Organometallics **2007,** *26,* 5003−5009

Syntheses and Structural Characterizations of Iron(II) Complexes Containing Cyclic Diphosphine Ligands with Positioned Pendant Nitrogen Bases

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Received June 19, 2007

A series of new iron(II) complexes that contain cyclic diphosphine ligands with pendant amine bases, $P_2^RN_2^{R'}$, have been synthesized and characterized (where $P_2^RN_2^{R'}$ are substituted 1,5-diaza-3,7-diphosphacyclooctanes). These compounds include $[Fe(P_2^{Ph}N_2^{Ph})(CH_3CN)_4](BF_4)_2$ (**5**), *cis*-$[Fe(P_2^{Ph}N_2^{Ph})_2(CH_3CN)_2](BF_4)_2$ (**6a**), *cis*-$[Fe(P_2^{Ph}N_2^{Bz})_2(CH_3CN)_2](BF_4)_2$ (**6b**), *cis*-$[Fe(P_2^{Cy}N_2^{Bz})_2(CH_3CN)_2](BF_4)_2$ (**6c**), *trans*-$[HFe(P_2^{Ph}N_2^{Ph})_2(CH_3CN)](BF_4)$ (**7**), and *cis*-$Fe(P_2^{Ph}N_2^{Ph})_2(Cl)_2$ (**8**). The molecular structures of **5**, **6b**, and **7** have been confirmed by X-ray diffraction studies. For all complexes the cyclic diphosphine ligands contain one six-membered ring in a chair conformation and one six-membered ring in a boat conformation. For complex **7**, the two rings that are in boat conformations result in N−H distances between the pendant amine nitrogens and the hydride ligand of 2.6 to 2.7 Å. Protonation of the pendant bases in complex **7** has been found to form several products. A structural assignment for a dominant protonated isomer has been assigned on the basis of ^1H, ^{31}P, and ^{15}N NMR spectroscopic techniques.

Introduction

The study of the role of the second coordination sphere in the reactivity of synthetic metal complexes has been inspired by the structures of several metalloproteins[1−3] and has led to the design of new ligands that result in the precise positioning of an acidic or basic site near the metal ion. Such ligands have been shown to stabilize unusual co-ligands by intramolecular hydrogen bonding, promote unusual reactivity, and lead to catalytic applications.[4−7] In the cases of metal hydrides with positioned acids in the second coordination sphere, proton−hydride bonding interactions, intra- and intermolecular exchange processes, concerted hydride−proton transfers to substrates, and catalytic transformations have been studied.[8−21] In our laboratories, the chemistry of first-row metal complexes containing diphosphine ligands that incorporate a pendant base has proven to be a rich area of study, and factors that contribute to the role of the base as a proton relay and participant in hydrogen activation have been established.[17]

In our previous studies of iron complexes that contain the PNP ligand, where PNP = bis(diethylphosphinomethyl)-

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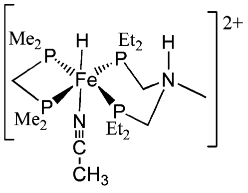
10.1021/om700601h CCC: $37.00

methylamine, we have shown that octahedral iron(II) complexes containing two chelating PNP ligands and two monodentate ligands adopt a cis geometry, while those containing one PNP ligand and one chelate with a smaller bite angle, such as bis(dimethylphosphino)methane, dmpm, favor trans structures.[17b] The endo isomer of the N-protonated hydride complex, *trans*-$[HFe(PNHP)(dmpm)(CH_3CN)]^{2+}$, **1**, was found to undergo intramolecular proton/hydride exchange with a rate of approximately 2×10^4 s^{-1} at room temperature.[17d]



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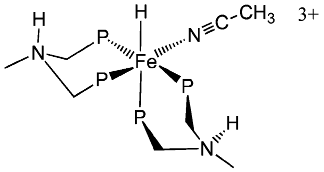

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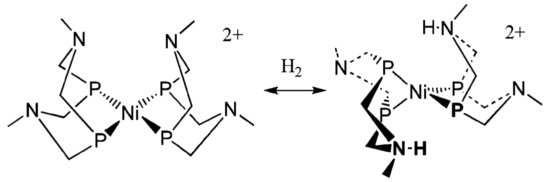

3 **4**

NMR studies of this complex also established that intermolecular proton exchange of the N−H proton with a weak external acid proceeds at rates even faster than the intramolecular exchange process. In contrast intramolecular proton/hydride exchange in *cis*-$[HFe(PNHP)_2(CH_3CN)]^{3+}$, **2**, was found to be slow on the NMR time with a rate of <1 s^{-1} at -25 °C.[17g] The slow intramolecular exchange is attributed to unfavorable steric interactions between the cis PNP ligands, as one of the chelate rings rearranges from the favored chair conformation to the boat form required for NH−FeH interactions.

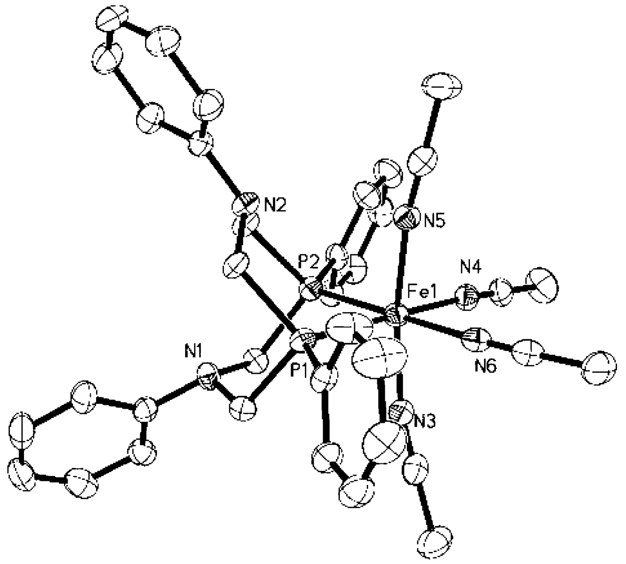

Figure 1. Perspective drawing of $[Fe(P^{Ph}_2N^{Ph}_2)(CH_3CN)_4]^{2+}$, **5**, indicating the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

We have shown previously that the related cyclic diphosphine ligand $P_2{}^RN_2{}^{R'}$ coordinates to a metal ion (Ni(II)) to form two six-membered chelate rings, and at least one of these is forced into the boat conformation. This conformation places the pendant amine base in close proximity to the metal ion, as shown in structure **3**.[17c] In the case of the four- and five-coordinate nickel derivatives, the conformations of the cyclic ligands allowed the pendant amine to participate with the metal ion in the formation or cleavage of a H−H bond as shown in the conversion of **3** to **4**, and effective electrocatalysts for hydrogen oxidation and production were characterized.[17c,e] In order to determine how the enforced boat conformation of the cyclic ligand influences the chemistry of the iron derivatives, we have synthesized a series of new octahedral Fe(II) complexes containing one or two of the $P_2{}^RN_2{}^{R'}$ ligands. Complexes of the formulas $[Fe(P_2{}^RN_2{}^{R'})CH_3CN)_4]^{2+}$, *cis*-$[Fe(P_2{}^RN_2{}^{R'})_2(CH_3CN)_2]^{2+}$, and *trans*-$[HFe(P_2{}^RN_2{}^{R'})_2(CH_3CN)]^{+}$ have been synthesized. The structures of these new complexes are of interest, and examples of both the cis and trans derivatives have been characterized by X-ray diffraction studies. Proton relay properties of the cyclic ligands in the iron complexes have been investigated.

Results and Discussion

Syntheses and Characterizations of Iron Complexes with P_2N_2 Ligands. The reaction of either 1 or 2 equiv of $P_2{}^{Ph}N_2{}^{Ph}$ with $[Fe(CH_3CN)_6](BF_4)_2$ in acetonitrile results in the formation of a new complex that shows a singlet in the ^{31}P NMR spectrum at 50.2 ppm. The ^1H NMR spectrum of the isolated product in CD_3CN shows resonances for the P_2N_2 ligand and a singlet at 1.96 ppm consistent with the presence of free protio-acetonitrile. Integration of the proton resonances suggests that the product undergoes rapid exchange of four acetonitriles relative to only one cyclic ligand, consistent with the formulation $[Fe(P_2{}^{Ph}N_2{}^{Ph})(CH_3CN)_4](BF_4)_2$, **5**. Elemental analyses are also consistent with this formula, and the electrospray ionization mass spectrum shows a peak for the fluorinated parent cation minus all four acetonitriles, $\{Fe(P_2{}^{Ph}N_2{}^{Ph})F\}^+$. Single crystals of **5** were grown from a CH_2Cl_2/Et_2O solution, and an X-ray diffraction study was carried out to confirm this formulation.

A perspective drawing of the iron dication is shown in Figure 1, and selected bond distances and angles are given in Table 1.

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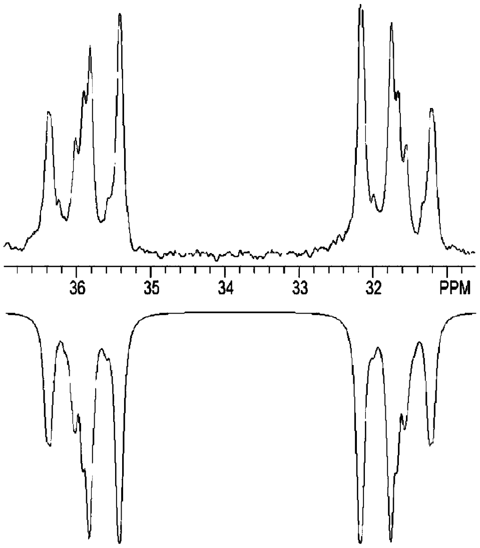


Figure 2. Experimental (top) and simulated (bottom) ^{31}P NMR spectra for **6a** recorded at 400 MHz.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for $[Fe(P_2^{Ph}N_2^{Ph})(CH_3CN)_4](BF_4)_2$, 5

	Bond Distances		
Fe(1)−P(1)	2.197(1)	Fe(1)−N(4)	1.969(4)
Fe(1)−P(2)	2.196(1)	Fe(1)−N(5)	1.923(4)
Fe(1)−N(3)	1.930(4)	Fe(1)−N(6)	1.986(4)
	Bond Angles		
P(1)−Fe(1)−P(2)	80.39(5)	N(3)−Fe(1)−N(5)	170.59(16)
N(3)−Fe(1)−N(4)	86.89(16)	P(1)−Fe(1)−N(4)	172.64(12)
N(4)−Fe(1)−N(5)	89.46(16)	P(2)−Fe(1)−N(6)	177.67(12)
N(5)−Fe(1)−N(6)	85.88(16)	P(2)−Fe(1)−N(4)	93.41(12)
P(1)−Fe(1)−N(6)	97.48(12)	P(2)−Fe(1)−N(5)	93.35(12)
P(1)−Fe(1)−N(3)	89.73(12)	P(1)−Fe(1)−N(5)	94.84(12)

The structure confirms the presence of a distorted octahedral iron(II) complex with a single diphosphine ligand.

The Fe−P distances are equivalent at 2.20 Å, and the P−Fe−P angle is 80.39 (5)°. Small bite angles have been found to be characteristic of these cyclic diphosphine ligands. The P−Fe−P angle for this iron complex is even smaller than the P−Ni−P angles (81.53(7)° and 82.63(7)°) observed in the five-coordinate nickel complex with the same ligand, $[Ni(P_2^{Ph}N_2^{Ph})_2(CH_3CN)](BF_4)_2$.[17c] The Fe−N distances for the acetonitrile ligands trans to the phosphines are slightly longer than those for the two acetonitriles trans to each other, as indicated in Table 1. The N−Fe−N angle between the two trans acetonitrile ligands is 170.59(16)°, with these two nitriles slightly bent away from the diphosphine. In fact the N−Fe−P angles for almost all of the nitriles adjacent to the phosphine donors are >90° and in the range 93−97°. One of the chelate rings of the diphosphine ligand is positioned in a boat conformation with the Fe(1)−N(2) distance equal to 3.53 Å.

Characterization of *cis*-$[Fe(P_2^{R}N_2^{R'})_2(CH_3CN)_2](BF_4)_2$ Derivatives. When the reaction of $[Fe(CH_3CN)_6](BF_4)_2$ with 2 equiv of $P_2^{Ph}N_2^{Ph}$ is carried out in acetone rather than acetonitrile, the product with two cyclic diphosphine ligands, *cis*-$[Fe(P_2^{Ph}N_2^{Ph})_2(CH_3CN)_2](BF_4)_2$, **6a**, is isolated exclusively. The ^{31}P NMR spectrum of this product at room temperature shows an AA′BB′ pattern with two multiplets at 31.7 and 35.8 ppm, consistent with a cis geometry. Observed and simulated spectra are shown in Figure 2. Other spectroscopic data and elemental analyses are given in the Experimental Section. In CD_3CN the coordinated acetonitrile ligands in **6a** underwent exchange with the solvent, and the rate for this process was determined by monitoring the disappearance of the singlet at 2.38 ppm assigned to the coordinated ligands. A half-life of 16 min was determined for this exchange process. No evidence for dissociation of a diphosphine ligand in acetonitrile to form **5** was observed. In contrast, **5** displays limited stability in acetone solution, and when **5** is dissolved in this solvent, formation of the bis(diphosphine) complex, **6a**, is observed by NMR spectroscopy.

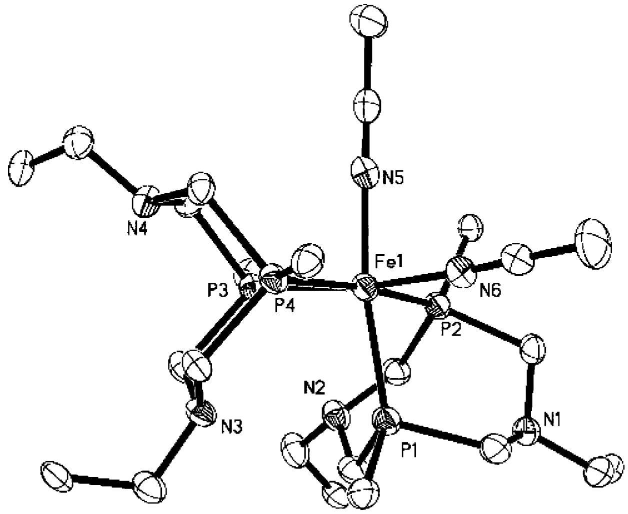


Figure 3. Perspective drawing of $[Fe(P^{Ph}{}_2N^{Bz}{}_2)_2(CH_3CN)_2]^{2+}$, **6b**$^+$, indicating the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Only ipso carbons of phenyl substituents are shown for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[Fe(P_2^{Ph}N_2^{Bz})_2(CH_3CN)_2](BF_4)_2$, 6b

	Bond Distances		
Fe(1)−P(1)	2.261(1)	Fe(1)−P(4)	2.265(1)
Fe(1)−P(2)	2.264(1)	Fe(1)−N(5)	1.951(3)
Fe(1)−P(3)	2.259(1)	Fe(1)−N(5)	1.951(3)
	Bond Angles		
P(1)−Fe(1)−P(2)	79.54(3)	N(5)−Fe(1)−N(6)	85.88(10)
P(3)−Fe(1)−P(4)	79.15(3)	P(1)−Fe(1)−P(3)	99.38(3)
P(1)−Fe(1)−N(5)	170.81(8)	P(2)−Fe(1)−P(4)	173.05(4)
P(2)−Fe(1)−N(5)	94.18(8)	P(2)−Fe(1)−P(3)	95.79(3)
P(4)−Fe(1)−N(5)	90.41(8)	P(3)−Fe(1)−N(5)	87.86(8)
P(1)−Fe(1)−N(6)	87.68(8)	P(2)−Fe(1)−N(6)	92.41(8)
P(3)−Fe(1)−N(6)	170.02(8)	P(4)−Fe(1)−N(6)	93.12(8)

Reactions of $[Fe(CH_3CN)_6](BF_4)_2$ with other cyclic diphosphine ligands under similar conditions resulted in the formation of analogous products *cis*-$[Fe(P_2^{Ph}N_2^{Bz})_2(CH_3CN)_2](BF_4)_2$, **6b**, and *cis*-$[Fe(P_2^{Cy}N_2^{Bz})_2(CH_3CN)_2](BPh_4)_2$, **6c**, which have been isolated and characterized. Each of the complexes shows two multiplets in the ^{31}P NMR spectrum, as expected for AA′BB′ spin systems, and these spectra have been simulated (see Figure S4). The mass spectral data provide evidence for the [parent cation]BF_4 and an ion with *m*/*z* corresponding to P − 2 CH_3CN.

Single crystals of *cis*-$[Fe(P_2^{Ph}N_2^{Bz})_2(CH_3CN)_2](BF_4)_2$, **6b**, have been isolated from an acetone/ether solution, and an X-ray diffraction study has been carried out. A drawing of the dication is shown in Figure 3, and selected bond distances and angles are given in Table 2. The structure confirms that the complex is the cis isomer in a distorted octahedral geometry. The Fe−P distances of 2.26 Å are equivalent within experimental error and are significantly longer than those observed in **5**. The P−Fe−P angles of the ligand chelates are smaller than those observed previously for complexes of the $P_2^{Ph}N_2^{Ph}$ ligand, with values of 79.54° and 79.15(3)°. The N(5)−Fe−N(6) angle between the cis nitrile ligands is compressed to 85.88°, presumably as a result of the steric demands of the cyclic ligands. In **6b** each diphosphine ligand contains one chelate ring in a chair conformation and the second in a boat. Although the iron−nitrogen distance is quite short, e.g., Fe(1)−N(2) = 3.43 Å, the amine base in each boat conformation points toward a phosphine in the other ligand and is therefore not positioned to allow involvement in a cooperative interaction at a vacant metal site generated by a labile ligand.

Synthesis of *trans*-[HFe($P_2^{Ph}N_2^{Ph}$)$_2$(CH_3CN)]BF_4, 7. The reaction of **6a** with excess bis(triphenyphosphino)iminium borohydride, $PPNBH_4$, in acetonitrile solution resulted in the formation of an iron hydride derivative, **7**. Similar reactions of **6b** and **6c** with borohydride reagents produced mixtures of products that were not successfully separated or further characterized. An alternate route to related hydride derivatives was investigated briefly by using anhydrous $FeCl_2$ as the starting reagent. The reaction of $FeCl_2$ with 2 equiv of $P_2^{Ph}N_2^{Ph}$ in methylene chloride resulted in the formation of a purple product that was isolated and identified as *cis*-Fe($P^{Ph}{}_2N^{Ph}{}_2$)$_2$$Cl_2$, **8**. Characterization data for **8** are included in the Experimental Section. However reaction of **8** with hydride reagents, such as $PPNBH_4$ or $NaBH_4$, did not lead to the formation of clean products, and this route was not investigated further.

The hydride product derived from **6a** showed limited stability in solution, and attempts at recrystallization often resulted in the decomposition of the product and observation of resonances for the free P_2N_2 ligand in the NMR spectra. Nevertheless the product was consistently isolated in low yields in reasonably pure form, although a small amount of PPN[BF_4] was a common contaminant. Spectroscopic data for the product at room temperature are consistent with the formulation *trans*-[HFe($P_2^{Ph}N_2^{Ph}$)$_2$(CH_3CN)]BF_4, **7**. In the ^{1}H NMR spectrum a hydride resonance is observed as a pentet (J_{P-H} = 45 Hz) at −20.0 ppm at room temperature, and the ^{31}P NMR spectrum shows a slightly broadened singlet at 50.8 ppm. Variable-temperature NMR studies reveal that at −50 °C in acetone solution the resonance in the ^{31}P NMR spectrum splits into two multiplets of an AA′BB′ pattern (57.9 and 45.9 ppm), and the hydride resonance in the ^{1}H NMR spectrum now appears as an overlapping triplet of triplets. The coalescence temperature occurs at 5 °C. These data are consistent with a fluxional process in which two pairs of nonequivalent phosphorus atoms are frozen out at the lower temperatures.

In acetonitrile-d_3, the ^{1}H NMR resonance at 3.44 ppm, assigned to coordinated acetonitrile, disappeared with a half-life of 67 min. The half-life is longer that that observed for the cis P_2N_2 derivative discussed above, but the rate is significantly faster than rates reported for other trans derivatives of iron(II), such as *trans*-[HFe(PNP)(dmpm)(CH_3CN)]$^+$, for which $t_{1/2}$ = 7 h.[17b] In **7**, the large distortion from octahedral geometry imposed by steric repulsions between trans P_2N_2 ligands, discussed below, is likely to result in loss of ligand field stabilization energy associated with the low-spin octahedral structure and permit relatively rapid acetonitrile exchange.

Single crystals of **7** were successfully isolated by diffusing diethyl ether into a dichloromethane solution at −80 °C. The single-crystal X-ray structure of the complex cation is shown in Figure 3, and selected bond distances and angles are given in Table 3. The structure confirms that the complex is a distorted octahedron with trans hydride and acetonitrile ligands; the H−Fe−N(5) angle is 178.4(6)°. The chelate rings in each of the cyclic ligands display one boat and one chair conformation. One of the N atoms, N(2), is nearly planar. The average distance between the boat N and Fe is 3.445 Å, similar to the Ni−N distances observed in the nickel complex with this ligand. The Fe−H distance is 1.430(5) Å, while the Fe−N(5) distance is 1.947 Å. The latter bond is shorter than the Fe−N distances observed for nitrile ligands trans to phosphine donors in the structures of **5** and **6b** discussed above. The N−H distances between the two N atoms in the boat conformations and the hydride ligand are 2.60 and 2.68 Å, slightly less than the sum of the van der Waals radii (2.75 Å). The coordination of each diphosphine ligand in **7** is unsymmetrical. For example, Fe−P(1) is 2.145(2) Å, while the second bond (Fe−P(2)) in the chelate is significantly longer, 2.213 (2) Å. The chelate bite angles of the diphosphine ligands are small, P(1)−Fe−P(2) = 81.64(7)° and P(3)−Fe−P(4) = 81.23°. These angles are similar to those observed for the same cyclic diphosphine ligand coordinated to nickel.[17c]

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for [HFe($P_2^{Ph}N_2^{Ph}$)$_2$(CH_3CN)](BF_4), 7

Bond Distances

Fe(1)−P(1)	2.146(2)	Fe(1)−P(4)	2.158(2)
Fe(1)−P(2)	2.214(2)	Fe(1)−H(1)	1.430(5)
Fe(1)−P(3)	2.194(2)	Fe(1)−N(5)	1.947(5)

Bond Angles

P(1)−Fe(1)−P(2)	81.70(7)	H(1)−Fe(1)−N(5)	178.4(6)
P(3)−Fe(1)−P(4)	81.22(7)	P(1)−Fe(1)−P(3)	100.26(7)
P(1)−Fe(1)−N(5)	106.22(18)	P(2)−Fe(1)−P(4)	100.58(7)
P(2)−Fe(1)−N(5)	86.69(15)	P(3)−Fe(1)−N(5)	86.64(15)
P(4)−Fe(1)−N(5)	106.08(19)	P(4)−Fe(1)−P(1)	147.69(7)
P(3)−Fe(1)−P(2)	173.33(7)		

The complex shows a very significant distortion from octahedral geometry in the nonplanarity of the four phosphorus atoms. For example, while one angle between trans phosphines, P(3)−Fe−P(2), is 173.33(7)°, the other trans angle P(4)−Fe−P(1) is significantly smaller, with a value of 147.69(7)°, and the dihedral angle formed by the two planes defined by the P atoms of the diphosphine ligands and iron is 34.4°. These angles are consistent with a twisting motion between the two diphosphine ligands to avoid steric interactions between the substituents on phosphorus. This distortion of the octahedral geometry about iron may be responsible for the low stability of this iron hydride complex. A similar distortion and dihedral angle of 34.9° were observed for the [Ni($P_2^{Cy}N_2^{Bz}$)$_2$]$^{2+}$ cation.[17c] The fluxional behavior indicated by the variable-temperature NMR studies described above likely involves a twisting motion in which the dihedral angle between the P−Fe−P planes varies.

Protonation Studies of *trans*-[HFe($P_2^{Ph}N_2^{Ph}$)$_2$(CH_3CN)]-BF_4, 7. The structure of **7** indicates that the pendant amines in two of the ligand chelate rings are positioned near the hydride ligand. Protonation of the amines in this complex was studied in order to explore the intramolecular proton/hydride exchange process. The addition of acids ranging in strength from triflic to anisidinium to **7** at room temperature in acetone-d_6 results in the loss of the hydride ligand over a period of about 30 min, presumably by the elimination of dihydrogen. This reactivity is similar to that observed for the other iron hydride derivatives with diphosphine ligands studied previously.[17b,d,g] Identification of products formed as a result of the protonation of **7** at low temperatures is complicated by the presence of four amine sites in the cyclic ligands and by conformational changes possible for the ligand chelate rings that would give rise to many possible isomers. Several resonances between 7 and 15 ppm in the ^{1}H NMR spectrum that are attributed to NH protons were observed when stepwise equivalents of triflic acid were added to the complex at −50 °C in acetone-d_6. Selective formation of a single or major product corresponding to each equivalent addition was

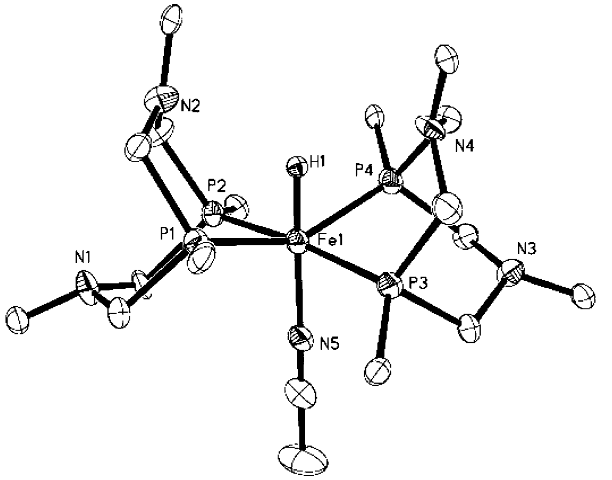


Figure 4. Perspective drawing of $[HFe(P^{Ph}{}_2N^{Ph}{}_2)_2(CH_3CN)]^+$, **7**, indicating the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Only ipso carbons of phenyl substituents are shown for clarity.

not observed, and structural assignments were not made for the stepwise protonation products.

However a species that is consistently formed in varying amounts when triflic acid is added to **7** at −50 °C, and which is the predominant species (ca. 80%) when four or more equivalents of acid are added, displays an NH singlet in the ^{1}H NMR spectrum at 14.6 ppm. In the hydride region of the spectrum, a new pentet is observed at −20.6 ppm, while the ^{31}P NMR spectrum shows a broad singlet at 30 ppm. In an effort to observe intramolecular exchange between the iron-hydride and the protonated nitrogen, a GOESY experiment was performed at −60 °C with a mixing time of 300 ms. The magnetization of the hydride peak at −20.6 ppm was selectively inverted, and the resonances of the NH peaks were monitored. However, no inverted exchange peak was observed, indicating that fast hydrogen exchange between Fe−H and NH groups is not occurring. Additional variable-temperature NMR data indicate that hydrogen elimination from this isomer at room temperature is relatively slow. As the solution is warmed to room temperature, the hydride resonance broadens and phosphorus coupling is no longer resolved, but when the solution is recooled to −50 °C, the pentet of the protonated hydride complex is again observed.

More detailed information on the structure of this relatively stable protonated isomer of **7** was obtained through the synthesis and NMR studies of the ^{15}N-labeled complex. The complex **7**(^{15}N) was prepared using the labeled ligand synthesized from ^{15}N-aniline. The isomer resulting from the addition of excess (ca. 4 equiv) triflic acid at −50 °C to **7**(^{15}N) showed two resonances in the ^{15}N NMR spectrum at 59.0 and 58.2 ppm, Figure 5a. The trans hydride and acetonitrile ligands in **7** remove a potential plane of symmetry through the four Fe−P bonds and make the two nitrogens in each ligand chelate inequivalent. In the ^{1}H NMR spectrum of the protonated labeled complex (Figure 5d), a doublet of doublets pattern is observed for the NH protons at 14.2 ppm with $J_1 = 26.7$ and $J_2 = 43.0$ Hz. Selective low power decoupling of the upfield nitrogen results in a single doublet in the ^{1}H NMR spectrum with the smaller coupling constant (Figure 5c), while selective decoupling of the downfield nitrogen gives a doublet with the larger *J* value (Figure 5b). When broadband high-power ^{15}N decoupling is applied, the signal at 14.2 ppm collapses to a singlet. The data support the structure shown in structure **9** for a diprotonated complex where each proton is stabilized by interaction with two inequivalent amines from ligand chelates in the chair conformation.

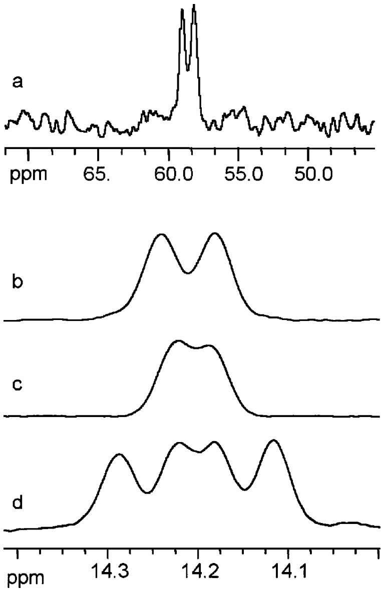
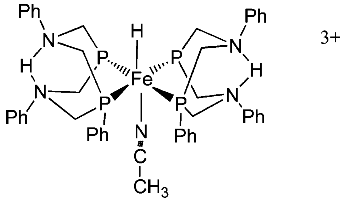


Figure 5. (a) ^{15}N{^{1}H decoupled} NMR of spectrum of the ^{15}N-labeled form of *trans*-$[HFe(CH_3CN)(P^{Ph}{}_2NH^{Ph}N^{Ph})_2]^{3+}$ (structure **9**). The NH region of the ^{1}H NMR spectrum of **9** (^{15}N-labeled) (b) with selective ^{15}N decoupling of the 59.0 ppm nitrogen resonance, (c) with selective ^{15}N decoupling of the 58.2 ppm nitrogen resonance, and (d) with no ^{15}N decoupling. Spectra were recorded in acetone-d_6 at −50 °C.



9

The predominance of this isomer helps to explain why facile Fe−H and N−H exchange and dihydrogen elimination are not observed for this system. A diprotonated nickel(0) structure in which the protons are similarly stabilized by two amine nitrogens of a related cyclic ligand has been identified previously.[17e] In the nickel system this is a minor isomer that is formed upon addition of hydrogen to the nickel(II) complex, $[Ni(P_2{}^{Cy}N_2{}^{Bz})_2]^{2+}$. The more favored nickel(0) isomers involve conformations of the ligand chelate rings that permit interaction of the amine proton with the electron-rich nickel center. In contrast, in the protonation of the iron(II) hydride derivative, the greater proton stabilization appears to be gained by formation of isomer **9**.

Summary and Conclusions

Both cis and trans derivatives of new iron complexes containing diazadiphosphacyclooctane ligands have been synthesized and characterized by X-ray diffraction techniques. In the structure of *trans*-$[HFe(P_2{}^{Ph}N_2{}^{Ph})_2(CH_3CN)]^+$, two pendant amines are positioned 2.6−2.7 Å from the iron-hydride ligand as a result of two chelate rings with boat conformations. However, upon protonation, no intramolecular NH−FeH exchange is observed by GOESY NMR experiments, indicating a relatively slow rate of exchange. Additional NMR studies of the ^{15}N-labeled complex indicate that upon protonation the flexible chelate rings favor two chair conformations that remove the protons from proximity to the metal center and permit simultaneous interactions of both amines in each diphosphine ligand with a single proton (see structure **9**). This work highlights the need for additional design and study of how ligands may incorporate optimum features of flexibility and positioning of pendant bases to promote catalytic H^+/e^- transfers.

Experimental Section

General Methods and Materials. All reactions were performed under an argon atmosphere using standard Schlenk line techniques. Solvents were dried using standard procedures and distilled under nitrogen. Deuterated NMR solvents were dried over molecular sieves and degassed using the freeze−pump−thaw method. Sodium tetraphenyl borate, triflic acid, and fluoroboric acid (48% aqueous solution) were obtained from commercial sources and used without further purification. $[Fe(CH_3CN)_6](BF_4)_2$[22] and the ligands $P_2^{Ph}N_2^{Ph}$, $P_2^{Cy}N_2^{Bz}$, and $P_2^{Ph}N_2^{Bz}$ [17c,f] were prepared as described previously.

^{1}H NMR, ^{31}P NMR, and ^{15}N NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. ^{31}P spectra were proton-decoupled and referenced to a phosphoric acid external standard. ^{1}H chemical shifts are referenced to residual solvent proton shifts. ^{15}N chemical shifts are reported relative to external ammonia, referenced indirectly to the frequency of the deuterated solvent. One-dimensional ^{15}N NMR spectra were acquired with continuous broadband irradiation of the protons to provide sensitivity enhancement from both the NOE interaction and from decoupling J_{NH}. VT NMR experiments were allowed to equilibrate for 5 min at each temperature. Exchange studies were done using a GOESY (gradient-enhanced NOE spectroscopy) pulse sequence. The NUTS software package by Acron NMR Inc. was used to simulate second-order spectra.[23] Electrospray ionization (ESI) mass spectra were collected using an HP 5989B mass spectrometer with a HP 59987A electrospray. Infrared spectroscopy was performed on a ThermoNicolet Avatar 360 FT-IR ESP spectrometer using potassium bromide pellets.

Syntheses. $[Fe(P^{Ph}{}_2N^{Ph}{}_2)(CH_3CN)_4](BF_4)_2$, 5. A one to one ratio of $[Fe(CH_3CN)_6](BF_4)_2$ (0.42 g, 0.86 mmol) and 1,3,5,7-tetraphenyl-1,5-diaza-3,7-diphosphacyclooctane ($P^{Ph}{}_2N^{Ph}{}_2$) (0.39 g, 0.86 mmol) was reacted in acetonitrile at room temperature. The suspension was stirred for 2 h, undergoing a change in color to a red solution. The volume of the solution was reduced to approximately 5 mL by applying a vacuum, and ether was layered on top. The resulting red-orange precipitate was filtered and washed with ether. Single crystals were grown through vapor diffusion of diethyl ether into a methylene chloride solution of the complex. Yield: 0.45 g, 62%. Anal. Calc for $C_{36}H_{40}B_2F_8FeN_6P_2$: C, 50.98; H, 4.75; N, 9.91. Found: C, 50.66; H, 4.55; N, 9.87. ^{31}P NMR (CD_3CN): 50.2 (s, sharp). ^{1}H NMR (CD_3CN, ppm): 7.76 (m), 7.71 (m), 7.31 (m), 7.19 (m), 6.94 (m) (20 H total, C_6H_5); 4.27 (m) (8 H total, PCH_2N); 1.96 (s) (12 H total, $NCCH_3$). ESI$^+$-MS, *m/z* (CH_3CN): 529 $\{[Fe(P^{Ph}{}_2N^{Ph}{}_2)](F)\}^+$.

***cis*-$[Fe(P^{Ph}{}_2N^{Ph}{}_2)_2(CH_3CN)_2](BF_4)_2$, 6a.** A one to two ratio of $[Fe(CH_3CN)_6](BF_4)_2$ (0.35 g, 0.71 mmol) and $P^{Ph}{}_2N^{Ph}{}_2$ (0.65 g, 1.4 mmol) was reacted in acetone at room temperature. The suspension was stirred overnight, undergoing a change to an orange solution. The volume of the solution was reduced to approximately 5 mL by applying a vacuum, and 20 mL of diethyl ether was layered on top. The resulting orange precipitate was filtered and washed with ether. Yield: 0.87 g, 58%. Anal. Calc for $C_{60}H_{62}B_2F_8FeN_6P_4$: C, 59.04; H, 5.12; N, 6.89. Found: C, 58.67; H, 5.27; N, 6.84. ^{31}P NMR (CD_3CN): $\delta_A = \delta_{A'} = 31.7$ ppm, $\delta_B = \delta_{B'} = 35.8$ ppm, $^2J_{AA'} = 14.2$ Hz, $^2J_{BB'} = -23.6$ Hz, $^2J_{AB} = 95.3$ Hz, $^2J_{AB'} = 60.3$ Hz. ^{1}H NMR (CD_3CN, ppm): 7.76 (m), 7.64 (m), 7.50 (m), 7.32 (m), 7.03 (m), 6.74 (m) (40 H total, C_6H_5); 4.31 (m), 4.09 (m), 3.65 (m), 3.34 (m), 2.84 (m) (16 H total, PCH_2N); 2.38 (s) (6 H total, $NCCH_3$). ESI$^+$-MS, *m/z* (CH_3CN): 1133 $\{[Fe(P^{Ph}{}_2N^{Ph}{}_2)_2(CH_3CN)_2](BF_4)\}^+$; 983 $\{[Fe(P^{Ph}{}_2N^{Ph}{}_2)_2](F)\}^+$; 482 $\{Fe(P^{Ph}{}_2N^{Ph}{}_2)_2\}^{2+}$.

***cis*-$[Fe(P^{Cy}{}_2N^{Bz}{}_2)_2(CH_3CN)_2](BF_4)_2$, 6b.** A one to two ratio of $[Fe(CH_3CN)_6](BF_4)_2$ (0.349 g, 0.709 mmol) and $P^{Cy}{}_2N^{Bz}{}_2$ (0.701 g, 1.42 mmol) was reacted in acetone at room temperature. The suspension was stirred overnight, undergoing a change to an orange-yellow solution. The volume of the solution was reduced to approximately 5 mL by applying a vacuum, and 15 mL of ether was layered on top. This solution was placed in a −15 °C freezer overnight. The yellow-orange solid that precipitated was isolated via filtration and recrystallized from methanol. Yield: 0.519 g, 57%. Anal. Calc for $C_{64}H_{94}B_2F_8FeN_6P_4{\cdot}2CH_3OH$: C, 58.08; H, 7.53; N, 6.16. Found: C, 57.92; H, 7.48; N, 5.89. ^{31}P NMR (CD_3CN): $\delta_A = \delta_{A'} = 30.8$ ppm, $\delta_B = \delta_{B'} = 32.2$ ppm, $^2J_{AA'} = 35.3$ Hz, $^2J_{BB'} = -76.1$ Hz, $^2J_{AB} = 100.3$ Hz, $^2J_{AB'} = 51.4$ Hz. ^{1}H NMR (CD_3CN, ppm): 7.55 (m), 7.41 (m), 7.36 (m), 7.26 (m), 6.85 (m) (20 H total, C_6H_5); 3.82 (m), 3.59 (m) (8 H total, NCH_2Ph); 3.21 (m), 2.93 (m), 2.40 (m), 2.16 (m) (16 H total, PCH_2N); 1.96 (s) (6 H total, free CH_3CN); 1.93−0.85 (br, m) (40 H total, C_6H_{11}). ESI$^+$-MS, *m/z* (CH_3CN): 1213 $\{[Fe(P^{Cy}{}_2N^{Bz}{}_2)_2(CH_3CN)_2](BF_4)\}^+$; 1131 $\{[Fe(P^{Cy}{}_2N^{Bz}{}_2)_2](BF_4)\}^+$; 1063 $\{[Fe(P^{Cy}{}_2N^{Bz}{}_2)_2](F)\}^+$.

***cis*-$[Fe(P^{Ph}{}_2N^{Bz}{}_2)_2(CH_3CN)_2](BPh_4)_2$, 6c.** A one to two ratio of $[Fe(CH_3CN)_6](BF_4)_2$ (0.42 g, 0.86 mmol) and $P^{Ph}{}_2N^{Bz}{}_2$ (0.82 g, 1.71 mmol) along with excess $NaBPh_4$ (1.46 g, 4.27 mmol) was reacted in 25 mL of acetone at room temperature. The suspension was stirred overnight undergoing a change to an orange solution. Fifteen milliliters of methanol was stirred in, and the volume of the solution was reduced to approximately 5 mL. The yellow-orange solid that formed was isolated via filtration and crystallized from acetone/ether (0.922 g, 62%). Anal. Calc for $C_{112}H_{110}B_2FeN_6P_4$: C, 77.24; H, 6.37; N, 4.83. Found: C, 76.88; H, 6.17; N, 4.73. ^{31}P NMR (CD_3CN): $\delta_A = \delta_{A'} = 35.1$ ppm, $\delta_B = \delta_{B'} = 38.2$ ppm, $^2J_{AA'} = 10.3$ Hz, $^2J_{BB'} = -20.6$ Hz, $^2J_{AB} = 92.3$ Hz, $^2J_{AB'} = 62.7$ Hz. ^{1}H NMR (CD_3CN, ppm): 7.27 (m), 6.99 (m), 6.84 (m) (40 H total, BC_6H_5); 7.70 (m), 7.55 (m), 7.37 (m), 7.30 (m), 7.18 (m), 7.06 (m), 6.45 (m) (40 H total, C_6H_5); 4.27 (m), 3.71 (m) (8 H total, NCH_2Ph); 3.18 (m), 2.61 (m), 1.86 (m), 1.28 (m) (16 H total, PCH_2N); 1.96 (s) (6 H total, free CH_3CN). ESI$^+$-MS, *m/z* (CH_3CN): 1422 $\{[Fe(P^{Ph}{}_2N^{Bz}{}_2)_2(CH_3CN)_2](BPh_4)\}^+$; 1381 $\{[Fe(P^{Ph}{}_2N^{Bz}{}_2)_2(CH_3CN)](BPh_4)\}^+$; 1340 $\{[Fe(P^{Ph}{}_2N^{Bz}{}_2)_2](BPh_4)\}^+$; 510 $\{[Fe(P^{Ph}{}_2N^{Bz}{}_2)_2]\}^{2+}$.

***cis*-$Fe(P^{Ph}{}_2N^{Ph}{}_2)_2(Cl)_2$, 8.** One equivalent of $FeCl_2$ (62 mg, 0.490 mmol) was added to 2 equiv of $P^{Ph}{}_2N^{Ph}{}_2$ (448 mg, 0.985 mmol) in methylene chloride. The reaction was allowed to stir at RT overnight, during which a color change to purple occurred. The solvent was reduced to approximately 5 mL, and hexanes was layered on top. Upon letting the flask sit at −15 °C for 12 h, a purple solid formed, which was filtered off and washed with hexanes (274 mg, 54%). Anal. Calc for $C_{56}H_{56}Cl_2FeN_4P_4$: C, 64.94; H, 5.45; N, 5.41. Found: C, 64.51; H, 5.39; N, 5.41. ^{31}P NMR ($CDCl_3$): $\delta_A = \delta_{A'} = 29.9$ ppm, $\delta_B = \delta_{B'} = 42.8$ ppm, $^2J_{AA'} = 56.3$ Hz, $^2J_{BB'} = -10.2$ Hz, $^2J_{AB} = 103.1$ Hz, $^2J_{AB'} = 69.3$ Hz. ^{1}H NMR ($CDCl_3$, ppm): 7.89, 7.58, 7.36, 7.01, 6.92, 6.51, 6.43 (br, 40 H total, C_6H_5); 5.13, 4.45, 4.16, 3.69, 3.28, 3.12, 2.42 (br, 16 H total, PCH_2N). ESI$^+$-MS (CH_3CN): 1000 *m/z* $[Fe(P^{Ph}{}_2N^{Ph}{}_2)_2(Cl)]^+$.

***trans*-$[HFe(P^{Ph}{}_2N^{Ph}{}_2)_2(CH_3CN)](BF_4)$, 7.** $[Fe(P^{Ph}{}_2N^{Ph}{}_2)_2(CH_3CN)_2](BF_4)_2$ (0.51 g, 0.42mmol) and a large excess of $PPNBH_4$ (1.61 g, 2.91 mmol) were added to acetonitrile (20 mL). An evolution of hydrogen took place followed by a gradual change in color to a yellow solution. The solution was stirred for 4 h and then filtered to remove the excess solid. The solvent was removed

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[22] (a) Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc*. **1960**, 3705−3711. (b) Heintz, P. A.; Smith, J. A.; Szalay, P. X. Weisgerber, A. *Inorg. Syn*. **2002**, *33*, 77.

[23] Stott, K.; Keeler, J.; Van, Q. N. and Shaka, A. J. *J. Magn. Reson.* **1997**, *125*, 302−324.

from the filtrate with a vacuum, and the resulting yellow solid was dissolved in 5 mL of methanol. After letting the flask sit for 24 h at −15 °C, the yellow solid that formed was filtered off. The recrystallization from methanol was repeated, and then a final recrystallization from methylene chloride/ether was performed, yielding a product that is pure according to ^{1}H and ^{31}P NMR spectroscopy. Yield: 35 mg, 8%. ^{31}P NMR (CD_3CN): δ 50.1 ppm (br s). ^{1}H NMR (CD_3CN, ppm): 7.26 (m), 7.17 (m), 7.13 (m), 6.91 (m) (40 H total, C_6H_5); 4.02 (br), 3.79 (br), 3.75 (br), 3.27 (br) (16 H total, PCH_2N); 3.44 (s) (3 H total, $NCCH_3$); −20.02 (p), $^2J_{PH} = 45.3$ Hz (1H total, Fe-*H*). ESI$^+$-MS, *m/z* (CH_3CN): 1025 {$[Fe(P^{Ph}_2N^{Ph}_2)(CH_3CN](F)$}$^+$; 965 {$(Fe(P^{Ph}_2N^{Ph}_2)(H)$}$^+$; 482 {$Fe(P^{Ph}_2N^{Ph}_2)_2$}$^{2+}$.

Alternatively, the tetraphenylborate salt of this complex was made by stirring $[Fe(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)_2](BF_4)_2$ (0.30 g, 0.24mmol), $PPNBH_4$ (0.80 g, 1.45 mmol), and excess $NaBPh_4$ (0.837 g, 2.42 mmol) in acetonitrile. After stirring for 4 h excess solid was filtered off. The solution was taken to dryness, and approximately 10 mL of methanol was added. The solution was then reduced to ∼4 mL and filtered. The resulting product was isolated as a mixture of $PPN(BPh_4)$ and product. Recrystallization from dichloromethane/methanol improves purity (73 mg, 27%). While this method produces a higher yield, a completely pure product is difficult to obtain.

Variable-temperature NMR was performed by dissolving approximately 20 mg of $[Fe(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)(H)]^+$ in acetone-d_6 and cooling to −50 °C in the NMR probe. ^{31}P NMR (acetone-d_6): at 23 °C, $\delta = 50.9$ ppm (br); at −50 °C, $\delta_A = \delta_{A'} = 45.7$ ppm, $\delta_B = \delta_{B'} = 57.2$ ppm, $^2J_{AA'} = 32.5$ Hz, $^2J_{BB'} = -4.8$ Hz, $^2J_{AB} = 56.1$ Hz, $^2J_{AB'} = 106.2$ Hz. ^{1}H NMR (acetone-d_6, ppm): at 23 °C, −19.81 (p), $^2J_{PH} = 44.6$ (1H, Fe-*H*); at −70 °C, −19.74 (tt), $J_1 = J_2 = 26.5$ Hz $J_3 = J_4 = 62.2$ Hz, (1H, Fe-*H*). The coalescence point occurs at approximately 5 °C.

Protonation of $[HFe(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)](BF_4)$, 7. $[HFe(CH_3CN)(P^{Ph}_2N^{Ph}_2)_2](BPh_4)$ (25 mg, 0.019 mmol) was dissolved in acetone-d_6 in an NMR tube and cooled to −50 °C. Triflic acid (6.7 μL, 0.076 mmol) was rapidly added, the tube was placed into the precooled (−50 °C) NMR probe, and low-temperature ^{31}P and ^{1}H NMR spectra were recorded. ^{31}P NMR (acetone-d_6): 30.1 ppm (br). ^{1}H NMR (acetone-d_6, ppm): major isomer (structure **9**): 14.15 (s, 2H, N-*H*-N); −20.63 (p, 1H, Fe-*H*, $^2J = 49.8$ Hz); isomer 2: 12.18 (s, 0.33 H, N-*H*); −21.32 (p, 0.14 H, Fe-*H*, $^2J = 47$ Hz). Other isomers: 9.74, 9.89 (0.25 H, N-*H*).

A GOESY experiment was performed on a similarly prepared sample at −60 °C with a mixing time of 300 ms. The magnetization of the hydride peak at −20.63 ppm was selectively inverted, and the resonances of the NH peaks were monitored. However, no inverted exchange peak was observed.

The ^{15}N-enriched version of $[HFe(CH_3CN)(P^{Ph}_2N^{Ph}_2)_2](BPh_4)$ was synthesized via use of ^{15}N-enriched aniline in the original ligand reaction. Protonation with triflic acid and low-temperature NMR were performed according to the above procedure. ^{1}H NMR (acetone-d_6): major isomer (structure **9**): 14.21 (dd) $J_1 = 26.7$ Hz, $J_2 = 43.0$ Hz, (2 H, N-*H*-N); isomer 2: 12.21 (d) $J = 74$ Hz, (0.33 H, N−H). Other isomers: 9.80 (d), 9.96 (d), $J = 56$ Hz, (0.25 H, N-*H*). ^{15}N NMR (acetone-d_6): 59.0 (br); 58.2 (br). ^{1}H NMR (acetone-d_6) using low-power selective ^{15}N deoupling: 14.21 (d) $J = 16$ Hz (upfield nitrogen (59.0 ppm) decoupled); 14.21 (d) $J = 29$ Hz (downfield nitrogen (58.2 ppm) decoupled). ^{1}H NMR (acetone-d_6) using broadband high-power ^{15}N deoupling: 14.21 (s).

Acetonitrile Exchange. *cis*-$[Fe(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)_2](BF_4)_2$, **6a** (approximately 20 mg), was dissolved in 0.7 mL of acetonitrile-d_3 at 23 ± 2 °C. The integral of the acetonitrile resonance at 2.38 ppm was followed as a function of time. A first-order plot ($\ln(I/I_o)$ vs time) was used to obtain a rate constant of $7.3 \times 10^{-4}\ s^{-1}$, which corresponds to a half-life of 16 min. Similar experiments showed rate constants of $> 1.1 \times 10^{-2}\ s^{-1}$ ($t_{1/2} = <1$ min) for *cis*-$[Fe(P^{Ph}_2N^{Ph}_2)(CH_3CN)_4](BF_4)_2$, **5**, and $1.7 \times 10^{-4}\ s^{-1}$ ($t_{1/2} = 67$ min) for *trans*-$[HFe(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)](BF_4)$, **7**.

Attempted Hydride Exchange with D_2O. *trans*-$[HFe(P^{Ph}_2N^{Ph}_2)_2(CH_3CN)](BF_4)$, **7** (20 mg, 0.015 mmol), was weighed into a NMR tube and dissolved in CD_3CN. An initial spectrum was taken, and D_2O (50 μL, 2.50 mmol) was added. The integration of the hydride resonance at −20.0 ppm was monitored over time. After 2 days the hydride resonance had maintained its original integral versus the integral of a single NCH_2P resonance.

X-ray Analysis of $[Fe(P^{Ph}_2N^{Ph}_2)(CH_3CN)_4](BF_4)_2$, 5. Crystals suitable for X-ray diffraction studies were grown from acetonitrile/methylene chloride/ether. A crystal of appropriate size was mounted on a glass fiber using Paratone-N oil, transferred to a Siemens SMART diffractometer/CCD area detector, centered in the beam (Mo Kα; $\lambda = 0.71073$ Å; graphite monochromator), and cooled to −122 °C. Preliminary orientation matrix and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. A minimum of a hemisphere of data was collected using 0.3° ω scans at 30 s per frame. The raw data were integrated and the unit cell parameters refined using Saint. Data analysis was performed using XPREP. Absorption correction was applied using SADABS. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Structure solutions and refinements were performed (SHELXTL-Plus V5.0) on F^2.

Preliminary data indicated a monoclinic cell. The choice of the $P2(1)/c$ space group was supported by the successful solution and refinement of the structure. All non-H atoms were refined anisotropically. All H-atoms were placed in idealized positions and were included in structure factor calculations but were not refined.

X-ray Analysis of $[Fe(P^{Ph}_2N^{Bz}_2)_2(CH_3CN)_2](BPh_4)_2$, 6b. The crystal structure for **6b** was performed in a similar manner as reported for **5**, except the crystals were grown from acetone/ether vapor diffusion. Preliminary data indicated a monoclinic cell. The choice of the $P2(1)/n$ space group was supported by the successful solution and refinement of the structure.

X-ray Analysis of $[HFe\ (P^{Ph}_2N^{Ph}_2)_2(CH_3CN)](BF_4)$, 7. The crystal structure for **7** was performed in a similar manner as reported for **5**, except the crystals were grown from methylene chloride/ether vapor diffusion. Preliminary data indicated a monoclinic cell. The choice of the $P2(1)$ space group was supported by the successful solution and refinement of the structure. All H-atoms except the hydride (H1) were placed in idealized positions and were included in structure factor calculations but were not refined. The hydride (H1) was located in a difference Fourier map and was refined isotropically. The Flack parameter refined to 0.0040 with an esd of 0.0243. The conformation was chosen because inversion of the structure gave a value near 1.

Acknowledgment. This work was supported by Grant CHE-0240106 from the National Science Foundation. D.L.D. acknowledges the support of the Office of Basic Energy Sciences of the Department of Energy, by the Chemical Sciences program. The Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy.

Supporting Information Available: Tables of crystal and refinement data, positional and equivalent isotropic thermal parameters, bond distances and angles, and torsional angles and figures with complete numbering schemes for **5**, **6b**, and **7**. Experimental and simulated ^{31}P NMR spectra for **6b** and **6c**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM700601H