Protonation of Nickel–Iron Hydrogenase Models Proceeds after Isomerization at Nickel

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ABSTRACT: Theory and experiment indicate that the protonation of reduced NiFe dithiolates proceeds via a previously undetected isomer with enhanced basicity. In particular, it is proposed that protonation of \((OC)_3Fe(pdt)-Ni(dppe)\) \(\text{I}\); pdt\(^+\) = \(\text{S(CH}_2)_3\text{S}\); dppe = \(\text{Ph}_2\text{P(CH}_2)_2\text{PPh}_2\) occurs at the Fe site of the two-electron mixed-valence \(\text{Fe}(0)\text{Ni}(II)\) species, not the \(\text{Fe}(I)\text{Ni}(I)\) bond for the homovalence isomer of \(\text{I}\). The new pathway, which may have implications for protonation of other complexes and clusters, was uncovered through studies on the homologous series \(L(OC)_2Fe(pdt)M(dppe)\), where \(M = \text{Ni, Pd (2), and Pt (3)}\) and \(L = \text{CO, PCy}_3\). Similar to \(\text{I}\), complexes 2 and 3 undergo both protonation and \(1e^–\) oxidation to afford well-characterized hydrides \((2\text{H}^+)^\text{−}\) and \((3\text{H}^+)^\text{−}\) and mixed-valence derivatives \((2\text{H}^+)^\text{+}\) and \((3\text{H}^+)^\text{+}\), respectively. Whereas the Pd site is tetrahedral in complexes \(2\) and \(3\), the Pt site is square-planar in \(3\), indicating that this complex is best described as \(\text{Fe}(0)\text{Pt}(II)\). In view of the results on \(2\) and \(3\), the potential energy surface of \(\text{I}\) was reinvestigated with density functional theory. These calculations revealed the existence of an energetically accessible and more basic \(\text{Fe}(0)\text{Ni}(II)\) isomer with a square-planar Ni site.

INTRODUCTION

The protonation of metal complexes and clusters continues to attract much attention because of its relevance to catalysis involving proton and hydride transfer reactions. In organometallic and heterogeneous catalysis, protonation is a step in substrate hydrogenation and hydrogen evolution.\(^1,2\) In biology, metal protonation is implicated in the reduction of \(\text{CO}_2\) and \(\text{N}_2\), not to mention hydrogen evolution.\(^2,3\) For all of these opportunities for translating biological insights into practical functional models for the active sites of these enzymes present metal protonation can in principle occur at a single metal or at the metal–metal bond.

The regiochemistry of protonation is relevant to a mechanistic understanding of the \([\text{NiFe}^-]\) and \([\text{FeFe}^-]\) hydrogenases, which also feature Ni–Fe and Fe–Fe bonding interactions.\(^4,5\) By proton transfer, these complexes equilibrate protons and dihydrogen, i.e., \(2\text{H}^+ + 2e^- = \text{H}_2\) in accordance with the local redox environment and activities of \(\text{H}^+\) and \(\text{H}_2\). Functional models for the active sites of these enzymes present opportunities for translating biological insights into practical catalytic systems.\(^6\) In addition to being fast and operating at low overpotentials, the hydrogenases are attractive targets for functional modeling because they utilize earth abundant metals.\(^7\) For the above reasons, much effort has been directed, both computationally\(^8\) and experimentally,\(^9\) at understanding the details of proton transfer to and from synthetic NiFe and FeFe complexes.

While many complexes engage separately in acid–base and redox reactions, few exhibit both kinds of reactivity, providing a possible explanation for the paucity of functional hydrogenase (H\(_{\text{ase}}\)ase) models. With respect to the \([\text{NiFe}^-]\)–H\(_{\text{ase}}\) (Figure 1, left), the premier example of such a model is \((OC)_3Fe(pdt)-Ni(dppe)\) \((1)\).\(^10\) Tricarbonyl \(1\) and analogous phosphine-substituted derivatives undergo: (i) protonation to afford rare examples of nickel–iron hydrides and (ii) \(1e^-\) oxidation to give Fe(II)Ni(II) derivatives (Figure 1, right). Several examples of charge-neutral Fe(I)Ni(II) species, as well as their related Fe(II)Ni(II) hydrides\(^11–13\) and Fe(II)Ni(II) cations,\(^14,15\) have been characterized.

The \([\text{NiFe}^-]\)–H\(_{\text{ase}}\) active site features Ni bound to four Cys ligands in a distorted tetrahedral (SF\(_4\)-like) arrangement. Two of the thiolates link to an Fe center whose coordination sphere includes the unusual CO and CN\(^–\) cofactors, the latter H-bonding to neighboring Ser and Arg residues.\(^4\) In the active states of the enzyme, the FeNi core appears to be relatively conformationally rigid, with the Fe–Ni distance and coordination geometry being rather insensitive both to redox state and the presence/absence of \(\text{H}^+\) substrate.\(^16\) The rigidity of the active site is undoubtedly a factor in the high rates and low overpotentials at which the interconversion of \(\text{H}^+\) and \(\text{H}_2\) is mediated.

Received: June 10, 2014
Published: August 5, 2014
In contrast to the rigid active site, small molecule mimics are conformationally dynamic. For example, 1 undergoes a tetrahedral → square-planar twist at Ni upon oxidation or protonation (Figure 1). While the structures of 1, [1]⁺, and [1H⁺] are established, those of any intermediates are not. Such transformations may, for example, involve “pre-twisting” of the Ni coordination in 1 (Scheme 1, top).

Distortion of the ground-state structure of 1 could well affect oxidation states by inducing 2e⁻ mixed-valency. Furthermore, the degree of Fe−Ni bonding and, most importantly, reactivity would also be perturbed. While ligand-centered isomerism is a common theme in the chemistry of multimetallic compounds, drastic differences in coordination geometry and metal−metal bonding between two (or more) interconverting species are extremely rare. They are, however, not without precedent; for example, Jones and co-workers reported X-ray structures for two complexes of formula (OC)₂Rh(μ-PR₂)₂Rh(CO)₂ (Scheme 1, bottom). One species takes the form of a red compound featuring Rh−Rh bonding (2.761 Å), in which one Rh center is square-planar and the other tetrahedral. A second (orange) isomer was also observed, in which non-interacting Rh centers (3.717 Å) adopt square-planar geometries.

The present study involves parallel experimental and density functional theory (DFT) investigations to obtain a complete structural, energetic, and mechanistic picture of complexes derived from FeNi complex 1. This work was extended to FePd and FePt species such that a homologous series can be interrogated for information regarding conformational motions and metal−metal bonding.

**RESULTS AND DISCUSSION**

The major routes to low-valent FeNi complexes of type (OC)₃Fe(pdt)Ni(diphosphine) involve treatment of (pdt)Ni-(diphosphine) with either (i) Fe₃(CO)₉ or (ii) Fe₂(CO)₆/CoCp₂. As applied to the Pd and Pt derivatives, the second route proved more attractive, giving the diamagnetic heterobimetals (OC)₃Fe(pdt)Pd(dppe) (2) and (OC)₃Fe(pdt)Pt-(dppe) (3) (Scheme 2).

Isolated as dark-green needles, 2 is sensitive to O₂ (decomposing to CO-free paramagnetic species) but is thermally stable in the solid state under N₂. The energies of the two νCO bands (A + E modes) compare well with those observed for 1 (Table 1).

The FePd species 2 is similar to 1 in that its room temperature ³¹P{¹H} NMR spectrum features a broad singlet resonance (δ 51.3) for the dppe ligand. At lower temperature, the resonance for 1 decoalesces into two peaks (well-resolved at -68 °C), consistent with a dynamic process that interconverts the ³¹P sites. The previously reported coalescence temperature (-30 °C) corresponds to a free energy barrier of 9.5 kcal/mol for the FeNi species 1. This process presumably occurs via an intermediate or transition state with square-planar Ni. No decoalescence was observed for 2 even at -85 °C, behavior suggestive of either: (i) a tetrahedral Pd ground state with a particularly low rotational barrier or (ii) a square-planar Pd ground state. The second possibility is ruled out based on the similarity of the IR data for 1 and 2. The structure of 2 in the solid state was confirmed crystallographically (Figure 2).

Given the covalent radii of Pd (1.39 Å) and low-spin Fe (1.32 Å), the Fe−Pd distance of 2.561 Å suggests the presence of bonding between the metal centers in 2. The intermetallic separation is somewhat shorter in 1 (2.467 Å). Metal−metal interactions aside, the Pd and Fe centers in 2 exist

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**Figure 1.** Active site of [NiFe]-H₂ase, a bidirectional catalyst, participates in redox and acid−base chemistry (left). Similar behavior is observed for the prototypical model complex 1 (right).

**Scheme 1**

**Scheme 2**
consistent with previous DFT analyses of this system.\textsuperscript{10} NBO analysis of FeNi\textsubscript{d} orbitals with a Pd-centered metal bonding (Figure S56a) is only modestly shifted from those of FePd\textsubscript{d} complexes, for which theory indicated an Fe-centered doublet ground-state singly occupied molecular orbital (SOMO).\textsuperscript{15} These computational results, as well the implied shift and the absence of \textsuperscript{31}P hyperfine coupling (Figure 4, top; for simulated EPR spectra and parameters see Figure S23 and Table S1, respectively). The data are similar to those for Fe(II)Ni(II) complexes, for which theory indicated an Fe-centered d(\textsuperscript{2}) doublet ground-state singly occupied molecular orbital (SOMO).\textsuperscript{15} These computational results, as well the implied absence of spin–orbit coupling expected for a d(\textsuperscript{2}) ground state, are consistent with a resonance in the vicinity of g_e. Owing to the inversion of the pdt\textsuperscript{2} ring, the \textsuperscript{[OC]Fe(pdt)-M(dppe)]\textsuperscript{+} radicals exist as two conformers, one giving rise to an axial pattern and the other to a rhombic pattern.

Table 1. IR Data (\(\nu_{CO}/\text{cm}^{-1}\)) for FeM (M = Ni, Pd, Pt) Compounds in CH\(_2\)Cl\(_2\) Solution

<table>
<thead>
<tr>
<th>compound</th>
<th>FeNi</th>
<th>FePd</th>
<th>FePt</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{OC})_3\text{Fe(pdt)M(dppe)})</td>
<td>2028, 1952\textsuperscript{20}</td>
<td>2024, 1955</td>
<td>1962, 1883, 1870</td>
</tr>
<tr>
<td>(\text{[(OC)}_3\text{FeH(pdt)M(dppe)]BF}_4)</td>
<td>2082, 2024\textsuperscript{20}</td>
<td>2081, 2020</td>
<td>2081, 2022</td>
</tr>
<tr>
<td>(\text{[(OC]}_3\text{Fe(pdt)M(dppe)]BF}_4)</td>
<td>2057, 1986\textsuperscript{13}</td>
<td>2058, 1986</td>
<td>2058, 1987</td>
</tr>
<tr>
<td>(\text{[Cy}<em>3\text{P(O)C}</em>{2}\text{Fe(pdt)M(dppe)]BF}_4)</td>
<td>1966, 1899\textsuperscript{12}</td>
<td>1964, 1900</td>
<td>1966, 1900</td>
</tr>
</tbody>
</table>

\(\text{C}_32, 1.798 (1.77)\). Selected angles (deg) (mean DFT values in parentheses): Pd1\textsubscript{−}−Pd1\textsubscript{−}S1, 122.5 (135.1); S1\textsubscript{−}Pd1\textsubscript{−}C30, 1.795; Fe1−C31, 1.793; Fe1−C32, 1.798 (1.77). Selected distances (Å) (mean DFT values in parentheses): Pd1\textsubscript{−}C32, 1.798 (1.77). Selected distances (Å) (mean DFT values in parentheses): Pd1−Pd1−S1, 122.5 (135.1); S1−Pd1−C30, 1.795; Fe1−C31, 1.793; Fe1−C32, 1.798 (1.77). Selected angles (deg) (mean DFT values in parentheses): P1−Pd1−S1, 135.2; P1−Pd1−S2, 118.83; P2−Pd1−S1, 115.7; P2−Pd1−S2, 122.5 (135.1); S1−Fe1−C30, 162.2; S2−Fe1−C32, 163.1 (161.1).

The structures of several complexes reported here were calculated using DFT, and the optimized structures were in excellent agreement with available crystal structures (selected metrics are presented in Tables S3 and S4). In the case of 2, calculations accurately predicted the geometry of Pd, as well as its proximity to Fe. Additional isomers characterized as minima with DFT will be discussed below. NBO (natural bond orbital)\textsuperscript{23} analysis revealed the Fe−Pd bond to arise from overlap of an Fe-centered \(d(\text{z}^2)\) orbital with a Pd-centered orbital with d character (Figure S56b). NBO analysis of FeNi congener 1 also revealed metal−metal bonding (Figure S56a) consistent with previous DFT analyses of this system.\textsuperscript{10} NBO analysis of other Fe−M complexes discussed herein did not indicate mixing of metal d orbitals; hence, no Fe−M bonding is expected for these species.

Mixed-Valence Derivatives. The cyclic voltammogram of 2 features reversible and quasi-reversible oxidations at \(E_{1/2} = -0.87\) and +0.26 V, respectively (vs ferrocene/ferrocenium, Fe\textsuperscript{0}/\textsuperscript{2+}; Figure 3). The reversible wave, assigned to the \textsuperscript{[2]\textsuperscript{0}/\textsuperscript{+}} couple, is 300 mV more negative than the wave for \textsuperscript{[1]\textsuperscript{0}/\textsuperscript{+}}. The quasi-reversible wave (Figure 3). The reversible wave, assigned to the \textsuperscript{[2]\textsuperscript{0}/\textsuperscript{+}} couple, is 300 mV more negative than the wave for \textsuperscript{[1]\textsuperscript{0}/\textsuperscript{+}}. The quasi-reversible wave (Figure 3). The reversible wave, assigned to the \textsuperscript{[2]\textsuperscript{0}/\textsuperscript{+}} couple, is 300 mV more negative than the wave for \textsuperscript{[1]\textsuperscript{0}/\textsuperscript{+}}.
Table 2. Redox Potentials (V vs Fe(0)/+, Experimental and DFT-Calculated) and Associated Electrochemical Data (Recorded at 0.1 V/s) for FeNi, FePd, and FePt Complexes (1 mM) in NBu4PF6 Electrolyte (100 mM CH2Cl2 Solution)

<table>
<thead>
<tr>
<th>[2]′BF4−</th>
<th>E1/2 (FeII/FeIII) (Eg/s,</th>
<th>∆Eg/l)</th>
<th>E° (FeII/FeIII) (Eg/s,</th>
<th>∆Eg/l)</th>
<th>E1/2 (FeII/FeIII) (Eg/s,</th>
<th>∆Eg/l)</th>
<th>E° (FeII/FeIII) (Eg/s,</th>
<th>∆Eg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[2]BF4−</td>
<td>1.34</td>
<td>0.52</td>
<td>−0.59</td>
<td>0.09</td>
<td>0.09</td>
<td>−0.62</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td>[2]BF4−</td>
<td>0.26</td>
<td>0.39</td>
<td>−0.87</td>
<td>0.09</td>
<td>0.09</td>
<td>−0.87</td>
<td>0.09</td>
</tr>
<tr>
<td>3</td>
<td>[2]BF4−</td>
<td>0.20</td>
<td>0.24</td>
<td>−1.14</td>
<td>0.08</td>
<td>0.08</td>
<td>−1.14</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>[3]BF4−</td>
<td>0.33</td>
<td>0.168</td>
<td>−0.93</td>
<td>0.07</td>
<td>0.07</td>
<td>−0.93</td>
<td>0.07</td>
</tr>
<tr>
<td>5</td>
<td>[3]BF4−</td>
<td>0.49</td>
<td>0.168</td>
<td>−0.93</td>
<td>0.07</td>
<td>0.07</td>
<td>−0.93</td>
<td>0.07</td>
</tr>
</tbody>
</table>

*E1/2 (FeII/FeIII) = 0.064 V under these conditions. Anodic potential for irreversible oxidation. Calculated and experimental values for [1]BF4 agree by construction and were used as references for the corresponding [2] waves. Calculated and experimental values for [2]′BF4 agree by construction and were used as references for the corresponding [2]′, [3], [4], and [5] waves. This value was not determined as difficulties arising from local minima led to inconclusive results. This wave is assigned to a FePdII/FePdIII couple (vide infra).
of 3 is also distinctive, with the $\nu_{CO}$ bands (1962, 1883, 1870 cm$^{-1}$) observed at energies ~70 cm$^{-1}$ lower than those for Fe(1)Ni(1) and Fe(1)Pd(1) analogs. The $^{31}P$($^1$H) NMR spectrum for 3 consists of a singlet (and $^{195}$Pt-coupled doublet) and is temperature-invariant down to ~85 °C. The chemical shift ($\delta$ 44.1) and $J_{PtP}$ (3277 Hz) are close to those of the (pdt)Pt$^{111}$dppe precursor ($\delta$ 44.5, $J_{PtP} = 2177$ Hz). While NMR data are in line with Pt coordination being either (i) high fluxional tetrahedral or (ii) square-planar, the latter is most consistent with low-energy $\nu_{CO}$ CO bands. Square planarity at Pt is corroborated by DFT geometry optimization (Figure 6).

Indeed, rather than being isostructural to 1 and 2, 3 is predicted to feature a square-planar Pt site, with the angle between the PtP$_2$ and PtS$_2$ planes being 4°. The calculated Fe–Pt distance (2.87 Å) exceeds the sum of the covalent radii (2.68 Å), suggesting an absence of Fe–Pt bonding and a purely pentacoordinate Fe. This site, in contrast to the square-planar Fe(I) in 2, is distorted trigonal bipyramidal ($\tau = 0.54$). As mentioned previously, NBO analysis did not reveal $d$ orbital mixing, which was observed in 1 and 2. Overall, the coordination geometries are consistent with an Fe(0)Pt(II) description for 3.

Quasi-reversible oxidations for (CO)$_3$Fe(pdt)Pt(dppe) were observed at ~0.93 and +0.33 V (Figure S29), potentials similar to those for the FePd analog 2. The proposed sequence of 1e$^-$ events: Fe(0)Pt(II) $\Rightarrow$ Fe(I)Pt(II) $\Rightarrow$ Fe(II)Pt(II). This sequence is supported by the IR spectrum for [(OC)$_3$Fe(dpdt)-Pt(dppe)]BF$_4$ ([3]BF$_4$) prepared from 3 and FeCBF$_4$, in which the $\nu_{CO}$ bands (2058, 1987 cm$^{-1}$) are at virtually identical energies to the bona fide Fe(1)M(II) species $^{[1]}$ and $^{[2]}$. While the EPR spectrum of $^{[3]}$ indicates some unpaired spin resides on Pt ($A^{(195)Pt} \approx 97$ MHz, $A^{(31P)} \approx 11$ MHz), the g-shifts suggest an Fe(I)Pt(II) description to be appropriate, as mirrored in the spin density calculations (Table 3). The paramagnetic salt [3]BF$_4$ undergoes ligand substitution with PCy$_3$ to afford dicarboxyl [Cy$_3$P(OC)$_3$Fe(dpdt)Pt(dppe)]BF$_4$ ([3]BF$_4$), the characterization for which mirrors that for [2]BF$_4$.

As expected, reaction of low-valent 3 with HBF$_4$ furnished the hydride salt [(OC)$_3$FeH(dpdt)Pt(dppe)]BF$_4$ ([3H]BF$_4$), for which a $^1$H NMR resonance at $\delta = -3.57$ is particularly diagnostic. The small coupling observed for the satellites ($J_{HPP} = 173$ Hz) indicates that the H--Pt interactions are rather weak. For comparison, square-planar platinum hydrides exhibit $J_{HPP}$ from ~650 to 1700 Hz, with $J_{HPP}$ being at the low end of this range for five-coordinate complexes of the type [Pt(PR$_3$)$_2$H]$^{+}$.25 Thus, [3H] is similar to its FePd analog in that the H$^-$ ligand can be considered terminally Fe-bound, as also supported by the $^{31}P$ NMR resonances for 3 being insensitive to protonation at Fe (for [3H]$^-$ $\delta = 46.4$, $J_{HPP} = 3220$ Hz). In contrast, the energies of the $\nu_{CO}$ bands for the FePt conjugate acid and base species are very different—those for [3H]$^+$ (2081, 2022 cm$^{-1}$) are greatly shifted relative to those for (CO)$_3$FeH(pdt)Pt(dppe) (2058, 1987 cm$^{-1}$). Overall, the proposed sequence of 1e$^-$ events: Fe(0)Pt(II) $\Rightarrow$ Fe(I)Pt(II) $\Rightarrow$ Fe(II)Pt(II) for 3, [3]BF$_4$, and [3H]BF$_4$, respectively.

While only a handful of FePt complexes bearing H$^-$ and CO ligands exist, the compounds (CO)$_3$FeH($\mu$-PR$_3$)Pt(PR$_3$)$_2$, are particularly pertinent. These complexes interconvert between isomers with terminal ([H]Fe$^+$Pr$_4$) and bridging (Fe$_5$($\mu$-
(OC)₃Fe(pdt)Pt(dppe) (3)\(^{-}\) −30.42 ND \(^{b}\) ND

\(^{a}\)The potential energy surface was found to be extremely flat along the isomerization pathway. As a result, the single imaginary frequency for the transition state (TS) was <20 cm\(^{-1}\) for the two barriers given in this table. Each TS was verified to lead to the relevant tetrahedral and square-planar geometries by following the intrinsic reaction coordinate (IRC) for 4 or 5 steps in both directions and subsequently optimizing the geometries. As the imaginary frequencies may be below the numerical accuracy of the methodology, and the complete IRC was not obtained, the free energy barriers should be viewed with caution. Moreover, multiple TSs were found for 1, suggesting a ruffled potential energy surface connecting the two isomers, and only the highest free energy barrier is reported. \(^{b}\)The TS was not determined for 3 as the isomerization was found to be significantly exergonic.

\(^{c}\)Estimated according to the Gutowsky–Holm relation using the coalescence temperature of 243 K (detected in SI), but the DFT free energies were calculated at 298 K for consistency with other experiments. Note that the calculated and experimental free energy barriers are not exactly equivalent.

the reaction free energies (\(\Delta G^0\)) and free energy barriers (\(\Delta G^1\)) associated with tetrahedral to square-planar isomerization are presented in Table 4. For the FeNi and FePd congeners, the isomerization is close to thermoneutral (\(\Delta G^0 = -0.67\) and +0.99 kcal/mol, respectively). Given the error associated with the calculations, it is not possible to determine a thermodynamic preference for the coordination geometry at Ni/Pd. The reaction free energies calculated using various other density functionals and basis sets with geometry optimization in CH₂Cl₂ solvent are qualitatively consistent with the results presented here, although certain

**Comparison of CO Frequencies.** Good agreement was found between experimental and calculated shifts in weighted average CO vibrational frequency (\(\Delta \nu\)) induced by protonation and oxidation of bimetallics 1–3 (Scheme 3). Protonation of the FeNi and FePd complexes is predicted to shift \(\nu\) \(\text{CO}\) by \(\sim 50 \, \text{cm}^{-1}\). In contrast, the shift induced by protonation of the FePt analog is much greater, with \(\Delta \nu\) \(\text{CO}\) \(\sim 110 \, \text{cm}^{-1}\). These \(\Delta \nu\) \(\text{CO}\) values correlate with the formal changes in Fe oxidation state: from +I to +II upon protonation of 1 and 2 as well as from 0 to +II upon protonation of 3. Trends in \(\Delta \nu\) \(\text{CO}\) for the couples [1]\(^{0/\pm}\), [2]\(^{0/\pm}\), and [3]\(^{0/\pm}\) are similar to those seen for protonation, the effects again being greater for the Pt case. The \(\Delta \nu\) \(\text{CO}\) values for these oxidations are consistent with their occurring remote from the Fe(\(\text{CO}\))₃ center in [1] and [2] but directly at this center in [3].

**Stereochemical Non-Rigidity.** As discussed above, the fluxionality of 1 and 2, evidenced by the broad singlet in their \(\text{³P}[\text{H}]\) NMR spectra, implicate the presence of a transient or intermediate species featuring square-planar Ni/Pd centers (Scheme 1, top). This conformational motion is likely to perturb both the oxidation states and intermetallic bonding of the Fe and M centers. Two optimized DFT structures characterized as minima were calculated for each bimetallic 1–3: one in which the (pdt)M(dppe) fragment is tetrahedral, and one in which it is square-planar. Selected bond lengths and angles are provided in Table S5. In each case, the Fe center is within bonding distance of M when the latter adopts a tetrahedral geometry, while the Fe–M distance is elongated when M is planar. The Fe–M elongation is subtle in the FeNi case (0.13 Å) but more pronounced for FePd and FePt (0.30 Å). The relative stability of the two isomers was computed, and
levels of theory do not predict a stable square-planar intermediate for geometry optimizations in the gas phase (see Tables S6–S8). The calculated free energy barriers are relatively low, consistent with the fluxionality of 1 and 2 observed in their room temperature NMR spectra. Because the potential energy surfaces for 1 and 2 were found to be extremely flat along the isomerization pathway, the calculated free energy barriers may not be quantitatively accurate and can be analyzed only qualitatively. The calculated free energy barrier of 6.66 kcal/mol for 1 is qualitatively consistent with, although somewhat lower than, the free energy barrier of 9.5 kcal/mol estimated from the coalescence temperature in the NMR measurement. Moreover, the lower calculated free energy barrier of 3.29 kcal/mol for 2 is consistent with the lack of decoalescence observed in the NMR experiments for 2. The observation of a particularly flat potential energy surface along the isomerization pathway has implications for the enzymatic system, where the geometry at the Ni site is between tetrahedral and square-planar.

The similarity in free energies and the relatively low free energy barriers suggest that the two isomers of 1 and 2 may interconvert. In addition, the free energy change associated with oxidation of 1 and 2 is similar for the two different isomers, with the calculated reduction potentials of the square-planar and tetrahedral isomers differing by only ~0.03 V, which is within the estimated error of the methodology. It is thus a distinct possibility that the Ni/Pd centers in 1 and 2 “preorganize” into square-planar geometries prior to 1e− loss. In the case of FePd complex 3, the square-planar isomer is overwhelmingly favored, consistent with the high stability characteristic of square-planar Pt(II) centers. Calculations indicate that ν CO energies for the tetrahedral isomer of 3, which was found to be a local minimum, are within 10 cm−1 of those for 1 and 2. Square-planar isomers of 1 and 2, while not observed experimentally, have calculated ν CO bands 55–65 cm−1 lower in energy than the respective tetrahedral conformers. This ν CO shift is consistent with the change in conformation inducing a change in oxidation state.

Given the dynamics in the neutral species 1 (as well as 2), we set about investigating hydride [1H]+ to yield further insight into the mechanism of protonation. At room temperature, [(CO)3FeH(pdt)Ni(dppe)]+ displays a single 31P NMR peak owing to its C2-symmetry. In view of the difficulty with determining whether or not Ni(dppe) twisting is occurring here, we interrogated an analogous hydride of lower symmetry, which entailed preparation of the new bimetallic (CO)3Fe-(pdt)Ni(S,S-chiraphos) (S,S-chiraphos = 2S,3S-bis(diphenylphosphino)butane, Scheme 4). Analogous to 1, this (S,S-chiraphos)+ (Scheme 4, center) give rise to two broad signals (resolved into two 31P-coupled doublets at ~70 °C). If twisting and equivalencing of the 31P sites were to be facile, it would be necessary for a tetrahedral hydride (Scheme 4, right) to be energetically accessible, which appears not to be the case. In general, it is proposed that twisting of neutral species is associated with “on/off” switching of Fe−M bonding in the FeNi and FePd (but not FePt) complexes. It is now evident that the twisting of hydride species is slower, perhaps reflecting the rigidifying influence of the H···M interactions (despite their weakness).

These observations are supported by computational work: the twisting of hydride [1H]+ was investigated, and two optimized DFT structures characterized as minima were calculated for the isomers of [1H]+. The relative free energies of the structures, which feature either square-planar or tetrahedral (pdt)Ni(dppe) fragments (Figure 7), were also calculated.

![Figure 7. Energy-minimized structures obtained with DFT for [1H]+ with the (pdt)Ni(dppe) moiety either square-planar (red) or distorted tetrahedral (blue). The optimized geometries are superimposed and presented in two views. Other (higher energy) isomers/tautomers proposed can be found in Figure S57.](image)

Twisting of the square-planar (pdt)Ni(dppe) site in [1H]+ to adopt a tetrahedral geometry was calculated to be significantly endergonic (ΔG0 = +11.47 kcal/mol). The tetrahedral conformer is predicted by DFT to be far (~104 ×) more acidic than the square-planar state (the experimental pK0(MeCN) for [1H]+ is 10.7).11 Considering the conjugate bases for the two isomers of [1H]+, these results suggest that 1 has greatly enhanced basicity when in the square-planar form, consistent with its description as Fe(0)Ni(II) (Scheme 1). Thus, it is reasonable that this isomer is responsible for the rich acid−base and redox chemistry exhibited by 1 and related complexes.

### CONCLUSIONS

Numerous studies have examined the protonation and 1e− oxidation of complexes of the type (CO)3Fe(pdt)Ni(diphosphine) and substituted derivatives thereof. This paper presents evidence that the protonations, and possibly the oxidations, proceed via a latent 2e− mixed-valence intermediate (Scheme 5).

Despite previous computational analyses,10,13,15 this key square-planar species had not been identified as an energetically accessible isomer of 1. The first clue for this unsuspected structure was provided by the 31P NMR properties of 1, which implicate a transient or intermediate square-planar species that interconverts the 31P sites. The new and compelling evidence for the intermediate comes from (i) DFT calculations that suggested thermodynamically accessible rotation at the non-Fe

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**Scheme 4**

![Scheme 4](image)
For small molecule [NiFe]-H2ase mimics, it has been underlining the role of latent, but highly reactive intermediates. Analogy to the results in this paper, such rotated diiron distorted nature of the Ni(Cys)4 site is likely an important demonstrated that perturbation of the Ni site greatly alters chiraphos),33 (pdt)Pd(dppe), and (pdt)Pt(dppe)34 were prepared of 1 invariably feature Fe2(SR)2L6 cores wherein terminal coordination sites are unavailable for H+ binding. Protonation of these Fe(I)Fe(I) complexes has been proposed to proceed via a rotated intermediate.

Overall, the work reported here shows that the geometry at the NiFe center and (ii) spectroscopic and electrochemical properties of the H2ases. Prior to protonation, model complexes almost invariably feature Fe2(SR)2L6 cores wherein terminal coordination sites are unavailable for H+ binding. Protonation of these Fe(I)Fe(I) complexes has been proposed to proceed via a "rotated intermediate" (Scheme 6).31 Models for this rotated state have been crystallized, revealing that Fe—Fe bonding is weakened and a terminal site on one Fe center is vacant.12 By analogy to the results in this paper, such rotated diiron complexes should perhaps be described as Fe(II)Fe(0), thus underlining the role of latent, but highly reactive intermediates.

The rotation-induced 2e− mixed-valence behavior also has implications for understanding active site mimics of the [FeFe]-H2ases. Prior to protonation, model complexes almost invariably feature Fe2(SR)2L6 cores wherein terminal coordination sites are unavailable for H+ binding. Protonation of these Fe(I)Fe(I) complexes has been proposed to proceed via a "rotated intermediate" (Scheme 6).31 Models for this rotated state have been crystallized, revealing that Fe—Fe bonding is weakened and a terminal site on one Fe center is vacant.12 By analogy to the results in this paper, such rotated diiron complexes should perhaps be described as Fe(II)Fe(0), thus underlining the role of latent, but highly reactive intermediates.

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2.87 (m, 4H, PCH2CH2P), 2.63 (m, 1H, equatorial CH2CH2CH3), 2.30 (m, 4H, CH2CH2CH3), 1.29 (m, 1H, axial CH2CH2CH3), −4.3 (s, 1H, FeH). 31P[H] NMR (CD2Cl2): δ 62.8. ESI-MS: m/z 750.8 [M − BF4]−. Orange blocks of [2H][BF4]THF-0.5Et2O formed upon slow diffusion of Et2O vapor into a THF solution of the title compound at −28 °C. One crystal (0.377 × 0.232 × 0.088 mm3) was subjected to X-ray diffraction at 178 K. Its space group was determined to be monoclinic P21/n with cell parameters a = 11.466 Å, b = 20.692 Å, c = 34.720 Å, β = 90.00°, γ = 90.00°. Integration of 9956 reflections and solution by direct methods using SHELXTL V6.12 afforded a model with R1 = 0.0369 and wR2 = 0.0754.

([OC]Fe(Pd)Pd(dppe))BF4 ([2B]Fe). A solution of 2 (22.5 mg, 30 μmol) in CH2Cl2 (1 mL) and CD3OD (0.1 mL) was treated with HBF4 (54% Et3O solution, 14.6 mg, 90 μmol) in CD3OD (0.5 mL). The solution was evaporated to dryness, and the oily residue triturated with Et2O (3 mL). The resulting solid was isolated by filtration, washed with Et2O (2 × 1 mL), and dried briefly to afford the title compound as an orange powder (19.6 mg, 23–25% yield). ESI-MS: m/z 719. [M − BF4]−. Anal. calc. for C32H30FeO3P2PtS2: C, 45.78; H, 3.60; N, 0.00. Found: C, 44.10; H, 3.69; N, 0.00. For the title compound as a brown powder (17.0 mg, 20.2% yield), ESI-MS: m/z 716. [M − BF4]−. Anal. calc. for C32H28FeO3P2PtS2: C, 44.99; H, 3.69; N, 0.00. Found: C, 45.03; H, 3.82; N, 0.00.

([Cy3P(OC)2Fe(pdt)Pt(dppe)]BF4 ([2B]Pt). A mixture of solid Fe2(CO)9 (25.3 mg, 60 μmol) and (pdt)Pt(dppe) (42.0 mg, 60 μmol) was cooled to −28 °C and dissolved in CH2Cl2 (2 mL) with stirring. After 1 min, the solution was treated with CoCp2 (22.7 mg, 120 μmol) and dissolved in CH2Cl2 (1 mL) and pentane (2 × 15 mL) was added, and the mixture allowed to stand overnight at −28 °C. The solids were isolated by filtration, washed with pentane (−28 °C, 2 × 2 mL), and dried briefly to afford the title compound as a yellow-brown powder (5.9 mg, 54.0 μmol, 27%). ESI-MS: m/z 1002.4 [M − BF4]−, 974.3 [M − Co − BF4]−. Anal. calc. for C68H50Fe2O3P2Pt2S2BF4: C, 48.09; H, 5.23; N, 0.00. Found: C, 48.06; H, 5.42; N, 0.52.

([Cy3P(OC)2Fe(pdt)Pd(dppe)]BF4 ([2B]Pd). This compound was prepared analogously to [2B]FeBF4 instead using 3 as the precursor. Yield: 28%, yellow powder. ESI-MS: m/z 838.9 [M − BF4]−. Anal. calc. for C68H48FeO3P2PtS2BF4: C, 51.44; H, 6.12; N, 0.00. Found: C, 51.60; H, 6.09; N, 0.00.

([Cy3P(OC)2Fe(pdt)Pd(dppe)]BF4 ([2B]Pd). This compound was prepared analogously to [2B]FeBF4 instead using 3 as the precursor. Yield: 28%, yellow powder. ESI-MS: m/z 1091.7 [M − BF4]−. Anal. calc. for C68H48FeO3P2PtS2BF4: C, 51.44; H, 6.12; N, 0.00. Found: C, 51.60; H, 6.09; N, 0.00.
square-planar isomerization were identified using the synchronous
transit-guided quasi-Newton method,26,47 and the resulting structures
were confirmed to have only a single imaginary frequency. Each TS
was verified to lead to the relevant tetrahedral and square-planar
geometries by following the IRC using the local quadratic
approximation25 for 4 or 5 steps in both directions and subsequently
optimizing the geometries. Because the potential energy surface
was found to be very flat, the single imaginary frequencies were small,
and the complete IRC connecting the two isomers through the TS could
not be obtained.

Thermochemical data were calculated at T = 298.15 K. The reaction
free energies (ΔG°) and free energy barriers (ΔG‡) associated with
the tetrahedral to square-planar isomerization in solution included
zero-point energy, entropic contributions, and solvation effects. The
relative reduction potentials and pK's were calculated from the
corresponding reaction free energies using methodology described
elsewhere.48 Chemical bonding analysis was performed using NBO.23

S Supporting Information
experimental and computational data.

* These authors contributed equally.

Notes
The authors declare no competing financial interest.

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