ORGANOMETALLICS

Spectroscopic and DFT Study of Ferraaziridine Complexes Formed in the Transfer Hydrogenation of Acetophenone Catalyzed Using *trans*-[Fe(CO)(NCMe)(PPh₂C₆H₄CH=NCH₂-)₂- κ^4 P,N,N,P](BF₄)₂

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Supporting Information

ABSTRACT: The reaction of the iron complex *trans*-[Fe(CO)(MeCN)(PPh₂C₆H₄CH=NCH₂-)₂- $\kappa^4 P$, *N*, *N*, *P*]-(BF₄)₂ (1) with KOiPr in benzene produced the unusual complex [Fe(CO)(PPh₂C₆H₄CH=NCH₂CH₂NHCHC₆H₄PPh₂)- $\kappa^5 P$, *N*, *C*, *N*, *P*][BF₄] (2), which has been characterized by spectroscopy and by single-crystal X-ray diffraction. The C–N bond length in this complex indicates that it is best viewed as an iron(II) ligand-folded ferraaziridine- $\kappa^2 C$, *N* complex instead of an iron(0) η^2 -iminium complex. Density functional theory (DFT) calculations have been employed on simplified



structural models to support a mechanism of formation of this complex via the transfer of a hydride from the alkoxide complex *trans*-[Fe(CO)(OCHMe₂)(PH₂C₆H₄CH=NCH₂-)₂- $\kappa^4 P_1N_1N_1P_1^{-1}$ (4_{DFT}) to an imine carbon on the ligand to produce the amide complex *trans*-[Fe(CO)(OC(CH₃)₂)(PH₂C₆H₄CH=NCH₂-CH₂NCH₂C₆H₄PH₂- $\kappa^4 P_1N_1N_1P_1^{-1}$ (5^{acet}_{DFT}) followed by liberation of acetone to afford 5_{DFT}. Two energetically similar pathways have been proposed in which deprotonation of the PNNP ligand of 5_{DFT} by strong base produces the experimentally observed ferraaziridinido complex Fe(CO)(PH₂C₆H₄CH=NCH₂- $P_2N_1N_2N_2P_1^{-1}$). Protonation of 3_{DFT} by free isopropyl alcohol produces the ferraaziridine complex $P_2(CO)(PH_2C_6H_4CH=NCH_2-)_2$ - $\kappa^4 P_1N_1N_1P_1$ (7_{DFT}). Protonation of 3_{DFT} by free isopropyl alcohol produces the ferraaziridine complex 2_{DFT}. Nuclear magnetic resonance and infrared spectroscopy data show that during the transfer hydrogenation of acetophenone catalyzed by 1 in basic isopropyl alcohol, free ligand is observed along with one major iron-containing species identified as 3. On the basis of our calculations of relative free energies and a CO scale factor, we predict that 2 is easily deprotonated to form the electron-rich iron complex 3 and the square-pyramidal Fe(0) complex 7, which are responsible for the two observed CO stretches below 1900 cm⁻¹ in catalytic mixtures. Mass balance studies indicate that the catalytically active species is not observable by NMR. Although 2 and 3 are poor transfer hydrogenation catalysts, we present experimental and theoretical evidence that ligand folding/ distortion is feasible.

INTRODUCTION

The hydrogenation of carbonyl compounds to alcohols is a vital process in the pharmaceutical, fine chemical, and perfume industries. The alcohols may be prepared via direct hydrogenation, hydrosilylation, or transfer hydrogenation (TH) reactions, usually utilizing catalysts based on expensive and sometimes toxic platinum metals.¹ Several attempts have been made to develop iron catalysts that would be cheaper and nontoxic for these kinds of reactions.¹⁻¹³ The first studies were carried out by Vancheesan et al.^{14,15} and Gao et al.,¹⁶ who introduced the asymmetric iron-catalyzed TH of ketones. In this regard, we recently reported highly efficient iron catalysts for the asymmetric TH of ketones to the corresponding alcohols using isopropyl alcohol as a hydrogen source.^{17–24} As a common structural feature in the new catalysts, an iron(II) atom is coordinated by a tetradentate diimine ligand, a carbonyl or isonitrile, and an acetonitrile or bromide ligand, as depicted in Figure 1. The catalysts work at room temperature with



Figure 1. Iron precatalysts for the TH of ketones with 6.5.6 (left) and 5.5.5 (right) metallacycles prepared by our group.

excellent turnover frequencies (TOF) and enantioselectivities (TOF up to 28 000 h^{-1} , ee up to 99%). While the mechanism of ruthenium-catalyzed TH has been extensively studied, ^{12,25,26} little is known about the mechanism of iron-catalyzed TH. A detailed knowledge of the mechanism will be essential to optimize the design of our systems to make more efficient and

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enantioselective iron catalysts, to make them more competitive with the best platinum metal based systems. Hence, this is currently under extensive study in our laboratory.

In the present paper we discuss the species observable by NMR and IR spectroscopy during the TH of acetophenone to 1-phenylethanol using the iron complex *trans*-[Fe(CO)-(MeCN)(PPh₂C₆H₄CH=NCH₂-)₂- κ^4 P,N,N,P][(BF₄)₂] (1)²⁴ as the precatalyst (Scheme 1), isopropyl alcohol as the

Scheme 1. Reaction Scheme for TH of Ketones Using 1 As a Precatalyst in the Presence of Excess $Base^{a}$



^{*a*}8 equiv with respect to 1.

hydrogen source, and potassium *tert*-butoxide (KOtBu) as the base. To gain further insight into the species formed during catalysis, we investigated the reaction of precatalyst **1** with stoichiometric amounts of base and performed density functional theory (DFT) calculations on simplified models of the reactive species to further support our results.

RESULTS AND DISCUSSION

Catalysis. The use of 1 as a precatalyst for the TH of acetophenone to 1-phenylethanol with a TOF of 2200 h^{-1} has been previously reported.²⁴ When 1 is dissolved in a solution of acetophenone in basic isopropyl alcohol, the solution immediately becomes clear and dark brown. The activated catalyst mixture is highly air sensitive, and exposure to air results in an immediate color change to pale yellow, rendering it inactive for TH. A typical plot for the production of 1-phenylethanol versus time using 1 at a catalyst to base to substrate loading of 1:8:600 at 26 °C is shown in Figure 2.



Figure 2. Observed production of 1-phenylethanol from acetophenone (0.47 M) in isopropyl alcohol (12.36 M) by use of 1 (0.87 mM) and KOtBu (7.0 mM) at 26 $^{\circ}$ C.

Investigation of the Catalysis by Spectroscopic Methods. The reaction mixture of a typical TH experiment was analyzed via NMR and IR techniques by using 1 as a precatalyst. ¹H and ³¹P{¹H} NMR spectra were recorded when the TH was carried out using relatively high catalyst loadings (catalyst:substrate = 1:43). ${}^{31}P{}^{1}H{}$ NMR spectra were recorded for reaction mixtures in isopropyl alcohol using C₆D₆ as an internal NMR reference for locking. ¹H NMR spectra were carried out in deuterated isopropyl alcohol and showed only poorly resolved peaks. No hydride signals were observed in the region between 0 and -30 ppm; however, a hvdride mechanism cannot be dismissed, as such a hydride species may be only transient or may be present in low concentration. The formation of iron hydrides as intermediates was proposed earlier for TH with the precatalysts [(PP₃)Fe- $(H)(H_2)](BPh_4)$ (PP₃ = P(CH₂CH₂PPh₂)₃)²⁷ and $Fe_3(CO)_{12}^{16}$ but hydride species were not isolated or observed spectroscopically.

 $^{31}P{^{1}H}$ NMR spectra recorded during TH have a number of interesting features. Two related doublets at 84.1 and 68.7 ppm ($J_{PP} = 29$ Hz), various singlets around -13.0 ppm, and two singlets at 32.2 and 31.7 ppm were observed (Figure 3). The



Figure 3. ${}^{31}P{}^{1}H$ NMR spectrum (161 MHz, *i*PrOH, C_6D_6 internal reference) of a TH run in 0.65 mL of isopropyl alcohol for the production of 1-phenylethanol from acetophenone (0.60 M) by use of 1 (0.025 M) and KOtBu (0.14 M) at 26 °C.

peak at 32.2 ppm is due to the oxidized free PNNP ligand. This was confirmed by a ${}^{31}P{}^{1}H{}$ NMR spectrum of an independently prepared sample of the PNNP ligand oxidized at phosphorus using hydrogen peroxide. The peak at 31.7 ppm is likely the mono-oxidized PNNP ligand, partially overlapped by the peak at 32.2 ppm. The peaks at -13.0 are due to the free PNNP ligand and unidentified PPh₂(aryl) species, possibly produced by ligand isomerization and fragmentation, as well as the phosphine of the mono-oxidized PNNP. Precatalyst 1 shows a singlet in the phosphorus spectrum at 50.8 ppm and is therefore completely consumed during the TH process.

To investigate the vibrational spectra of the catalytic mixture, the reaction mixture was concentrated under vacuum to dryness and the IR spectrum of the residue was taken as a KBr disk. The spectrum revealed weak broad absorptions for C=O vibrations at 1960 and 1946 cm⁻¹, and intense broad absorptions from 1835 to 1890 cm⁻¹, with distinct maxima at 1870 and 1846 cm⁻¹, indicating that a carbonyl ligand is still coordinated to a metal center during catalysis, possibly to the

active species. The broadness of the absorption below 1900 cm^{-1} is likely due to the presence of multiple, similar species in solution, with two major species giving rise to peaks at 1870 and 1846 cm⁻¹. While 1960 and 1946 cm⁻¹ are typical values for a monocarbonyl iron(II) compound, signals below 1900 cm⁻¹ are usually indicative of iron(0) complexes or bridging carbonyl ligands.^{28,29} Assignment of these two peaks was done in conjunction with density functional theory calculations (vide infra).

Isolation of a Ferraaziridine Complex (2). With the goal of isolating the intermediates observed by ³¹P NMR and IR spectroscopy, we investigated the reaction of precatalyst 1 with 2 equiv of sodium isopropoxide in neat benzene without acetophenone present. Surprisingly, we did not observe the formation of an octahedral iron alkoxide complex. Instead, the cationic ferraaziridine complex [Fe(CO)(PPh₂C₆H₄CH= NCH₂CH₂NHCHC₆H₄PPh₂)- $\kappa^{5}P$,*N*,*C*,*N*,*P*][BF₄] (2) was isolated in 65% yield. However, the reaction could only be carried out on a small scale, as the purity was diminished at larger scales (Scheme 2).

Scheme 2. Synthesis of 2



The single-crystal X-ray diffraction structure (Figure 4) revealed a distorted geometry where the C(10) carbon of the ferraaziridine moiety is bound approximately trans to the carbonyl ligand, with a C(10)-Fe-C(17) angle of $158.3(2)^{\circ}$. The complex appears to adopt a distorted-octahedral geometry, with a strained C(10)-Fe-N(2) angle of 42.0(1)° and obtuse P(1)-Fe-C(10) and C(17)-Fe-N(2) angles of 106.1(1) and 116.6(1)°, respectively (Figure 4). The complex is best viewed as an iron(II) κ^2 -ferraaziridine complex instead of an iron(0) η^2 iminium complex, given the N(2)-C(10) bond distance of 1.434(5) Å, characteristic for an N-C single bond. The bond distances from iron to the imine, amine, and alkyl functions are 1.980(3) Å (Fe–N(1)), 1.988(3) Å (Fe–N(2)), and 2.012(2) Å (Fe–C(10)), respectively (Table 1). The metal–carbonyl distance Fe-C(17) (1.781(4) Å) is typical for an ironcarbonyl bond and is similar to that of complex 1.24

We have also calculated the ground-state structures of $\mathbf{1}_{DFT}$ and $\mathbf{2}_{DFT}$ in the gas phase using DFT (simplified structural models, phenyls replaced with hydrogens). Both structures are in good agreement with those of 1 (see the Supporting Information) and 2 (Figure 4, Table 1). The gas-phase metrical parameters for $\mathbf{1}_{DFT}$ and $\mathbf{2}_{DFT}$ are nearly identical with those calculated with solvation effects (vide infra).

The Fe–NH and Fe–CH protons of **2** appear at 4.21 and 3.61 ppm, respectively, in the ¹H NMR spectrum. These assignments were confirmed by analysis of the ¹H–¹H-gCOSY and ¹H–¹³C-gHSQC NMR experiments. The ¹³C NMR chemical shift of the carbonyl carbon is found at 213 ppm as a doublet of doublets (² J_{CP} = 3.1, 24 Hz). The FeCH carbon is observed at 68 ppm as a doublet of doublets (² I_{CP} = 5, 11 Hz). The ³¹P{¹H} NMR spectrum has two sharp doublets at 84.3 and 70.1 ppm ($J_{P,P}$ = 43 Hz), consistent with the lack of

symmetry of the ligand. The 31 P NMR spectrum of the crude product by the reaction of Scheme 2 also shows a singlet at -13.4 ppm, consistent with free ligand being released.

Since we were able to measure clean and well-resolved NMR spectra without contact-shifted signals, we expect that the electronic state of the iron is low-spin iron(II) and the complex is diamagnetic (this is supported by unrestricted DFT calculations on a related Fe(II) complex, which will be discussed later). The ESI mass spectrum shows the cation for 2 at m/z 689.15. The IR spectrum shows a characteristic CO vibration band at 1940 cm⁻¹, similar to signals that have already been reported for six-coordinate, octahedral Fe(II) complexes with one CO ligand.^{30–33} The CO stretch is observed at wavenumbers lower than that for the starting material 1 (2002 cm⁻¹), as expected for a reduction in positive charge and increase in π back-bonding from Fe to CO on going from 1 to 2. This increase in bonding to the carbonyl is reflected in the relative reactivity of the complexes on stirring in acetonitrile: there is ligand exchange of acetonitrile for CO in 1 but not in 2.

To the best of our knowledge, there are only two other examples of a similar type of ferraaziridine iron coordination described in the literature. Siebenlist et al. reported that the reaction of an α -imine ester (ⁱPrN=CHC(OEt)=O) with $Fe_2(CO)_9$ in THF leads mainly to binuclear products with a small amount of the complex trans-Fe(CO)₂(ⁱPrNHCHC- $(OEt)=O)-\kappa N,C)_2$.³⁴ Evidence supported that the imine group was hydrogenated by hydrogen atom extraction from THF in an electron transfer process. As in 2, this ligand is coordinated to iron via both the amine nitrogen and the adjacent carbon atom, thus forming a three-membered azametallacycle. In addition, a photochemical reaction of $(EtO_2C)(NMe_2)C =$ NCPh=S with $Fe_2(CO)_9$ produced, among other products, $Fe(CO)_3(Me_2NC(CO_2Et)(N=C(Ph)S)-\kappa N,C,S))$, where the azametallacycle has geminal methyl groups on nitrogen.35a We have recently reported a related reaction involving the baseinduced formation of a ruthenaaziridine from a bis-(pyridylmethyl)amine complex.^{35b}

Reactivity of Complex 2. Complex 2 displays certain spectral features similar to those of the TH reaction mixture (Figure 3). It has an IR absorption at 1940 cm⁻¹ and doublets in the ³¹P{¹H} NMR spectrum at 84 and 69 ppm. However, the signal of the latter spectrum has a $J_{P,P}$ coupling constant of 43 Hz while the doublets of the TH solution have $J_{P,P} = 29$ Hz (Figure 3), thus indicating that the complexes are not the same. Complex 2 does not catalyze the TH of acetophenone in neat isopropyl alcohol without base at 26 °C. On the basis of the coupling constant mismatch between 2 and the TH mixture, it is not the species present during TH.

Compound 2 could also be observed (along with signals for free/oxidized ligand) by ³¹P{¹H} NMR via an NMR-scale reaction of 1 in isopropyl alcohol with 2 equiv of sodium isopropoxide, suggesting that it could be an intermediate toward the formation of the species with a similar $J_{P,P}$ value in the TH mixture as described above. An isolated, pure sample of 2 was reacted with a stoichiometric amount of KOtBu in isopropyl alcohol to afford the postulated ferraaziridinido complex $Fe(CO)(PPh_2C_6H_4CH=NCH_2CH_2NCH-C_6H_4PPh_2)-\kappa^5P,N,C,N,P$ (3) (Scheme 3), which only differs from 2 in that the ferraaziridine nitrogen atom is deprotonated. This structure is proposed on the basis of NMR/IR spectra and DFT calculations (vide infra). Complex 3 could not be isolated as a pure product, and therefore analysis was done on the crude solution after removal of excess base. The ³¹P{¹H} NMR



Figure 4. Molecular structure of 2 (top row, ellipsoids at 30% probability level) and calculated gas-phase structure of 2_{DFT} (bottom row). Phenyl hydrogens and counteranions have been omitted for clarity. Selected bond distances and angles are presented in Table 1.

Table 1. Comparison of Bond Lengths (Å) and Angles (deg) for Compounds 2 and $2_{\rm DFT}$

	length			angle	
param	2	2 _{DFT}	param	2	2 _{DFT}
Fe1-P1	2.203(1)	2.18	Fe1-C10-N2	68.06(2)	68.4
Fe1-P2	2.2178(9)	2.24	Fe1-N2-C10	69.92(2)	68.4
Fe1-N1	1.980(3)	1.99	H10-C10-Fe	119.15(3)	119.6
Fe1-N2	1.988(3)	1.97	H10-C10-N2	113.15(3)	112.0
Fe1-C10	2.012(4)	1.97	H10-C10-C11	114.56(3)	113.7
C10-C11	1.500(5)	1.49	N2-C10-C11	115.20(3)	114.6
C10-H10	0.974(3)	1.09	C10-N2-C1	119.56(3)	118.2
C10-N2	1.434(5)	1.46	C10-N2-H1N	118.07(2)	114.1
N2-C1	1.494(2)	1.46	C1-N2-H1N	107.62(3)	112.5

spectrum of the resulting solution shows two doublets at 84.1 and 68.7 ppm ($J_{\rm P,P}$ = 29 Hz) (along with singlets at -12 and -13.4 ppm for various isomers of the free ligand), which now matches the chemical shift and coupling constant of the phosphorus-containing complex in the TH mixture. The IR spectrum shows absorptions associated with carbonyl ligands at 1862 and 1870 cm⁻¹, as well as broad peaks at 1934 and 1957 cm⁻¹. From the similarities of the ³¹P{¹H} NMR and IR spectra between this reaction mixture and the TH solutions, we reason that **3** is present during TH.

Interestingly, when it is dissolved in neat isopropyl alcohol, the crude mixture of **3** is only minimally catalytically active (0.5% conversion of 3.85 mmol of acetophenone to 1-phenethanol at 26 $^{\circ}$ C in 1 h, 40% in 24 h). This supports the notion that, although **3** is the species seen by IR and 31 P{¹H} NMR, it is not the catalytically active species during TH.

Scheme 3. Observation of 3: Postulated Structure



This "noninnocent" behavior of the ligand is reminiscent of the PNP systems designed by Milstein³⁶ and Schneider³⁷ and PNNP complexes developed in our group,²³ whereby the ligand exhibits reversible protonation–deprotonation behavior. However, our system is flexible and preferentially adopts a folded/ distorted geometry, which is not observed for these other structurally rigid ligands.

Mass Balance Experiment. Line-broadening techniques were required for all ³¹P{¹H} NMR spectra due to very poor signal to noise, indicating that several species were likely not being detected by NMR experiments, possibly even the active species. For that reason, mass balance NMR experiments were carried out. Triphenylphosphine oxide (OPPh₃) is inert to catalysis and was therefore chosen as a standard to compare to other phosphorus integrations. A mixture of 2 equiv of OPPh₃ and 1 equiv of 1 was reacted with base and substrate in isopropyl alcohol, as per standard procedures. NMR conditions were optimized for accurate integration data. The doublets for 3 account for approximately 25% of the phosphorus introduced, and ligand and oxidized ligand account for

Scheme 4. Proposed Mechanisms for the Formation of 2_{DFT} and 3_{DFT} and the Fe(0) Species 7_{DFT}



approximately 18%. Therefore, only 43% of the phosphorus introduced for TH is detectable, leaving 57% of all phosphoruscontaining species unaccounted for and therefore NMR inactive. This is significant, because it shows that a maximum of 75% of the iron is either catalytically active and NMR inactive or is catalytically active and found in extremely low concentrations. We report elsewhere that the true identity of the active species is 4 nm iron(0) nanoparticles coated with the chiral ligand.³⁸

Calculated Mechanism for Formation of the Complexes 2_{DFT} , 3_{DFT} , and an Fe(0) Species (7_{DFT}). We have used density functional theory (DFT) calculations to rationalize

the formation of the experimentally observed complexes 2 and 3 and also propose the energetically favorable reduction to a five-coordinate Fe(0) species via two energetically similar pathways (Scheme 4). In order to reduce computational cost, the phenyl substituents on phosphorus have been truncated to hydrogen atoms in all calculated structures. In addition, solvent effects have been taken into account and all calculations have been performed using isopropyl alcohol as the solvent (see Computational Details).

Starting with the dicationic TH precatalyst 1_{DFT} , the labile acetonitrile ligand is replaced by an incoming isopropoxide



Figure 5. Calculated geometries and selected bond lengths for 4_{DFT} , $TS_{4,5}$ (-726i cm⁻¹), $TS_{6,3}$ (-1049i cm⁻¹), $TS_{6,7}$ (-1055i cm⁻¹), $TS_{3,7}$ (-319i cm⁻¹), and 7_{DFT} : gray, carbon; white, hydrogen; blue, nitrogen; red, oxygen; pink, phosphorus; orange, iron. Phenyl hydrogens have been omitted for clarity.

anion, which is exergonic by 16.3 kcal/mol to generate 4_{DFT} (Figure 6). Next, hydride transfer from the tertiary carbon on the alkoxido ligand reduces the imine moiety, generating the cationic Fe(II) imino-amido species 5_{DFT}^{acet} , which is endergonic by 7.3 kcal/mol and has a transition state barrier of 20.1 kcal/mol to overcome (TS_{4,5}, Figures 5 and 6). Dissociation of weakly coordinating acetone from 5_{DFT}^{acet} produces 5_{DFT} , a five-coordinate imino-amido species, which reacts with another 1 equiv of alkoxide, yielding the neutral octahedral complex 6_{DFT} , which is 24.9 kcal/mol lower in energy than 1_{DFT} .

The exergonic process of going from $\mathbf{S}_{\text{DFT}}^{\text{aceft}}$ to **6** is followed by two energetically similar pathways: simultaneous ligand folding/distortion and deprotonation to generate a neutral Fe(II) ferraaziridinido complex $(3_{\text{DFT}}^{\text{iPrOH}})$ with a barrier of 22.2 kcal/mol $(\mathbf{TS}_{6,3})$; alternatively, deprotonation *without* generation of an iron–alkyl bond reduces the metal center to form a distorted-square-pyramidal Fe(0) complex $(7_{\text{DFT}}^{\text{PrOH}})$ with a calculated barrier of 21.9 kcal/mol $(\mathbf{TS}_{6,7})$. The activation energy for these transitions differs by only 0.3 kcal/mol, and the free energies of products $3_{\text{DFT}}^{\text{iPrOH}}$ and $7_{\text{DFT}}^{\text{iPOH}}$ are lower than that of $6_{\rm DFT}$ by 8.6 and 5.8 kcal/mol, respectively. The transition-state geometries $TS_{6,3}$ and $TS_{6,7}$ are shown in Figure 5. The major difference between these transition states is the iron–alkoxide distance and the degree of ligand distortion during deprotonation. For $TS_{6,3}$, the alkoxide is further away from iron (Fe- - O = 3.05 Å) than in $TS_{6,7}$, where the Fe–O distance is close (Fe–O = 2.05 Å) and the alkoxide remains trans to the carbonyl (O–Fe–C = 175.8°). Tetradentate PNNP ligands are known to fold to produce cis-octahedral complexes.³⁹ The Fe(0) complex 7, with or without isopropyl alcohol, is proposed on the basis of the low carbonyl stretches in the IR spectrum of the catalytic mixture (vide supra), which will be discussed in the following section.

Dissociation of isopropyl alcohol from the deprotonated ferraziridine complex 3_{DFT}^{iPrOH} leads to 3_{DFT} + acetone + ⁱPrOH (Scheme 4), which has the lowest relative free energy of all the compounds calculated (-37.6 kcal/mol relative to 1_{DFT} + $2^{i}PrO^{-}$) and has been experimentally observed in the presence of more than 2 equiv of base (Figure 3 and Scheme 3). The metrical parameters of 3_{DFT} do not differ much from those of



Figure 6. Energy profile for the compounds shown in Scheme 4 with energies of free isopropoxide (ⁱPrO⁻), isopropyl alcohol (ⁱPrOH), and acetone (acet) used where appropriate. Energies are all calculated relative to **1** and 2 equiv of isopropoxide in isopropyl alcohol. Relative enthalpies are shown in parentheses.

 $2_{\rm DFT}$, but the electronics change dramatically. The relative carbonyl stretch of $2_{\rm DFT}$ is 83 cm⁻¹ lower than that of $3_{\rm DFT}$ in the gas phase, which suggests that iron is very electron rich when the ferraaziridine nitrogen is deprotonated (the difference is 86 cm⁻¹ when solvation effects are incorporated). We rationalize that $2_{\rm DFT}$ is formed by protonation of the tetrahedral nitrogen atom by free isopropyl alcohol, given a modest energy difference of 4.8 kcal/mol between $3_{\rm DFT}$ and $2_{\rm DFT}$.

Reduction to the square-pyramidal Fe(0) complex 7_{DFT} can also be accomplished by ligand "unfolding" of 3_{DFT} with a barrier of 14.6 kcal/mol ($TS_{3,7}$, Figures 5 and 6). The relative free energy of this electron-rich Fe(0) complex is similar to that of 3_{DFT} (1.8 kcal/mol lower) and can also form by simultaneous deprotonation/reduction of 6_{DFT} (vide supra).

All calculations were performed on low-spin iron complexes in the singlet state (S = 0). To account for the possibility of oddelectron intermediates, we also optimized an intermediate spin analogue of $4_{\rm DFT}$ (S = 1, two unpaired electrons; see the Supporting Information). Intermediate-spin $4_{\rm DFT}$ retains a distorted-octahedral geometry but is 10.6 kcal/mol higher in energy than low-spin $4_{\rm DFT}$. Attempts at calculating a high-spin analogue of $4_{\rm DFT}$ resulted in immediate CO loss from the coordination sphere. Since the metal–carbonyl bond is clearly intact in compound 2 and its synthesis is reproducible in open and closed systems, we do not think CO dissociation plays a role in its formation. However, decomposition of the metal complex cannot be ruled out if iron adopts a high-spin electron configuration.

Using a CO Scale Factor to Support the Proposed Structures of 3 and 7. Observed metal-carbonyl stretches in our Fe-PNNP infrared spectra are easily identifiable and sensitive to changes in the overall electronic structure. Although there have been studies reporting DFT scale factors^{42,43} for metal carbonyl complexes,^{44,45} they do not report scale factors using the mPW1PW91 functional. Furthermore, the theoretical models of 1_{DFT} and 2_{DFT} are not the same as their experimental analogues. A new CO scale factor was determined using simplified models of 1 and 2, along with simplified models of two other fully characterized iron(II) PNNP complexes, *trans*-(*R*,*R*)-[Fe(CO)(NCMe)(PPh₂CH₂CHNCHPhCHPhNCHC-H₂PPh₂)- $\kappa^4 P$,*N*,*N*,*P*][BPh₄]₂ (8)¹⁹ and *trans*-(*R*,*R*)-[Fe(CO)-(NCMe)(PPh₂C₆H₄CH=N-C₆H₁₀-N=CHC₆H₄PPh₂)- $\kappa^4 P, N, N, P]$ [BF₄]₂ (9)¹⁸ (see the Supporting Information). As for all other complexes, phenyl groups were truncated to hydrogen atoms and anions were removed to reduce computational cost. The experimental carbonyl stretches were then compared with the calculated carbonyl stretches, which resulted in a calculated⁴² CO scale factor of 0.917 ± 0.002.

The square-pyramidal complex $7_{\rm DFT}$ has a calculated carbonyl stretching frequency of 2020 cm⁻¹, which is only 8 cm⁻¹ lower than the calculated CO stretching frequency of complex $3_{\rm DFT}$ (2028 cm⁻¹), indicating electron-rich iron centers in both cases. Applying the CO scale factor to $3_{\rm DFT}$ and $7_{\rm DFT}$ results in predicted experimental CO stretches of 1860 ± 4 and 1852 ± 4 cm⁻¹, respectively (Figure 7). In comparison with the observed transfer



Figure 7. Experimental, calculated, and scaled carbonyl stretches for proposed complexes 3 and 7.

hydrogenation CO stretches of 1870 and 1862 cm⁻¹, we predict that complexes **3** and 7 are responsible for the two experimentally observed carbonyl stretches below 1900 cm⁻¹ in transfer hydrogenation mixtures.

CONCLUSION

We investigated the mechanism of transfer hydrogenation of acetophenone to 1-phenylethanol utilizing *trans*-[Fe(CO)- $(MeCN)(PPh_2C_6H_4CH=NCH_2-)_2-\kappa^4P,N,N,P][BF_4]_2$ (1) as a precatalyst and basic isopropyl alcohol as a hydrogen source. Spectroscopic and computational investigations were performed to determine the structures of any intermediates involved in catalysis. NMR data showed that, during catalysis,

free ligand is observed along with an iron-containing species thought to be the neutral ferraaziridinido complex Fe(CO)- $(PPh_2C_6H_4CH=NCH_2CH_2NCHC_6H_4PPh_2)-\kappa^5P_1N_1C_1N_1P$ (3). This is suggested on the basis of the synthesis, characterization, and reactivity of the unusual ligand-folded ferraaziridine complex $[Fe(CO)(PPh_2C_6H_4CH=NCH_2CH_2NHCH C_6H_4PPh_2$ - $\kappa^5P_1N_1C_1N_1P$ [BF₄] (2). Both of these complexes are mediocre catalysts in comparison with precatalyst 1. Using density functional theory, we proposed thermodynamically favorable mechanisms for the formation of 2_{DFT} and 3_{DFT} that involve simultaneous deprotonation/folding of the ligand arm or deprotonation without formation of an iron-alkyl bond. Infrared spectroscopy showed that, during catalysis, two electron-rich iron species form with CO stretches below 1900 cm⁻¹. On the basis of a calculated CO scale factor and relative free energies, we predict that 2 is easily deprotonated in the presence of excess base to form electron-rich iron complexes 3 and the square-pyramidal Fe(0) complex Fe- $(CO)(PPh_2C_6H_4CH=NCH_2-)_2-\kappa^4P,N,N,P$ (7), which are responsible for the two observed CO stretches below 1900 cm⁻¹ in catalytic mixtures. Some of us provide evidence elsewhere that the actual catalyst in the system is 4 nm Fe(0)nanoparticles coated with chiral ligand.³⁸

COMPUTATIONAL DETAILS

All calculations were performed using Gaussian09⁴⁶ and Gaussian03.⁴⁷ The mPW1PW91 density functional was used for all calculations.^{48,49} Iron was treated with the SDD basis set to include relativistic effective core potentials.⁵⁰ Atoms C, H, N, O, and P were treated with the 6-31++G(d,p) basis set, which includes diffuse⁵¹ and polarization⁵ functions. Unrestricted open-shell calculations of 4_{DFT} showed no evidence of significant spin contamination; therefore, only closed-shell structures were considered. The phenyl substituents on phosphorus atoms were replaced with hydrogen atoms to reduce computational cost. Such simplifications were shown in previous computational studies on iron and ruthenium systems to have no significant effect on the core structures.^{18,53} Lynch and Truhlar have reported that the mPW1PW91 functional is better for the prediction of transition states and energy barriers.⁵⁴ All structures were optimized with solvent correction (2-propanol) using the integral equation IEF-PCM protocol.⁴⁰ Radii and nonelectrostatic terms from the SMD solvation model were also used, which have been reported by Truhlar and coworkers to be more accurate in calculating the solvation free energy of bare ions such as isopropoxide.⁴¹ Ground-state structures of 1_{DFT}, $2_{\text{DFT}},\,3_{\text{DFT}},\,7_{\text{DFT}},\,8_{\text{DFT}},\,\text{and}\,\,9_{\text{DFT}}$ were performed in the gas phase for CO scale factor calculations. Optimized ground states were found to have zero imaginary frequencies, while optimized transition states were found to have one imaginary frequency. Three-dimensional visualizations of the calculated structures were generated by ChemCraft.55

EXPERIMENTAL DETAILS

General Procedures. All preparations and manipulations were carried out under an argon or nitrogen atmosphere using standard Schlenk line and glovebox techniques. Dry, oxygen-free solvents and acetophenone were prepared by distillation from appropriate drying agents and employed throughout. Precatalyst **1** and PNNP ligand were prepared by previously reported methods.²⁴ Mass spectroscopy and elemental analyses (EA) were performed at the University of Toronto, and all samples were handled under argon for the EA. Varian Gemini 400 and 300 MHz spectrometers were employed for recording ¹H (400 and 300 MHz), ¹³C{¹H} (100 and 75 MHz), and ³¹P{¹H} (121 MHz) NMR spectra at ambient temperature. The ¹H and ¹³C NMR spectra were referenced to solvent resonances, as follows: 7.26 and 77.16 ppm for CHCl₃ and CDCl₃, 5.32 and 54.0 ppm for CH₂Cl₂ and CD₂Cl₂, 1.94 and 1.24 ppm for CH₃CN and CD₃CN. The ³¹P NMR spectra were referenced to 85% H₃PO₄ (0 ppm). Gas chromatography

was done on a Perkin-Elmer Clarus 400 chromatograph equipped with a chiral column (CP chirasil-Dex CB 25 m \times 2.5 mm) and autosampling capabilities. Hydrogen gas was used as the mobile phase, and the oven temperature was set at 130 °C. Retention times are 7.58 and 8.03 min for phenylethanol and 4.56 min for acetophenone.

Formation of Oxidized PNNP. Free PNNP ligand (11 mg, 0.018 mmol) was dissolved in 0.6 mL of CDCl₃, an excess of aqueous hydrogen peroxide (H_2O_2 ; 0.05 mL of 30%, 0.6 mmol) was added, and the mixture was stirred at room temperature in air for 30 min. The reaction solution was then transferred to an NMR tube for analysis. ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 33.0 ppm (s), very minor singlets at 32.3 and 36.0 ppm.

Preparation of 2. In a nitrogen-filled glovebox, 3 mL of benzene was added to a solid mixture of 1 (56 mg, 0.093 mmol) and NaiOPr (15 mg, 0.18 mmol). The reaction mixture turned dark brown after ca. 15 min and was stirred for 12 h at ambient temperature. The solution was filtered off and was allowed to slowly evaporate for several days, to give the product as dark brown crystals. Crystals for X-ray analysis were selected directly from this crop. After washing with ether and pentane the pure product was obtained. Yield: 31 mg, 0.06 mmol, 65%. ¹H NMR (400 MHz, CD₃CN): δ 8.76 (d, $J_{H,P}$ = 3.1 Hz, 1 H, CH=N), 8.03 (m, 2 H, Ar), 7.75-6.74 (several m, 22 H, Ph), 6.42 (m, 2 H, Ar), 6.23 (m, 2 H Ar), 4.32 (m, 1 H, CH₂), 4.21 (br s, 1 H, NH), 3.80 (m, 1 H, CH₂), 3.61 (m, 1 H, CH), 2.55 (m, 1 H, CH₂). ³¹P{¹H} NMR (121 MHz, CD₃CN): δ 84.3 (d, $J_{P,P}$ = 43.4 Hz), 70.1 (d, $J_{P,P}$ = 43.3 Hz). ¹³C{¹H} NMR (100 MHz, CD₃CN): δ 213.3 (dd, $J_{C,P} = 3.1$ Hz, $J_{C,P} = 24.2$ Hz, CH=N), 170.0 (d, $J_{C,P} = 4.6$ Hz, Ar), 154.7 (d, $J_{C,P}$ = 32.1 Hz, Ar), 136.9–128.1 (several m, Ar), 70.1 (d, $J_{C,P}$ = 4.5 Hz, CH₂), 68.1 (dd, $J_{C,P}$ = 5.5 Hz, $J_{C,P}$ = 10.8 Hz, CH), 48.6 (d, $J_{C,P} = 1.8 \text{ Hz}$, CH₂). ¹⁹F NMR (CD₃CN): δ 152.3 (s). IR (KBr): ν_{CO} 1940 cm⁻¹. MS (ESI⁺, MeOH): m/z 689.2 for [M – BF₄]⁺. Anal. Calcd for C41H36BF4FeN2OP2·C6H6: C, 65.99; H, 5.30; N, 3.27. Found: C, 65.82; H, 5.30; N, 3.61.

Observation of 3. In a nitrogen-filled glovebox, 3 mL of isopropyl alcohol was added to a solid mixture of **2** (25 mg, 0.031 mmol) and KOtBu (5 mg, 0.044 mmol). The reaction mixture turned dark brown immediately and was stirred for 1 h at ambient temperature. The solution was filtered to remove excess base, and NMR and IR measurements of the crude solution were run. ³¹P{¹H} NMR (121 MHz, *i*PrOH, C₆D₆ insert): δ 84.1 (d, *J*_{P,P} = 30.7 Hz), 68.7 (d, *J*_{P,P} = 30.7 Hz). IR (KBr): ν_{CO} 1862 and 1870 cm⁻¹, as well as broad peaks at 1934 and 1957 cm⁻¹.

Transfer Hydrogenation. In a vial containing precatalyst 1 (5 mg, 0.0055 mmol) and KOtBu (5 mg, 0.044 mmol), isopropyl alcohol (6 mL, 78 mmol) and acetophenone (0.35 mL, 3 mmol) were added at room temperature, in an argon-filled glovebox. A dark brown solution was immediately formed, which was stirred vigorously. Samples were taken from the mixture, quenched by exposure to air, and analyzed by gas chromatography. When the samples are exposed to air, the solution turns yellow and the reaction stops immediately. The alcohol/ketone concentration does not change in these solutions, even after several days. All of the catalytic results were reproduced to ensure consistency.

NMR Scale Transfer Hydrogenation. In a vial containing precatalyst 1 (18 mg, 0.020 mmol) and KOtBu (10 mg, 0.088 mmol), isopropyl alcohol (0.6 mL, 7.8 mmol) and acetophenone (0.1 mL, 0.86 mmol) were added at room temperature, in an argon-filled glovebox. Immediately a dark brown solution was formed, which was stirred vigorously for 10 min before being transferred to a J. Young NMR tube containing a D_2O insert, and ${}^{31}P{}^{1}H{}$ NMR measurements were run immediately on a Varian 400 MHz spectrometer. All results were reproduced to ensure consistency.

Mass Balance Experiments. Prior to addition of solvent, OPPh₃ (11 mg, 0.040 mmol) was added to a vial prepared as outlined above. The dark brown solution was stirred for 10 min and transferred to a J. Young NMR tube containing a D₂O insert. ³¹P NMR was run immediately on a Varian 400 MHz spectrometer, with a 90° pulse, decoupled NOE, and a relaxation decay of 3.7 s. Parameters were optimized by determining the T_1 relaxation times of all species present in the ³¹P NMR spectrum. All results were reproduced to ensure consistency.

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ASSOCIATED CONTENT

S Supporting Information

Figures, tables, and CIF files giving NMR and IR spectra, details of mass balance experiments, details of the DFT calculations, and crystal structure data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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