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# Iron-Catalyzed Homogeneous Hydrogenation of Alkenes under Mild Conditions by a Stepwise, Bifunctional Mechanism

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ABSTRACT. Hydrogenation of alkenes containing polarized C=C double bonds has been achieved with iron-based homogeneous catalysts bearing a bis(phosphino)amine pincer ligand.  $(PNHP^{iPr})Fe(H)_2(CO), PNHP^{iPr} =$ mol% standard catalytic conditions (5 Under NH(CH<sub>2</sub>CH<sub>2</sub>P*i*Pr<sub>2</sub>)<sub>2</sub>), 23 °C , 1 atm H<sub>2</sub>), styrene derivatives containing electron-withdrawing para-substituents reacted much faster than both the parent styrene and substituted styrenes with an electron-donating group. Selective hydrogenation of C=C double bonds occurs in the presence of other reducible functionalities such as  $-CO_2Me$ , -CN, and N-heterocycles. For the  $\alpha,\beta$ unsaturated ketone benzalacetone, both C=C and C=O bonds have been reduced in the final product, but NMR analysis at the initial stage of catalysis demonstrates that the C=O bond is reduced much more rapidly than the C=C bond. Although Hanson and coworkers have proposed a non-bifunctional alkene hydrogenation mechanism for related nickel and cobalt catalysts, the iron system described here operates via a stepwise metal-ligand cooperative pathway of Fe-H hydride transfer, resulting in an ionic intermediate, followed by N-H proton transfer from the pincer ligand to form the hydrogenated product. Experimental and computational studies indicate that the polarization of the C=C bond is imperative for hydrogenation with this iron catalyst.

#### **1. INTRODUCTION**

The chemistry community has been aiming towards the use of Earth-abundant catalysis in recent years.<sup>1</sup> Although alkene hydrogenation is well-known with Rh,<sup>2</sup> Ir,<sup>3</sup> and Ru<sup>4</sup> catalysts,<sup>5,6</sup> only a handful of catalysts with Earth-abundant, first row metals have been discovered. Notably, the use of Fe,<sup>7</sup> Co,7<sup>89-10</sup> and Ni9<sup>,11</sup> catalysts with pincer supporting ligands have been highly successful in the past few years.6 For example, Peters, *et al.* discovered that the (PBP<sup>tBu</sup>)Co(N)<sub>2</sub> complex (PBP<sup>tBu</sup> = bis(phosphino)boryl with *t*-butyl substituents on the phosphines) can catalyze

hydrogenation of terminal alkenes quantitatively with TOF's of 1000 h<sup>-1</sup>; dimeric  $[(PBP^{Cy})CoH]_2$  catalyzes hydrogenation of terminal and internal olefins, albeit at much slower rates with TOF's from 2.5 to 8 h<sup>-1</sup> (1 atm H<sub>2</sub>, C<sub>6</sub>D<sub>6</sub>, 2 mol% catalyst, 23 °C).9 The Ni analogue of the Peters catalyst forms a monomer which also hydrogenates terminal (TOF = 25 h<sup>-1</sup>) and internal (TOF = 0.6 h<sup>-1</sup>) olefins catalytically (1 atm H<sub>2</sub>, C<sub>6</sub>D<sub>6</sub>, 2 mol% catalyst, 23 °C).9 The Ni-boryl catalyst is more active than Hanson's (PNHP<sup>Cy</sup>)Ni(H)<sup>+</sup> catalyst (PNHP<sup>Cy</sup> = HN(CH<sub>2</sub>CH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>) based on the latter having only 0.2 – 0.4 h<sup>-1</sup> TOF for hydrogenation of terminal alkenes (hydrogenate alkenes via 1,2-insertion of the alkene into the Ni–H bond. Chirik's cobalt-diphosphine catalysts hydrogenate allyl alcohols and other unhindered, activated olefins at 25 °C under 4 atm H<sub>2</sub>.<sup>10</sup> Milstein *et al.* have reported an acridine-based (PNP)Fe catalyst that can partially hydrogenate alkynes to *E*-alkenes.<sup>12</sup>



Figure 1. Examples of bifunctional catalysts with a metal-hydride and ligand-proton.<sup>13,14</sup>

The (PNP<sup>iPr</sup>)Fe(H)(CO) (PNP<sup>iPr</sup> = N(CH<sub>2</sub>CH<sub>2</sub>P*i*Pr<sub>2</sub>)<sub>2</sub>) catalyst (1) can hydrogenate (using 2 in Figure 1) and dehydrogenate CN and CO bonds.<sup>15,16</sup> The latter underwent experimental and computational mechanistic studies to conclude that a bifunctional mechanism with a concerted six-membered cyclic transition state of hydride (Fe–H) and proton (N–H) transfer to the C and O atoms of C=O substrates, respectively, was operating.<sup>16</sup> This metal-ligand cooperativity, yielding a bifunctional hydrogenation mechanism, has been proposed for a number of catalysts. Figure 1 displays a few selected examples, including species **2** formed from the catalyst used in this paper

(1); note that these hydride complexes possess an acidic proton on the supporting ligand. Metalligand cooperativity can occur via a simultaneous (concerted) hydride/proton transfer step or via consecutive steps. Interestingly, DFT calculations of Milstein's *trans*-[Ru(H)<sub>2</sub>(PNN)(CO)] catalyst (PNN = 2-CH<sub>2</sub>NEt<sub>2</sub>-6-CH<sub>2</sub>P*t*Bu<sub>2</sub>-pyridine) for dimethylcarbonate hydrogenation to methanol propose the metal-ligand cooperative pathway to be higher in energy than hydride transfer followed by C–OMe cleavage.<sup>17</sup> In the present work, hydrogenation of polar C=C bonds is investigated under mild conditions with catalyst 1 and the *in situ* formed 2. Non-polarized C=C bonds cannot be hydrogenated by this catalyst. DFT calculations suggest a stepwise, bifunctional mechanism of hydride transfer followed by proton transfer that only occurs for polarized C=C bonds. This stepwise mechanism is in contrast to the concerted hydride/proton transfer to C=O substrates. Experiments and calculations suggest that polarization of the C=C bond is necessary for hydrogenation with this catalyst system.

#### 2. RESULTS AND DISCUSSION

*Hydrogenation of Olefins.* The present investigation was initiated by employing iron complexes **1**, **3**, and **4** as homogeneous catalysts (or catalyst precursors) for the hydrogenation of styrene. At 23 °C under 1 atm of H<sub>2</sub> pressure, styrene was quantitatively hydrogenated to form ethylbenzene with 5 mol% of either catalyst **1** or **3** within a day (Table 1). In the case of the iron complex **3**, a slight excess of KO'Bu (3 equiv. with respect to the iron catalyst) was required to initiate catalysis (entry 2), but it gives results identical to those seen with **1** as catalyst. No catalytic activity was observed in the absence of a base. On the other hand, catalyst **1** did not require any base to carry out the hydrogenation reaction. The iron hydrido-borohydride complex **(4)** was reported to be the best catalyst for ester<sup>18</sup> and nitrile hydrogenation<sup>19</sup> at higher temperatures (100 – 135 °C). When this catalyst was used for the hydrogenation of styrene at





ethylbenzene

H<sub>2</sub> 1 atm

styrene

	$N = F_{e} = CO$ $H$ $(^{i}Pr)_{2}$ $H$ $(^{i}Pr)_{2}$ $1$	H N P H ( <sup>i</sup> Pr) <sub>2</sub> 3	P( <sup>i</sup> Pr) <sub>2</sub> H N -CO N ( <sup>i</sup> F	BH <sub>3</sub> -P( <sup>i</sup> Pr) <sub>2</sub> -Fe-CO P H r) <sub>2</sub> 4	
entry	catalyst (loading)	<i>p</i> H <sub>2</sub> (atm)	time (h)	temp. (°C)	NMR conv. (%)
1	1 (5 mol %)	1	24	23	100
$2^b$	<b>3</b> (5 mol %)	1	24	23	100
	+ KO <sup>t</sup> Bu (15 mol %)				
3 <sup><i>c</i></sup>	<b>3</b> (5 mol %)	1	24	23	0
4	<b>4</b> (5 mol %)	1	24	23	37
5	<b>4</b> (5 mol %)	1	24	100	86
6	1 (2 mol %)	1	48	23	23
7	-	1	24	23	0

<sup>*a*</sup>solvent: ~0.7 mL of  $C_6D_6$ , monitored over time by <sup>1</sup>H NMR spectroscopy; <sup>*b*</sup>solvent: 1 mL of THF; <sup>*c*</sup>no base added.

23 °C (1 atm H<sub>2</sub>), only 37% conversion was achieved after one day. From the current mechanistic understanding of the hydrogenation reactions involving these iron catalysts,<sup>20</sup> it is proposed that complex **1** is one of the active intermediates in all of these reactions. But generating this species from the iron hydrido-borohydride pre-catalyst requires either heating or a BH<sub>3</sub>-trapping reagent like trimethylamine.<sup>21</sup> Therefore, the low catalytic activity of complex **4** is attributed to the lack of BH<sub>3</sub> dissociation at room temperature, so the active iron dihydride catalyst is not formed.

To probe this hypothesis, hydrogenation of styrene was carried out at 100 °C using catalyst 4; in this case a much higher conversion was achieved after one day (86%, entry 5). From these catalytic studies, it was evident that complex 1 was the best catalyst for the hydrogenation of styrene under these conditions. However, when the catalyst loading of 1 was reduced from 5 mol% to 2 mol%, only 23% of styrene was converted to ethylbenzene after two days, suggesting that the reaction has a strong dependence on the concentration of the iron catalyst. A control experiment in the absence of an iron catalyst did not produce any ethylbenzene indicating that this reaction is indeed catalytic in iron. The solution stayed homogeneous during the course of the reaction with no visible particles being formed. A mercury poisoning test did not affect the hydrogenation activity.<sup>22,23</sup> However, mercury does not always inhibit iron nanoparticle catalysts.<sup>24</sup> We also observed reproducible kinetic behavior with no induction period for this catalytic process which is supportive of the homogeneous nature of the catalyst.<sup>22b</sup> Furthermore, a successive addition experiment was also performed to reinforce the homogeneity of the catalytic system.<sup>25</sup>

Next, the alkene substrate scope was expanded to investigate the electronic and steric factors involved in this reaction (Table 2). Under standard catalytic conditions (5 mol% 1, 23 °C, 1 atm  $H_2$ ), styrene derivatives containing electron-withdrawing substituents reacted much faster than both the parent styrene and styrenes with electron-donating groups. For example, 4-(CF<sub>3</sub>)-styrene was quantitatively hydrogenated in 1.5 hours, but styrene and 4-(CH<sub>3</sub>)-styrene were completed in 24 h and 48 h, respectively. For an even more electron rich substrate, 4-(OCH<sub>3</sub>)-styrene, no hydrogenation product was formed at 23 °C and a higher temperature (60 °C) and a much longer reaction time of 168 h were required to achieve full conversion (entry 3). These results suggest that the hydrogenation reactions are strongly dependent on the electronic

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entry	substrate	product	time (h)	temperature	NMR conv. (%)
1			24	23 °C	100
2			48	23 °C	96
3	MeO	MeO	168	60 °C	100
4	F <sub>3</sub> C	F <sub>3</sub> C	0.3	23 °C	100
5	MeO <sub>2</sub> C	MeO <sub>2</sub> C	0.7	23 °C	100
6	NC	NC	53	23 °C	30
7	N	N	1	23 °C	100
8	Ph Ph	Ph Ph	240	60 °C	100
9	OMe	OMe	0.8	23 °C	100
10			144	80 °C	44
11		OH	2.5 <sup>b</sup>	23 °C	100

## **Table 2.** Iron-catalyzed hydrogenation of alkenes.<sup>*a*</sup>

<sup>*a*</sup> Conditions: 0.7 mL of C<sub>6</sub>D<sub>6</sub>; [1] = 0.014 M; [alkene] = 0.285 M; catalytic reactions were performed in a J. Young NMR tube with a large head–space (~9 mL).

<sup>b</sup> Time to reduce both alkene and ketone.

properties of the substrate, i.e., the *polarity* of the C=C double bond. DFT calculations, reported below, will investigate the electronic effect of the substrates on the rate of hydrogenation. These

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 hydrogenation reactions were found to follow good first order kinetics ( $R^2 > 0.997$ ), with rate constants of 8.31(5) x 10<sup>-5</sup>, 2.18(7) x 10<sup>-5</sup>, and 8.8(9) x 10<sup>-4</sup> s<sup>-1</sup> for styrene, 4-methylstyrene, and 4-trifluoromethylstyrene, respectively (Figure 2).



**Figure 2.** Kinetic traces for the hydrogenation of styrenes at 23 °C by 1.  $\bullet$  = 4-CF<sub>3</sub>-styrene;  $\blacksquare$  = styrene;  $\blacklozenge$  = 4-Me-styrene. Conditions: [1] = 0.014 M, [styrene] = 0.285 M, 1 atm of H<sub>2</sub>, 0.7 mL C<sub>6</sub>D<sub>6</sub>, 23 °C. Lines are first order fits.

The rate of hydrogenation was increased for 4-(CO<sub>2</sub>Me)-styrene, consistent with rate effects of other electron-withdrawing *para*-substituents (entry 5, Table 2). Notably, under 1 atm of H<sub>2</sub> pressure and at room temperature, hydrogenation of the C=C double bond occurred in a *chemoselective* fashion as the ester functionality remained intact after the reaction.<sup>18a</sup> Similarly, methyl methacrylate, a non-benzylic alkene containing a polar ester group adjacent to the C=C double bond, readily yielded the desired hydrogenation product methyl isobutyrate, keeping the ester moiety intact (entry 9). Although the –CN group is generally considered to be an electron-withdrawing group, *p*-CN-styrene reacted much more sluggishly and only reached ~30% conversion after 53 hours. As mentioned earlier, Beller and coworkers have reported nitrile hydrogenation product was not observed under these mild reaction conditions with 1. The slow

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rate of hydrogenation observed in the present case could be a result of catalyst inhibition by substrate coordination to the five-coordinate iron center in **1**. In fact, when a stoichiometric amount of *p*-(CN)-styrene was added to a C<sub>6</sub>D<sub>6</sub> solution of **1**, there was significant broadening of the resonances of the vinyl group of the styrene, suggesting an interaction between the iron complex and the substrate double bond (eq 1). An IR spectrum of a similar reaction in THF showed a CN stretch that was identical to that of free 4-cyanostyrene in THF (2228 cm<sup>-1</sup>), arguing against coordination through the nitrile. Based on these results, we conclude that under catalytic conditions of excess *p*-(CN)-styrene substrate, the substrate can coordinate to (PNP<sup>iPr</sup>)Fe(CO)(H) through the double bond and thereby inhibit catalysis. This effect is not seen with excess styrene, which is likely due to the olefin of *p*-(CN)-styrene being a better  $\pi$ -acceptor ligand than styrene.



The pyridine analogue of styrene, 2-vinylpyridine, was also hydrogenated at a much faster rate than styrene, affording 2-ethylpyridine quantitatively within 1 h (entry 7, Table 2). It is thought that the presence of the electronegative nitrogen atom adjacent to the C=C double bond in 2-vinylpyridine increases the polarity of the alkene C=C bond and therefore the reaction proceeds with a faster rate than styrene. Notably, no product resulting from the hydrogenation of the pyridine ring was detected under these conditions even though **2** has been shown to hydrogenate 2,6-dimethylpyridine (3 mol% **3**, 10 mol% KO<sup>t</sup>Bu, 80 °C, 10 atm H<sub>2</sub>).<sup>15</sup> Remarkably, catalytic

hydrogenation of 2-vinylpyridine could also be performed under *neat conditions* affording 100% conversion in four hours.

If only electronic effects dictate the outcome of the hydrogenation activity, then installing a second phenyl ring at the  $\alpha$ -position of styrene should in theory increase the rate of reaction. However, for such a substrate, no reactivity was observed at room temperature and in fact it reacted much more slowly even at a higher temperature (entry 8). We rationalize this behavior on the basis of the steric crowding imposed by the second phenyl ring at the alkene moiety which likely increases the related kinetic barrier. An internal alkene,  $\beta$ -methylstyrene, also reacted slowly possibly for both steric and electronic reasons.

Although several research groups have independently performed hydrogenation of carbonyl groups utilizing these iron catalysts,<sup>16,18,19</sup> it was of interest to examine a substrate, benzalacetone (entry 11, Table 2), which contains both C=O and C=C bonds to determine if the hydrogenation reaction would proceed in a chemoselective fashion at room temperature (23 °C) and low hydrogen pressure (1 atm) in benzene. Interestingly, when benzalacetone was subjected to catalysis, a mixture containing the starting material (**a**), two partially reduced species (**b** and **c**), and the fully hydrogenated species (**d**) resulted in a relative ratio of 1:1:10:7 after 15 min with an overall ~95% conversion of the reactant (Figure 3). With a longer reaction time, **b** and **c** both converted to the fully reduced species **d**. Although both C=O and C=C bonds are ultimately hydrogenated by this iron catalyst, the product distribution at the early stage of the reaction suggests that the rate of hydrogenation of the C=C bond is much slower than that of the C=O bond.



Figure 3. Iron-catalyzed hydrogenation of benzalacetone at different times. Conditions: [1] = 0.014 M, [benzalacetone] = 0.285 M, 1 atm of H<sub>2</sub>, 0.7 mL C<sub>6</sub>D<sub>6</sub>, 23 °C.

Under 1 atm of H<sub>2</sub> pressure, hydrogenation of non-polar aliphatic alkenes such as 1-hexene and tert-butylethylene did not occur in the presence of catalyst **1** (Figure 4). Attempts to hydrogenate these substrates even under a higher H<sub>2</sub> pressure (5 atm) and higher temperatures (100 - 150 °C) were not successful. Nonetheless, these results are consistent with our hypothesis that the C=C double bond needs to be sufficiently polarized in order to interact with the active iron dihydride complex. DFT calculations support the hypothesis that the activation barriers of non-polarized (ethylene) C=C bonds are higher (*vide infra*). In the case of 1-hexene, products resulting from the isomerization of the terminal C=C double bond were not observed. Aliphatic alkenes containing functional groups such as –OH and –CO<sub>2</sub>H were also not viable substrates as these groups reacted with the five-coordinate iron center present in complex **1** to generate the catalytically inactive iron alkoxide or carboxylate complexes, respectively (Figure 4).<sup>26</sup> Although Hazari, Schneider, and Bernskoetter have reported increased rates for iron-catalyzed dehydrogenation and hydrogenation reactions in the presence of a Lewis acidic co-catalyst such

as  $LiBF_4$  or  $LiOTf^{27}$  such effects were not observed in the alkene hydrogenation reaction with iron catalyst **1**.



Figure 4. Incompatible hydrogenation substrates.

Hanson and coworkers have reported nickel<sup>11</sup> and cobalt<sup>28</sup> catalysts, supported by a similar  $PNHP^{Cy}$  ligand (Cy = cyclohexyl), for alkene hydrogenation. Interestingly, for both the nickel and cobalt-based systems, hydrogenation of alkenes proceeded smoothly without the involvement of the protic N-H moiety in the pincer ligand indicating that the PNHP<sup>Cy</sup> ligand is not participating in these hydrogenation reactions. For the nickel system, migratory insertion of 1-octene into the Ni-H bond generated the corresponding linear nickel-octyl species, which was isolated and characterized.<sup>11</sup> The insertion proved to be reversible as the parent nickel hydride complex reformed upon heating the nickel-octyl complex to 80 °C. The nickel hydride species, in the absence of H<sub>2</sub>, also catalyzed isomerization of 1-octene to form internal octene isomers at 80 °C. In the case of the cobalt system, a similar alkene isomerization activity was observed in the absence of dihydrogen; however, formation of the corresponding cobalt alkyl species via the insertion of a C=C double bond into a Co-H bond was not experimentally observed. As the N-H moiety on the pincer ligand is not involved in the hydrogenation of alkenes, a direct hydrogenolysis of nickel or cobalt alkyl intermediates was proposed to release the product during catalysis.

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Scheme 1. Experiments to support a metal-ligand cooperative pathway.

In contrast to the aforementioned cobalt and nickel complexes, when complex 1 or *in-situ* generated iron dihydride complex (2) was treated with 1-hexene (1 : 5 ratio), neither an iron alkyl intermediate nor the internal hexene isomers were formed (eq 3, Scheme 1). When a stoichiometric reaction between 1 and styrene was performed, no insertion product was generated at room temperature (eq 2). Chemical shifts associated with 1 and styrene did not change, indicating there is minimal interaction between these two species. On the other hand, the reaction between 2 and styrene quantitatively produced ethyl benzene and 1 at room temperature (eq 4). No iron alkyl species was detected during this reaction (Scheme 1). These results seem to indicate that the mechanism of the C=C double bond hydrogenation using the iron system differs from the nickel and cobalt systems discussed above. To test if the iron system operates via a metal-ligand cooperative pathway, we synthesized the related PN*Me*P derivative of one of the active iron catalysts (4-Me)<sup>18b,29</sup> and investigated its catalytic activity. 4-

Me turned out to be catalytically inactive in the hydrogenation of styrene under 1 atm of  $H_2$  pressure at 100 °C (eq 5, Scheme 1).<sup>30</sup> No ethyl benzene was formed after 24 h. This result is in contrast to what has been previously observed for the related nickel and cobalt systems and implies that these iron catalysts act in a bifunctional pathway even for a much less-polar C=C double bond as compared to the more highly polarized C=O and C=N bonds. Further discussion of this point is presented below in the context of DFT simulations.

DFT Calculations of the Mechanism. The mechanism of styrene hydrogenation with the truncated complex  $(PNP^{Me}-H)Fe(H)_2(CO)$  (<sup>(PMe2)</sup>2 -with methyl substituents on the phosphines) was modeled using a DFT level of theory similar to that used in simulating the mechanism of alcohol dehydrogenation by Chakraborty and co-workers.<sup>16</sup> Truncation of the ligand is not expected to have a substantial influence on the activation barriers due to minimal steric hindrance between the flanking phosphine substituents and the  $\beta$ -CH<sub>2</sub> of the styrene substrates. Previous mechanistic studies of the hydrogenation and dehydrogenation of substrates with complex  $(^{PMe2})_2$  were proposed to occur via a concerted, bifunctional  $H^-/H^+$  transfer mechanism through a 6-membered transition state, *i.e.*, a Novori-style H<sub>2</sub> transition state.4 Interestingly, a transition state for the concerted transfer of the NH-proton and FeH-hydride for styrene could not be found in the present case. Instead, a transition state for Fe-H transfer ("hydride transfer") to the  $\beta$ -carbon of the substrate was found (**TS-A**) with an imaginary vibrational mode at 545i cm<sup>-1</sup> corresponding to the Fe-H bond breaking and the C-H bond forming. The hydride transfer activation barrier in benzene is  $\Delta G^{\ddagger} = 14.1$  kcal/mol and  $\Delta H^{\ddagger} = 0.9$  kcal/mol. An intrinsic reaction coordinate (IRC) calculation of this transition state revealed formation of an ionic intermediate complex (int-C) with a sigma-complexed C-H bond (C-H = 1.22 Å). The intermediate is endergonic relative to the starting materials by only 13.3 kcal/mol in free energy.

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The separation of these charged species is highly endergonic in benzene at  $\Delta G = 44.7$  kcal/mol  $(\Delta H = 58.4 \text{ kcal/mol})$ . Note that in continuum THF solvent, the separation of charged species is also endergonic, but much less so than calculated in benzene,  $\Delta G = 15.4$  kcal/mol ( $\Delta H = 29.1$ kcal/mol) for THF. After int-C, the transition state for the N-H proton transfer (TS-B) was located with a single imaginary vibrational mode at 792i cm<sup>-1</sup> corresponding to N-H bond breaking and C–H bond forming. This barrier is  $\Delta G^{\ddagger} = 14.0 \text{ kcal/mol} (\Delta H^{\ddagger} = 0.5 \text{ kcal/mol})$  from the starting materials, and thus 1.0 kcal/mol *lower* in energy than int-C. An IRC calculation indicated that this transition state connects int-C to  $(PMe^2)$ 1 + ethylbenzene. The stability of the wavefunction of each complex was checked to ensure it is a true minimum energy solution. The present result indicates that the potential energy surface for proton transfer is very flat and that although the bifunctional hydride/proton transfer occurs through a calculated stepwise mechanism, the second step is facile, essentially making this an asynchronous ionic hydrogenation (Figure 5).<sup>31</sup> With an electron withdrawing *para*-NO<sub>2</sub> substituent on styrene, the PES (Figure S1b) becomes less shallow with a small barrier to proton transfer of  $\Delta G^{\ddagger} = 3.6$ kcal/mol ( $\Delta H^{\ddagger} = -3.2$  kcal/mol). With an electron donating *para*-NMe<sub>2</sub> substituent on styrene, the barrier to proton transfer (Figure S1a) becomes even more endergonic from the ionic intermediate,  $\Delta G^{\ddagger} = -1.3$  kcal/mol ( $\Delta H^{\ddagger} = -1.9$  kcal/mol). Comparing the relative energies of the ionic intermediates to the hydride and proton transfer transition states suggests that the ionic intermediate becomes less stable (increases in free energy) with electron donating substituents on the *para* position of the styrene phenyl moiety.

![](_page_16_Figure_2.jpeg)

**Figure 5.** Calculated potential energy diagram for the hydrogenation of styrene in benzene (black) and THF (red) by <sup>(PMe2)</sup>2. Free energies and (enthalpies) are given in kcal/mol at STP.

Table 3 presents the calculated barriers for hydride transfer from  $(PMe^2)^2$  to *para*-X-styrene substrates where X = NMe<sub>2</sub>, OMe, Me, H, CF<sub>3</sub>, CN, and NO<sub>2</sub>. The transition state structure of hydride transfer significantly changes with the electronic character of the styrene substrate. As the *para*-substituent becomes more electron withdrawing, the FeH···C<sub>β</sub> and NH···C<sub>α</sub> distances increase, thereby yielding even earlier transition states (Figure 6). This indicates that the more polarized the C=C bond, the earlier the TS, and the lower the activation barrier for hydrogenation. The Hammett plot in Figure 7 shows a strong correlation between the electronic influence of the X-substituent and the rate where the calculated  $\rho = 3.00$  in the gas-phase,  $\rho =$ 3.13 in benzene, and  $\rho = 3.65$  in THF. Overall, hydrogenation activation barriers decreased markedly as the substituent became more electron withdrawing, which is consistent with experimental results. The increase in polarity of the solvent increases the influence of the *para*substituent because of the significant electronic charge buildup present in the transition state. For example, the activation barriers in benzene ( $\varepsilon = 2.27$ ) are less than those in THF ( $\varepsilon = 7.43$ ) by *ca*.

2 kcal/mol. The increase in activation barrier in a more polar solvent may be due to the early transition state of hydride transfer. The  $\beta$ -carbon of styrene must be polarized to have significant partial positive charge for the hydride to transfer. This partial positive site may be stabilized by the polar, THF solvent, thus decreasing the carbon's electrophilicity and increasing the activation barrier for hydride transfer. This conclusion was also seen experimentally. Side-by-side reaction of 1 with styrene and H<sub>2</sub> (1 atm) in C<sub>6</sub>D<sub>6</sub> vs. THF- $d_8$  were monitored by <sup>1</sup>H NMR spectroscopy at 23 °C. The first order rate constants were 9.6 (3) x  $10^{-5}$  s<sup>-1</sup> and 4.4 (1) x  $10^{-5}$  s<sup>-1</sup>, respectively (see Supporting Information).

Table 3. Calculated activation parameters for hydrogenation of *p*-X-styrene substrates in kcal/mol.

$\sigma_p^{32}$	Х	$\Delta G^{\ddagger} (\Delta H^{\ddagger}),$ gas	$\Delta G^{\ddagger} (\Delta H^{\ddagger}),$ THF	$\Delta G^{\ddagger} (\Delta H^{\ddagger}),$ benzene
-0.83	NMe <sub>2</sub>	14.0 (0.3)	19.5 (5.8)	17.5 (3.8)
-0.27	OMe	12.6 (-0.6)	17.6 (4.4)	15.8 (2.6)
-0.17	Me	11.4 (-1.5)	16.4 (3.4)	14.6 (1.6)
0	Н	11.2 (-2.1)	15.9 (-2.3)	14.1 (0.9)
+0.54	CF <sub>3</sub>	9.4 (-3.9)	14.0 (0.7)	12.4 (-1.0)
+0.66	CN	8.1 (-4.8)	12.3 (-0.6)	12.1 (-0.8)
+0.78	NO <sub>2</sub>	7.2 (-5.7)	11.1 (-1.8)	9.7 (-3.1)

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![](_page_18_Figure_2.jpeg)

**Figure 6.** Plot of C···H distances in hydride transfer transition states between the alpha and beta carbon of *p*-X-styrene substrates and the N–H proton and Fe–H hydride of  $(^{PMe2})_2$ , respectively.

![](_page_18_Figure_4.jpeg)

Figure 7. Calculated Hammett plot in gas-phase (black, y = 3.00x + 0.17), benzene (blue, y = 3.13x + 0.06), and THF (red, y = 3.65x + 0.10).

The present calculations indicate that the polarizability of the C=C bond significantly influences the activation barrier. Therefore, it is of interest to ask, why doesn't **2** hydrogenate *less* polarized C=C bonds, *e.g.*, that of ethylene or 1-hexene? The hydrogenation of ethylene was calculated to have an activation barrier of  $\Delta G^{\ddagger} = 19.1$  kcal/mol ( $\Delta H^{\ddagger} = 7.4$  kcal/mol) in continuum benzene solvent with an imaginary frequency of 456i cm<sup>-1</sup>. It is interesting that this barrier is only 5 kcal/mol higher in free energy than the barrier to hydrogenation of styrene, yet aliphatic mono-olefins cannot be hydrogenated. Even more interesting, the IRC calculation of the ethylene hydrogenation transition state revealed a *concerted* transfer of the hydride and proton,

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suggesting a different mechanism for ethylene hydrogenation than for the styrene hydrogenations. Based on these differences between ethylene and styrene hydrogenation, we propose that C=C hydrogenation only occurs when there is sufficient polarization of the double bond to permit the stepwise hydrogenation by hydride transfer followed by proton transfer. Calculations of the hydrogenation of O=C bonds show a hydrogen bonded adduct between  $O=CH_2$  and  $(PNP^{Me}-H)Fe(H)_2(CO)$  only 1.1 kcal/mol lower in free energy than the concerted hydrogenation TS.<sup>16</sup> For Noyori's catalyst, hydrogen bonded adducts between X=C (X = N, O) and the model complex ( $C_6H_6$ )Ru(H)(H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>O) are more stable than the starting materials.<sup>13</sup> This initial outer-sphere interaction between the trans-dihydride complex and the X=C substrate may be the first necessary step for hydrogenation to proceed.

## **3. CONCLUSIONS**

In summary, we have shown that the five-coordinate iron complex (1) bearing a bis(phosphino)amine ligand can effectively catalyze the base-free hydrogenation of a variety of alkenes under mild conditions. Polarity of the C=C double bond seems to be critical and therefore a large electronic influence on the rate of the hydrogenation of different styrene derivatives was observed. This catalytic system is tolerant of other reducible functional groups such as  $-CO_2Me$ , -CN, *N*-heterocycle and the catalytic reaction can be performed under solvent-free conditions. Unlike the similar nickel and cobalt systems developed by Hanson and coworkers,<sup>11,28</sup> the iron catalyst described in this report operates via a metal-ligand cooperative pathway via a stepwise hydride transfer then proton transfer mechanism.

#### **4. EXPERIMENTAL DETAILS**

General Experimental Information. Unless otherwise noted, all of the organometallic compounds were prepared and handled under a nitrogen atmosphere using standard Schlenk and

glovebox techniques. Dry and oxygen-free solvents (pentane) were collected from an Innovative Technology PS-MD-6 solvent purification system and used throughout the experiments. THF, toluene, C<sub>6</sub>D<sub>6</sub>, and THF-*d*<sub>8</sub> were vacuum distilled from purple solutions of Na and benzophenone under a nitrogen atmosphere. All other commercially available chemicals were used as received. <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra were recorded on a Bruker Avance-400 MHZ or Avance-500 MHz spectrometers. Chemical shift values in <sup>1</sup>H NMR spectra were referenced internally to the residual solvent resonances. <sup>31</sup>P NMR spectra were referenced externally to 85% H<sub>3</sub>PO<sub>4</sub> (0 ppm). [PNP<sup>iPr</sup>]Fe(H)(CO) (1), [PNHP<sup>iPr</sup>]Fe(H)(CO)Br (3), [PNHP<sup>iPr</sup>]Fe(H)(CO)(HBH<sub>3</sub>) (4), and [PNMeP<sup>iPr</sup>]Fe(H)(CO)(HBH<sub>3</sub>) (4-Me) were prepared according to previously published procedures.<sup>18a,18b,33</sup>

General Procedure for the Hydrogenation of Alkenes. In a typical catalytic experiment, complex 1 (4 mg, 10  $\mu$ mol), a substrate (0.2 mmol), and 0.7 mL of C<sub>6</sub>D<sub>6</sub> were placed in a J. Young NMR tube adapted with a 9 mL cylindrical bulb just below the valve. Before passing H<sub>2</sub> into this reaction mixture, a <sup>1</sup>H NMR spectrum was recorded. Then the NMR tube was thoroughly degassed by performing three freeze-pump-thaw cycles and 1 atm of H<sub>2</sub> was introduced. The resulting solution was mixed either at 23 °C or at a higher temperature and the progress of the reaction was monitored periodically by <sup>1</sup>H NMR spectroscopy. The percentage conversion values were obtained from the relative <sup>1</sup>H NMR integrations of the reactants and products.

Stoichiometric Reaction between Complex 1 and Styrene. In a glovebox, a J. Young NMR tube was charged with complex 1 (8 mg, 20  $\mu$ mol), styrene (2.3  $\mu$ L, 20  $\mu$ mol) and 0.7 mL of C<sub>6</sub>D<sub>6</sub>. The resonances associated with the iron complex and styrene did not change at all indicating that there is no molecular interaction between these two species at room temperature.

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Stoichiometric Reaction between Complex 1 and 4-Cyanostyrene. 10 mg (26  $\mu$ mol) of complex 1 was introduced into a J-Young tube. 3.3 mg (0.11 mmol) 4-cyanostyrene was diluted in 0.5ml C<sub>6</sub>D<sub>6</sub> in a small vial, then this solution was added to the J-Young tube. About 0.5 mL C<sub>6</sub>D<sub>6</sub> was added which was used to wash the vial contents into the J-young tube. A <sup>1</sup>H NMR spectrum showed that the olefinic resonances of the substrate broadened substantially (See Supporting Information).

Side-by-side Reaction of 1 with Cyanostyrene in C<sub>6</sub>D<sub>6</sub> and THF-*d*<sub>8</sub>. 4 mg (12.3 µmol) of 1 was measured in a vial. C<sub>6</sub>D<sub>6</sub> was used to dissolve the catalyst and wash the vial contents into a J-Young NMR tube. The total volume of C<sub>6</sub>D<sub>6</sub> was 0.7 mL. 23.5 µL (0.205 mmol) styrene was added and the sample placed under 1 atm H<sub>2</sub> following freeze-pump-thaw degassing. The progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy. A similar sample was prepared using 0.75 mL THF-*d*<sub>8</sub>, 4.3 mg (11.0 µmol) **1**, and 25.3 µL (0.221 mmol) styrene and monitored by <sup>1</sup>H NMR spectroscopy. The samples were slowly rotated to invert the sample and mix the liquid with the H<sub>2</sub> gas at 23 °C. The rate of reaction was monitored by <sup>1</sup>H NMR spectroscopy.

Stoichiometric Reaction between the Iron Dihydride Species and Styrene. H<sub>2</sub> (1 atm) was passed to a J. Young NMR tube containing a red C<sub>6</sub>D<sub>6</sub> solution of complex 1 (8 mg, 20  $\mu$ mol). The formation of the *trans*-Fe(H)<sub>2</sub> and *cis*-Fe(H)<sub>2</sub> (62 : 38) was supported by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and the color of the solution turned yellow. To this solution, styrene (2.3  $\mu$ L, 20  $\mu$ mol) was quickly added via a syringe and the resulting mixture was mixed at 23 °C. Over a period of 14 h, the color of the yellow solution changed to orange and <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra recorded at this point showed a mixture containing ethyl benzene, 1, and iron dihydride species. Styrene was completely consumed at this point.

> Iron-Catalyzed Hydrogenation of 2-vinylpyridine under Neat Conditions. In a glovebox, complex 1 (4 mg, 10  $\mu$ mol) and 2-vinylpyridine (21.6  $\mu$ L, 0.2 mmol) were placed in a J. Young NMR tube. H<sub>2</sub> (1 atm) was introduced to this reaction mixture after performing freeze-pumpthaw cycles. The resulting solution was mixed at 23 °C for 4 h, ~0.6 mL of C<sub>6</sub>D<sub>6</sub> was added, and a <sup>1</sup>H NMR spectrum was recorded to calculate the percent conversion. Quantitative conversion of 2-vinylpyridine to 2-ethylpyridine was observed under these conditions.

> Isomerization of 1-Hexene. In a glovebox, complex 1 (4 mg, 10  $\mu$ mol) or in-situ formed 2 (10  $\mu$ mol), 1-hexene (0.2 mmol, 24.8  $\mu$ L), and 0.7 mL of C<sub>6</sub>D<sub>6</sub> were placed in a J. Young NMR tube equipped with a Teflon stopcock. The reaction mixture was heated to 60 °C for 1 day and monitored by <sup>1</sup>H NMR spectroscopy. No isomerization reaction leading to the formation of internal isomers was observed during this time period.

**Computational Details.** All calculations were performed using Gaussian09<sup>34</sup> using a DFT level of theory similar to that used in calculating the mechanism of alcohol dehydrogenation.<sup>16</sup> Geometry optimizations were performed in the gas-phase with the B3LYP functional and def2-SVP basis set and enthalpy and free energy corrections were obtained at 298 K using unscaled vibrational frequencies. Single point calculations were performed on the gas-phase optimized structure with the B3PW91/def2-QZVPP level of theory including the GD3 parameters for empirical dispersion. Solvent corrections were performed at optimized stationary points (B3PW91/def2-QZVPP) with the SMD solvent model<sup>35</sup> for benzene ( $\varepsilon = 2.3$ ) and tetrahydrofuran ( $\varepsilon = 7.4$ ). Free energies are reported in kcal/mol at STP unless otherwise noted. See Supporting Information for a sample input file.

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## ASSOCIATED CONTENT

**Supporting Information**. Spectroscopic data for reactions are included. Kinetic data and fits, and xyz coordinates of calculated structures with single point energies (in Hartrees) and free energy and enthalpy corrections. This material is available free of charge via the internet at http://pubs.acs.org.

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## Notes

The authors declare no competing financial interest.

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