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Pendant Bases as Proton Relays in Iron Hydride and Dihydrogen Complexes

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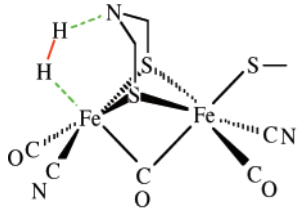
Abstract: The complex *trans*-[HFe(PNP)(dmpm)(CH_3CN)]BPh_4, **3**, (where PNP is $Et_2PCH_2N(CH_3)CH_2PEt_2$ and dmpm is $Me_2PCH_2PMe_2$) can be successively protonated in two steps using increasingly strong acids. Protonation with 1 equiv of *p*-cyanoanilinium tetrafluoroborate in acetone-d_6 at −80 °C results in ligand protonation and the formation of endo (**4a**) and exo (**4b**) isomers of *trans*-[HFe(PNHP)(dmpm)(CH_3CN)]-$(BPh_4)_2$. The endo isomer undergoes rapid intramolecular proton/hydride exchange with an activation barrier of 12 kcal/mol. The exo isomer does not exchange. Studies of the reaction of **3** with a weaker acid (anisidinium tetrafluoroborate) in acetonitrile indicate that a rapid intermolecular proton exchange interconverts isomers **4a** and **4b**, and a pK_a value of 12 was determined for these two isomers. Protonation of **3** with 2 equiv of triflic acid results in the protonation of both the PNP ligand and the metal hydride to form the dihydrogen complex $[(H_2)Fe(PNHP)(dmpm)(CH_3CN)]^{3+}$, **11**. Studies of related complexes [HFe-(PNP)(dmpm)(CO)]$^+$ (**12**) and [HFe(depp)(dmpm)(CH_3CN)]$^+$ (**10**) (where depp is bis(diethylphosphino)-propane) confirm the important roles of the pendant base and the ligand trans to the hydride ligand in the rapid intra- and intermolecular hydride/proton exchange reactions observed for **4**. Features required for an effective proton relay and their potential relevance to the iron-only hydrogenase enzymes are discussed.

Introduction

The recent determination of the structures of iron-only hydrogenases has revealed that the active sites consist of bimetallic iron complexes bridged by a 1,3-dithiolate ligand.[1−8] Based on the scattering of X-rays alone, it is difficult to precisely identify the three atom backbone in the dithiolate ligand of this enzyme. Certain structural and spectroscopic features of the enzyme have been interpreted to suggest that the central atom of the chelate is a secondary amine as shown in structure **1**.[1] In addition, DFT calculations have shown that the nitrogen atom of the azadithiolate ligand is a competent base for assisting the heterolytic cleavage of hydrogen, and its presence provides a low energy pathway for the heterolytic cleavage of hydrogen to form a terminal hydride ligand and protonated nitrogen base.[9]



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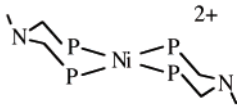

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A number of recent model studies have described dithiolate[10−22] or phosphido[23,24] bridged diiron complexes, and in some cases

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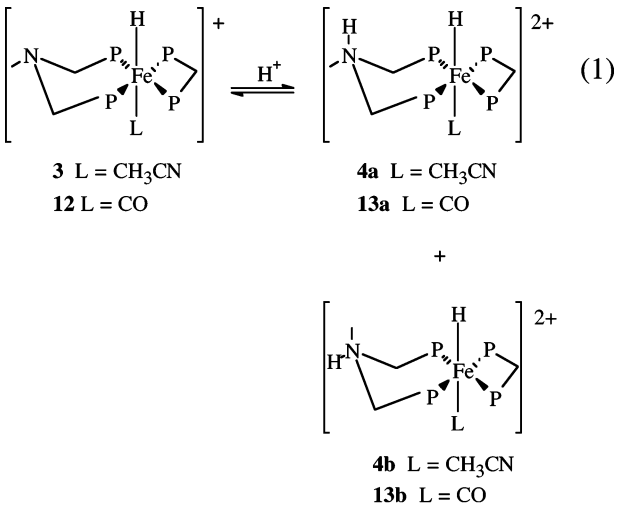
these have included the attachment of a 4Fe4S cluster or the presence of azadithiolate[20,25] or azadiphosphido bridges.[24] Electrochemical studies of [(μ-ADT)$Fe_2(CO)_6$] (where ADT = SCH_2NRCH_2S, R = *p*-bromobenzyl) which contains a diiron core indicate that the presence of a bridging azadithiolate ligand shifts the potential for hydrogen production to more positive potentials by 230 mV compared to the complex [(μ-PDT)$Fe_2(CO)_6$] (where PDT = $SCH_2CH_2CH_2S$) which does not contain a pendant nitrogen atom in the dithiolate bridge.[20] These results suggest that the pendant nitrogen atom of the dithiolate ligand in [(μ-ADT)$Fe_2(CO)_6$] plays a role in the delivery of protons to the catalytically active site. However the effects are not large, and this complex still has a large overpotential of more than a volt for H_2 production. Other experimental[11,26,27] and theoretical[28,29] studies of model compounds indicate that bridging hydride ligands may be involved in the catalytic cycle of hydrogenase enzymes and that there are other possible low energy pathways for the cleavage of hydrogen that do not require a nitrogen in the dithiolate chelate. Finally, the role of interactions between the active site and the surrounding protein is not understood. As a result, there is no clear consensus on the mechanism of operation of the active site of the iron-only hydrogenase enzyme.

Studies of organometallic complexes have shown that pendant bases are important in proton/hydride exchange reactions,[30−37] which suggests an understanding of proton relays will be necessary for developing efficient hydrogen production/hydrogen oxidation catalysts. Our laboratories have previously studied the reactivities of **2** and its corresponding hydride derivative.[38] It was found that the secondary amine in the PNP ligand of **2** acts as a fast proton relay for intermolecular exchange between D_2O and the metal hydride. The exchange was proposed to proceed through a nickel(IV) dihydride or a nickel(II) dihydrogen intermediate, but neither of these species could be detected. These results prompted us to study the role of a pendant base in proton/hydride exchange in iron diphosphine complexes that are known to readily form dihydrogen and hydride complexes.[39−43] In this work we demonstrate experimentally that a pendant nitrogen base in a six-membered chelate ring can promote very rapid intra- and intermolecular proton/hydride exchange in octahedral Fe(II) PNP complexes and function as a proton relay for oxidized Fe(III) hydrides as well. Our experimental results are consistent with models proposed previously for iron-only hydrogenase enzymes based on theoretical studies[9] and structural inference.[1]

Results and Discussion

Previous work has shown that octahedral iron(II) complexes containing two chelating PNP ligands and two monodentate ligands adopt a cis geometry, while those containing one PNP and one dmpm chelate favor trans structures.[44] The complex *trans*-[HFe(PNP)(dmpm)(CH_3CN)](BF_4)$_2$, **3**, was selected for studying the role of the PNP ligand in hydride/proton exchange reactions. Compound **3** is easily prepared in pure form, and its crystal structure has been previously determined.[44] This structure indicates that the PNP ligand adopts a chair conformation in the solid state. This same conformation is likely the most stable in solution, but the boat conformation should also be easily accessible. Previous work demonstrated that protonation of **3** in acetonitrile with even relatively weak acids such as anisidinium tetrafluoroborate, which has a pK_a in acetonitrile of 11.3, leads to the evolution of hydrogen and the formation of the dication [Fe(PNP)(dmpm)$(CH_3CN)_2]^{2+}$. However NMR experiments conducted at low temperatures have made it possible to slow this hydrogen evolution reaction and observe the protonated intermediates. Quantitative data have been obtained on the rate of intramolecular proton/hydride exchange in this system. Selected reactions of *trans*-[HFe(PNP)(dmpm)(CO)]$^+$, **12**, and *trans*-[HFe(depp)(dmpm)(CH_3CN)]$^+$, **10**, are also described for comparison.

Intramolecular Proton/Hydride Exchange. Reaction of **3** with 1 equiv of *p*-cyanoanilinium tetrafluoroborate (pK_a = 7.6 in acetonitrile)[45] in acetone-d_6 at −80 °C results in the formation of endo and exo isomers, **4a** and **4b**, as shown in eq 1. The



(1)

3 L = CH_3CN **4a** L = CH_3CN

12 L = CO **13a** L = CO

+

4b L = CH_3CN

13b L = CO

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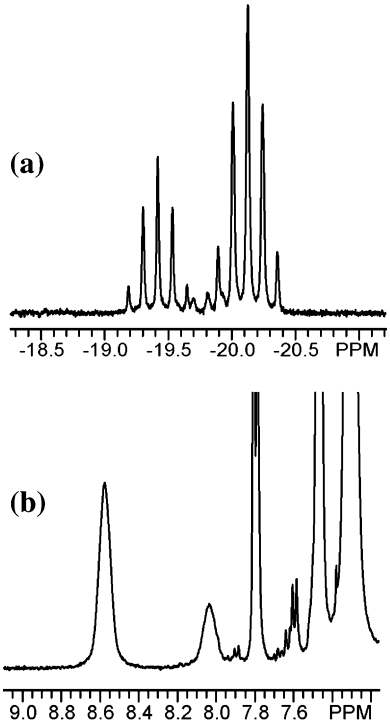
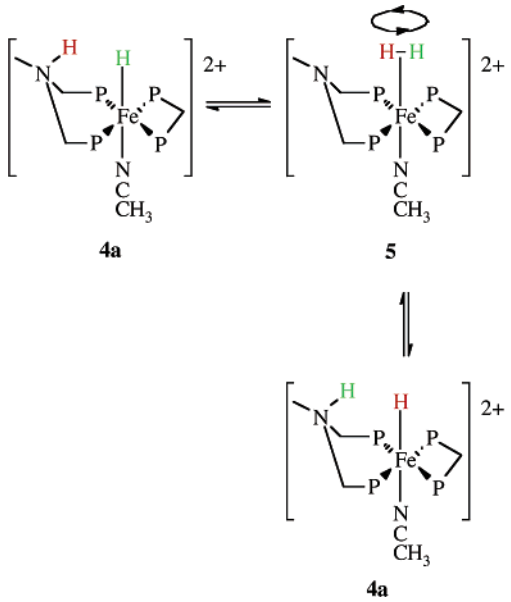


Figure 1. (a) 400 MHz ^{1}H NMR spectrum of the hydride region of **4a** and **4b** recorded in acetone-d_6 at −80 °C; the pentet centered at −20.06 ppm is assigned to **4a**, and the pentet centered at −19.42 ppm is assigned to **4b**. (b) 400 MHz ^{1}H NMR spectrum of the NH region in acetone-d_6 at −80 °C; the singlet at 8.56 ppm is assigned to **4a**, and the resonance at 8.03 ppm is assigned to **4b**.

hydride region of the ^{1}H NMR spectrum at −80 °C consists of two pentets at −20.06 ppm ($^2J_{PH}$ = 47.0 Hz) and −19.42 ppm ($^2J_{PH}$ = 46.2 Hz) assigned to **4a** and **4b**, respectively (Figure 1, trace a). Corresponding to these two hydride resonances are two singlets assigned to the NH protons of **4a** and **4b** at 8.56 and 8.03 ppm, respectively (Figure 1, trace b). The ^{31}P NMR spectrum at −80 °C also indicates the presence of two isomers (see Experimental Section and Figure S1). Upon warming the solution, the hydride resonance assigned to the endo isomer broadens and disappears, while the hydride resonance assigned to the exo isomer remains unchanged even at room temperature. When the reaction with acid is repeated at room temperature in acetonitrile, a single hydride pentet is observed at −19.66 ppm ($^2J_{PH}$ = 46.2 Hz). This resonance is assigned to the exo isomer, **4b**. A hydride resonance for the endo isomer is not observed due to rapid exchange of the hydride ligand and the proton on the PNHP ligand. The ^{31}P NMR spectrum exhibits resonances assigned to both the endo and exo isomers (see Experimental Section) indicating that these two isomers are not interconverting rapidly on the NMR time scale at room temperature. These data confirm that **4a** undergoes rapid intramolecular hydride/proton exchange while **4b** does not.

The exchange mechanism is proposed to involve a proton transfer from the PNHP$^+$ ligand to the hydride ligand to form a dihydrogen complex, **5**, followed by rotation of the dihydrogen ligand and heterolytic cleavage as shown in eq 2. Hydride/proton



exchange is not observed for the exo isomer **4b** because the proton of the PNHP$^+$ ligand cannot approach the hydride ligand in the boat conformation. As a result a reaction analogous to eq 2 cannot occur. Loss of hydrogen from the protonated complexes is observed at room temperature over the course of 0.5 h with formation of [Fe(PNP)(dmpm)(CH$_3$CN)$_2$]$^{2+}$ which has been previously characterized. This reaction also presumably proceeds through intermediate **5**.

To obtain kinetic data on the proton/hydride exchange of **4a**, GOESY NMR experiments were performed on a mixture of **4a** and **4b** in acetone-d_6 at −60 °C. Inversion of the pentet at −20.06 ppm resulted in the appearance of an inverted peak at 8.28 ppm. The ratio of the intensity of the inverted NH resonance to the intensity of the inverted hydride resonance can be plotted as a function of the mixing time and analyzed to yield a rate constant of 7.3 s^{-1} at −60 °C (see Figure S2) and a free energy of activation of 12 kcal/mol for the exchange of the hydride and NH proton of **4a**.[46] This corresponds to an exchange rate at room temperature of approximately 1×10^4 s^{-1}. This is consistent with rapid exchange broadening the hydride and NH resonances of **4a** in the NMR spectrum at room temperature.

In contrast, a GOESY NMR experiment in acetone-d_6 at −60 °C, in which the hydride resonance at −19.42 ppm assigned to the exo isomer **4b** was inverted, did not result in the appearance of any inverted peaks. No exchange is observed between the metal hydride and the proton on the nitrogen of **4b**, consistent with the hydride resonance for this isomer being observed as a pentet at room temperature.

Several examples of intramolecular interactions between a metal hydride and a ligand proton in synthetic complexes have been reported previously,[30−37] and example complexes are shown by structures **6**−**9**. For complexes **6**−**8**, intramolecular

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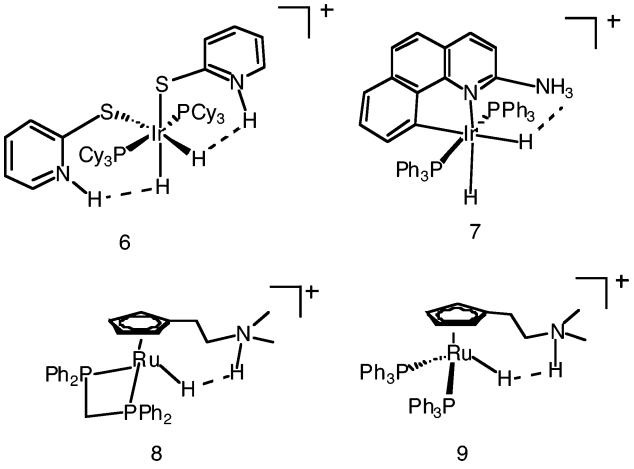

6 7 8 9

proton/hydride exchange is observed, but it is relatively slow as indicated by the observation of distinct resonances for both the hydride ligand and NH protons.[30,31,33,35] In all of these cases, it has been proposed that the intramolecular proton/hydride exchange proceeds through a dihydrogen complex similar to that proposed for **4a**. Only complex **9** exhibits a fast intramolecular proton/hydride exchange[36] comparable to that observed for **4a**. In this case it has been proposed that the proton/hydride exchange proceeds through a trans dihydride intermediate and not through a dihydrogen complex.[35] Our results for **4a** demonstrate that a dihydrogen intermediate can also participate in rapid (10^4 s^{-1}) intramolecular hydride/proton exchange. A similar high rate of hydride/proton exchange (on the order of 10^4 s^{-1}) has been observed previously for the nickel complex $[HNi(PNHP)(PNP)]^{2+}$,[38] but the nature of the intermediate has not been established. At least part of the reason for the relatively slow intramolecular exchange rates observed for several of these complexes is the mismatch in pK_a values of the protonated ligand and the pK_a of the incipient dihydrogen or dihydride complex that results from proton transfer. In this regard, the failure of complex **7** to undergo rapid proton/hydride exchange is surprising. The ability to form either the protonated nitrogen complex or the corresponding dihydrogen complex by varying the nature of the phosphine ligand suggests the pK_a values of the ammonium group of **7** and the dihydrogen complex resulting from proton transfer are very similar. In this case, the failure to observe rapid proton/hydride exchange may be due to the restricted motion of the nitrogen atom of the pendant amine caused by its attachment to an extended aromatic chelating ring system and not to a mismatch in pK_a values. This suggests two requirements for an effective proton relay: (1) matched pK_a values of the incipient dihydrogen or dihydride complex and the protonated pendant base, and (2) a flexible attachment of the base that permits close approach to the metal center without requiring significant rearrangement of the inner coordination sphere of the complex.

Intermolecular Proton Exchange. Interconversion of **4a** and **4b** involves deprotonation of the N atom of the $PNHP^+$ ligand to form **3**, inversion at nitrogen, and reprotonation, an intermolecular proton exchange process. When a relatively strong acid (cyanoanilinium, pK_a = 7.6 in acetonitrile) is used, the protonation of the nitrogen atom of **3** is quantitative, and the interconversion of the endo and exo isomers is slow even at room temperature in acetonitrile-d_3. For weaker acids with pK_a values close to that of **4a** and **4b** (see below), rapid interconversion of the endo and exo isomers is observed. For example, upon dissolving a mixture of anisidinium tetrafluoroborate (pK_a = 11.3 in acetonitrile)[47] and **3** in acetonitrile-d_3, two broad resonances are observed in the ^{31}P NMR spectrum for the PNP (55.18 ppm) and dmpm (1.33 ppm) ligands at room temperature and at −40 °C. These results are consistent with the rapid protonation of **3** to form isomers **4a** and **4b** as shown in reaction 1 and the reverse reaction so that an equilibrium distribution is reached. In this case the observed chemical shifts for the PNP and dmpm ligand are a weighted average of the chemical shifts for **3**, **4a**, and **4b**. No hydride resonance is observed in the ^{1}H NMR spectrum at room temperature. This is attributed to rapid intramolecular exchange between the hydride ligand and the PNHP ligand of **4a** (reaction 2) *and* the rapid intermolecular exchange of the protons of the PNHP ligands of **4a** and **4b** with anisidinium (reaction 1). At −40 °C, a broad pentet is observed at −20.07 ppm in the ^{1}H NMR spectrum. This indicates that the hydride ligand is not exchanging sufficiently fast with the protons of anisidinium or the PNHP ligand at this temperature to collapse the PH coupling (46.0 Hz). Hence the intermolecular exchange process between the PNHP ligand of **4a** and **4b** and anisidinium (reaction 1) is faster than the intramolecular exchange of the hydride and the proton on the PNHP ligand of **4a** (reaction 2) at −40 °C in acetonitrile.

When D_2O is added to $[HFe(CH_3CN)(PNP)(dmpm)]^+$, complete disappearance of the hydride resonance at −19.86 ppm occurs in less than 5 min (the time required to record the spectrum) in CD_3CN. The observed exchange of deuterium with the hydride ligand of **3** presumably involves the protonation of the pendant base in an intermolecular process followed by rapid intramolecular H/D exchange. To probe the role of the PNP ligand in the D_2O/hydride exchange of **3**, we prepared the complex $[HFe(CH_3CN)(depp)(dmpm)](BPh_4)$, **10**, in which the NMe group of the PNP ligand has been replaced with a methylene group of the depp ligand (depp = 1,3-bis(diethylphosphino)propane). This complex has been fully characterized and exhibits spectral characteristics very similar to those of **3** as expected (see Experimental Section). Addition of D_2O to $[HFe(CH_3CN)(depp)(dmpm)]^+$ results in only 60% incorporation of deuterium after 2.2 h. The much slower rate of exchange of the depp complex supports the importance of the N atom in the backbone of the PNP ligand for the rapid intermolecular exchange of protons from the bulk solution into the hydride position.

Observation of a Dihydrogen Complex by Protonation of 3 with Strong Acids. Protonation of **3** with fluoroboric acid in acetone-d_6 at −80 °C results in the formation of a mixture of **4a** and **4b** as well as a new product $[(H_2)Fe(CH_3CN)(PNHP)(dmpm)]^{3+}$, **11**, which is protonated both on the PNP ligand and at the hydride ligand to form a dihydrogen complex, reaction 3. The presence of the dihydrogen ligand is indicated by the disappearance of the hydride resonance of **3** at −19.85 ppm (a triplet of triplet of doublets) and the appearance of a broad resonance at −17.24 ppm assigned to a dihydrogen ligand. The observation of an AA′XX′ pattern in the ^{31}P NMR spectrum indicates that a trans geometry is preserved in the product, with the dihydrogen ligand trans to acetonitrile. As shown in reaction 3, both endo and exo isomers are possible for complex **11**, but

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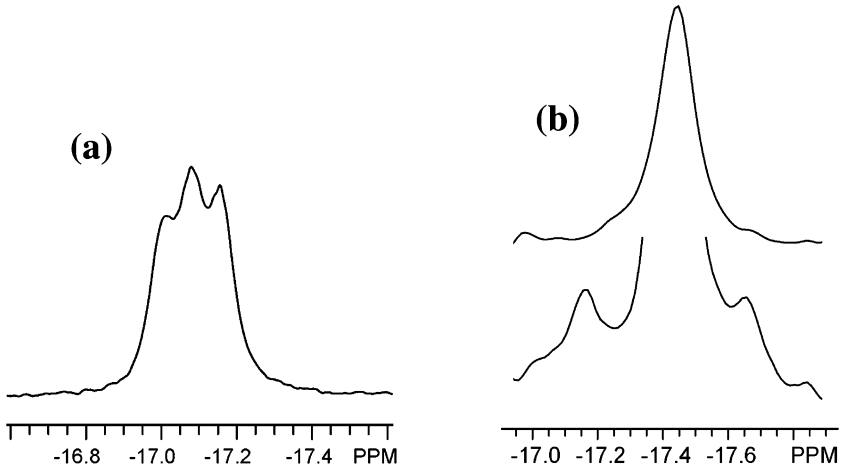
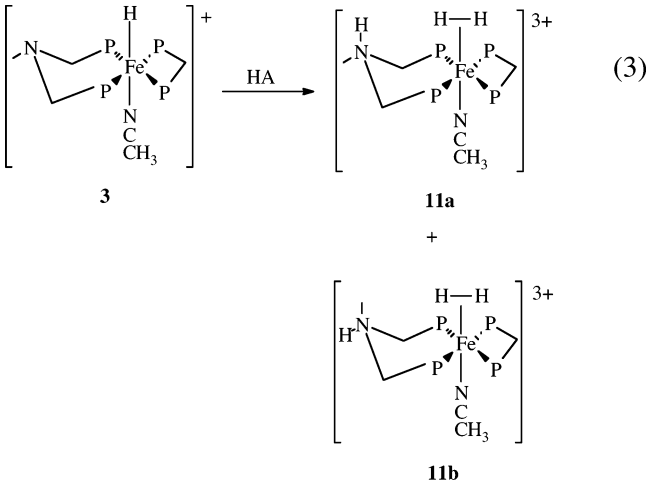


Figure 2. (a) Hydride region of 400 MHz ^{1}H NMR spectrum of **11(HD)** in acetone-d_6 at −80 °C. (b) 400 MHz ^{2}H NMR spectrum of **11(HD)** proton-coupled (bottom) and proton-decoupled (top) in acetone-d_6 at −80 °C.

only one isomer is observed in the NMR spectra. We tentatively assign this species as the endo isomer on the basis of changes in chemical shifts similar to those of **4a**.



(3)

When **3** is protonated with triflic acid in acetone-d_6 at −80°C, only **11(HD)** is formed. The isotope composition arises from H/D exchange of triflic acid with acetone-d_6. In this case, a 1:1:1 triplet is observed in the ^{1}H NMR spectrum at −17.08 ppm with $^1J_{HD} = 30.4$ Hz (trace a of Figure 2). In the ^{2}H NMR spectrum, a doublet ($^1J_{HD} = 30.4$ Hz) and a singlet are observed at −17.40 and −17.43 ppm, respectively (trace b of Figure 2). The doublet is assigned to an HD ligand and the singlet to a D_2 ligand. When the ^{2}H NMR spectrum is ^{1}H-decoupled, the doublet collapses to a singlet as expected. Using relationships between $^1J_{HD}$ and H−H bond distances suggested by Morris[48] and Heinekey,[49] an H−H bond distance of 0.92 Å can be calculated for **11**. This distance is in good agreement with previously reported iron dihydrogen complexes.[39−43]

Thermodynamic Considerations. As described above, **3** can be successively protonated in two steps using increasingly strong acids. The first protonation occurs on the nitrogen atom of the PNP ligand to form a nearly 50:50 mixture of endo and exo isomers, **4a** and **4b**. The average pK_a of the protonated ligand in these two isomers in acetonitrile can be determined experimentally. Reaction 1 is reversible when anisidinium tetrafluoroborate is used as the acid in acetonitrile. Loss of H_2 also occurs after protonation, but this reaction is much slower than the rate at which equilibrium 1 is established. The observed ^{31}P NMR chemical shifts of the PNP ligand as a function of added anisidinium tetrafluoroborate were used to determine an equilibrium constant of 6.2 ± 0.2 for reaction 1 with B = anisidine. From this equilibrium constant, a pK_a value of 12.1 ± 0.2 was calculated for the N-protonated ligand in the mixture of **4a** and **4b** (see Experimental Section for details). This compares to pK_a values of 9.4 for *trans*-[Fe(PNHP)(dmpm)$(CH_3CN)_2]^{3+}$ and 10.5 for *trans*-$[HFe(PNHP)(dmpm)(CO)]^{2+}$.[44] Both charge and the electron-withdrawing ability of the trans ligands exert an influence on the acidity of the PNHP ligand.

The second protonation occurs on the hydride ligand of **4** to form the dihydrogen complex **11**. The pK_a of the dihydrogen ligand in **11** can be bracketed between those of triflic acid (2.6 in acetonitrile)[50] and *p*-cyanoanilinium (7.5 in acetonitrile). The pK_a value for **11** is apparently similar to that of HBF_4 in acetone, because, as noted above, addition of tetrafluoroboric acid to a solution of **3** in acetone-d_6 at −80 °C results in the formation of a mixture of **4a**, **4b**, and **11** based on ^{1}H and ^{31}P NMR spectra (see Experimental Section).

Reactions of [HFe(CO)(PNP)(dmpm)][BF_4], 12. Studies of the analogous carbonyl hydride complex, **12**, have shown that the nature of the ligand trans to the hydride in these Fe(II) complexes has a significant effect on the chemistry of the hydride ligand. Protonation of **12** in acetone-d_6 with excess triflic acid results only in the protonation of the nitrogen atom of the PNP ligand to form primarily the endo isomer, **13a** (see reaction 1). In contrast to the protonation of **3**, formation of a doubly protonated dihydrogen complex is not observed in the NMR spectrum at −80 °C. However dihydrogen is evolved from the protonated complex at rt upon addition of excess triflic acid.

In addition, fast intra- and intermolecular exchange processes which are proposed to involve a dihydrogen intermediate are not observed for the carbonyl complex. Protonation of [HFe(PNP)(dmpm)(CO)][BF_4], **12**, with tetrafluoroboric acid in acetonitrile results in the formation of the endo (**13a**) and exo (**13b**) isomers of $[HFe(PNHP)(dmpm)(CO)]^{2+}$ analogous

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to **4a** and **4b**. However, hydride resonances for both **13a** and **13b** are observed at room temperature, indicating that rapid intramolecular proton/hydride exchange is not occurring for either isomer. Replacement of acetonitrile with CO trans to the hydride ligand turns off the rapid intramolecular exchange observed for **4a**. Although the BF_4^- anion is known to affect proton-transfer rates in some systems through ion-pairing effects,[51] the exchange between the proton of the PNHP ligand and the hydride ligand is slow for **13** when HBF_4 is used and fast for **4a** when [*p*-cyanoanilinium]BF_4 is used. This indicates that the anion is not playing a significant role in this proton/hydride exchange.

The nature of the trans ligand in these octahedral iron complexes can also have a major influence on the rate of intermolecular H/D exchange. While Fe−H/D_2O exchange is very fast for the PNP complex containing an acetonitrile ligand trans to the hydride, the rate of deuterium exchange into the hydride position is orders of magnitude slower when the trans ligand is CO. When excess D_2O is added to [HFe(CO)(PNP)-(dmpm)]$^+$ in CD_3CN or acetone-d_6, no change is observed in the hydride resonance at −7.18 ppm after 24 h.

These differences are attributed to the fact that a dihydrogen ligand trans to a CO ligand is known to be much more acidic than one trans to acetonitrile.[52−55] As a result the energy barrier for the formation of a dihydrogen intermediate by proton transfer from the $PNHP^+$ ligand is expected to be large in this system, and formation of the doubly protonated dihydrogen complex analogous to **11** is not observed.

Electrochemical Studies. Cyclic voltammograms of [HFe-(PNP)(dmpm)(CH_3CN)](BPh_4), **3**, and [HFe(depp)(dmpm)(CH_3-CN)](BPh_4), **10**, were obtained at 200 mV/s in acetonitrile solutions (Figure 3). For **10** the one-electron oxidation at −0.33 V (ΔE_p = 69 mV) is reversible, while the Fe^{II}/Fe^{III} oxidation wave obtained for **3** under identical conditions is irreversible (E_p = −0.31 with $E_p - E_{p/2}$ = 61 mV). For complex **3** there is also an additional irreversible oxidation wave at −0.03 V. The cyclic voltammograms of both compounds have been studied as a function of scan rate. The wave assigned to the Fe^{II}/Fe^{III} couple of **10** remains reversible over scan rates of 0.2 to 2 V/s, and a linear plot of peak current versus the square root of the scan rate for **10** indicates that the electron-transfer process is diffusion controlled. Scan rates below 0.2 V/s are quasi-reversible with i_c/i_a less than 0.90, corresponding to a slow proton migration to solution from the Fe^{III} hydride.

For complex **3**, no return cathodic wave is observed after the Fe^{II}/Fe^{III} oxidation couple is recorded for scan rates up to 75 V/s. At 100 V/s a small cathodic wave that corresponds to the Fe^{III}/Fe^{II} couple is observed (Figure S3). At these higher scan rates the second oxidation wave at −0.03 V nearly disappears (Figure S4). These results are consistent with an EC mechanism in which the one-electron oxidation of **3** is followed by a fast chemical reaction. For a reversible electron-transfer reaction followed by a fast irreversible chemical reaction, a 30 mV shift in the peak potential is expected for each 10-fold increase in scan rate.[56] For scan rates between 0.05 V/s and 5 V/s, a 65 mV shift toward a more positive potential is observed for the first oxidation wave of **3** corresponding to a 32 mV shift in E_p for each 10-fold increase in scan rate. The EC mechanism proposed for **3** involves a reversible oxidation to form an Fe^{III} hydride (**14**) followed by rapid proton transfer from the iron to the PNP ligand to form an Fe^{I} species (**15**), as shown in reaction 4. A cathodic wave is not observed for **14** until the scan rate

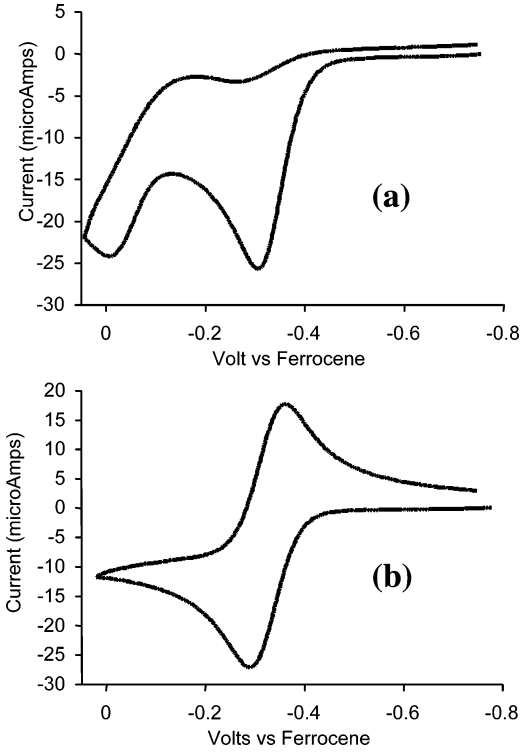
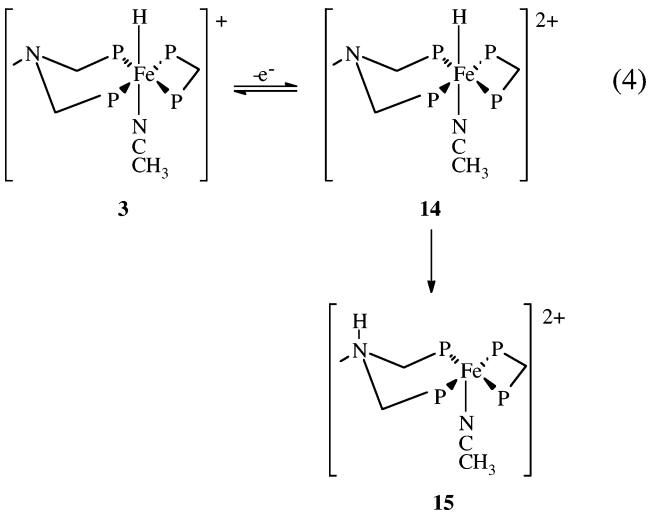


Figure 3. (a) Cyclic voltammogram of a 3.0 mM solution of [HFe(PNP)-(dmpm)(CH_3CN)](BPh_4), **3**, in a 0.3 M solution of Bu_4NBF_4/CH_3CN (E_p = −0.31 V). The scan rate is 0.2 V/s. (b) Cyclic voltammogram of a 3.0 mM solution of [HFe(depp)(dmpm)(CH_3CN)](BPh_4), **10**, in a 0.3 M solution of Bu_4NBF_4/CH_3CN ($E_{1/2}$ = −0.33 V). The scan rate is 0.2 V/s.



(4)

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reaches 100V/s and the time between the oxidation and reduction events is 8 ms. This result is consistent with a half-life of approximately 10 ms for this hydride species or a proton-transfer rate from intermediate **14** of approximately 100 s^{-1}. The second oxidation wave observed at lower scan rates is assigned to the Fe^{I} species **15** that results from proton transfer from Fe to N. This species forms rapidly following oxidation, and as a result it is observed at slower scan rates. To obtain more quantitative data, double potential step chronoamperometric experiments[57] were performed on complex **3**. In this experiment the potential was stepped from an initial potential of −0.56 V to a potential of +0.15 V for a variable amount of time and then back to the initial potential. From working curves and the ratio of the anodic and cathodic currents (see Figure S5), a rate constant of $(1.1 \pm 0.2) \times 10^2$ s^{-1} was obtained for the proton-transfer reaction in the conversion of **14** to **15** shown in reaction 4. It is clear from the different results for **3** and **10** that proton migration following oxidation of the iron center is assisted by the PNP ligand.

Summary and Relevance to Fe-Only Hydrogenases. The results described in this work establish that a nitrogen base in the backbone of a six-membered chelate ring is capable of serving as a very efficient proton relay in iron hydride and dihydrogen complexes. The intramolecular proton/hydride exchange process for **4a** is proposed to involve the heterolytic cleavage of a dihydrogen ligand on iron in the same manner as has been proposed for the distal iron atom of iron-only hydrogenase. The pendant base in **3** also facilitates (a) intermolecular exchange of the N−H proton of the $PNHP^{+}$ ligand with protons in solution at rates faster than the intramolecular exchange process, and (b) the transfer of the proton from iron to solution upon oxidation of Fe^{II} to Fe^{III}. These reactions provide a potential model for the movement of protons from the active site of the enzyme to the proton conduction channel. Important requirements for an effective proton relay in these synthetic systems have been found to include the matching of the pK_a values of the incipient dihydrogen complex with the protonated pendant base and a flexible ligand which allows close approach of the protonated base to the hydride ligand without significant reorganization of the inner coordination sphere of iron. Similar features are likely to be important in the enzyme active site. In the system studied here, the elimination of H_2 from intermediate **5** was found to be too slow to permit the development of a rapid electrocatalytic cycle for proton reduction. Nevertheless, determining the features responsible for the efficient movement of protons from a metal center to the bulk solution will be important in designing synthetic catalysts for a range of reactions that involve the transfer of both protons and electrons to or from the substrate during reduction/oxidation processes.

Experimental Section

General Methods and Materials. All reactions were performed using standard Schlenk techniques under argon or handled in a glovebox under nitrogen, and all solvents were degassed with argon. Solvents were dried by conventional distillation methods.[44] Complex **3**[44] and bis(diethylphosphino)propane (depp)[58] were synthesized as reported previously. ^{1}H NMR, ^{31}P NMR, GOESY (Gradient Selected Overhauser Effect Spectroscopy), and variable-temperature NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. ^{1}H chemical shifts (ppm) are reported relative to residual solvent protons, and ^{31}P chemical shifts (ppm) are referenced to external phosphoric acid. VT NMR experiments were allowed to equilibrate for 5 min at each temperature before spectra were recorded. In the GOESY experiments, the exchange rate constants were determined by performing selective one-dimensional dynamic exchange experiments using the selective DPFGSE (Double Pulsed Field Gradient Spin−Echo) pulse sequence.[59] SigmaPlot 2002 for Windows version 8.02 was used to curve-fit the data for the dynamic exchange experiments.

Electrochemical measurements were carried out at room temperature in a 0.30 M Bu_4NBF_4/acetonitrile solution with 3.0 mM concentration of iron complex under a nitrogen flow. Cyclic voltammetry and chronoamperometric data were collected using a Cypress Systems model CS-1200 computer-aided potentiostat with a three electrode system. The working electrode was a glassy carbon disk with a 2 mm diameter, and the counterelectrode was a glassy carbon rod with a 3 mm diameter. The reference electrode was a silver/silver chloride wire in a 0.30 M Bu_4NBF_4/acetonitrile solution with a Vycor tip. All potentials are referenced to the ferrocene/ferrocenium couple which was used as an internal standard.

Synthesis of [HFe(CH$_3$CN)(depp)(dmpm)](BPh$_4$), 10. A mixture of depp[58] (0.244 g, 1.11 mmol) and dmpm (0.150 g, 1.10 mmol) in THF (5 mL) was added to a suspension of $FeCl_2$ (0.140 g, 1.11 mmol) in 25 mL of THF, and the resulting green solution was stirred for 3 h. This solution was filtered onto a suspension of bis(triphenylphosphine)-iminium borohydride (0.917 g, 1.66 mmol) in THF (25 mL) and an orange solution with a white precipitate formed after stirring for 1.5 h. The reaction mixture was filtered, and the solvent was removed forming a red-orange tar. $NaBPh_4$ (3.78 g, 11.05 mmol) and acetonitrile (150 mL) were added to the flask, and the resulting yellow solution was stirred for 2 h. A yellow solid (0.533 g, 60%) precipitated on addition of water. This solid was collected by filtration and washed with ether. Yellow crystals were grown from acetonitrile/ether solutions at −15 °C (0.154 g, 17%). Anal. Calcd for $C_{42}H_{64}BFeNP_4$: C, 65.22; H, 8.34; N, 1.81. Found: C, 65.35; H, 8.60; N, 1.76. ^{31}P NMR (CD_3CN): AA′XX′ spin pattern; $\delta_A = 2.35$ (dmpm), $\delta_X = 42.60$ (depp). ^{1}H NMR (CD_3CN): −19.48 (ttd, $^{2}J_{PH} = 45$ Hz, $^{2}J_{PH} = 40$ Hz, $^{4}J_{HH} = 3.6$ Hz, 1.0 H, *H*Fe); 1.05 (br m, 12.0 H, PCH_2CH_3); 1.45 (t), 1.53 (t) ($^{2}J_{PH} = 4.4$ Hz, 13.0 H total, PCH_3); 1.41 (m), 1.62 (m), 1.69 (m) (11.8 H total, PCH_2CH_3 and PCH_2CH_2); 2.09 (br m, 1.3 H, $PCH_2CH_2CH_2P$); 2.95 (m), 3.12 (m) (1 H each, PCH_2P); 2.24 (s, 2.6 H, $NCCH_3$); 6.84 (m), 6.99 (m), 7.27 (m) (17.8 H total, $B(C_6H_5)_4$). MS, ESI (CH_3CN; *m*/*z*): 731 $\{[Fe(depp)(dmpm)](BPh_4)\}^{+}$, 413 $\{[HFe(depp)(dmpm)]\}^{+}$. IR (KBr, cm^{-1}); $\nu_{FeH} = 1829$; $\nu_{CN} = 2237$. A cyclic voltammogram recorded in 0.30 M Bu_4NBF_4/CH_3CN solution at 200 mV/s consisted of one irreversible oxidation wave at 0.56 V (E_p, $E_p - E_{p/2} = 76$ mV), one reversible oxidation wave at −0.33 V ($E_{1/2}$, $\Delta E_p = 69$ mV, $i_a/i_c = 0.91$), and one irreversible reduction wave at −2.54 V (E_p, $E_p - E_{p/2} = 56$ mV). For comparison, the cyclic voltammogram of [HFe(CH_3-CN)(PNP)(dmpm)]BPh_4 recorded under the same conditions consisted of three irreversible oxidation waves at 0.53 V (E_p, $E_p - E_{p/2} = 66$ mV), −0.03 V, and −0.31 V (E_p, $E_p - E_{p/2} = 61$ mV) and an irreversible reduction at −2.26 V(E_p, $E_p - E_{p/2} = 96$ mV).

Selective ^{31}P-Decoupled ^{1}H NMR Spectra of [HFe(CH$_3$CN)-(depp)(dmpm)](BPh$_4$), 10. Selective ^{31}P decoupled (depp) ^{1}H NMR (CD_3CN): −19.48 (t, $^{2}J_{PH} = 45$ Hz, *H*Fe), 1.03 and 1.08 (two t, $^{3}J_{HH} = 7.6$ Hz, PCH_2CH_3), 1.45 and 1.53 (two t, $^{2}J_{PH} = 3.8$ Hz, PCH_3), 1.41, 1.62 and 1.69 (three m PCH_2CH_3 and PCH_2CH_2), 2.09 (br m, 1.3 H, $PCH_2CH_2CH_2P$), 2.95 and 3.12 (two m, PCH_2P), 2.24 (s, $NCCH_3$).

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Selective ^{31}P decoupled (dmpm) ^1H NMR (CD_3CN): −19.48 (t, $^2J_{PH}$ = 40 Hz, *H*Fe), 1.05 (broad m, PCH_2CH_3), 1.45 and 1.53 (two s, PCH_3), 1.41, 1.62 and 1.69 (three broad m, PCH_2CH_3 and PCH_2CH_2), 2.09 (br m, 1.3 H, $PCH_2CH_2CH_2P$), 2.95 (d, $^2J_{HH}$ = 14.5 Hz) and 3.12 (dq, $^2J_{HH}$ = 14.5 Hz $^4J_{HH}$ = 3.6 Hz, PCH_2P), 2.24 (s, $NCCH_3$).

Observation of [Fe(D$_2$)(CH$_3$CN)(PNDP)(dmpm)]$^{3+}$, 11(D$_2$), and [Fe(DH)(CH$_3$CN)(PNDP)(dmpm)]$^{3+}$, 11(HD). [HFe(CH_3CN)(PNP)(dmpm)](BPh_4) (0.015 g, 0.019 mmol) was dissolved in acetone-d_6, purged with H_2, and cooled to −80 °C. Triflic acid (5.1 μL, 0.057 mmol) was syringed into the NMR tube, and the sample was kept at −80 °C until VT NMR experiments were performed (0.5 h). ^{31}P NMR (acetone-d_6, −80 °C): −6.00 (m, *dmpm*); 41.60 (m, *PNP*). ^1H NMR (acetone-d_6, −80 °C): −17.08 (1:1:1 t, $^1J_{HD}$ = 30.4 Hz, [Fe(*H*D)(CH_3-CN)(PNHP)(dmpm)]$^{2+}$). ^2H NMR (acetone, −80 °C): −17.43 (s, [Fe(D_2)(CH_3CN)(PNHP)(dmpm)]$^{2+}$), −17.40 (d, $^1J_{HD}$ = 30.4 Hz, [Fe(H*D*)(CH_3CN)(PNHP)(dmpm)]$^{2+}$). This doublet collapsed to a singlet when the spectrum was proton decoupled. The same results were observed when triflic acid-*d* was used. Using this $^1J_{HD}$ value and d_{HH} = 1.42−0.0167(J_{HD}), a value of 0.91 Å was calculated for the HH bond distance.[48] Using d_{HH} = 1.44−0.0168(J_{HD}), a value of 0.93 Å was calculated for the HH bond distance.[49]

Observation of [HFe(CH$_3$CN)(PNHP)(dmpm)]$^{2+}$, 4a and 4b. [HFe(CH_3CN)(PNP)(dmpm)](BPh_4) (15 mg, 0.019 mmol) and *p*-cyanoanilinium tetrafluoroborate (3.90 mg, 0.019 mmol) were accurately weighed into an NMR tube. A ^{31}P NMR spectrum was taken immediately after this sample was dissolved in acetonitrile-d_3 (0.7 mL) at 23 ± 2 °C. ^{31}P NMR (acetonitrile-d_3, 20 °C): 54.87 (*PNHP*, endo, 37%), 59.00 (*PNHP*, exo, 31%), 0.67 (*dmpm*, endo), and 1.66 (*dmpm*, exo). See text for the structures of the endo (**4a**) and exo isomers (**4b**). The weighted average for the two PNHP chemical shifts is 56.00 ppm. Additional resonances were observed and assigned to [Fe(PNHP)(dmpm)($CH_3CN)_2$]$^{2+}$: −5.03 (m, dmpm), 29.35 (m, *PNHP*, 32%). ^1H NMR (acetonitrile-d_3, 20 °C, ppm): −19.79 (br pentet, $^2J_{PH}$ = 46.8 Hz).

This experiment was repeated at −80 °C in acetone-d_6. ^1H NMR: −20.06 (*H*Fe, $^2J_{PH}$ = 47.0 Hz, endo, **4a**); −19.42 (*H*Fe, $^2J_{PH}$ = 46.4 Hz, exo, **4b**); 8.56 (br s, PN*H*P, endo); 8.03 (br s, PN*H*P, exo). ^{31}P NMR (acetone-d_6, −80 °C): 53.03 (m, *PNHP*, endo, 66%), 58.56 (m, *PNHP*, exo, 25%), 2.50 (m, *dmpm*, endo), 3.86 (m, *dmpm*, exo); resonances at −3.78 and 31.31 for [Fe(PNHP)(dmpm)($CH_3CN)_2$]$^{2+}$ (9%) are also observed. The second acetonitrile in the last product arises from an acetonitrile present in the crystal lattice.

Reaction of [HFe(CH$_3$CN)(PNP)(dmpm)](BPh$_4$), 3, with HBF$_4$. [HFe(CH_3CN)(PNP)(dmpm)](BPh_4) (15 mg, 0.019 mmol) was accurately weighed into an NMR tube and dissolved in acetone-d_6 (0.7 mL). The sample was cooled to −80 °C, and HBF_4 (48% aqueous solution) (7.45 μL, 0.057 mmol) was syringed into the NMR tube. Spectra were recorded immediately. The distribution of products based on integration of the ^{31}P NMR spectra is endo-[HFe(PNHP)(dmpm)(CH_3CN)]$^{2+}$, **4a** (71%), exo-[HFe(PNHP)(dmpm)(CH_3CN)]$^{2+}$, **4b** (21%), and [Fe(H_2)(PNHP)(dmpm)(CH_3CN)]$^{3+}$, **11** (8%). ^1H NMR, −80 °C (hydride region): −17.24 (br s, **11**); −20.19 (pentet, **4a**) and −19.4 (pentet, **4b**). ^{31}P NMR, −80 °C: −6.13 (dmpm), 41.05 (PNHP), **11**; 2.38 (dmpm), 52.46 (PNHP) **4a**; 3.64 (dmpm), 57.99 (PNHP) **4b**.

Protonation of [HFe(CO)(PNP)(dmpm)]$^+$, 12, with Triflic Acid. The synthesis of [HFe(CO)(PNP)(dmpm)]$^+$ consistently results in a mixture of [HFe(CO)(PNP)(dmpm)]$^+$/[Fe(Cl)(CO)(PNP)(dmpm)]$^+$.[44] In a typical experiment, this mixture (15 mg, 0.024 mmol) in acetone-d_6 is treated with triflic acid (6.5 μL, 0.072 mmol) at −80 °C. ^1H NMR (acetone-d_6, −80 °C): −7.68 (pentet, $^2J_{PH}$ = 48.1 Hz, endo-*H*Fe, 94%); −7.07 (pentet, $^2J_{PH}$ = 46.4 Hz, exo-*H*Fe, 6%). ^{31}P NMR (acetone-d_6, −80 °C): three complexes: 1.24 and 51.08 (endo isomer [HFe(CO)(PNHP)(dmpm)]$^{2+}$, **13a**, 61%); 3.02 and 55.03 (exo isomer [HFe(CO)(PNHP)(dmpm)]$^{2+}$, **13b**, 3%); and −7.55 and 37.57 [Fe(Cl)(CO)(PNHP)(dmpm)]$^{2+}$ (36%). The last complex has been independently synthesized and characterized previously.[44]

Protonation of [HFe(PNP)(dmpm)(CH$_3$CN)](BPh$_4$), 3, with Anisidinium Tetrafluoroborate. In a typical experiment [HFe(CH_3CN)(PNP)(dmpm)](BPh_4) (15 mg, 0.019 mmol) and anisidinium tetrafluoroborate (0.010 g, 0.047 mmol) were placed in an NMR tube and dissolved in CD_3CN (0.7 mL) at room temperature. ^{31}P NMR, rt: 1.33 and 55.18 ([HFe(PNHP)(dmpm)(CH_3CN)]$^{2+}$, 70%) and −4.84 and 29.25 ([Fe(PNP)(dmpm)($CH_3CN)_2$]$^{2+}$, 30%). These shifts remained constant for 4.0 h. No hydride resonance is observed due to exchange of the proton on the PNHP$^+$ ligand with the hydride and with the conjugate base in solution. At −40 °C, the hydride is seen in the ^1H NMR as a broad pentet centered at −20.07 ($^2J_{PH}$ = 46.0 Hz). The ^{31}P NMR at −40 °C is similar to the room-temperature spectrum. The ^{31}P chemical shift of 55.18 ppm observed in the protonation experiment is the weighted average of a rapidly exchanging mixture of [HFe(PNHP)(dmpm)(CH_3CN)]$^{2+}$ (**4a** and **4b**) and [HFe(PNP)(dmpm)(CH_3CN)]$^+$ (**3**). From this chemical shift value and the weighted average of 56.00 ppm for the fully protonated PNHP ligand of [HFe(PNHP)(dmpm)(CH_3-CN)]$^{2+}$ (see **Observation of [HFe(CH$_3$CN)(PNHP)(dmpm)]$^{2+}$, 4a and 4b**) and 44.86 ppm for the unprotonated PNP ligand of [HFe(CH_3-CN)(PNP)(dmpm)]$^+$, an equilibrium constant (K_{eq} = {[HFe(CH_3CN)(PNHP)(dmpm)]$^{2+}$}{anisidine}/{[HFe(CH_3CN)(PNP)(dmpm)]$^+$}{anisidinium}) can be calculated for the reaction of [HFe(CH_3CN)(PNP)(dmpm)]$^+$ with anisidinium to form [HFe(CH_3CN)(PNHP)(dmpm)]$^{2+}$ and anisidine. Five similar experiments were carried out in which varying ratios of anisidine/anisidinium were added to **3**, and the data were used to calculate a value of K_{eq} of 6.2 ± 0.2. Addition of log K_{eq} to the pK_a of anisidinium (11.3) gives a pK_a value of 12.1 ± 0.2 for [HFe(CH_3CN)(PNHP)(dmpm)]$^+$ in acetonitrile.

Kinetics of Intramolecular Hydride/Proton Exchange for [HFe(CH$_3$CN)(PNHP)(dmpm)]$^{2+}$. [HFe(CH_3CN)(PNP)(dmpm)](BPh_4) (0.015 g, 0.019 mmol) and *p*-cyanoanilinium tetrafluoroborate (0.0039 g, 0.019 mmol) were accurately weighed into an NMR tube and dissolved in acetone-d_6 (0.7 mL) at 0 °C. GOESY NMR (acetone-d_6; −60 °C): The pentet at −20.10 was selectively inverted (endo-[*H*Fe(CH_3CN)(PNHP)(dmpm)]$^{2+}$), and an inverted exchange peak was observed at 8.28 (endo-[HFe(CH_3CN)(PN*H*P)(dmpm)]$^{2+}$) (mixing times (s), {normalized integration of exchange peak}), 0.050 {0.15}, 0.075 {0.24}, 0.100 {0.30}, 0.150 {0.42}, 0.200 {0.48}, 0.250 {0.57}, 0.300 {0.64}, 0.400 {0.75}. The plot of [integration (exchange peak)/integration (selected peak)] versus mixing time (s) gives a rate of 7.3 s^{-1} for the exchange of the hydride with the proton of the endo isomer of the protontated PNHP ligand. Using the relationship $\Delta G^{\ddagger} = aT[10.319 + \log(T/k)]$, where a = 4.575 × 10^{-2} ($\Delta G^{\ddagger}$ in kcal mol^{-1}), T is temperature in Kelvin, and k is the rate of exchange in s^{-1}, a free energy of activation for exchange of protons was calculated to be 12.0 ± 0.2 kcal mol^{-1}.[45] No exchange occurred, for mixing times of 0.10 s to 0.50 s, between the hydride and the protonated PNHP ligand of the exo isomer when the pentet at −19.42 ppm was selectively inverted.

HD Exchange of Fe−H with D$_2$O. [HFe(CH_3CN)(PNP)(dmpm)](BPh_4) (15 mg, 0.019 mmol) was placed into an NMR tube and dissolved in 0.7 mL of CD_3CN at 23 ± 2 °C. D_2O (20 μL, 1.1 mmol) was added to this sample. The disappearance of the hydride resonance at −19.86 ppm was followed by ^1H NMR by comparing the hydride integral with that of the resonance of the PCH_2CH_3 group on the PNP ligand. Complete deuterium incorporation occurred in less than 5 min.

Similar procedures were used to establish the rate of deuterium incorporation for [HFe(CH_3CN)(depp)(dmpm)](BPh_4) and [HFe(CO)(PNP)(dmpm)]PF_6. In the latter case, no deuterium incorporation occurred at the hydride site over a period of 24 h. For [HFe(CH_3CN)(depp)(dmpm)](BPh_4), integration of the hydride resonance at −19.48 ppm indicated 60% deuterium incorporation after 2.2 h under conditions identical to those described for [HFe(CH_3CN)(PNP)(dmpm)](BPh_4).

Double Potential Step Chromoamperometry Studies of 3. An acetonitrile solution of [HFe(CH_3CN)(PNP)(dmpm)]$^+$ (3.0 mM in 0.3 M NEt_4BF_4) was used for these studies. The potential of the glassy carbon electrode was stepped from an initial resting potential of −0.56

V to a potential of +0.15 V and then back to the initial potential. The time of potential reversal, τ, was varied from 10 to 1500 ms; however the best kinetic data were obtained for τ at 10 ms and 20 ms. Using the working curves for the double potential step chronoamperometry for an EC mechanism,[57] a rate constant of $(1.1 \pm 0.2) \times 10^2$ s^{-1} was calculated (average of two 10 ms and two 20 ms reversal times).

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Supporting Information Available: ^{31}P NMR spectrum of endo and exo isomers of $[HFe(CH_3CN)(PNHP)(dmpm)]BPh_4$, **4a** and **4b**; plot of GOESY data for **4a**; cyclic voltammograms of $[HFe(CH_3CN)(PNP)(dmpm)]BPh_4$, **3**; double potential step chronoamperometry of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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