[FeFe]hydrogenase mimics for proton reduction catalysis: Supramolecular proton reduction catalysts with appended redox-active and proton-responsive ligands towards application in a molecular artificial leaf

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The Role of Redox-Active Phosphole Ligands in Proton Reduction Catalysis using [FeFe]H$_2$ase Mimics

**Abstract.** In this chapter we elucidate the behavior of various related phosphole-appended [FeFe]H$_2$ase mimics and show that their protonation reactivity is induced by the structural integrity of these compounds upon/after reduction. The structural integrity is in turn affected by the electron-accepting nature of the phosphole ligands, resulting in appreciable amounts of spin density being located on this organic fragment. The resulting catalytic efficiency is similar for all catalysts, even though the catalytic mechanism changes drastically with regards to the order of elementary steps, redox potentials and the rate of proton transfer. In the context of photocatalytic proton reduction, it is mandatory to carefully balance the kinetic and thermodynamic properties of chromophores and catalysts. We show here that by selecting ‘the right ligand for the right job’, a catalyst can operate at the desired mode without adversely affecting its catalytic merits.
Introduction

In the search for efficient proton reduction catalysts inspired by the [FeFe]H\textsubscript{2}ase active site, various types of synthetic [2Fe-2S] clusters have been thoroughly investigated and characterized.\textsuperscript{1,2} In the late '90s the structure of the native [FeFe]H\textsubscript{2}ase active site was elucidated, although the exact configuration of the organic co-factor bridging the iron atoms was still unknown.\textsuperscript{3} The similarity of the enzyme’s active site to known propanedithiolato (pdt)-bridged [2Fe-2S] clusters led to a well-characterized first generation of [FeFe]H\textsubscript{2}ase mimics studied mainly by the groups of Darzensbourg\textsuperscript{4–7} and Pickett,\textsuperscript{8–11} although the high overpotential for catalysis combined with the many decomposition pathways limited the use of this class of compounds for further study and application.\textsuperscript{12,13} Since that time, two main classes of [FeFe] H\textsubscript{2}ase mimics have emerged: the azadithiolato (adt)-bridged and benzenedithiolato (bdt)-bridged [2Fe-2S] clusters. The adt-based mimics have been thoroughly investigated and studied by the group of Rauchfuss,\textsuperscript{14} ultimately leading to a functional and structural mimic containing an electron reservoir and proton relay akin the natural enzyme.\textsuperscript{15,16} On the other hand, the bdt-based [2Fe-2S] clusters have been studied to a much lesser extent,\textsuperscript{17} as in contrast to the pdt and adt-mimics,\textsuperscript{18,19} the mono-anions of the reported bdt hexacarbonyl complex are not protonated by weak acids.\textsuperscript{20,21} Activation of the Fe-Fe bond by substitution of a carbonyl for phosphorus-based ligands can lead to structures with increased Brønsted basicity due to the lower π-acidity of the latter. Although in the case of phosphite complex (μ-bdt) Fe\textsubscript{2}(CO)\textsubscript{5}(P(OME))\textsubscript{3}, the basicity indeed increased, the intrinsic efficiency of the catalyst decreased.\textsuperscript{22,23}

Figure 1. Chemical structures of the previously reported pyridylphosphole-functionalized H\textsubscript{2}ase mimic 6, compounds 2–5 and the hexacarbonyl parent compound 1.
In Chapter 4 we have shown that the incorporation of a redox-active phosphole ligand into a bdt-based H₂ase mimic leads to efficient proton reduction catalysis in aqueous media. Before entering its catalytic cycle, this pyridylphosphole-appended complex 6 needs to be activated by a two-electron reduction and di-protonation in an overall ECCE process occurring at unexpectedly mild potentials. In contrast, the parent hexacarbonyl complex 1 [(μ-bdt)Fe₂(CO)₆] needs to be activated by two-electron reduction (at similar potentials) before protonation takes place in an overall EEC process. We wanted to understand the underlying principles of the different behavior in catalytic proton reduction catalysis of these complexes, and why in complex 1 mono-reduction is insufficient to affect protonation. Our hypothesis is that the increased Brønsted basicity of the mono-reduced state of 6 compared to 1 is explained by either (a) an increase in σ-donor ability of the phosphorus ligand compared to a carbonyl ligand, (b) the redox-activity or (c) the combined redox- and proton-reactivity of the phosphole ligand. To rule out two of the three hypotheses, we bridged the gap between complexes 1 and 6 by synthesizing and characterizing a series of Fe₂(μ-bdt)(CO)₅L complexes 2–5 (Figure 1). These complexes contain a phosphine or phosphole ligand, allowing for the separation of redox-active, proton-reactive and ‘innocent’ behavior of the phosphorus ligands in complexes 2–6.

The electron transfer (ET) and proton transfer (PT) behavior (including electrocatalysis) for compounds 1–5 was fully elucidated by cyclic voltammetry (CV) in CH₂Cl₂ combined with peak potential analysis and fitting to digital simulation. To gain insight in the structure-reactivity relationships of the various reduced and protonated forms of complexes 2–5 we calculated the geometries, frontier orbitals localization and spin density distribution of X, X⁺, X²⁻ and XH⁻ (X = 2–5) by DFT. The electrochemical properties and DFT calculations are presented in the Results section. In the Discussion section we elaborate on the observed differences and similarities in the electrochemistry, which we explain by the DFT calculated geometries and frontier orbital localization of the involved intermediate species. For complexes 2–5 the reduction potentials of their intermediates are strikingly similar, whereas the protonation reactivity of the intermediates changes dramatically with the nature of the phosphorous ligand. The redox-activity of the phosphole ligands in 3–5 leads to electron delocalization after mono-reduction, which avoids rupture of one of the Fe-S bonds. This leads to an [2Fe-2S] cluster that is structurally intact and sufficiently basic to react with weak acids. The difference in reactivity facilitates alternative catalytic pathways, leading to a change in redox potentials throughout the catalytic cycle. One implication of this finding is that lowering catalytic overpotentials might be more straightforward through facilitating proton transfer than
through decreasing the intrinsic reduction potentials of the complexes.

Results

Synthesis and characterization

The four [FeFe]H_2ase mimics 2–5 bearing a benzenedithiolato (μ-bdt) bridge and one phosphorus ligand were synthesized by reacting the hexacarbonyl precursor 1 [(μ-bdt)Fe_2(CO)_6] with trimethylamine N-oxide, followed by addition of the corresponding ligand in a mixture of dichloromethane and acetonitrile at room temperature. Purification by column chromatography yielded the target compounds as air-stable red solids in moderate yields (40–60%). All new compounds (3, 4 and 5) were characterized by ^1H NMR, ^31P NMR, HR-MS, IR and X-ray analysis. The spectroscopic data of compound 2 matched those reported in literature. Infrared analysis showed that all complexes are electronically similar in their neutral state, i.e. the carbonyl stretching frequencies are all shifted by approximately 30 cm⁻¹ with respect to the hexacarbonyl precursor.

Single crystal X-ray diffraction of complexes 3–5 reveals very similar structural features for all complexes, with the phosphorus ligands in apical position (Figure 2). For dibenzophosphole complex 3, the fused benzene rings π–π stack to the bdt bridge (centroid-centroid distance 3.424 Å), similar to the previously reported X-ray structure of 2 (centroid-centroid distance 3.556 Å). The Fe-Fe bond length in complexes 2–5 is approximately 2.52 Å, slightly larger than the 2.48 Å reported for 1, and the dihedral angle between phosphorus and the two iron atoms is 151±3° for all structures. However, the Fe-P bond is slightly longer for phosphine complex 2 (2.252 Å) compared to 3–5 (2.218±0.005), which is most likely related to a difference in π-backbonding from iron to phosphorus. The amount of backbonding is in this case not affected by the electron density on the metal, as this would be translated into differences in the infrared vibrational energies, but rather to the smaller cone angles of the phospholes compared to triphenylphosphine. The DFT calculated geometries of 2–5 are in good agreement with their respective crystal structures, with slight overestimation of Fe-S and Fe-Fe bond lengths by 1.2% and underestimation of Fe-C bond lengths by 0.5% (cf. Figure 20 and Table 2).
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Figure 2. Molecular structures of 2–5 as determined by X-ray diffraction with displacement ellipsoids at the 50% probability level.

Table 1. Spectroscopic properties of complexes 1–6 in CH₂Cl₂ (IR) or CD₂Cl₂ (NMR). (Unresolved = the NMR signals belonging to the bdt bridge overlap with various aromatic signals in the NMR spectrum.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR (CO stretch)</th>
<th>¹H-NMR (μ-bdt)</th>
<th>³¹P-NMR</th>
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<td>1</td>
<td>2078/2042/2002</td>
<td>7.13/6.63</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2050/1993/1979/1936</td>
<td>6.13</td>
<td>52.5</td>
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<td>4</td>
<td>2049/1992/1979/1936</td>
<td>6.97/6.64</td>
<td>74.9</td>
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<tr>
<td>5</td>
<td>2053/1995/1983/1940</td>
<td>(unresolved)</td>
<td>76.8</td>
</tr>
<tr>
<td>6</td>
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<td>75.1</td>
</tr>
</tbody>
</table>
Elucidation of electron and proton transfer processes using cyclic voltammetry

Solutions of compounds 1–5 were subjected to cyclic voltammetry at a static mercury drop (for peak potential analysis) or a glassy carbon (for catalysis) working electrode in CH₂Cl₂ containing 0.1 M nBu₄NPF₆. In absence of acid, two-electron reduction waves with potential inversion were observed, with peak reduction potentials around –1.8 V (all reported potentials are vs. Fc/Fc⁺) for 2–5. A scan rate dependent study of these redox waves combined with peak potential analysis and electrochemical simulations proved to be insufficient to accurately determine the redox behavior of the compounds. In presence of acid (HNEt₃PF₆) and using similar analytical techniques, the first reduction potentials could be accurately determined. These potentials were used to fully elucidate the redox behavior in absence of acid (including disproportionation/comproportionation pathways). In presence of acid, peak potential analysis of the first redox wave (at varying scan rates and acid concentration) was sufficient to accurately determine all electron and proton transfer processes occurring at the first redox wave. Catalytic mechanisms were elucidated by electrochemical simulation of the catalytic waves using the data from the first redox wave. A full description of the electrochemical and chemical processes including cyclic voltammograms, fits to digital simulation and peak potential analysis is given in the Experimental Section.

Behavior of hexacarbonyl complex 1

In a previous report the parent hexacarbonyl complex 1 was subjected to electrochemical analysis in CH₂Cl₂ at a glassy carbon electrode. A two-electron reduction wave at a half-wave potential of –1.44 V was observed with ca. 35 mV potential inversion. The authors addressed the difficulties in determining the extent of potential inversion \( \Delta E^0 = |E_1 - E_2| \), as well as the pronounced influence of the electrode material on heterogeneous charge transfer. In a separate gas-phase DFT study, \( \Delta E^0 \) was calculated to be ca. 460 mV, with an experimental lower limit of 150 mV for CH₃CN solvent (Gutmann donor number (DN) = 14.1 kcal mol⁻¹) and a normal potential ordering for THF solvent (DN = 20 kcal mol⁻¹). Because the authors correlate the \( \Delta E^0 \) value to the DN (or Lewis basicity) of the solvent, it is expected that \( \Delta E^0 \) should be larger than 150 mV for a non-coordinating solvent. Cyclic voltammetry of a 1.0 mM solution of 1 in CH₂Cl₂ (DN = 0 kcal mol⁻¹; virtually non-coordinating) at a static mercury drop electrode showed a fully reversible two-electron reduction wave at a half-wave potential of –1.48 V with a peak-to-
peak separation of 43 mV for scan rates 0.03–3.0 V s\(^{-1}\) (Figure 3, top left). Simultaneous fitting of digital simulations on voltammograms acquired in the absence and presence of increasing amounts of HNEt\(_3\)PF\(_6\) (Figure 3, top right) revealed that the extent of potential inversion of 1 in CH\(_2\)Cl\(_2\) is ca. 280 mV, a value that could only be reliably determined when a disproportionation equilibrium reaction (1\(^-\) + 1\(^-\) \rightleftharpoons 1^{2-} + 1) was included. This analysis also yielded the rate constant for protonation of the dianion 1\(^{2-}\) as well as the redox potential for the hydride couple 1H|1H\(^+\). The electron transfer, proton transfer and disproportionation processes are summarized schematically in Figure 3 (bottom).

After two-electron reduction of 1, one of the Fe-S bonds breaks and one carbonyl ligand bridges both Fe centers.\(^{21}\) The resulting species 1\(^{2-}\) is sufficiently basic to react with weak acids.\(^{20,21}\) However, the molecular structure and reactivity of the mono-anion 1\(^-\) have not yet been unambiguously assigned, and the question addressed by Capon and co-workers (“We were particularly interested in determining whether the protonation step of the initial reduction product competes kinetically with...
the second reduction step”) still stands. Recently, Mirmohades et al. addressed this question in a laser flash quench study, and it was found that the mono-anion could only be protonated by moderately strong acids with a $pK_a < 12.7$. They did experimentally observe the mono-anion $1^–$ (and supported its structure by DFT), which did not contain any bridging carbonyls but had one of the Fe$_d$-S bonds elongated by 1.25 Å, and the resulting spin density most likely located on the five-coordinate Fe$_d$ atom. After a second electron transfer, the resulting di-anion $1^{2–}$ shows a fully cleaved Fe$_d$-S bond with a carbonyl ligand moving into a bridging position, and the resulting basicity increase can therefore be ascribed to the second electron being (at least partly) localized on iron.

We found that protonation of $1^–$ by weak acids is thermodynamically (and not kinetically) unfavorable on the basis of thermochemical analysis of the redox and acid-base equilibria presented in Figure 4. The free energy related to the overall electron/proton transfer $\Delta G(1^-|1H^-)$ when going from $1^–$ to $1H^–$ is equal, regardless of the chemical pathway. This free energy is the sum of free energies for the redox equilibrium and acid-base equilibrium according to the formulae in Figure 4. The $pK_a$ of the $1^{2–}|1H^–$ couple is 23, which leads to a $pK_a$ value of 13 for the $1^-|1H$ couple. Because this value is in line with the previously reported data, combined with the fact that the disproportionation reaction observed here is relatively slow ($k_f = 5\times10^4$ M$^{-1}$ s$^{-1}$), we conclude that the mono-anion is not sufficiently basic to react with weak acids.

$$\Delta G (1^-|1H^-) = FE (1^-|1^{2–}) + 2.3RTpK_a (1^{2–}|1H^-)$$

Figure 4. ET-PT square scheme for thermochemical analysis of the redox and acid-base equilibria observed for 1.

$$\Delta G (1^-|1H^-) = 2.3RTpK_a (1^-|1H) + FE (1H|1H^-)$$
Behavior of triphenylphosphine complex 2

In absence of acid, triphenylphosphine complex 2 undergoes two sequential (quasi-reversible) reduction events (through potential inversion) at -1.80 V and -1.62 V to form di-anion \( 2^{2-} \) (Figure 5, top left). DFT calculated frontier orbital plots of neutral 2 show that its LUMO is delocalized over the [2Fe-2S] cluster and the bdt bridge, and population of this LUMO by one electron leads to a structurally reorganized mono-anion \( 2^- \) with a cleaved (3.41 Å) \( Fe_d-S \) bond and the distal iron atom (\( Fe_d \)) in a distorted square pyramidal configuration, resulting most likely in the \( Fe^0 \) (d^8) formal oxidation state (Figure 5, bottom). Due to this chemical transformation, the spin density distribution of \( 2^- \) (90% on \( Fe_d \)) is markedly different from the LUMO localization of 2. Through dissociation of the thiolate ligand, the Fe-Fe bond in \( 2^- \) is not destabilized sufficiently to affect protonation, which was observed from the cyclic voltammograms in presence of acid. In these experiments, the cathodic peaks did not shift to more positive potentials on addition of acid (Figure 23A), indicating that there is no (rate-limiting) proton transfer between the electron transfers. However, the anodic re-oxidation wave shifted to potentials roughly 0.6 V more positive (-1.03 V; Figure 21), indicating that the di-reduced species \( 2^{2-} \) reacts with a proton to form the hydride \( 2H^- \) (Figure 5, bottom). DFT calculations on the di-anion \( 2^{2-} \) reveal a geometry with a bridging carbonyl ligand and one \( Fe_d-S \) bond completely ruptured (3.90 Å), with both distal and proximal (\( Fe_p \)) iron centers in \( 2^{2-} \) in a distorted octahedral conformation. According to its DFT calculated geometry, \( 2H^- \) features a similarly exposed geometry as the di-anion, although now with a bridging hydride instead of a bridging carbonyl ligand.

Thus, 2 reacts in a similar fashion as the parent complex 1 and only the di-anion \( 2^{2-} \) is sufficiently basic to react with a proton to form \( 2H^- \). Simulation of the catalytic waves (Figure 25) show that the only plausible catalytic mechanism is of the (E)ECCE type, wherein neutral 2 is activated by one-electron reduction and then enters the cycle as the active species \( 2^- \) (Figure 5, bottom). This mono-anion then accepts an additional electron and undergoes protonation under diffusion control to form \( 2H^- \). Next, a rate-determining protonation equilibrium is followed by (dissociative) electron transfer (-2.09 V) to release \( H_2 \) with reformation of the mono-anion \( 2^- \).
Figure 5. Top left: Cyclic voltammetric response of 1.0 mM complex 2 in CH$_2$Cl$_2$ containing 0.1 M nBu$_4$NPF$_6$ in absence of acid at various scan rates (glassy carbon). Top right: Catalytic waves at 4/8/32/56 equivalents of Et$_3$NHPF$_6$ at 0.1 V/s (glassy carbon). Bottom: Simplified ET-PT scheme and catalytic cycle (light orange) with DFT calculated geometries and frontier orbital plots of the various reduced and protonated forms of 2.
Figure 6. Top left: Cyclic voltammetric response of 1.0 mM complex 3 in CH₂Cl₂ containing 0.1 M nBu₄NPF₆ in absence of acid at various scan rates (glassy carbon). Top right: Catalytic waves at 4/8/16/32/56 equivalents of Et₃NHPF₆ at 0.1 V/s (glassy carbon). Bottom: Simplified ET-PT scheme and catalytic cycle (light orange) with DFT calculated geometries and frontier orbital plots of the various reduced and protonated forms of 2.
Behavior of dibenzophosphole complex 3

The redox behavior of 3 in absence of acid deviates from 2, in that the cyclic voltammograms show ‘textbook’ redox waves at low scan rates (Figure 6, top left). The redox potentials of this two-electron process are at $-1.80$ V (reversible) and $-1.67$ V (quasi-reversible). DFT calculated frontier orbital plots reveal that the LUMO of 3 is delocalized over the [2Fe-2S] cluster and the bdt bridge, similar to the LUMO localization found for 2. In contrast to 2$^-$, the calculated geometry of 3$^-$ shows that after mono-reduction of 3 the [2Fe-2S] butterfly structure remains intact, with 60% of spin density in 3$^-$ distributed over the two iron atoms and 26% spin density on the dibenzophosphole ligand. This mono-anion 3$^-$ is sufficiently basic to be protonated because it is still structurally intact after reduction. In presence of increasing amounts of acid the cathodic peaks in the cyclic voltammograms shift to more positive potentials (Figure 26), indicative of a rate-limiting homogeneous follow-up reaction after electron transfer. Peak potential analysis on these voltammograms indicates an ECE mechanism (Figure 6, top right). The mono-anion 3$^-$ is protonated to form the hydride species 3H, which is then further reduced at $-1.03$ V to form the anionic hydride species 3H$^-$. DFT calculations indicate that this hydride is in a bridging position, with the [2Fe-2S] butterfly structure remaining intact with Fe$_{distal}$-S bond elongation (2.54 to 2.61 Å). The chemical pathway from 3 to 3H$^-$ does not go via the di-anion 3$^{2-}$, which shows a DFT calculated geometry with an opened-up [2Fe-2S] cluster (Fe$_d$-S at 3.90 Å) and a bridging carbonyl ligand, and its HOMO localized mainly on iron and the bdt bridge (Figure 6, bottom). Scanning to more negative potentials, catalytic waves appear around $-2.0$ V (Figure 6, top right). Through digital simulation of the voltammograms (Figure 27), we find that the catalytic mechanism (starting from the pre-catalyst 3) is of the (E)CECE type (one-electron activation followed by catalysis via CECE). In this mechanism, hydride 3H$^-$ is first protonated in a rate-determining equilibrium followed by reduction at $-1.90$ V with release of H$_2$, reforming the active catalytic species 3$^-$.

Behavior of phosphole complexes 4

The redox and protonation behavior for complex 5 is identical (within experimental error) to the behavior of 4 unless stated otherwise. In absence of acid, a two-electron reversible reduction with potential inversion is observed at $-1.85$ V/$-1.67$ V ($-1.80$ V/$-1.62$ V for 5) (Figure 7, top left). Frontier orbital plots show that the LUMO of 4 is delocalized over the di-iron complex and the backbone of the phosphole ligands (Figure 7, bottom). Calculated geometries of 4$^-$ show that the complex re-
The Role of Redox-Active Phosphole Ligands in Proton Reduction Catalysis using [FeFe]H₂ase Mimics

Figure 7. Top left: Cyclic voltammetric response of 1.0 mM complex 4 in CH₂Cl₂ containing 0.1 M nBu₄NPF₆ in absence of acid at various scan rates (glassy carbon). Top right: Catalytic waves at 4/8/16/32/56 equivalents of Et₃NHPF₆ at 0.1 V/s (glassy carbon). Bottom: Simplified ET-PT scheme and catalytic cycle (light orange) with DFT calculated geometries and frontier orbital plots of the various reduced and protonated forms of 2.
mains structurally intact on mono-reduction with partial aromatization of the phosphole backbone. The resulting spin density occupies what used to be the neutral molecule’s LUMO with 46% (39% for 5) spin density on the two iron atoms and 47% (56% for 5) on the phosphole ligand. Further reduction to the di-anion $4^{2-}$ leads to full aromatization of the phosphole backbone, with structural changes to the [2Fe-2S] core structure limited to elongation of the Fe-Fe bond to around 2.71 Å. The HOMO of the di-anion shows the same distribution as the LUMO of the neutral complex and the spin density distribution of the mono-anion, and it can thus be concluded that on reduction both electrons simply occupy this delocalized orbital without inducing structural changes to the complex. From electrochemical analysis it follows that the mono-anion $4^-$ is rapidly protonated to form the respective hydride species, which is in turn further reduced to form the mono-anionic hydride species $4\text{H}^-\text{ in an overall process very similar to the process observed for 3. DFT calculations on this hydride species show a bridging hydride ligand with one of the Fe-S bonds elongated from 2.30 Å to 2.83 Å (3.08 Å for 5H$^-$. Catalysis occurs via an (E)CECE mechanism at identical potentials, rates and equilibrium constants as observed for 3 (Figure 7, bottom).

Discussion

In the absence of acid, complexes 2–5 follow similar electrochemistry, with the first reduction around $-1.8$ V and the second reduction around $-1.6$ V. For complexes based on phosphole ligands (4 and 5), both mono-anions and di-anions show geometries similar to the neutral complexes, and the potential inversion is explained by electron delocalization with concomitant ligand aromatization. For the dibenzophosphole-based complex 3, the first reduction process ($3^-|3^{2-}$) is similar to the one observed for 4 and 5. However, the second reduction ($3^{2-}|3^{3-}$) leads to a distorted geometry, which is due to lower electron delocalization onto the dibenzophosphole ligand compared to $4^{2-}$ and $5^{2-}$. The reduction of phosphine-based complex 2 leads to a mono-anion with a distorted geometry, as the triphenylphosphine ligand is not susceptible to store electron density after reduction and the resulting charge cannot be stabilized on an intact [2Fe-2S] butterfly structure. The di-anions $2^{2-}$ and $3^{2-}$ are also very close in both geometry and orbital localization. The geometric changes on reduction of 2 and 3 closely resemble the changes observed in the parent complex 1, i.e. mono-reduction leads to elongation of one of the Fe$_d$S bonds and di-reduction induces complete rupture of this Fe-S bond with a carbonyl ligand moving into a bridging position.
In the presence of acid, the mono-anion of 2 is not sufficiently basic to react with weak acid. Similarly to 1, two-electron reduction is necessary for this complex to afford a reactive Fe-Fe framework amenable to protonation by a weak acid. In contrast, mono-anions of 3–5 readily react with a proton to form the respective hydride intermediates. Within these complexes, the redox-activity of the phosphole ligands leads to electron delocalization after reduction, which avoids rupture of the
Fe₄S bond, leading to an [2Fe-2S] cluster that is structurally intact and therefore sufficiently basic to be protonated. It should be stressed here that not the inherent electronic properties or redox-activity of the metal-ligand combination but rather how these parameters affect the structural integrity of the complex after reduction influences the catalytic performance. Upon overall di-reduction and protonation, all complexes form the anionic hydride species XH⁻ (where X is 2–5). The potential of all hydride redox couples XH|XH⁻ is around –1.0 V, which is 0.6 V more positive than the second reduction in absence of acid, irrespective of how these hydride species were formed (ECE for 3–5 and EEC for 2).

Advancing from the hydride species XH⁻ into the catalytic wave, the next equilibrium protonation (XH⁻|XH₂) is the rate determining step for catalysis. This step is followed by electron transfer, liberating H₂ and reforming the mono-anion (XH₂|H₂ + X ). The overall free energy ΔG(XH⁻|H₂ + X ) associated with this sequence of proton transfer (PT) and electron transfer (ET) is again the sum of the free energies of PT and ET, respectively (vide supra). This free energy shows to be very similar for 2–5. The separate PT and ET steps are strongly affected by the nature of the ligand: For phosphole-based complexes 3–5 the equilibrium constant \( K = 0.04 \text{ M}^{-1} \) (pK = 1.4) and the redox potential is –1.90 V. For 2, \( K = 150 \text{ M}^{-1} \) (pK = –2.2) and the redox potential is –2.09 V. Following the typical ET-PT relationship of 59 mV per pK unit, it can be easily deduced that the difference in potential between 2 and 3–5 (190 mV) is counterbalanced by their differences in pK (3.6). This last PT/ET step demonstrates the intimate relationship between the rate and the overpotential for catalysis.

Conclusion

Comparing the reactivity of compounds 1–6 to the structure of their various reduced and protonated species, some general conclusions can be drawn (Figure 8). In the case of redox-innocent ligands (CO and PPh₃; compounds 1 and 2) an Fe₄-S bond is cleaved on reduction, leading to a opened-up [2Fe-2S] butterfly structure that is not sufficiently basic to get protonated. The use of redox-active phosphole ligands (3–6) avoids the rupture of the aforementioned Fe₄-S bond by withdrawing electron density onto the phosphole backbone. This leads to an intact [2Fe-2S] butterfly structure that can get protonated, with the second electron transfer at milder potentials than was the case for redox-innocent ligands. The incorporation of proto-reactivity in the ligand (compound 6, cf. Chapter 4) leads to charge stabi-
lization during reduction, and therefore to a milder reduction potential than was the case for the similar compound without proto-reactivity (4). In the search for efficient H₂ase mimics, we envision that reducing the overpotential is easier to attain by opening up novel reduction/protonation pathways, both by geometric tuning of the complexes and by inclusion of functionalities that facilitate PCET. Moreover, it was shown that the incorporation of redox-active phosphole ligands allows for an alternative catalytic mechanism at modified redox potentials in the catalytic cycle, without affecting the overall catalytic performance.
Chapter 5

Experimental

Materials and methods

General procedures. All syntheses were carried out under a nitrogen atmosphere using standard Schlenk techniques. All purifications involving column chromatography were performed in air with non-degassed solvents. Dichloromethane used for synthesis and electrochemistry was distilled over calcium hydride prior to use. Acetonitrile was used for synthesis (p.a. grade) as received. The supporting electrolyte nBu₄NPF₆ (prepared from saturated solutions of KPF₆ and nBuN₄Br in water) was recrystallized from hot methanol and dried under vacuum at 80 °C overnight. The phosphole ligands were synthesized according to literature procedures.38,39 The acid HNEt₃PF₆ was synthesized according to a literature procedure.40 All commercially available chemicals were used as received. The ¹H and ³¹P NMR spectra were measured on a Bruker AV400 spectrometer. Mass spectra were collected on an AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer (JEOL, Japan). FD probe equipped with FD Emitter, Carbotec (Germany), FD 10 μm. Current rate 51.2 mA/min over 1.2 min. Typical measurement conditions are: Counter electrode –10 kV, ion source 37V.

Synthesis

Synthesis of (µ-bdt)Fe₂(CO)₅L. A Schlenk flask was charged with (µ-bdt)Fe₂(CO)₆, phosphorus ligand (1.0 equivalent) and CH₂Cl₂ (100 ml/mmol). A solution of trimethylamine N-oxide dihydrate in CH₃CN (50 mM; 1.0 equivalent) was added dropwise and the solution was stirred at room temperature for 2 hours. The crude product was pre-adsorbed on silica and purified by column chromatography (SiO₂; gradient elution: pentane to CH₂Cl₂/pentane 1:3). This gave the target products in moderate yields (40%–60%) as air-stable red solids.

Characterization of 2 (40% yield). ¹H NMR (300 MHz, CD₂Cl₂) δ 7.57–7.45 (m, 6H), 7.43–7.29 (m, 9H), 6.53 (dd, J = 5.4, 3.2 Hz, 2H), 6.22 (dd, J = 5.4, 3.2 Hz, 2H). ³¹P NMR (121 MHz, CD₂Cl₂) δ 61.94. IR (CD₂Cl₂, cm⁻¹) 2050 (vs), 1993 (vs), 1979 (s, sh), 1936 (w).

Characterization of 3 (40% yield). ¹H NMR (300 MHz, CD₂Cl₂) δ 8.00–7.87 (m, 2H), 7.78–7.66 (m, 2H), 7.58–7.49 (m, 2H), 7.47–7.34 (m, 7H), 6.16–6.03 (m, 4H). ³¹P NMR (121 MHz, CD₂Cl₂) δ 52.82. IR (CD₂Cl₂, cm⁻¹) 2050 (vs), 1993 (vs), 1979 (s, sh), 1936 (w).
The Role of Redox-Active Phosphole Ligands in Proton Reduction Catalysis using [FeFe]H₂ase Mimics

MS (FD+) for C₂₉H₁₇Fe₂O₅PS₂: m/z calculated 651.89538, observed 651.90908 (Δ(m/z) 21.0 ppm).

Characterization of 4 (45% yield). ¹H NMR (300 MHz, CD₂Cl₂) δ 7.92 (ddd, J = 11.0, 7.5, 2.1 Hz, 2H), 7.63–7.53 (m, 3H), 7.27–7.19 (m, 6H), 7.17–7.08 (m, 4H), 6.98 (dd, J = 5.5, 3.2 Hz, 2H), 6.64 (dd, J = 5.5, 3.2 Hz, 2H), 2.67–2.51 (m, 2H), 2.39–2.25 (m, 2H), 1.66–1.44 (m, 4H, overlaps with water peak). ³¹P NMR (121 MHz, CD₂Cl₂) δ 74.86. IR (CH₂Cl₂, cm⁻¹) 2049 (vs), 1992 (vs), 1979 (s, sh), 1936 (w). MS (FD+) for C₃₇H₂₇Fe₂O₅PS₂: m/z calculated 757.97363, observed 757.98919 (Δ(m/z) 20.5 ppm).

Characterization of 5 (60% yield). ¹H NMR (300 MHz, CD₂Cl₂) δ 8.08 (ddd, J = 10.5, 6.4, 3.0 Hz, 2H), 7.61 (m, 3H), 7.21–6.92 (m, 16H), 6.92–6.82 (m, 2H), 6.74–6.63 (m, 6H). ³¹P NMR (121 MHz, CD₂Cl₂) δ 76.78. IR (CH₂Cl₂, cm⁻¹) 2053 (vs), 1995 (vs), 1983 (s, sh), 1940 (w). MS (FD+) for C₄₅H₂₉Fe₂O₅PS₂: m/z calculated 855.98928, observed 856.01426 (Δ(m/z) 29.2 ppm).

Infrared spectroscopy

Figure 9. Infrared spectra of compounds 2–5 (1 mM in CH₂Cl₂).
NMR spectroscopy

Figure 10. $^1$H NMR (300 MHz) spectrum of 2 in CD$_2$Cl$_2$.

Figure 11. $^{31}$P NMR (121 MHz) spectrum of 2 in CD$_2$Cl$_2$.

Figure 12. $^1$H NMR (300 MHz) spectrum of 3 in CD$_2$Cl$_2$. 
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Figure 13. $^{31}$P NMR (121 MHz) spectrum of 3 in CD$_2$Cl$_2$.

Figure 14. $^1$H NMR (300 MHz) spectrum of 4 in CD$_2$Cl$_2$.

Figure 15. $^{31}$P NMR (121 MHz) spectrum of 4 in CD$_2$Cl$_2$. 
Figure 16. $^1$H NMR (300 MHz) spectrum of 5 in CD$_2$Cl$_2$. 

Figure 17. $^{31}$P NMR (121 MHz) spectrum of 5 in CD$_2$Cl$_2$. 

**Single crystal X-ray diffraction analysis**

X-ray intensities were measured on a Bruker D8 Quest Eco diffractometer equipped with a Triumph monochromator ($\lambda = 0.71073$ Å) and a CMOS Photon 50 detector at a temperature of 150(2) K. Intensity data were integrated with the Bruker APEX2 software. Absorption correction and scaling was performed with SADABS. The structures were solved with the program SHELXL. Least-squares refinement was performed with SHELXL-2013 against $F^2$ of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times $U_{eq}$ of the attached C atoms.
The Role of Redox-Active Phosphole Ligands in Proton Reduction Catalysis using [FeFe]H\textsubscript{2}ase Mimics

C29H17Fe2O5PS\textsubscript{2} (3), Fw = 652.24, dark-red diamonoid, 0.363×0.237×0.189 mm, monoclinic, \(P_2_1/n\) (No: 14), \(a = 10.0681(6)\), \(b = 17.3783(9)\), \(c = 15.5640(8)\) Å, \(\beta = 95.619(3)\), \(V = 2710.1(3)\) Å\(^3\), \(Z = 4\), \(D_x = 1.596\) g/cm\(^3\), \(\mu = 1.322\) mm\(^{-1}\). 44332 reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.65\) Å\(^{-1}\). 10371 reflections were unique, of which 6065 were observed \([I > 2\sigma(I)]\). 352 parameters were refined with 0 restraints. R1/\(wR_2\) \([I > 2\sigma(I)]\): 0.0527/0.1258. R1/wR2 \([\text{all refl.}]\): 0.122/0.1675. S = 0.876. Residual electron density between -0.635 and 0.570 e/Å\(^3\).

C37H27Fe2O5PS\textsubscript{2} (4), Fw = 758.40, dark-red diamonoid, 0.382×0.131×0.078 mm, monoclinic, \(P_2_1/n\) (No: 14), \(a = 10.407(3)\), \(b = 17.562(5)\), \(c = 18.126(5)\) Å, \(\beta = 91.982(5)\), \(V = 3310.9(16)\) Å\(^3\), \(Z = 4\), \(D_x = 1.521\) g/cm\(^3\), \(\mu = 1.094\) mm\(^{-1}\). 42080 reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.74\) Å\(^{-1}\). 8113 reflections were unique, of which 4018 were observed \([I > 2\sigma(I)]\). 424 parameters were refined with 0 restraints. R1/\(wR_2\) \([I > 2\sigma(I)]\): 0.0709/0.1405. R1/wR2 \([\text{all refl.}]\): 0.1910/0.1910. S = 0.895. Residual electron density between -0.509 and 0.542 e/Å\(^3\).

C45H29Fe2O5PS\textsubscript{2} (5), Fw = 856.50, dark-red diamonoid, 0.446×0.112×0.084 mm, monoclinic, \(P_2_1/c\) (No: 14), \(a = 15.2560(7)\), \(b = 15.3674(7)\), \(c = 17.9400(9)\) Å, \(\beta = 97.672(2)\), \(V = 4168.3(3)\) Å\(^3\), \(Z = 4\), \(D_x = 1.500\) g/cm\(^3\), \(\mu = 1.01\) mm\(^{-1}\). 38582 reflections were measured up to a resolution of \((\sin \theta/\lambda)_{\text{max}} = 0.84\) Å\(^{-1}\). 7333 reflections were unique, of which 5837 were observed \([I > 2\sigma(I)]\). 523 parameters were refined with 0 restraints. R1/\(wR_2\) \([I > 2\sigma(I)]\): 0.0335/0.0899. R1/wR2 \([\text{all refl.}]\): 0.0520/0.0899. S = 0.947. Residual electron density between -0.792 and 0.687 e/Å\(^3\).

Figure 18. Molecular structure of 3 with displacement ellipsoids at the 50% probability level.

Figure 19. Molecular structure of 4 with displacement ellipsoids at the 50% probability level.

Figure 20. Molecular structure of 5 with displacement ellipsoids at the 50% probability level.
Chapter 5

Figure 21. Bar graph of the parameters in Table 2, showing underestimation and overestimation of selected parameters by DFT with respect to the parameters determined by XRD for compounds 2–5.

Table 2. Selected bond lengths and (dihedral) angles as determined by X-ray diffraction (XRD) and the comparison to the DFT calculated geometries.

<table>
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<tr>
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<th>2 (DFT)</th>
<th>3 (XRD)</th>
<th>3 (DFT)</th>
<th>4 (XRD)</th>
<th>4 (DFT)</th>
<th>5 (XRD)</th>
<th>5 (DFT)</th>
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<td>2.303</td>
<td>2.276</td>
<td>2.302</td>
<td>2.274</td>
<td>2.303</td>
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<td>2.306</td>
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<tr>
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<td>2.283</td>
<td>2.297</td>
<td>2.273</td>
<td>2.303</td>
<td>2.280</td>
<td>2.303</td>
<td>2.297</td>
<td>2.301</td>
</tr>
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<td>2.528</td>
<td>2.474</td>
<td>2.520</td>
<td>2.482</td>
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<td>2.523</td>
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<tr>
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<td>2.306</td>
<td>2.273</td>
<td>2.300</td>
<td>2.280</td>
<td>2.304</td>
<td>2.269</td>
<td>2.303</td>
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<tr>
<td>Fe\textsubscript{p}-S\textsubscript{2}</td>
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<td>1.779</td>
<td>1.784</td>
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<td>1.780</td>
<td>1.793</td>
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<td>1.761</td>
<td>1.765</td>
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<td>66.5°</td>
<td>65.9°</td>
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<td>66.1°</td>
<td>66.3°</td>
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<tr>
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<td>66.7°</td>
<td>65.9°</td>
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<td>66.3°</td>
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</tr>
<tr>
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<td>100.8°</td>
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<td>100.2°</td>
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</table>
The Role of Redox-Active Phosphole Ligands in Proton Reduction Catalysis using [FeFe]H₂ase Mimics

Electrochemistry

Cyclic voltammetry was performed on 1 mM solutions in CH₂Cl₂ containing 0.1 M nBu₄NPF₆ as the supporting electrolyte. The voltammograms were recorded using a 663 VA stand with a PGSTAT302N potentiostat (Metrohm/Autolab), a static mercury drop electrode (SMDE; drop size 2) or glassy carbon disk (diameter 2 mm) as a working electrode, a platinum wire as an auxiliary electrode and a leakless Ag⁰/Ag⁺ reference electrode (eDAQ ET069). Single equivalents of Et₃NHPF₆ were added as a 25% m/V solution in CH₂Cl₂. To convert the potential values of the Ag⁰/Ag⁺ reference to Fe/Fe⁺, a correction factor was used as determined by cyclic voltammetry of 1 mM ferrocene in CH₂Cl₂ using the same reference electrode. At the end of each experiment, ferrocene was added to the solution to check for reference electrode drift. All cyclic voltammetric experiments were iR compensated to around 95% of solution resistance. Digital simulation of cyclic voltammograms was performed using DigiElch version 7.FD (build 7.096; ElchSoft.com).

Elucidation of redox and chemical processes using cyclic voltammetry was conducted by the following step-wise protocol:

- In presence of (increasing amounts of) acid, the mechanism of protonation was established by peak potential analysis in the pure kinetic region:
  - In the case $\partial E_{p,c}/\partial \ln([\text{Et}_3\text{NHPF}_6]) = \partial E_{p,c}/\partial \ln(\nu) \approx 12.8$ mV an ECE mechanism was assumed on the basis of the analysis laid down by Parker and others.\(^{30,31,44-46}\)
  - In the case $\partial E_{p,c}/\partial \ln([\text{Et}_3\text{NHPF}_6]) = 0$ and the anodic re-oxidation wave moved to potentials more positive, it was assumed that the formed di-anion was (slowly) protonated in an overall EEC mechanism
- For ECE mechanism: From digital simulation of the cyclic voltammograms in presence of acid the first reduction potential and the protonation rate were determined:
  - $X + e^- \leftrightarrow X^- (E_0^1; k_s)$
  - $X^- + H^+ \rightarrow XH (k_d)$
  - The second reduction potential in presence of acid ($XH + e^- \leftrightarrow XH^-$) was determined from its half-wave potential $E_{1/2}$ by cycling over the anodic re-oxidation wave
- In absence of acid and using the first reduction potential, the second reduction potential and the disproportionation/comproportionation equilibrium were determined by digital simulation:
  - $X^- + e^- \leftrightarrow X^{2-} (E_0^2; k_s)$
• $2\,X^- \leftrightarrow X + X^{2-}$ \((k_f)\), with \(K = \exp(F/RT|E^*_1 - E^*_2|)\)
• Then, using all known parameters, multiple electrocatalytic mechanisms were simulated digitally, of which in all cases only one mechanism could unambiguously be fitted on the catalytic waves.

**Cyclic voltammetry in presence of acid at a static mercury electrode**

![Cyclic voltammograms](image)

Figure 22. Cyclic voltammograms of complexes 2 (top left), 3 (top right) and 4 (bottom) in presence of 4 mM Et₃NHPF₆ at a mercury electrode.
Cyclic voltammetry of 1

Cyclic voltammograms of 1 in absence and presence of acid are shown in the main text. For kinetic analysis, it was attempted to make the proton transfer reaction \((1^+ + \text{H}^+)\) rate limiting by applying the slowest scan rate possible without introducing too much natural convection (0.03 V/s). However, this yielded peak potential variations that could not be interpreted by the analysis method laid down by Parker. However, digital simulation using the parameters from Table 3 showed perfect overlap with the experimental voltammograms.

![Figure 23](image1.png)

Figure 23. Peak potential analysis of 1 at (left) various scan rates (0.03/0.1/0.3/1.0/3.0 V/s) and (right) various acid concentrations (4/8/16/32/64 mM) at a mercury electrode.

Cyclic voltammetry of 2

![Figure 24](image2.png)

Figure 24. Peak potential analysis of 2 at (left) various scan rates (0.03/0.1/0.3/1.0/3.0 V/s) and (right) various acid concentrations (4/8/16/32 mM) at a mercury electrode.
Figure 25. Experimental (solid) and simulated (dashed) cyclic voltammograms of 2 (left) in absence of acid (0.3 V/s) and (right) in presence of acid (0.1 V/s) at 8 mM and 32 mM concentration Et$_3$NHPF$_6$.

Cyclic voltammetry of 3

Figure 26. Peak potential analysis of 3 at (left) various scan rates (0.03/0.1/0.3/1.0/3.0 V/s) and (right) various acid concentrations (4/8/16/32 mM) at a mercury electrode.

Figure 27. Experimental (solid) and simulated (dashed) cyclic voltammograms of 3 (left) in absence of acid (0.3 V/s) and (right) in presence of acid (0.1 V/s) at 8 mM and 32 mM concentration Et$_3$NHPF$_6$. 
Cyclic voltammetry of 4 and 5

The main redox processes in absence of acid occurring for complex 4 in dichloromethane have been described in the main text. However, in-depth analysis of the voltammograms shows that the di-anions slowly decompose in solution to a species with a 0.2 V milder reduction potential (~1.47 V). This intramolecular process is relatively slow (ca. 3 s⁻¹), but still accounts to a large extent for the shape of the anodic re-oxidative part of the voltammograms. In presence of acid this chemistry is not observed, since the di-anion is never accessed. For complex 5 the same additional intramolecular process was observed, albeit twice as slow at 1.5 s⁻¹.

Figure 28. Peak potential analysis of 4 at (left) various scan rates (0.03/0.1/0.3/1.0/3.0 V/s) and (right) various acid concentrations (4/8 mM) at a mercury electrode. Peak potentials at higher acid concentrations (16/32 mM) could not be determined due to the onset of the catalytic wave.
Figure 29. Experimental (solid) and simulated (dashed) cyclic voltammograms of 4 in absence of acid at (top left) 0.03 and (top right) 3.0 V/s. Bottom: in presence of acid (0.1 V/s) at 8 mM and 32 mM concentration Et$_3$NHPF$_6$.

Catalytic overpotential determination

The overpotential for proton reduction is generally defined against the reversible redox couple of proton reduction/hydrogen oxidation in the respective solvent-acid mixture, which in this case is 2 Et$_3$NHPF$_6$ + 2 e$^-$ ↔ 2 Et$_3$N + H$_2$ + 2 PF$_6^-$ (not taking into account homoconjugation equilibria). This redox couple can generally be described by the standard potential for proton reduction together with the $pK_a$ of the acid, both in the solvent used. However, in CH$_2$Cl$_2$ no $pK_a$ values nor proton reduction standard potentials are available. For this reason, we used a crude method to estimate the standard potential for this redox couple by performing proton reduction/hydrogen oxidation on a platinum working electrode under catalytic conditions (in absence of a homogeneous catalyst), leading to a half-wave potential $E_{1/2} = -1.25$ V (vs. Fe$^{0/+}$). Overpotentials for proton reduction were then determined relative to this potential.
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**Simulation parameters**

Table 3. Fitting parameters used in the simulation of cyclic voltammograms for compounds 1–5.

<table>
<thead>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<td><strong>Electron transfer.</strong> Potentials in V vs. Fe⁰/⁰⁺. Reversibility (in brackets) denoted as ‘rev’ ($k_s &gt; 10$ cm s⁻¹) or as $k_s$ value in [cm s⁻¹] if known.</td>
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<td>X</td>
<td>X⁻</td>
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<td>-1.80 (0.1)</td>
<td>-1.80 (rev)</td>
<td>-1.85 (rev)</td>
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<td>X²⁻</td>
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**Disproportionation reactions.** Forward rate constants $k_i$ given in [M⁻¹ s⁻¹]. Equilibrium constant $K$ = exp($F/RT\cdot\Delta E^\circ$), where $\Delta E^\circ$ is the difference in potentials between the two electron transfers.

<table>
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<tr>
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<td>X + XH⁺</td>
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<td>x</td>
<td>4</td>
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**Protonation reactions.** Forward rate constants $k_i$ given in [M⁻¹ s⁻¹]. Equilibrium constant $K$ (in brackets) given in [M⁻¹].

<table>
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<td>XH</td>
<td>x</td>
<td>x</td>
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<tr>
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<td>&gt; 10⁹</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
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<td>XH₂</td>
<td>x</td>
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<td>&gt; 10⁶ (0.04)</td>
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<tr>
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<td>X⁻ + H₂</td>
<td>2×10⁵</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

**DFT calculations**

The gas-phase geometries of the molecules 2–5 were optimized with the Turbomole program package at the ri-DFT/BP86 level. We used the def2-TZVP basis set for all atoms. These calculations also yielded the frontier orbital plots (isovalue 0.05) and spin density plots (isovalue 0.005).
Chapter 5

Total energies of neutral complexes

LUMO frontier orbital plots shown.

Lowest energy structure is in agreement with the XRD structure of 2.

Lowest energy structure is in agreement with the XRD structure of 5.
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0 kcal/mol +0.6 kcal/mol +1.5 kcal/mol

Lowest energy structure is in agreement with the XRD structure of 3.
Table 4. DFT calculated total energies (in hartree) for the closed-shell singlet (CSS), open-shell singlet (OSS) and triplet (T) states of the di-anions $2^{2-}$ through $5^{2-}$. For $4^{2-}$ and $5^{2-}$, the CSS state is lowest in energy. For $2^{2-}$ and $3^{2-}$, both CSS and OSS states are similar in energy. For sake of comparison, all DFT calculated di-anions were analyzed in their CSS state.

<table>
<thead>
<tr>
<th></th>
<th>$2^{2-}$</th>
<th>$3^{2-}$</th>
<th>$4^{2-}$</th>
<th>$5^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSS</td>
<td>-5159.45279</td>
<td>-5158.27402</td>
<td>-5469.232582</td>
<td>-5775.41586</td>
</tr>
<tr>
<td>OSS</td>
<td>-5159.45279</td>
<td>-5158.27402</td>
<td>-5469.232578</td>
<td>-5775.41581</td>
</tr>
<tr>
<td>T</td>
<td>-5159.42695</td>
<td>not converged</td>
<td>-5469.23336</td>
<td>-5775.41419</td>
</tr>
</tbody>
</table>

Table 5. DFT calculated spin density distribution of mono-anions $2^-$ through $5^-$. Localization designated by: CO = all carbonyl ligands, Fe$_d$ = distal iron atom, Fe$_p$ = proximal iron atom, S$_1$ = the least dissociated sulfur atom, S$_2$ = the most dissociated sulfur atom, bdt = all six carbon atoms in the bdt bridge, P = phosphorus atom, phosphole = all four carbon atoms in the phosphole ring, backbone = all remaining non-hydrogen atoms.

<table>
<thead>
<tr>
<th></th>
<th>$2^-$</th>
<th>$3^-$</th>
<th>$4^-$</th>
<th>$5^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>9.0%</td>
<td>3.9%</td>
<td>2.9%</td>
<td>0.7%</td>
</tr>
<tr>
<td>Fe$_d$</td>
<td>89.5%</td>
<td>26.0%</td>
<td>17.3%</td>
<td>15.7%</td>
</tr>
<tr>
<td>Fe$_p$</td>
<td>-</td>
<td>33.9%</td>
<td>29.0%</td>
<td>23.6%</td>
</tr>
<tr>
<td>S$_1$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S$_2$</td>
<td>1.4%</td>
<td>6.8%</td>
<td>4.4%</td>
<td>3.6%</td>
</tr>
<tr>
<td>bdt</td>
<td>-</td>
<td>3.7%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
<td>5.5%</td>
<td>3.0%</td>
<td>3.4%</td>
</tr>
<tr>
<td>phosphole</td>
<td>11.0%</td>
<td>34.6%</td>
<td>38.9%</td>
<td></td>
</tr>
<tr>
<td>backbone</td>
<td>-</td>
<td>9.2%</td>
<td>8.8%</td>
<td>14.2%</td>
</tr>
</tbody>
</table>
The Role of Redox-Active Phosphole Ligands in Proton Reduction Catalysis using [FeFe]H₂ase Mimics

Table 6. DFT calculated spin density distribution of hydrides 2H⁻ through 5H⁻. For explanation on localization designation, see caption of Table 5.

<table>
<thead>
<tr>
<th></th>
<th>2H⁻</th>
<th>3H⁻</th>
<th>4H⁻</th>
<th>5H⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>5.1%</td>
<td>13.0%</td>
<td>10.5%</td>
<td>10.5%</td>
</tr>
<tr>
<td>Fe_d</td>
<td>107.2%</td>
<td>91.8%</td>
<td>90.1%</td>
<td>95.0%</td>
</tr>
<tr>
<td>H</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe_p</td>
<td>66.4%</td>
<td>49.1%</td>
<td>41.8%</td>
<td>36.4%</td>
</tr>
<tr>
<td>S¹</td>
<td>-</td>
<td>8.6%</td>
<td>9.9%</td>
<td>8.5%</td>
</tr>
<tr>
<td>S²</td>
<td>5.6%</td>
<td>7.8%</td>
<td>4.0%</td>
<td>2.0%</td>
</tr>
<tr>
<td>bdt</td>
<td>-</td>
<td>13.7%</td>
<td>9.5%</td>
<td>4.8%</td>
</tr>
<tr>
<td>P</td>
<td>6.9%</td>
<td>7.2%</td>
<td>5.3%</td>
<td>5.1%</td>
</tr>
<tr>
<td>phosphole</td>
<td>7.5%</td>
<td>27.5%</td>
<td>33.4%</td>
<td></td>
</tr>
<tr>
<td>backbone</td>
<td>8.8%</td>
<td>1.3%</td>
<td>1.3%</td>
<td>4.3%</td>
</tr>
</tbody>
</table>

Table 7. Selected bond lengths for reduced and protonated forms of 2 and 3. Carbons C₁⁻C₄ are in the phosphole ring.

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>2⁺</th>
<th>2⁻</th>
<th>2H⁻</th>
<th>3</th>
<th>3⁻</th>
<th>3²⁻</th>
<th>3H⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe_d-S¹</td>
<td>2.297</td>
<td>2.264</td>
<td>2.343</td>
<td>2.4</td>
<td>2.303</td>
<td>2.305</td>
<td>2.341</td>
<td>2.543</td>
</tr>
<tr>
<td>Fe_d-L²⁺</td>
<td>2.059</td>
<td>1.652</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe_d-Fe_p</td>
<td>2.528</td>
<td>2.61</td>
<td>2.626</td>
<td>2.762</td>
<td>2.520</td>
<td>2.647</td>
<td>2.615</td>
<td>2.753</td>
</tr>
<tr>
<td>Fe_p-S¹</td>
<td>2.304</td>
<td>2.27</td>
<td>2.268</td>
<td>2.299</td>
<td>2.299</td>
<td>2.299</td>
<td>2.267</td>
<td>2.345</td>
</tr>
<tr>
<td>Fe_p-S²</td>
<td>2.306</td>
<td>2.343</td>
<td>2.345</td>
<td>2.317</td>
<td>2.300</td>
<td>2.349</td>
<td>2.339</td>
<td>2.343</td>
</tr>
<tr>
<td>Fe_p-P</td>
<td>2.256</td>
<td>2.247</td>
<td>2.154</td>
<td>2.518</td>
<td>2.226</td>
<td>2.254</td>
<td>2.139</td>
<td>2.325</td>
</tr>
<tr>
<td>P-C₁</td>
<td>1.834</td>
<td>1.826</td>
<td>1.850</td>
<td>1.824</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-C₂</td>
<td>1.832</td>
<td>1.820</td>
<td>1.843</td>
<td>1.827</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁-C₃</td>
<td>1.855±0.011 Å</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂-C₄</td>
<td>1.415</td>
<td>1.422</td>
<td>1.418</td>
<td>1.419</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃-C₄</td>
<td>1.472</td>
<td>1.464</td>
<td>1.467</td>
<td>1.467</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) For the dianions, L = μ-CO. For the hydrides, L = μ-H.
Table 8. Selected bond lengths for reduced and protonated forms of 4 and 5. Carbons C₁–C₄ are in the phospole ring.

<table>
<thead>
<tr>
<th></th>
<th>4</th>
<th>4⁻</th>
<th>4²⁻</th>
<th>4H⁻</th>
<th>5</th>
<th>5⁻</th>
<th>5²⁻</th>
<th>5H⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feₐ-S₁</td>
<td>2.303</td>
<td>2.318</td>
<td>2.326</td>
<td>2.411</td>
<td>2.306</td>
<td>2.320</td>
<td>2.333</td>
<td>2.359</td>
</tr>
<tr>
<td>Feₐ-S₂</td>
<td>2.303</td>
<td>2.355</td>
<td>2.425</td>
<td>2.827</td>
<td>2.301</td>
<td>2.340</td>
<td>2.388</td>
<td>3.081</td>
</tr>
<tr>
<td>Feₐ-H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.648</td>
<td></td>
</tr>
<tr>
<td>Feₐ-Feₚ</td>
<td>2.521</td>
<td>2.614</td>
<td>2.714</td>
<td>2.753</td>
<td>2.523</td>
<td>2.605</td>
<td>2.700</td>
<td>2.771</td>
</tr>
<tr>
<td>Feₚ-H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feₚ-S₁</td>
<td>2.304</td>
<td>2.298</td>
<td>2.297</td>
<td>2.319</td>
<td>2.303</td>
<td>2.299</td>
<td>2.301</td>
<td>2.299</td>
</tr>
<tr>
<td>Feₚ-S₂</td>
<td>2.304</td>
<td>2.339</td>
<td>2.349</td>
<td>2.343</td>
<td>2.305</td>
<td>2.333</td>
<td>2.344</td>
<td>2.348</td>
</tr>
<tr>
<td>Feₚ-P</td>
<td>2.244</td>
<td>2.310</td>
<td>2.362</td>
<td>2.400</td>
<td>2.246</td>
<td>2.301</td>
<td>2.347</td>
<td>2.393</td>
</tr>
<tr>
<td>P-C₁</td>
<td>1.837</td>
<td>1.820</td>
<td>1.814</td>
<td>1.818</td>
<td>1.835</td>
<td>1.818</td>
<td>1.809</td>
<td>1.818</td>
</tr>
<tr>
<td>P-C₂</td>
<td>1.831</td>
<td>1.822</td>
<td>1.811</td>
<td>1.820</td>
<td>1.835</td>
<td>1.819</td>
<td>1.809</td>
<td>1.818</td>
</tr>
<tr>
<td>C₁-C₃</td>
<td>1.375</td>
<td>1.402</td>
<td>1.431</td>
<td>1.395</td>
<td>1.375</td>
<td>1.400</td>
<td>1.424</td>
<td>1.395</td>
</tr>
<tr>
<td>C₂-C₄</td>
<td>1.365</td>
<td>1.395</td>
<td>1.425</td>
<td>1.386</td>
<td>1.371</td>
<td>1.401</td>
<td>1.425</td>
<td>1.393</td>
</tr>
<tr>
<td>C₃-C₄</td>
<td>1.477</td>
<td>1.442</td>
<td>1.412</td>
<td>1.450</td>
<td>1.486</td>
<td>1.454</td>
<td>1.434</td>
<td>1.459</td>
</tr>
</tbody>
</table>
The Role of Redox-Active Phosphole Ligands in Proton Reduction Catalysis using [FeFe]H₂ase Mimics
Frontier orbital plots of 2

2 (HOMO)

2 (LUMO)

2⁻ (SOMO)

2⁻ (LUMO)

2⁻ (spin density)
The Role of Redox-Active Phosphole Ligands in Proton Reduction Catalysis using [FeFe]H₂ase Mimics

\[ 2^+ \text{ (SOMO)} \]

\[ 2^+ \text{ (LUMO)} \]

\[ 2\text{H}^- \text{ (SOMO1)} \]

\[ 2\text{H}^- \text{ (SOMO2)} \]

\[ 2\text{H}^- \text{ (LUMO)} \]

\[ 2\text{H}^- \text{ (spin density)} \]
Frontier orbital plots of 3

3 (HOMO)

3 (LUMO)

3⁻ (SOMO)

3⁻ (LUMO)

3⁻ (spin density)
The Role of Redox-Active Phosphole Ligands in Proton Reduction Catalysis using [FeFe]H₂ase Mimics
Chapter 5

Frontier orbital plots of 4

4 (HOMO)

4 (LUMO)

4⁻ (SOMO)

4⁻ (LUMO)

4⁻ (spin density)
The Role of Redox-Active Phosphole Ligands in Proton Reduction Catalysis
using [FeFe]H₂ase Mimics

$4^\pm$ (SOMO)

$4^\pm$ (LUMO)

$4H^-$ (SOMO1)

$4H^-$ (SOMO2)

$4H^-$ (LUMO)

$4H^-$ (spin density)
Frontier orbital plots of 5

5 (HOMO)

5 (LUMO)

5⁻ (SOMO)

5⁻ (LUMO)

5⁻ (spin density)
The Role of Redox-Active Phosphole Ligands in Proton Reduction Catalysis using [FeFe]H₂ase Mimics
References


The Role of Redox-Active Phosphole Ligands in Proton Reduction Catalysis using [FeFe]H$_2$ase Mimics


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