake, Y.; Nishibayashi, Y. *Nat. Chem.* **2011**, *3*, 120.
- (22) The yields of fixed-N products were highly sensitive to the concentration of  $\mathbf{1}$ , with higher dilutions proving detrimental.
- (23) Rittle, J.; Peters, J. C. *J. Am. Chem. Soc.* **2016**, *138*, 4243.
- (24) (a) Crossland, J. L.; Zakharov, L. N.; Tyler, D. R. *Inorg. Chem.* **2007**, *46*, 10476. (b) Field, L. D.; Li, H. L.; Magill, A. M. *Inorg. Chem.* **2009**, *48*, 5.
- (25) Aqueous base distillation (KOH) of  $\text{Ph}_2\text{NH}$  did not produce  $\text{NH}_3$ , thus confirming that the source of  $\text{NH}_3$  cannot be from the organic base.
- (26) Mass spectrometric analysis (EI and ES) of the solution unfortunately did not provide evidence for the identity of the unknown Fe-containing species.