Catalytic N$_2$-to-NH$_3$ Conversion by Fe at Lower Driving Force: A Proposed Role for Metallocene-Mediated PCET

Matthew J. Chalkley,† Trevor J. Del Castillo,† Benjamin D. Matson,† Joseph P. Roddy, and Jonas C. Peters*

Division of Chemistry and Chemical Engineering, California Institute of Technology (Caltech), Pasadena, California 91125, United States

ABSTRACT: We have recently reported on several Fe catalysts for N$_2$-to-NH$_3$ conversion that operate at low temperature (−78 °C) and atmospheric pressure while relying on a very strong reductant (KC$_8$) and acid ([H(OEt$_2$)$_2$][BArF$_4$]). Here we show that our original catalyst system, P$_3$BFe, achieves both significantly improved efficiency for NH$_3$ formation (up to 72% for e$^-$ delivery) and a comparatively high turnover number for a synthetic molecular Fe catalyst (84 equiv of NH$_3$ per Fe site), when employing a significantly weaker combination of reductant (Cp$_*^\dagger$Co) and acid ([Ph$_2$NH$_2$][OTf] or [PhNH$_3$][OTf]). Relative to the previously reported catalysis, freeze-quench Mössbauer spectroscopy under turnover conditions suggests a change in the rate of key elementary steps; formation of a previously characterized off-path borohydrido−hydrido resting state is also suppressed. Theoretical and experimental studies are presented that highlight the possibility of protonated metallocenes as discrete PCET reagents under the present (and related) catalytic conditions, offering a plausible rationale for the increased efficiency at reduced driving force of this Fe catalyst system.

The reduction of N$_2$ to NH$_3$ is critical for life and is performed on a massive scale both industrially and biologically. The high stability of the N≡N triple bond necessitates catalysts and high-energy reagents/conditions to achieve the desired transformation. Synthetic studies of catalytic N$_2$-to-NH$_3$ conversion by model complexes are of interest to constrain hypotheses concerning the mechanism/s of biological (or industrial) N$_2$-fixation and to map fundamental catalyst design principles for multielectron reductive transformations. Interest in Fe model systems that catalyze N$_2$-to-NH$_3$ conversion has grown in part due to the postulate that one or more Fe centers in the FeMo-cofactor of FeMo-nitrogenase may serve as the site of N$_2$ binding and activation during key bond-breaking and -making steps. Previous examples of synthetic molecular Fe catalysts that mediate N$_2$-to-NH$_3$ conversion operate with high driving force, relying on a very strong acid (pK$_a$ ca. 0) and reductant (E$^0$ ≤ −3.0 V vs Fe$^{+/0}$). In contrast, several Mo catalysts have been shown to facilitate N$_2$-to-NH$_3$ conversion with significantly lower driving force. There is thus interest in exploring the viability of Fe-mediated catalytic N$_2$-to-NH$_3$ conversion under less forcing conditions from a practical perspective, and to continue assessing these systems as functional models of biological nitrogenses, in which 8 ATP are consumed per NH$_3$ formed providing a total driving force of 58 kcal/mol.

Such conditions additionally afford unusually high selectivity and catalytic turnover for NH$_3$. Moreover, we note that the use of milder reagents as reductant (E$^0$; eq 1) and acid (pK$_a$; eq 1) engenders a higher effective bond dissociation enthalpy (BDE$_{\text{effective}}$; eq 1). This may in turn afford access to proton-coupled electron transfer (PCET) pathways (e.g., FeN$_2$ + H$^+$ → FeN$_2$H) in addition to electron transfer (ET)/proton transfer (PT) pathways, thus enhancing overall catalytic.

Received: January 9, 2017

Figure 1. Summary of conditions used for catalytic N$_2$-to-NH$_3$ conversion by P$_3$BFe$^+$ highlighting the estimated enthalpic driving force (ΔΔH$_{\text{f}}$).
efficiency. Theoretical considerations, including DFT calculations, and experimental details are discussed that suggest the viability of a decamethylcobaltocene-mediated PCET pathway in this system; by extension we suggest that metallocene-mediated (e.g., Cp²⁺Co) PCET pathways may be operative in previously studied Mo and Fe N₂-fixing systems that use metallocene reductants.¹⁰–¹³,²⁰

\[ \text{BDE}_{\text{effective}} = 1.37(pK_a) + 23.06(E^f) + C_H \]  

Various observations of P₃Fe complexes in the presence of acids and reductants suggested that this system might be capable of N₂-to-NH₃ conversion with lower driving force than that originally reported. Accordingly, we had observed that the treatment of P₃FeN₂⁺ with KC₈ and weaker acids (pKₐ > 0) led to greater than stoichiometric NH₃ formation (e.g., under unoptimized conditions [2,6-dimethylanilinium][OTf] afforded 2.1 equiv of NH₃ per Fe).²² Similarly, the treatment of P₃FeN₂⁺ with [H(OEt)]₃[BAF₄] (HBArF₄ = tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate) and weaker reductants led to modest yields of NH₃. For example, under unoptimized conditions we had observed that decamethylcobaltocene (Cp²⁺Co) and HBArF₄ afforded 0.6 equiv of NH₃ per Fe.²²,²³

Most recently, an apparent catalytic response was observed during a cyclic voltammetry experiment at the p₄FeN₆⁰⁻/⁰-couple (−2.1 V vs Fe⁰/⁰⁺) upon addition of excess HBArF₄ under a N₂ atmosphere. Electrolytic NH₃ generation by p₄FeFe' was observed at −2.4 V vs Fe⁰/⁰⁺ in Et₂O,²₅ and Na/Hg (−2.4 V vs Fe⁰/⁰⁺ in THF).¹⁶ could instead be used for N₂-to-NH₃ conversion (albeit less selectively and with low turnover). Finally, mixing P₃FeFe' with Cp²⁺Co in Et₂O at −78 °C under N₂ generates some P₃FeN₂⁺ as observed by X-band EPR and Mössbauer spectroscopy (see the Supporting Information), suggesting that Cp²⁺Co is in principle a sufficiently strong reductant to trigger catalysis by P₃FeFe'.

Treatment of P₃FeFe' with Cp²⁺Co and [Ph₂NH₂][OTf], [Ph₂NH₂][BAF₄] or [PhNH₂][OTf] in Et₂O at −78 °C under an N₂ atmosphere affords catalytic yields of NH₃. (Table 1). Notably, the highest selectivity for NH₃ obtained among this series (72% at standard substrate loading; entry 1) is significantly improved compared to all previously described (molecular) Fe catalysts for N₂-to-NH₃ conversion.²⁰,²₄

Table 1. N₂-to-NH₃ Conversion with P₃Fe Complexes (M = Fe, Co)₄

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Cp²⁺Co (equiv)</th>
<th>acid (equiv)</th>
<th>equiv of NH₃/Fe</th>
<th>% yield of NH₃/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P₃FeFe'</td>
<td>54</td>
<td>108</td>
<td>12.8 ± 0.5</td>
</tr>
<tr>
<td>2</td>
<td>P₃FeFe'</td>
<td>162</td>
<td>32²</td>
<td>34 ± 1</td>
</tr>
<tr>
<td>3</td>
<td>P₃FeFe'</td>
<td>322</td>
<td>63²</td>
<td>26.7 ± 0.9</td>
</tr>
<tr>
<td>4</td>
<td>P₃FeFe'</td>
<td>[322] × 2</td>
<td>[32²] × 2²</td>
<td>56 ± 9</td>
</tr>
<tr>
<td>5</td>
<td>P₃FeFe'</td>
<td>[322] × 3</td>
<td>[32²]</td>
<td>84 ± 8</td>
</tr>
<tr>
<td>6</td>
<td>P₃FeFe'</td>
<td>54</td>
<td>108²</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>7</td>
<td>P₃FeFe'</td>
<td>162</td>
<td>32²</td>
<td>16 ± 1</td>
</tr>
<tr>
<td>8</td>
<td>P₃FeFeN₂⁺</td>
<td>162</td>
<td>32²</td>
<td>12.1 ± 0.1</td>
</tr>
<tr>
<td>9</td>
<td>P₃FeCoN₂⁺</td>
<td>54</td>
<td>108²</td>
<td>1.1 ± 0.4</td>
</tr>
<tr>
<td>10</td>
<td>P₃FeCoN₂⁺</td>
<td>54</td>
<td>108²</td>
<td>0 ± 0</td>
</tr>
</tbody>
</table>

*The catalyst, acid, Cp²⁺Co, and Et₂O were sealed in a vessel at −196 °C under an N₂ atmosphere following warming to −78 °C and stirring. Yields are reported as an average of at least 2 runs; for individual experiments see the Supporting Information, b. For these experiments the reaction was allowed to proceed for 3 h at −78 °C before cooling to −196 °C and furnishing with additional substrate and solvent. c[Ph₂NH₂][OTf], d[Ph₂NH₂][BAF₄] e[PhNH₂][OTf].

ACS Central Science
assignment, but its high isomer shift and large quadrupole splitting are suggestive of a tetrahedral, \( S = 2 \) Fe(II) complex.\(^{31,32}\) The Mössbauer spectrum of a catalytic reaction mixture after 30 min was also analyzed (see the Supporting Information). The spectrum still shows \( P_3 \) FeN\(_2\) (53%), the same unknown \( P_3 \) Fe species (18%), and again a tetrahedral, high-spin Fe(II) component (22%). However, \( P_3 \) Fe\(^+\) is now present (\( \delta = 0.75 \) mm/s, \( \Delta E_Q = 2.55 \) mm/s, 8%) and \( P_3 \) FeN\(_2\)\(^-\) is no longer observed. The reloading experiments described above provide strong evidence that “\( P_3 \) Fe” species represent an “active catalyst” population; interpretation of the relative speciation via spectroscopy should hence bear on the mechanism of the overall catalysis.

The appearance of a presumed high-spin (\( S = 2 \)), tetrahedral Fe(II) species during catalysis (ca. 25%) might arise via dechelation of a phosphine arm. This species could represent an off-path state or a downstream deactivation product. Interestingly, under the present catalytic conditions we do not observe the borohydrido–hydrido species \( P_3 \) Fe\(^+\)(\( \mu \)-H)Fe(H)\(_2\)\( (L) (L = N_2 \) or \( H_2 \) ); this species was postulated to be an off-path state during \( N_2 \)-to-NH\(_3\) conversion catalysis using HBAr\(^+\) and KC\(_8\) and was the major component observed at early times (ca. 60% at 5 min).\(^{23}\) It therefore appears that a larger fraction of the “\( P_3 \) Fe” species are in a catalytically on-path state at early reaction times under these new catalytic conditions.

Additionally, the presence of a significant degree of \( P_3 \) Fe\(^+\)N\(_2\)\(^-\) (Figure 2) at an early time point is distinct from conditions with HBAr\(^+\) and KC\(_8\).\(^{23}\) This observation is consistent with the notion that protonation of \( P_3 \) FeN\(_2\)\(^-\) is slowed under the present conditions, likely as a result of the insolubility of the triflate salt [Ph\(_2\)NH\(_2\)][OTf] and its attenuated acidity relative to HBAr\(^+\).\(^{17,18,33}\) Clearly, differences in the rates of key elementary steps under the new conditions described here may lead to new mechanistic scenarios for \( N_2 \)-to-NH\(_3\) conversion.

The improved catalytic efficiency at significantly lower driving force warrants additional consideration. When using HBAr\(^+\) and KC\(_8\), we have previously suggested that protonation of \( P_3 \) FeN\(_2\)\(^-\), which itself can be generated by reduction of \( P_3 \) FeN\(_2\) to produce \( P_3 \) Fe–N=NH is a critical first step; \( P_3 \) Fe–N=NH can then be trapped by acid to produce spectroscopically observable \( P_3 \) Fe=NH–NH\(_2\).\(^{29}\) These steps, shown in eqs 2a and 2b, represent an ET–PT pathway. A PT–ET pathway, where \( P_3 \) FeN\(_2\) is sufficiently basic to be protonated to generate \( P_3 \) Fe–N=NH as a first step, followed by ET, is also worth considering (eqs 3a and 3b).

A direct PCET pathway (eq 4), where H atom delivery to \( P_3 \) FeN\(_2\) occurs, thus obviating the need to access either \( P_3 \) FeN\(_2\)\(^-\) or \( P_3 \) Fe–N=NH\(_2\), needs also to be considered.

\[
\begin{align*}
(P_3 \text{FeN}_2) & + e^- \rightarrow (P_3 \text{FeN}_2)^- \\
(P_3 \text{FeN}_2)^- & + H^+ \rightarrow (P_3 \text{Fe} - \text{N}=\text{NH})^+ \\
(P_3 \text{Fe} - \text{N}=\text{NH})^+ & + e^- \rightarrow (P_3 \text{Fe} - \text{N}=\text{NH}) \\
(P_3 \text{FeN}_2) + H^+ & \rightarrow (P_3 \text{FeN}_2)^- \\
(P_3 \text{FeN}_2)^- & + H^+ \rightarrow (P_3 \text{Fe} - \text{N}=\text{NH})^+ \\
(P_3 \text{Fe} - \text{N}=\text{NH})^+ & + e^- \rightarrow (P_3 \text{Fe} - \text{N}=\text{NH}) \\
(P_3 \text{FeN}_2) + H^+ & \rightarrow (P_3 \text{FeN}_2)^- \\
(P_3 \text{FeN}_2)^- & + H^+ \rightarrow (P_3 \text{Fe} - \text{N}=\text{NH})^+ \\
(P_3 \text{Fe} - \text{N}=\text{NH})^+ & + e^- \rightarrow (P_3 \text{Fe} - \text{N}=\text{NH})
\end{align*}
\]

Initial PT to \( (P_3 \text{FeN}_2)^- \) to generate \( (P_3 \text{Fe} - \text{N}=\text{NH})^+ \) (eq 3a) is unlikely under the present conditions due to the high predicted acidity of \( (P_3 \text{Fe} - \text{N}=\text{NH})^+ \) (pK\(_a\) = −3.7; estimated via DFT; see the Supporting Information); efficient generation of such a species seems implausible for acids whose pK\(_a\)'s are calculated at 1.4 (Ph\(_2\)NH\(_2\))\(^+\) and 6.8 (PhNH\(_3\))^\(^+\) in EtO\(_2\) (Table 2). We note that [Ph\(_2\)NH\(_2\)][OTf] does not react productively with \( (P_3 \text{FeN}_2)^- \) at −78 °C in EtO\(_2\), as analyzed by Mössbauer spectroscopy.

<table>
<thead>
<tr>
<th>species</th>
<th>pK(_a)</th>
<th>BDEa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph(_2)NH(_2^+)</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>PhNH(_3^+)</td>
<td>6.8</td>
<td>31</td>
</tr>
<tr>
<td>lutidinium</td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td>endo-Cp(^+)Co(η(^5)-C(_5)Me(_5)H)(^+)</td>
<td>16.8</td>
<td>31</td>
</tr>
<tr>
<td>exo-Cp(^+)Co(η(^5)-C(_5)Me(_5)H)(^+)</td>
<td>16.8</td>
<td>31</td>
</tr>
<tr>
<td>endo-Cp(^+)Cr(η(^5)-C(_5)Me(_5)H)(^+)</td>
<td>17.3</td>
<td>37</td>
</tr>
<tr>
<td>exo-Cp(^+)Cr(η(^5)-C(_5)Me(_5)H)(^+)</td>
<td>12.1</td>
<td>30</td>
</tr>
<tr>
<td>( P_3 \text{Fe} - \text{N}=\text{NH} )(^+)</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>( P_3 \text{Fe} - \text{N}=\text{NH} )(^+)</td>
<td>38.7</td>
<td>35</td>
</tr>
<tr>
<td>( P_3 \text{Fe} = \text{N}=\text{NH}_2 )(^+)</td>
<td>14.4</td>
<td>51</td>
</tr>
<tr>
<td>( P_3 \text{Fe} = \text{N}=\text{NH}_2 )(^+)</td>
<td>47.0</td>
<td></td>
</tr>
<tr>
<td>( \text{[HIPTN}N\text{]} \text{M}=\text{N}=\text{NH} )(^+)</td>
<td>51.0</td>
<td></td>
</tr>
</tbody>
</table>

\(^\text{a}\)Calculated using the MO06-L\(3\) functional with a def2-TZVP basis set on Fe and Mo and a def2-SVP basis set on all other atoms\(^{15}\) (see the Supporting Information). \(^\text{b}\)In kcal/mol. \(^\text{c}\)Values and BDEs of Selected Species

Focusing instead on the PCET pathway (eq 4), the DFT-calculated BDE\(_{N = H}\) for \( P_3 \) Fe–N=NH (35 kcal/mol; Table 2; see the Supporting Information for details)\(^{30}\) is larger than the effective BDE\(^{21}\) of either Cp\(^+\)Co/Ph\(_2\)NH\(_2\)\(^+\) or Cp\(^+\)Co/PhNH\(_3\)\(^+\) (25 and 31 kcal/mol, respectively). This suggests that PCET (eq 4) is plausible on thermodynamic grounds. Given that we have employed Cp\(^+\)Co in this study, and that this and also Cp\(_2\)Co and Cp\(^+\)Cr have been effective in other \( N_2 \)-fixing molecular catalyst systems,\(^{10,13,30}\) we have explored via DFT several putative metallocene-derived PCET reagents. Independent studies of \( H_2 \) evolution from cobaltocene have invoked a protonated cobaltocene intermediate.\(^{37–39}\) The observation of a background \( H_2 \) evolution reaction (HER) when employing metallocene reductants, but in the absence of an \( N_2 \)-to-NH\(_3\) conversion catalyst, suggests that metallocene protonation is kinetically competent.\(^{13,30}\) Based on the analysis we describe below, we propose that protonated metallocenes may serve as discrete and highly active H\(^+\) sources for PCET.

We find that the formation of endo- and exo-Cp\(^+\)Co(η\(^5\)-C\(_5\)Me\(_5\)H)\(^+\) is predicted to be thermodynamically favorable via
protonation of Cp*Co by either Ph3NH+ or PhNH3+ (−21 and −13 kcal/mol, respectively; Figure 3A).21,42 We have calculated the BDEs of both endo- and exo-Cp*Co(η5-C5Me5H) as 31 kcal/mol (Figure 3B; Table 2), indicating that they should be among the strongest PCET reagents accessible in this catalyst cocktail. Indeed, they would be among the strongest PCET reagents known.21

We anticipate that these species would be extremely unstable in solution and hence difficult to detect in situ, but via trapping in the solid state by rapid precipitation from toluene we have isolated a species whose EPR data and chemical behavior are consistent with {Cp*Co(η5-C5Me5H)}{OTf}. Accordingly, slow addition of a toluene solution of Cp*Co to −78 °C to triflic acid (HOTf) leads to the instantaneous precipitation of a purple solid that can be handled only at low temperature. The purple solid is characterized at 77 K by powder EPR spectroscopy via its highly structured signal. By contrast, at room temperature either as a solid or as a stirred suspension in toluene leads to the formation of H2 and Cp*Co(η5-C5Me5H)+, as is to be expected given that they are predicted to be nearly isoenergetic. Allowing the purple precipitate to warm to room temperature leads to the formation of H2 and Cp*Co+.

Figure 3. (A) Calculated free-energy changes for the protonation of Cp*Co. (B) DFT optimized structure of endo-Cp*Co(η5-C5Me5H) (methyl protons omitted for clarity). (C) The unfavorable reduction of 2,6-lutidinium by Cp*Cr with the calculated free energy change. (D) The favorable protonation of Cp*Cr by lutidinium with the calculated free energy change.

To better understand the potential role of PCET in N2-to-NH3 conversion catalysis by Cp*Fe, we have additionally calculated the N–H bond strengths (Table 2) of several early stage candidate intermediates, including the aforementioned P3*Fe=N=NH (35 kcal/mol), P3*Fe=N=NH2+ (51 kcal/mol), and P3*Fe=N=NH2- (47 kcal/mol). We conclude that PCET from Cp*Co(η5-C5Me5H)+ to generate intermediates of these types is thermodynamically favorable in each case.43 To generate the first and most challenging intermediate (eq 5), the enthalpic driving force for PCET is estimated at ~4 kcal/mol (ΔGcalc = −9 kcal/mol). This driving force and, hence, the plausibility of PCET steps, increase sharply as further downstream Fe=N=NH2 intermediates are considered.44-47

\[
P3*FeN2+ + Cp*Co(\eta^5-C_5Me_5H)^+ \rightarrow P3*Fe=N=NH + Cp*Co^{2+}
\]

(5)

Stage candidate intermediates, including the aforementioned P3*Fe=N=NH (35 kcal/mol), P3*Fe=N=NH2+ (51 kcal/mol), and P3*Fe=N=NH2- (47 kcal/mol). We conclude that PCET from Cp*Co(η5-C5Me5H)+ to generate intermediates of these types is thermodynamically favorable in each case.43 To generate the first and most challenging intermediate (eq 5), the enthalpic driving force for PCET is estimated at ~4 kcal/mol (ΔGcalc = −9 kcal/mol). This driving force and, hence, the plausibility of PCET steps, increase sharply as further downstream Fe=N=NH2 intermediates are considered.44-47

Given the prevalence of metallocene reductants in N2-to-NH3 (or -N2H4) conversion, especially for the well-studied Mo catalyst systems, it is worth considering metallocene-mediated PCET more generally. For instance, a role for ET/PT steps (or conversely PT/ET) in N2-to-NH3 conversion catalyzed by [HIPTN3N]Mo (HIPTN3N = [(3,5-(2,4,6-Pr3C6H3)$_2$C$_6$H$_4$NCH2CH2)N]$_3^-$, a bulky triamidoamine ligand) has been frequently posited.48-52 But PCET steps may play a critical role, too. In the latter context, we note reports from Schrock and co-workers that have shown that both acid and reductant are required to observe productive reactivity with [HIPTN3N]MoN2. These observations are consistent with PCET to generate [HIPTN3N]Mo−N=N=NH.53 A PCET scenario has been discussed in the general context of N2-to-NH3 conversion, where a lutidinyl radical intermediate formed via ET from Cp*CoCr was suggested as a PCET reagent that can be generated in situ.40,53 However, our own calculations predict that the lutidinyl radical should not be accessible with Cp*CoCr as the reductant (ΔGcalc = +10 kcal/mol; Figure 3C).54,55 We instead propose protonation of Cp*CoCr by the lutidinium acid as more plausible (ΔGcalc = −5.3 kcal/mol; Figure 3D) to generate a highly reactive decamethylchromocene-derived PCET reagent.

While N–H bond strengths have not been experimentally determined for the [HIPTN3N]Mo system, using available published data we deduce the N–H bond of [HIPTN3N]Mo−N=N=NH to be ca. 49 kcal/mol and we calculate it via DFT (truncated HIPTN3N; see the Supporting Information) as 51 kcal/mol.57
hence much larger than we predict for P₃Fe−N≡NH (35 kcal/mol), perhaps accounting for its higher stability. A PCET reaction between endo-Cp₈Cr(η⁴-C₅Me₂H₂)₅ (BDEend = 37 kcal/mol) and [HIPTN,N,MoN₂] to generate [HIPTN,N,Mo−N≡NH and Cp₈Cr⁺] would be highly exergonic. Furthermore, we predict a similarly weak BDE for Cp-protonated cobalocene, CpCo(η⁶-C₅H₅)₄ (BDEend = 35 kcal/mol). These considerations are consistent with the reported rapid formation of [HIPTN,N,Mo−N≡NH using either Cp₈Cr or Cp₈Co in the presence of lutidinium acid.₆₀

To close, we have demonstrated catalytic N₂-to-NH₃ conversion by P₃Fe at a much lower driving force (nearly 100 kcal/mol) than originally reported via combination of a weaker reductant (Cp₂Cr or Cp₂Co in the presence of lutidinium acid.₆₀

**, freeze-quench Mo reagent. Indeed, the achievement of high efficiency for NH₃ formation is observed (up to 72% at standard substrate loading), and by reloading additional substrate at low temperature a turnover number that is comparatively high for a synthetic molecular Fe catalyst (84 ± 8 equiv of NH₃ per Fe) has been achieved. Freeze-quench Mössbauer spectroscopy under turnover conditions reveals differences in the speciation of P₃Fe compared to previous studies with HBAr₄ and KCₘₙ suggesting changes in the rates of key elementary steps. Using DFT calculations we have considered the viability of a decamethylcobalocene-mediated PCET pathway as an additional contributor to the previously formulated ET−PT and PT−ET pathways. Based on our calculations, we propose that protonated metallocenes should serve as discrete, very reactive PCET reagents in N₂-to-NH₃ conversion catalysis. Furthermore, we present preliminary experimental data that suggests that protonated decamethylcobalocene can be accessed synthetically and that such a species may be a potent PCET reagent. Indeed, the achievement of high efficiency for N₂-to-NH₃ conversion by both P₃Fe and various Mo catalysts that benefit from metallocene reductants raises the intriguing possibility that metallocene-based PCET reactivity is a potentially widespread and overlooked mechanism. Efforts are underway to experimentally probe such pathways.

**REFERENCES**


The enthalpic driving force (∆ΔH) has been estimated here by taking 3(BDE₁₁₁₁ − BDEefficiency), where BDE is bond dissociation enthalpy. This allows for an evaluation of the driving force for a given reaction with respect to that for a hypothetical N₂-to-NH₃ conversion catalyst that uses H₂ as the proton and electron source. This is achieved by using Bordwell’s equation (with the assumption that S(•••) = S(XH)): see the Supporting Information) and literature values (see refs 15–19 and 21 for pKₐ redox potential, the enthalpy of reaction for H⁺ + e⁻ → H⁻ (CH₃ = 66 kcal/mol in THF), and the energy of H⁻ in THF (52 kcal/mol).


(20) While initiating our studies we became aware of a phosphine-supported Fe system that catalyzes N₂-to-NH₃ conversion using Cp*Fe(PCy)₃ as a catalyst and [Fe(NH₃)₃]²⁻ as a ligand. This system was found to be highly selective, achieving >95% selectivity towards NH₃ formation with N₂ as the sole reactant.


(23) Del Castillo, T. J.; Thompson, N. B.; Peters, J. C. A Synthetic Single-Site Fe Nitrogenase: High Turnover, Freeze-Quench ⁵⁷Fe Reductant Loading. Lower selectivities are observed with higher loading of the reductant. A redox equilibrium between P₃ and P₃⁻ is observed in the Mo nitrogenase. Spectroscopy experiments (see the Supporting Information).


(25) In catalytic runs performed with labeled [P₃H₃]²⁻ and [Fe(NH₃)₃]²⁻ under an atmosphere of natural abundance, the production of exclusively NH₃ is observed, demonstrating that the NH₃ formed during catalysis is derived from N₂ and not degradation of the acid (see the Supporting Information).


(29) The distinct properties of tetrahedral, high spin Fe(II) lead to higher isomer shifts (0.9–1.3) and large quadrupole splittings (>2.5) that are characteristic of these types of species. Münch, E. in Physical Methods in Bioinorganic Chemistry: Spectroscopy and Magnetism; Que, L., Jr., Ed.; University Science Books: Sausalito, CA, 2000; pp 287–320.


(36) Experimental BDE₅₉ values for related species (P₃H₃)Fe(C=N=NH)₂, (P₃H₃)Fe(C=N=NH)₂, (P₃H₃)Fe(C=N=NH)₂, (P₃H₃)Fe(C=N=NH)₂ have been measured and are in good agreement with the BDE₅₉ values calculated using the DFT methods described in this work (see the Supporting Information for full details). Rittle, J.; Peters, J. C. N = H Bond Dissociation Enthalpies and Facile H Atom Transfers for Early Intermediates of Fe–N₂ and Fe–CN Reductions. J. Am. Chem. Soc. 2017, in press. DOI: 10.1021/jacs.6b12861.


(41) Efforts to instead optimize a metal hydride species, [CP₃FeH]²⁻, led to hydride transfer to the ring system. Nevertheless, reactive transition metal hydride radical cations are also known to exhibit PCET behavior.


(43) The dissolution equilibria and kinetics of the insoluble reagents used complicate analysis of the kinetics of individual ET, PT, and PCET steps. However, the low activation barriers (G° < 9 kcal/mol) calculated for all proposed PCET reactions are consistent with these reactions being kinetically accessible (see the Supporting Information for full details).

(44) Studies (see refs 45–47) have shown that the Marcus cross-reaction holds quite well for many PCET reactions. This is indicative of a substantial correlation between thermodynamic driving force and reaction kinetics; it is, however, unclear whether the proposed reactivity would demonstrate such behavior.


(50) Studt, F.; Tuczek, F. Theoretical, Spectroscopic, and Mechanistic Studies on Transition-Metal Dinitrogen Complexes:


(54) Although our calculations for a hypothetical lutidinyl radical predict a weak N–H bond (BDEN–H ~ 35 kcal/mol), the oxidation potential of this species is calculated to be −1.89 V vs Fc+/0 in THF (see the Supporting Information). Experimental determination of this reduction potential for calibration has been contentious; however, our calculated reduction potential is similar to that previously calculated for pyridinium in aqueous media (−1.37 V vs SCE; see refs 55 and 56).


(57) It has been reported that [HIPTN3N]MoN2/[HIPTN3N] Mo–N≡NH is in equilibrium with DBU/DBU+ (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; pKα ~ 18.5 in THF; see refs 17 and 18). Taken with the reported reduction potential of [HIPTN3N] MoN2 (E1/2 = −1.81 V vs Fc+/0 in THF, see ref 52), the experimental BDE can be approximated with the Bordwell equation and the enthalpy of reaction for H+ + e− → H+ (see refs 15 and 19).

(58) In addition to lutidinium salts, [Et3NH][OTf] has been shown to affect the formation of [HIPTN3N]Mo–N≡NH from [HIPTN3N] MoN2 in the presence of metalloocene reductants (see ref 52).