Fe-mediated HER vs N2RR: Exploring Factors that Contribute to Selectivity in P3EFe(N2¬) (E = B, Si, C) Catalyst Model Systems

Benjamin D. Matson, and Jonas C. Peters

ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.7b03068 • Publication Date (Web): 03 Jan 2018

Downloaded from http://pubs.acs.org on January 4, 2018

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.
Fe-mediated HER vs N₂RR: Exploring Factors that Contribute to Selectivity in P₃EFe(N₂) (E = B, Si, C) Catalyst Model Systems

Benjamin D. Matson and Jonas C. Peters*

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

Abstract: Mitigation of the hydrogen evolution reaction (HER) is a key challenge in selective small molecule reduction catalysis. This is especially true of catalytic nitrogen (N₂) and carbon dioxide (CO₂) reduction reactions (N₂RR and CO₂RR, respectively) using H⁺/e⁻ currency. Here we explore, via DFT calculations, three iron model systems, P₃EFe (E = B, Si, C), known to mediate both N₂RR and HER, but with different selectivity depending on the identity of the auxiliary ligand. It is suggested that the respective efficiencies of these systems for N₂RR trend with the predicted N–H bonds strengths of two putative hydrazido intermediates of the proposed catalytic cycle, P₃EFe(NNH₂)+ and P₃EFe(NNH₂). Further, a mechanism is presented for undesired HER consistent with DFT studies, and previously reported experimental data, for these systems; bimolecular proton-coupled-electron-transfer (PCET) from intermediates with weak N–H bonds is posited as an important source of H₂ instead of more traditional scenarios that proceed via metal hydride intermediates and proton transfer/electron transfer (PT/ET) pathways. Wiberg bond indices provide additional insight into key factors related to the degree of stabilization of P₃EFe(NNH₂) species, factors that trend with overall product selectivity.

KEYWORDS: nitrogen fixation, N₂RR, HER, hydrogen evolution, PCET, HAT, nitrogenase

Introduction

The reduction of nitrogen (N₂) to ammonia (NH₃) by nitrogenase enzymes (the nitrogen reduction reaction: N₂RR) has garnered substantial interest in the synthetic inorganic community for several decades. In particular, the structural characterization of the FeMo-cofactor active site of biological nitrogen fixation, and mechanistic uncertainties associated with this process, have motivated studies of synthetic (primarily Mo and Fe) model systems that mediate N₂RR in the presence of proton and electron equivalents in organic solvent. The mechanisms of these systems are at various stages of understanding. Experimental and theoretical (predominantly Mo) studies have been undertaken to provide insight.

Single-site iron model complexes, such as P₃BFe(N₂)⁺ (Figure 1), catalyze N₂RR under a variety of conditions and driving forces, with reported selectivities (to date) for NH₃ generation as high as 72% based on reductant consumed. In addition, conditions have been reported under which P₃BFe(N₂)⁺ also catalyze N₂RR to varying degrees, with the P₃BFe-system being far more efficient at the hydrogen evolution reaction (HER) than N₂RR compared to P₃BFe and P₃CFe. We are naturally interested in understanding the mechanism/s by which catalysis in these respective systems occurs, and in exploring alternative systems that might function similarly. Of interest to the present study is the interplay between efficiency for the N₂RR and HER on the P₃BFe scaffold and its isostructural congeners P₃SiFe and P₃CFe. In particular, can we elucidate some of the salient factors that dictate overall product selectivity for NH₃ versus H₂ in these respective systems?

Figure 1. Schematic depiction of N₂RR/HER iron catalysts studied herein to explore key factors dictating product selectivity.

Herein we use DFT calculations to explore this question. We examine the comparative...
feasibility of HER via proton-coupled electron
transfer (PCET)\(^9\) from several putative \(\text{Fe}(\text{N}_x\text{H}_y)\)
early intermediates, using electronic structure
calculations coupled with predicted N–H bond
strengths, thermodynamic driving forces, and
electron-transfer (ET) kinetics as mechanistic
probes. Acknowledging the likelihood that
numerous and potentially competing factors may be
at play, the formation, electronic structure, and
reactivity of a key common intermediate, \(\text{Fe}(\text{NNH}_2)^+\),
is highlighted to be an important factor in the
divergent selectivity profile of \(\text{P}_3\text{BiFe}\) (and \(\text{P}_3\text{CiFe}\))
relative to the \(\text{P}_3\text{SiFe}\) system.

\textbf{Computational Methods}

All calculations were performed using
dispersion corrected density functional theory (DFT-
D\(_3\)) using Grimmes dispersion correction.\(^{10}\) All
calculations were done using the full \(\text{P}_3\text{BiFe}\) scaffold
with the TPSS functional\(^{11}\) and a def2-TZVP basis
set on transition metals and a def2-SVP basis set on
all other atoms.\(^{12}\)

All stationary point geometries were
optimized using NWChem 6.3\(^{13}\) or Orca 3.0.3.\(^{14}\) To
ensure consistency in grid size, all reported single
point and thermodynamic energies were performed
using Orca 3.0.3. Frequency calculations were used
to confirm the presence of true minima and to obtain
gas phase free-energy values at 195 K (\(G_{\text{gas}}\)).
Solvation corrections were performed using the
COSMO-SMD continuum model.\(^{15}\) The solvation
free energy was approximated using gas phase and
solvated single point energies (\(\Delta G_{\text{solv}} \approx E_{\text{solv}} - E_{\text{gas}}\)).
Finally, the free-energy of the solvated species at
195 K was calculated using the gas-phase free-
energy and the solvation free-energy (\(G_{\text{solv,195K}} =
G_{\text{gas,195K}} + \Delta G_{\text{solv}}\)).\(^{16}\)

The accuracy of the described computational
methodology was measured by comparison to
several experimental benchmarks of interest. In
addition to ensuring good agreement between
computed and crystallographically determined
structural data, experimentally determined bond
dissociation enthalpies (BDFE\(_{\text{N,H}}\)) of the compounds
\(\text{P}_3\text{BiFe} (\text{CNH})^+\), \(\text{P}_3\text{SiFe} (\text{CNH})\), \(\text{P}_3\text{SiFe} (\text{CNMeH})\),
\(\text{P}_3\text{SiFe} (\text{CNMeH}) \) and \(\text{P}_3\text{SiFe} (\text{NNMe})^+\) could be
faithfully reproduced within ±2 kcal/mol (See SI for
total description).\(^{16}\) As a further point of calibration,
the calculated singlet-triplet energy gap and the
redox potentials of \(\text{P}_3\text{BiFe} (\text{NNMe})_2\) and
\(\text{P}_3\text{SiFe} (\text{NNMe})_2\) are in good agreement with the
experimentally determined values (within ±1.5
kcal/mol, and ±3 kcal/mol (±130 mV vs Fe\(^{0+}\),
respectively; see SI).\(^{6.b,17}\)

Reduction kinetics were calculated using the
standard Marcus equation relating activation barrier
with driving force and total reorganization energy
(\(\lambda_{\text{os}} = \lambda_{\text{is}} + \lambda_{\text{os}}\)).\(^{18}\) The inner-sphere reorganization
energy for electron transfer (\(\lambda_{\text{is,ET}}\)) was estimated
assuming non-adiabatic behavior and by calculating
the difference between the single point energies of
the relevant species in its ground state and the
corresponding single point energy of this ground
state in the oxidized or reduced geometry (Eq. 1).

\[
\lambda_{\text{is,ET}} = [E(\text{Fe}^{\text{ox}}) - E(\text{Fe}^{\text{red}})]
+ [E(\text{Fe}^{\text{red}}) - E(\text{Fe}^{\text{ox}})]
\]

The outer-sphere reorganization energy was
calculated by assuming a barrier of 1.0 kcal/mol for
the reduction of \(\text{P}_3\text{BiFe} (\text{NNH})^+\) followed by
calculation of \(\lambda_{\text{os}}\) using this barrier and \(\lambda_{\text{is}}\),
as calculated by Eq 1. A continuum solvation model
was used to confirm that \(\lambda_{\text{os}} \approx \lambda_{\text{is}}\) (See SI for full
description).\(^{18}\) Reduction barriers for
\(\text{P}_3\text{SiFe} (\text{NNH})^+\) were subsequently calculated
relative to \(\text{P}_3\text{BiFe} (\text{NNH})^+\).

\textbf{Results and Discussion}

To set the stage for the present study,
previously reported catalytic \(\text{N}_2\)-to-\(\text{NH}_3\) conversion
studies by \(\text{P}_3\text{BiFe} (E = \text{B, C, and Si})\) under an
atmosphere of \(\text{N}_2\) at −78 °C in Et\(_2\)O, using KC\(_8\) and
\([\text{Et}_2\text{O}]_2\text{H}[\text{BARF}_4]\) (\(\text{HBARF}_4\), \(\text{BARF}_4\) = tetrakis-(3,5-
bis(trifluoromethyl)phenyl)borate) as the reductant
and acid source,\(^{4a,d}\) established \(\text{P}_3\text{BiFe}\) as the most
efficient catalyst for \(\text{N}_2\)RR; the highest reported
efficiency for this system (under these conditions)
was 45 ± 3% (48 equiv acid; 58 equiv reductant).
For comparison, the \(\text{P}_3\text{SiFe}\) system provided a
conversion efficiency of only 5 ± 3%. The \(\text{P}_3\text{SiFe}\)
catalyst system was reasonably active at 36 ± 6%
(note: ~25% lower substrate loading was used for
this \(\text{P}_3\text{SiFe}\) value). Measurement of HER activity
established \(\text{P}_3\text{SiFe}(\text{N}_2)^+\) (88% per added acid equiv)
as a significantly more efficient HER catalyst than
\(\text{P}_3\text{BiFe} (\text{N}_2)\) (40% per added acid equiv) under
analogous conditions.\(^{46}\) \(\text{N}_2\)RR catalysis by \(\text{P}_3\text{Fe} (E = \text{B, Si})\) has also been studied in the presence of
milder reagents (e.g., Cp\(^2\)Co and [\(\text{H}_2\text{NPh}_2\)][\(\text{OTf}\)] or
[\(\text{H}_3\text{NPh}\)][\(\text{OTf}\)]); under these conditions only the
\(\text{P}_3\text{BiFe}\) system is catalytically active.
Figure 2. (top) Previous experimental work showing the formation of P₃Fe(NNH₂)⁺ (E = B or Si) via protonation with excess acid.⁴⁸⁻⁹ (bottom) Calculated free energy changes (in kcal/mol; 195 K) for the formation of P₃Fe(NNH₂)⁺ via P₃Fe(NNH) (E = B or Si).

Previous studies of the P₃Fe and P₃SiFe systems have also explored the generation and characterization of early stage intermediates of the N₂RR catalysis.⁴⁻⁷ Most salient, low temperature protonation of P₃Fe(N₂)⁻ (E = B, Si) with excess HBArF₄ affords the doubly protonated P₃Fe(NNH₂)⁺ species (Figure 2).⁴⁶⁻⁷ As expected, corresponding DFT calculations (this work) are consistent with thermodynamically favored formation of P₃Fe(NNH) via proton transfer (Figure 2); another favorable proton transfer forms P₃Fe(NNH₂)⁺.

DFT Support for Slow Fe Protonation and Fast Fe-NₓHᵧ Formation

Although metal hydride (M–H) species are most typically invoked as intermediates of transition-metal catalyzed HER,⁹ we do not think Fe–H species are the primary players in H₂ formation by the present systems. Several experimental observations are consistent with this idea. Foremost among them is that low temperature addition of stoichiometric acid (e.g., HBArF₄) to any of the anions, P₃Fe(N₂)⁻, causes overall oxidation to their corresponding neutral products, P₃Fe(N₂)(H), with release of 0.5 equiv H₂.⁴⁻⁷ This is noteworthy because for E = Si or C the diamagnetic hydride products, P₃Fe(N₂)(H), are very stable species and are formed during catalysis as end products.⁴⁻⁷ We posit that reactive P₃Fe(NₓHᵧ) intermediates instead undergo net bimolecular HAT reactions to liberate H₂ via NₓHᵧ-ligand-mediated steps (vida infra). While iron hydrides (Fe–H) can tie up the population of active catalyst, in our view they are unlikely to be intermediates of the dominant HER pathway.

To speak to this hypothesis computationally, we focus on one acid source, HBArF₄, as it has been the subject of the most extensive comparative study.⁴⁷ The solid-state empirical formula of HBArF₄ reveals the presence of two ethers per HBArF₄ ([(Et₂O)₂H][HBArF₄])⁴⁰ To determine the preferred solution-state structure of this acid, optimizations were performed in which a Et₂OH⁺ species was provided with 0, 1 or 2 explicit Et₂O molecules with which to hydrogen bond. We found that [(Et₂O)₂H]⁺ speciation was lowest in free-energy, with [(Et₂O)₃H]⁺ and [Et₂OH]⁺ higher in energy by +7.0 and +8.2 kcal/mol, respectively (see SI).

The structure of HBArF₄ is particularly crucial for Fe protonation, as a pre-equilibrium formation of the [Et₂OH]⁺ appears to be required, as evidenced by relaxed surface scans. The need for dissociation of Et₂O prior to Fe protonation provides a lower bound on the barrier of +8.2 kcal/mol. The requirement of [Et₂OH]⁺ as the active acid, as opposed to [(Et₂O)₂H]⁺, is presumably steric in origin and may speak, in part, to the importance of bulky isopropyl-phosphino substituents in these catalysts. Our lab recently reported that a structurally related P₃SiOs(N₂)⁻ complex is an active catalyst for N₂RR.⁴¹ In contrast to the P₃Fe(N₂)⁻ catalysts, stoichiometric HBArF₄ addition can protonate at the metal, generating Os–H species that are not catalytically active for N₂RR. Steric access to the larger Os center is presumably less restricted than it is for Fe.

The steric profile of the Fe(N₂) unit suggests that functionalization of the β-N should not be subject to the same pre-equilibrium. This is consistent with relaxed surface scans, which show that the N₂ unit can be protonated in a concerted, low energy step in which an Et₂O molecule is favorably displaced by the nucleophilic β N-atom. Subsequent proton transfers yield Fe(NH) with a low overall kinetic barrier (0.5–1.0 kcal/mol; see SI).

Fe–H formation is thermodynamically favored for all three scaffolds. We therefore presume that the dominant source of HER for these systems is not via Fe–H formation, but that hydride species are formed over the course of catalysis as thermodynamic products. We presume that both
HER and N₂RR, under the conditions explored in this work, are operating under kinetic control. In subsequent results and discussion, thermodynamics are assumed to be relevant within the context of kinetic parameters.

In addition to restricting our analysis to a single acid, HBAF₄, we focus on KC₈ as a reductant for several reasons. Most salient is that KC₈ is the only reductant that has been shown to produce catalytic yields of NH₃ for all scaffolds considered. This observation is attributed to the requirement of Fe(N₂) formation during catalysis. While P₃Fe(N₂)− can be formed with weaker reductants, namely Cp*₂Co, the more reducing P₃SiFe(N₂)− is believed to be inaccessible under these conditions. Additionally, it has been noted that, when using KC₈ and HBAF₄, HER and N₂RR proceed with similar initial rates on P₃Fe and P₃SiFe scaffolds, possibly due to Fe(N₂) reduction being a common rate limiting step. Further the initial rates of N₂RR are similar between the scaffolds, which makes this reductant/acid combination well suited for a comparative study.

Despite the need to restrict the scope of this study to a specific catalysis cocktail, many of the conclusions should extend to other conditions reported for N₂RR catalysis using P₃Fe (and related) complexes. In particular, the BDFE₉H values reported herein are acid and reductant independent and hence provide insight into the anticipated stability and reactivity profiles of key early intermediates of N₂RR.

Calculation of BDFE₉H Values for Fe–N₃H₄ Intermediates

Early stage intermediates of the type Fe(NNH) and Fe(NNH₂) are expected to be highly reactive; thermochemical calculations reveal the presence of extremely weak N–H bonds in these systems, as shown by their calculated bond dissociation enthalpies (BDFE₉H; Figure 3). In particular, as yet unobservable P₃EFe(NNH) intermediates are predicted to have extremely weak N–H bonds (< 40 kcal/mol), and should therefore be subject to rapid bimolecular loss of H₂ and generation of P₃Fe(N₂). By contrast, the BDFE₉H values of candidate P₃Fe(N₃H₄) intermediates that are further downstream (e.g., Fe(N₂H₄), Fe(NH), Fe(NH₂)) are predicted to be significantly larger (Figure 3). This notion is consistent with the solution stability of characterized examples of such downstream intermediates, contrasting the high degree of solution instability of earlier intermediates.

Of particular interest herein is that the BDFE₉H values for the P₃EFe(NNH₃)⁺ (n = 0, 1) system are lower than those for P₃Fe⁺, for a given overall charge. As discussed later, these different BDFE₉H values are rooted in the different valence electron counts, and hence electronic structures, of the respective P₃E systems.

For additional context, it is useful to consider reported BDFE₉H data for a related P₃SiFe(CN) system. The relevant P₃SiFe(CN) species, isoelectronic with P₃Fe(NNH), is calculated to have a weak BDFE₉H of 43.5 kcal/mol, in close agreement to that of 41.4 kcal/mol determined experimentally. Accordingly, P₃SiFe(CN) loses 0.5 equiv H₂ rapidly in solution to afford P₃SiFe(CN). In contrast, its oxidized cation, P₃SiFe(CN)+, has a much higher BDFE₉H (61.8 kcal/mol (calc); 61.9 kcal/mol (exp)); this species is stable to H₂ loss in solution and can be isolated and structurally characterized.

Considering these collected data and observations, and additional data discussed below, we presume that the earliest N₂RR intermediates in P₃EFe-systems are very important for determining N₂RR versus HER selectivity; they engage in bimolecular H₂-evolving reactions that compete with productive N₂RR. We next consider aspects of the H–H bond-forming steps in these early P₃EFe(N₃H₄) intermediates in more detail.

Figure 3. BDFE₉H values (in kcal/mol) for selected P₃EFe(N₃H₄) species.22

P₃EFe(NNH) species are plausible candidates to consider with respect to selectivity.
since bimolecular H$_2$-evolving reactions can presumably result from their extremely weak N–H bonds (Figure 3; 31-17 kcal/mol). P$_3^{E}$Fe(NNH)$_2$ with a BDFE$_{N-H}$ estimated to be 8.2 kcal/mol lower than for P$_3^{B}$Fe(NNH), might be reasonably expected to liberate H$_2$ more readily, thereby attenuating its N$_2$RR efficiency. However, the BDFE$_{N-H}$ for P$_3^{E}$Fe(NNH) is calculated to be even lower (17.3 kcal/mol) than for P$_3^{Si}$Fe(NNH) (23 kcal/mol), despite the fact that P$_3^{E}$Fe(N$_2$) is appreciably more efficient for N$_2$RR. Hence, a trend is not evident on the basis of the Fe(NNH) intermediates, at least as related to their relative BDFE$_{N-H}$ values. Fe(NNH) intermediates are readily protonated to form Fe(NNH)$_2^+$ species in solution at low temperature (Figure 2). This likewise suggests that Fe(NNH) intermediates are unlikely to be primarily responsible for HER under catalytic conditions when a large excess of acid is present.

P$_3^{E}$Fe(NNH)$_2$ BDFE$_{N-H}$ values provide a more tractable trend: the respective calculated values are 38.2 kcal/mol for P$_3^{B}$Fe, 34.4 kcal/mol for P$_3^{E}$Fe, and 22.9 kcal/mol for P$_3^{Si}$Fe; the P$_3^{E}$Fe–NNH$_2$ species that exhibits the most efficient N$_2$RR activity exhibits the strongest N–H bond, and the least efficient exhibits the weakest (Figure 3).

Calculated Reduction Kinetics of P$_3^{E}$Fe(NNH)$_2^+$

To gain further insight into the respective role P$_3^{E}$Fe(NNH)$_2$/$^+$0 (E = B, Si, C) species might play in dictating product selectivity, P$_3^{E}$Fe(NNH)$_2^+$ reduction kinetics were derived using the standard Marcus equation relating the driving force and total reorganization energy with the ET activation barrier.$^{18}$ Comparison of the optimized Fe(NNH)$_2^+$ and Fe(NNH)$_2^+$ redox pairs reveals significant differences in their respective reduction potentials and inner-sphere reorganization energies ($\lambda_{i,s,ET}$).

The P$_3^{E}$Fe(NNH)$_2^+$ species is predicted to have a considerably more positive reduction potential ($-1.2$ V vs Fe/Fe$^+$) than P$_3^{Si}$Fe(NNH)$_2^+$ ($-1.9$ V; Table 1), resulting from their different valence electronic counts and electronic structures (see below). Given their dramatic difference in reduction potentials, the barrier for reduction ($G^*$) is expected to sharply increase in moving from B to Si. Relative reduction barrier calculations, assuming G* = 1.0 kcal/mol for the reduction of P$_3^{B}$Fe(NNH)$_2^+$, predict activation barriers that are 4–5 times higher in energy for the reduction of P$_3^{E}$Fe(NNH)$_2^+$ versus P$_3^{Si}$Fe(NNH)$_2^+$ (Table 1). While the reduction of all three species should be more than readily accomplished by the strong reductant KC$_8$, P$_3^{C}$Fe(NNH)$_2$ species are predicted to be significantly longer lived than the P$_3^{B}$Fe(NNH)$_2^+$ congener.

To roughly quantify the differences in reduction rate between P$_3^{E}$Fe(NNH)$_2^+$ species, and hence get a sense of their relative expected lifetimes, we turned to transition state theory. By assuming a pre-exponential factor invariant across both scaffolds, reduction rates for P$_3^{E}$Fe(NNH)$_2^+$ and P$_3^{E}$Fe(NNH)$_2^+$, normalized to P$_3^{B}$Fe(NNH)$_2^+$ ($k_{rel}$), were calculated ($k_{rel} = 2x10^{-4}$ and 2x10$^{-5}$, respectively). Accordingly, we expect P$_3^{E}$Fe(NNH)$_2^+$ and P$_3^{C}$Fe(NNH)$_2^+$ to be ~10$^6$ times longer-lived, respectively, than P$_3^{B}$Fe(NNH)$_2^+$, with respect to one-electron reduction.

We conclude that facile reduction of P$_3^{B}$Fe(NNH)$_2^+$ to P$_3^{E}$Fe(NNH)$_2^+$, relative to that for P$_3^{Si}$Fe(NNH)$_2^+$ and P$_3^{C}$Fe(NNH)$_2^+$, is one important factor in determining its comparative efficiency for N$_2$RR. As further elaborated below, long-lived P$_3^{E}$Fe(NNH)$_2^+$ intermediates can, via bimolecular PCET pathways, instead lead to unproductive HER. This HER activity, however, is dependent on both a long-lived P$_3^{E}$Fe(NNH)$_2^+$ intermediate, and the presence of a highly reactive PCET reagent, such as a P$_3^{E}$Fe(NNH)$_2^+$ species. We have previously postulated that P$_3^{E}$Fe(NNH)$_2$ formation is required for the release of the first equivalent of NH$_3$ and thus suggest that this species may be a crucial intermediate in both HER and N$_2$RR.$^{46,17}$

<table>
<thead>
<tr>
<th>E$^0$ (vs Fe$^{+0}$)</th>
<th>$\lambda_{i,s,ET}$</th>
<th>G*$^a_{rel}$</th>
<th>k$^b_{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E = B</td>
<td>-1.2 V</td>
<td>23</td>
<td>1.0</td>
</tr>
<tr>
<td>E = Si</td>
<td>-1.9 V</td>
<td>30</td>
<td>4.4</td>
</tr>
<tr>
<td>E = C</td>
<td>-2.0 V</td>
<td>30</td>
<td>5.2</td>
</tr>
</tbody>
</table>

$^a$Energies are in kcal/mol, unless noted otherwise.

$^b$G*$^a_{rel}$ values were calculated assuming a P$_3^{B}$Fe(NNH)$_2^+$ reduction barrier of 1.0 kcal/mol. k$^b_{rel}$ = exp[(G*$^b_{rel}$ - G*$^E_{rel}$)/k$_B^b$T] where T = 195 K.

Calculated PCET Reactions

The differences in N–H bond strengths and relative rates of P$_3^{E}$Fe(NNH)$_2$/$^+$ reduction, with corresponding implications for product selectivity, are further highlighted by calculating the thermodynamic and kinetic parameters for several PCET reactions of interest (Figure 4ABC). In
particular, comparative driving forces were calculated for unproductive bimolecular PCET reactions that generate H2 between P3Fe(NNH2)n+ (n = 0, 1; E = B, Si, C) and P3Fe(NNH2). Consistent with the calculated BDFE values (Figure 3), the P3Fe, and to a lesser extent the P3Si, system shows a higher propensity to undergo PCET to liberate H2 and the corresponding reduced Fe–NNH2 species. This is especially apparent in the reaction between two P3Fe(NNH2)0 species, and in the cross-reaction between an P3Fe(NNH2)n+ cation and a neutral P3Fe(NNH2)2 species.

In the former case, two P3Fe(NNH2)0 (E = Si, C) species react in a very favorable step to form 0.5 equiv H2 and P3Fe(NNH)− (ΔGcalc = −17.5 kcal/mol and −16.5, respectively; Figure 4A). The reaction barrier is expected to be dominated in this case by the work required to bring two cationic species together in solution (~5 kcal/mol; see SI), highlighting the reactive nature of P3Fe(NNH2)0. In contrast, P3SiFe(NNH2)0 shows a correspondingly uphill PCET reaction (ΔGcalc = +3.1 kcal/mol) in its self-combination to liberate H2 and P3SiFe(NNH)0;23 P3Fe(NNH2)n+ is also much more readily reduced to P3Fe(NNH2)2 (Table 1).

**Figure 4.** Calculated free energy changes (ΔGcalc; in kcal/mol; 195 K) for several putative PCET reactions that evolve H2.

The bimolecular reaction between cationic P3Fe(NNH2)n+ with P3Fe(NNH2)0 to produce H2 and the corresponding P3Fe(NNH2)n+ and P3Fe(NNH)0 byproducts is predicted to be favorable for all three systems (Figure 4C). However, the P3Fe systems proceed with far more driving force than the P3SiFe system.

Favorable driving forces are also predicted for all three systems in self reactions of P3Fe(NNH2)0 to produce H2 and P3Fe(NNH), but again the P3SiFe systems proceed with far more driving force (Figure 4B). While the bimolecular reaction of P3Fe(NNH2)0 with itself is therefore a presumed source of H2 for each system, in sum the P3SiFe systems are more likely, under each of the considered bimolecular reactions, to liberate H2, in accord with their efficiency for HER versus N2RR relative to the P3SiFe system.

Given that the reduction of P3Fe(NNH2)0 is predicted to be comparatively slow, one might expect such a species to build-up as an intermediate. This possibility warrants future experimental studies aimed at in situ detection. At the present stage, we can suggest that a high (relative) concentration of P3Fe(NNH2)0, and a high predicted propensity for HER via reaction of this species with either itself or P3Fe(NNH), leads to unproductive PCET steps that evolve H2 as competitive with downstream N2 reduction steps that lead to N2RR. This is one important factor in determining selectivity.

**Figure 5.** Overview of predicted bimolecular HER and N2RR pathways for P3Fe(NNH2)0 species and pertinent BDFE values.

Since the P3Fe(NNH2)0 intermediate is predicted to have a lower propensity for H2-liberating PCET reactivity, and is also predicted to be reduced much more rapidly, the reaction of two P3Fe(NNH2)0 molecules is a more probable source of H2 for this scaffold; the efficiency for N2RR on P3SiFe should therefore be related to the rate at which
P$_3^{3\delta}$Fe(NNH$_2$) can be productively consumed (i.e., protonated to form a P$_3^{3\delta}$Fe(NNH$_2$)$_2$" or P$_3^{3\delta}$Fe(NNH$_3$)$_2"). Mechanistic experiments to address these scenarios are ongoing. For example, a recent study has shown that P$_3^{3\delta}$Fe(NNH$_2$) can be protonated by strong acid at low temperature to liberate P$_3^{3\delta}$Fe(N)" and NH$_3$, presumably via P$_3^{3\delta}$Fe(NNH$_3$)$_2$. While the P$_3^C$Fe scaffold provides a less definitive comparison, the calculated BDFE$_{N-H}$ values and H$_2$-evolving PCET thermodynamics suggest that the dominant source of HER on the P$_3^C$Fe scaffolds may be the reaction between Fe(NNH$_2$) and Fe(NNH$_3$)$_2$. The highly reducing nature of P$_3^C$Fe(NNH$_2$)$_2$, as for the P$_3^S$Fe scaffold, suggests it should be comparatively long-lived, and thus more likely to undergo PCET with P$_3^C$Fe(NNH$_3$)$_2$. The similarity between P$_3^C$Fe and P$_3^S$Fe in their thermodynamics for the reaction between two Fe(NNH$_2$)$_2$ species (Figure 4A) does not correlate with their disparate %NH$_3$ efficiencies. Substantial differences in their predicted thermodynamics for the reaction between Fe(NNH$_2$) and Fe(NNH$_3$)$_2$ (Figure 4C) are more in line with the observed trend. This type of bimolecular reactivity may be an important source of HER on the P$_3^C$Fe scaffolds (Figure 5).

**Wiberg Bond Indices of P$_3^E$Fe(NxHy) Species**

We next examine how each P$_3^E$ auxiliary, and the corresponding P$_3^B$Fe(NNH$_x$) valence at iron, confers variability in bonding to, and the electronic structure of, the NNH$_x$ ligand, as a means of further considering corresponding reactivity differences of P$_3^{3\delta}$Fe(NNH$_x$) species.

Wiberg bond indices provide a means to examine how the localized bonding between various atoms, expressed as a bond index, changes as a function of the NNH$_3$ reduction state (i.e., NNH to NNH$_3$). We have suggested elsewhere that the relative flexibility of the P$_3^B$ ligand, owing to a weak and dative Fe→B interaction, may allow for stabilization of Fe→NNH$_3$ intermediates where Fe→N pi-bonding is accompanied by pyramidalization at the Fe center, and a corresponding lengthening of the Fe→B distance. The P$_3^S$ ligand is expected to give rise to a more shared, covalent Fe–Si interaction, irrespective of the NNH$_3$ reduction state, and the P$_3^C$ system may be expected to fall in the middle of these extremes.

Changes in the respective bond indices of these frameworks have been determined between pairs of P$_3^E$Fe(NNH) and P$_3^E$Fe(NNH$_2$) species (E = B, C, Si), related by formal addition of an H-atom to the former. Interestingly, the N–H bond indices are essentially invariant across all complexes studied, indicating that differences in BDFE$_{N-H}$ are mostly dependent on the relative bonding through the E–Fe→N–N manifold. The most salient data, reproduced in Figure 6, are the total Wiberg bond indices for Fe–N$_a$, Fe–N$_b$, Fe–E, N–N and N–H. The total Fe–N–N bond order, $\Sigma$(Fe–N–N), is also provided, as is the net difference in the ABDFE$_{N-H}$ value, for each pair on moving from Fe(NNH) to Fe(NNH$_2$).

As expected, the Fe–E bond order weakens slightly from Fe(NNH) to Fe(NNH$_2$) for E = B, and stays constant for both Si and C. The respective change at Fe–N$_a$ is also informative. For the B system, a significant increase is observed (1.6 to 1.9), reflecting a build-up in pi-bonding in P$_3^B$Fe(NNH$_2$), akin to low-spin (pseudotetrahedral) iron imides of the type P$_3^{3\delta}$Fe(NR). For comparison, a previously characterized P$_3^{3\delta}$Fe(NR) species (R = 4-OMe-Ph) is predicted to have an Fe–N bond order of 1.8 (see SI).

By contrast, the Fe–N$_a$ index for Si is sharply attenuated (from 1.6 to 1.2), reflecting a corresponding decrease in pi bonding. While this difference must partly reflect a less flexible Fe–Si interaction, it also reflects the electronic structure resulting from an extra electron in the frontier orbitals of the $^2E$ {Fe-Si}$_7$ system relative to $^1A$ {Fe-B}$_7$. Interestingly, P$_3^{3\delta}$Fe(NNH$_2$) is pyramidalized at N$_b$ whereas N$_b$ is planar for P$_3^{3\delta}$Fe(NNH$_2$). This observation can again be rationalized by the assignment of a low-spin iron “imide-like” electronic structure to {Fe-B}$_7$P$_3^{3\delta}$Fe(NNH$_2$), but not for {Fe-Si}$_7$P$_3^{3\delta}$Fe(NNH$_2$), where substantial spin leaks onto the NNH$_2$ subunit (19% on P$_3^{3\delta}$Fe(NNH$_2$)). The C system provides an interesting further comparison, with spin leakage onto the NNH$_2$ unit falling between these two extremes (12% on P$_3^{3\delta}$Fe(NNH$_2$)). An increase in the Fe–N$_a$ index occurs from P$_3^C$Fe(NNH) to P$_3^C$Fe(NNH$_2$) (1.2 to 1.4), but N$_b$ is predicted to remain planar.

There also appears to be a strong trend between the degree of change in the total Fe–N–N bond order ($\Sigma$(Fe–N–N)) and the ΔBDFE$_{N-H}$; The B and C systems show little change in $\Sigma$(Fe–N–N), with a corresponding significant increase in BDFE$_{N-H}$ from Fe(NNH) to Fe(NNH$_2$) (7.0 and 17.9 kcal/mol, respectively). However, the P$_3^C$Fe system starts at a much weaker BDFE$_{N-H}$ of 17.3 kcal/mol for P$_3^{3\delta}$Fe(NNH) (compared to 31.2 kcal/mol for P$_3^{3\delta}$Fe). This observation is consistent with their total $\Sigma$(Fe–N–N) values (3.8 for B and 2.9 for C). Thus, the comparative stability of P$_3^{3\delta}$Fe(NNH$_2$), with its much higher BDFE$_{N-H}$ relative that in P$_3^C$Fe(NNH),
appears to reflect a higher degree of instability in
P$_3^{E}$Fe(NNH) (relative to the same comparison for E = B). This idea is further supported by Wiberg bond
indices of the P$_3^{Si}$Fe(N2) species, which show a total
bond order of 4.0 across the Fe–N–N unit for all
three scaffolds (Figure 6).

In sharp contrast, the P$_3^{Si}$Fe system has a
relatively high Σ(Fe–N–N) value in P$_3^{Si}$Fe(NNH),
but this value decreases dramatically in
P$_3^{Si}$Fe(NNH$_2$). There is correspondingly very little
change in the ABDFE$_{N,H}$, reflecting a comparatively
very weak N–H bond in P$_3^{Si}$Fe(NNH$_2$). The
instability of P$_3^{Si}$Fe(NNH$_2$), with an electronic
structure that places substantial unpaired spin on
NNH$_2$ owing to the {Fe–Si$^+$} configuration,
preumably contributes to the cathodically shifted
reduction potential predicted for P$_3^{Si}$Fe(NNH$_2$)$^+$
relative to P$_3^{B}$Fe(NNH$_2$)$^+$, and also its propensity for
facile PCET to liberate H$_2$.

The P$_3^{Si}$Fe system is unique within this
series in its ability to support a high total Fe–N–N
bond order from Fe(NNH) to Fe(NNH$_2$), facilitating
its trajectory along productive N$_2$RR.

**Figure 6.** Selected total Wiberg bond indices for
P$_3^{E}$Fe(N2), P$_3^{E}$Fe(NNH) and P$_3^{E}$Fe(NNH$_2$) species,
along with the total Fe–N–N bond order, Σ
(Fe–N–N). ABDFE$_{N,H}$ values are reported in kcal/mol.

**Conclusion**

Exploring the chemical basis for N$_2$RR
versus HER selectivity for a molecular catalyst is
important to future catalyst design. The DFT study
described herein suggests that PCET reactions
involving P$_3^{E}$Fe(NNH$_2$)$^{n+}$ species likely play an
important role in the efficiency of N$_2$-to-NH$_3$
conversion catalysis by P$_3^{E}$Fe model systems. These
calculations enable predictions qualitatively
consistent with previous stoichiometric and catalytic
experiments. The comparative stability of P$_3^{E}$Fe(NNH$_2$)$^{n+}$
intermediates, as predicted by calibrated BDFE$_{N,H}$ values and redox potentials,
emerges as one of the important factors in
determining selectivity for N$_2$RR versus HER in
these systems. Corresponding Wiberg bond indices
intimate P$_3^{B}$ as an especially well-equipped ligand
for supporting N$_2$RR at Fe, due to its high degree of
flexibility and the valence electron count it confers
to Fe in the reduced intermediate P$_3^{B}$Fe(NNH$_2$). Our
study suggests that increasing the rate at which an
P$_3^{Si}$Fe(NNH$_2$) intermediate is productively consumed
so as to avoid bimolecular HER, possibly via rapid
PCET reagents, may be a promising route to
increasing efficiency for NH$_3$ production.

Looking beyond these iron model systems,
our study underscores the potential utility of DFT-
predicted BDFE$_{N,H}$ determinations towards the
rational design of catalysts for N$_2$RR. Intermediates
with weak N–H bonds (e.g., M(NNH) and M(NNH$_2$)) are highlighted as important sources of
H$_2$ production via bimolecular PCET. Such a
scenario is distinct from HER activity via more
traditional metal-hydride intermediates.

**ASSOCIATED CONTENT**

**Supporting Information.**
The Supporting Information is available free of
charge on the ACS Publications website.

Complete computational details, molecular
geometries from the computations, additional
calculations and analysis (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*jpeters@caltech.edu*
Funding Sources
No competing financial interests have been declared.

ACKNOWLEDGMENT
This work was supported by the NIH (GM 070757) and the Gordon and Betty Moore Foundation, and the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number ACI-1053575. B.D.M. acknowledges the support of the NSF for a Graduate Fellowship (GRFP). We thank Matthew Chalkley for insightful input.

REFERENCE


8 Side-by-side comparisons of catalytic N2RR by P3Fe (E = B, and Si) using potassium graphite (KCa) and [(Et2O)2H][BArF2]2 (BArF2 = tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate) have revealed P3Fe to be the most efficient catalyst, with reported efficiencies up to 37%. N2RR catalysis by P3Fe is less efficient under these conditions, with reported efficiencies of 33% and 4%, respectively. Studies focused on HER catalysis have shown P3Fe(N2)3 (88% per H+) to be significantly more efficient than P3Fe(N2)2 (40% per H+) under analogous conditions. See 4d.

In this study, we do not distinguish between the terms H-atom transfer (HAT) vs PCET. For consistency, we refer to PCET throughout. For discussion of terminology see: (a) Warren, J. J.; Tronic, T. A.; Mayer, J. M. Chem. Rev. 2010, 110, 6961–7001. (b) Hammes-Schiffer, S. J. Am. Chem. Soc. 2015, 137, 8860–8871.


22 We have previously reported bond dissociation enthalpies (BDE\textsubscript{N-H}) for P\textsubscript{3}BFe(NNH) and P\textsubscript{3}BFe(NNH\textsubscript{2}) (see ref 4e). Here we reported BDFE\textsubscript{N-H} values as they have more theoretical justification in the absence of experimental knowledge of the entropy change associated with H\textperiodcentered loss.

23 While this discussion may seem at odds with the enhanced stability of P\textsubscript{3}SiFe(NNH\textsubscript{2})\textsuperscript{+} relative to P\textsubscript{3}BFe(NNH\textsubscript{2})\textsuperscript{+}, other factors are presumably responsible in solution, such as the more facile reduction of P\textsubscript{3}BFe(NNH\textsubscript{2})\textsuperscript{+} relative to P\textsubscript{3}SiFe(NNH\textsubscript{2})\textsuperscript{+}.


26 Similarly, the C\textsubscript{2}H\textsubscript{5} radical is predicted to have a very low BDFE\textsubscript{C-H} (34 kcal/mol) when compared to C\textsubscript{2}H\textsubscript{4} (100 kcal/mol), but the Wiberg bond indices for their respective C–H bonds do not change appreciably (See SI).
N2H4-mediated PCET Pathways Can Short-Circuit N2RR via HER