# ORGANOMETALLICS

# Iron Hydride Complexes Bearing Phosphinite-Based Pincer Ligands: Synthesis, Reactivity, and Catalytic Application in Hydrosilylation Reactions

Papri Bhattacharya, Jeanette A. Krause, and Hairong Guan\*

Department of Chemistry, University of Cincinnati, P.O. Box 210172, Cincinnati, Ohio 45221-0172, United States

Supporting Information

**ABSTRACT:** Treatment of resorcinol-derived bis(phosphinite) ligands 1,3-(R<sub>2</sub>PO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (R = <sup>i</sup>Pr and Ph) with Fe(PMe<sub>3</sub>)<sub>4</sub> furnishes iron POCOP-pincer hydride complexes [2,6-(R<sub>2</sub>PO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]Fe(H)(PMe<sub>3</sub>)<sub>2</sub> (R = <sup>i</sup>Pr, 1a; R = Ph, 1b) with two PMe<sub>3</sub> *cis* to each other. The isopropyl complex 1a undergoes ligand substitution upon mixing with CO to give [2,6-(<sup>i</sup>Pr<sub>2</sub>PO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]Fe(H)(PMe<sub>3</sub>)(CO). The kinetic product (2a) of this process contains a CO ligand *trans* to the hydride, whereas the thermodynamic product (2a') has a CO ligand *cis* to the hydride. The displacement of PMe<sub>3</sub> in 2a by



CO takes place at an elevated temperature, resulting in the formation of  $[2,6-({}^{i}Pr_{2}PO)_{2}C_{6}H_{3}]Fe(H)(CO)_{2}$  (3a). These new iron POCOP-pincer hydride complexes catalyze the hydrosilylation of aldehydes and ketones with different functional groups, and 1a is the most efficient catalyst for this process. Isotopic labeling experiments rule out the hydride ligand being directly involved in the reduction. The hydrosilylation reactions are more likely to proceed via the activation of silanes or carbonyl substrates after ligand (PMe<sub>3</sub>, or CO in the case of 3a) dissociation from the iron center.

## ■ INTRODUCTION

Hydrido complexes of iron are fundamentally important for their crucial roles in a wide variety of catalytic processes.<sup>1</sup> Studies on synthetic iron hydride complexes have shed light on the mechanisms by which nitrogenase and hydrogenase enzymes function.<sup>2,3</sup> In homogeneous catalysis, iron hydride species are often invoked as key intermediates in iron-catalyzed reactions.<sup>4</sup> Recent efforts have been made to elucidate structure—reactivity relationship of *well-defined* iron hydride complexes with the objective to provide mechanistic bases for the rational design of iron catalysis.<sup>5</sup> Meanwhile, several well-characterized iron hydride complexes have been directly employed as the catalysts for a number of reactions.<sup>6</sup>

Transition metal complexes with pincer-type ligands, especially those containing precious metals, have shown high reactivity for both stoichiometric bond activations and catalytic transformations.<sup>7</sup> One of the new focuses in this research area has been placed on the chemistry of 3d metals, among which iron is particularly attractive due to its relatively low cost and toxicity.<sup>8</sup> Although various iron compounds bearing either neutral<sup>9–11</sup> or anionic<sup>12</sup> pincer-type ligands have been synthesized, examples of the corresponding hydrido complexes are scarce in the literature.<sup>10d,f,12a,12i</sup> Of the known iron pincer hydride complexes, only two have been reported to be catalytically active. The first of such compounds is Chirik's (<sup>iPr</sup>PNP)FeH<sub>2</sub>(N<sub>2</sub>) (<sup>iPr</sup>PNP = 2,6-(<sup>i</sup>Pr<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>3</sub>N)), which can be used to catalyze the hydrogenation of olefins.<sup>10d</sup> The second example is Milstein's (<sup>iPr</sup>PNP)FeH(CO)Br, which has been shown

as a very efficient catalyst for the hydrogenation of ketones.<sup>10f</sup> Noticeably, in both cases the iron center is supported by a bis(phosphino)pyridine ligand that is typically synthesized from 2,6-bis(chloromethyl)pyridine and an expensive, pyrophoric secondary phosphine.<sup>13</sup>

Taking into account not only the prices of metals but also the costs of ligand synthesis, we have focused our studies on the catalysis of first-row transition metal complexes with phosphinitebased POCOP-pincer ligands as shown in Figure 1. This specific type of pincer ligands is readily accessible via P–O bond forming reaction of resorcinol or other diols with relatively inexpensive ClPR<sub>2</sub>.<sup>14</sup> The synthesis of POCOP-pincer complexes of nickel, in particular, is also straightforwardly accomplished via cyclometalation of the pincer ligands with simple metal salts such as NiCl<sub>2</sub>. For catalytic applications, we and other groups have demonstrated that these nickel pincer complexes are excellent catalysts for the reduction of carbonyl functionalities,<sup>15</sup> Michael addition of amines and alcohols to acrylonitrile derivatives,14g,k,m Kharasch addition of CCl<sub>4</sub> to alkenes,<sup>14f,g</sup> and C-S cross-coupling reactions.<sup>16</sup> In stark contrast to nickel chemistry, POCOP-pincer complexes of other first-row transition metals are exceedingly rare, largely due to the inability of common metal salts to activate the C-H bonds of the pincer ligands. To date, there are only two established cobalt systems<sup>12i,17</sup> and one iron system;<sup>12i</sup> however,

 Received:
 June 28, 2011

 Published:
 August 08, 2011



Figure 1. Transition metal complexes with POCOP-pincer ligands.

Scheme 1. Synthesis of an Iron Hydride Complex with a POCOP-Pincer Ligand



the catalytic applications of these complexes have yet to be reported. In this contribution, we describe our success of using  $Fe(PMe_3)_4$  to promote the cyclometalation of POCOP-pincer ligands, which leads to the synthesis of a series of new iron pincer hydride complexes. We also report catalytic hydrosilylation of aldehydes and ketones with these well-defined iron complexes. Our preliminary mechanistic studies of this catalytic process demonstrate the pitfalls along the path to understanding the chemistry of metal hydrides. One cannot always assume that a reduction reaction catalyzed by a metal hydride must involve the insertion of an unsaturated chemical bond into the metal—hydrogen bond.

#### RESULTS AND DISCUSSION

Synthesis and Structure of [2,6-(R<sub>2</sub>PO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]Fe(H)(PMe<sub>3</sub>)<sub>2</sub> (1a-c). One of the most efficient methods to synthesize transition metal hydride complexes is via cyclometalation or ligand-directed C-H bond activation with low-valent metal species.<sup>18,19</sup> This strategy has been applied to the synthesis of iron compounds involving imine functionalities as the anchoring groups.<sup>20,21</sup> Related chemistry with a pincer ligand has been described by Li and co-workers for the reaction between  $Ph_2PO(CH_2)_3OPPh_2$  and  $Fe(Me)_2(PMe_3)_4$ , where the postulated C-H bond activation step takes place following methane elimination (Scheme 1).<sup>12i</sup> Consistent with this mechanistic hypothesis, we found that mixing 1,3-bis(diisopropylphosphinito)benzene with an equimolar amount of  $Fe(PMe_3)_4$  at room temperature furnished iron hydride complex 1a in 67% isolated yield (eq 1). The <sup>1</sup>H NMR spectrum of 1a in THF- $d_8$  confirmed the presence of the hydride ligand, which appeared at -14.87 ppm as a well-resolved triplet of doublets of doublets with coupling constants of 78.4, 47.6, and 22.0 Hz (Figure 2).<sup>22</sup> This splitting pattern is in accordance with a  $C_s$  symmetry molecule bearing one bis(phosphinite) pincer ligand, one cis PMe<sub>3</sub> (relative to the hydride), and one trans PMe<sub>3</sub>. As



Figure 2. Characteristic hydride resonance of 1a observed by <sup>1</sup>H NMR spectroscopy.

expected, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum showed three phosphorus resonances: one doublet of doublets at 221.0 ppm for the phosphinite phosphorus nuclei and a pair of doublets of triplets at 13.7 ppm and 6.6 ppm for the two PMe<sub>3</sub> ligands. The analogous iron complex **1b**, with phenyl substituents, was prepared in 69% yield via a similar synthetic procedure. On the other hand, the synthesis of complex **1c** with a more bulky pincer ligand was unsuccessful; the isolated material contained mainly the starting materials along with a marginal amount of hydride species suggested by <sup>1</sup>H NMR spectroscopy. The characteristic triplet of doublets at  $-14.20 \text{ ppm} (^2J_{P-H} = 72.0 \text{ and } 29.6 \text{ Hz})$  implied that only one PMe<sub>3</sub> remained coordinated as a result of a crowded iron center.



In the X-ray crystal structure of **1a** (Figure 3), iron is situated in a distorted octahedral coordination sphere with P(1), P(2), and P(3) leaning toward the hydride ligand; the P(x)-Fe-P(4) angles [103.66(2)°, 99.42(2)°, and 97.38(3)°] are greater than the 90° of a perfect octahedral geometry. The aromatic ring of the pincer ligand is canted toward the neighboring PMe<sub>3</sub> with a 172.44(11)° angle for C(4)···C(1)-Fe. The Fe-P(4) [2.2583(7) Å] distance is longer than the Fe-P(3) distance [2.2167(7) Å], presumably due to the greater *trans* effect of the hydride than the aryl ring.

Ligand Substitution Reactions. The Fe-P bond distances of 1a suggested to us that the trans-PMe<sub>3</sub> (with respect to the hydride) would be more labile than the cis-PMe<sub>3</sub>. To test this hypothesis, a THF solution of 1a was stirred under 1 atm of CO at room temperature for 24 h. The substitution reaction proceeded quantitatively to form the mono-CO-substituted hydride species 2a (eq 2), which exhibited a strong CO stretching band at 1928 cm<sup>-1</sup> and a set of low-field multiplets (216.7–217.1 ppm) in the  ${}^{13}C{}^{1}H$  NMR spectrum. The *trans* relationship between CO and hydride is supported by fact that the hydride resonance of 2a is significantly downfield-shifted (a triplet of doublets at -9.58 ppm, in THF- $d_8$ ) compared to that of **1a** (-14.86 ppm). The stereoconfiguration of 2a was further established by singlecrystal structure determination (Figure 4). Having a "slim" CO ligand on iron appears to create more space on the hydride side. The P(x)-Fe-C(22) angles of **2a** [100.48(8)°, 97.86(8)°, and  $95.60(8)^{\circ}$ ] are roughly  $2^{\circ}$  smaller than the corresponding

ARTICLE



Figure 3. ORTEP drawing of  $[2,6-({}^{i}Pr_{2}PO)_{2}C_{6}H_{3}]Fe(H)(PMe_{3})_{2}$ (1a) at the 50% probability level. Selected bond lengths (Å) and angles (deg): Fe-H 1.42(2), Fe-C(1) 2.001(2), Fe-P(1) 2.1724(6), Fe-P(2) 2.1753(6), Fe-P(3) 2.2167(7), Fe-P(4) 2.2583(7), C(1)-Fe-P(1) 77.99(7), C(1)-Fe-P(2) 77.29(7), C-(1)-Fe-P(4) 83.44(6), P(1)-Fe-P(4) 103.66(2), P(2)-Fe-P(4) 99.42(2), P(3)-Fe-P(4) 97.38(3), P(1)-Fe-P(3) 102.68(2), P-(2)-Fe-P(3) 101.65(2).

P(x)-Fe-P(4) angles of 1a. The pincer aromatic ring is also canted toward CO in 2a, although the C(4)···C(1)-Fe angle has increased to 175.77(11)°.



The substituents on the phosphorus donors of the pincer ligand greatly influence the rate of ligand substitution at the iron center. In contrast to facile displacement of PMe<sub>3</sub> from 1a, the reaction of 1b under 1 atm of CO was markedly slower at room temperature. In THF-d<sub>8</sub>, the <sup>1</sup>H NMR spectrum showed that, even after 4 d, only 2% of 1b was converted to 2b, as evidenced by a triplet of doublets at -8.57 ppm (<sup>2</sup> $J_{P-H} = 55.2$  and 50.4 Hz). An attempt to accelerate this process by subsequently heating the same sample at 60 °C resulted in a new triplet of doublets at  $-11.20 \text{ ppm} (^2 J_{P-H} = 66.8 \text{ and } 28.8 \text{ Hz})$ . At that point, the signals of 2b became barely observable. The upfield-shifted resonance at -11.20 ppm suggested that the new hydride species **2b**<sup>'</sup> may no longer contain a *trans*-CO and could be a geometric isomer of 2b through a PMe<sub>3</sub>/CO ligand swap. Unfortunately, the substitution reaction at 60 °C remained sluggish; only 24% NMR conversion was observed after 3 d, and therefore the synthesis of 2b' was not pursued.

The above-mentioned reactivity of 1b led us to suspect that 2a might be the kinetic product of ligand substitution from 1a. Indeed at 60 °C and *in the absence of CO*, 2a underwent a slow isomerization to a new hydride species 2a' (eq 3) with a nearly



Figure 4. ORTEP drawing of  $[2,6-({}^{i}Pr_{2}PO)_{2}C_{6}H_{3}]Fe(H)(PMe_{3})-(CO)$  (2a) at the 50% probability level. Selected bond lengths (Å) and angles (deg): Fe-H 1.40(2), Fe-C(1) 2.013(2), Fe-P(1) 2.2002(6), Fe-P(2) 2.1888(7), Fe-P(3) 2.2198(6), Fe-C(22) 1.774(2), C(22)-O(22) 1.157(3), C(1)-Fe-P(1) 79.43(7), C-(1)-Fe-P(2) 77.58(7), P(1)-Fe-P(2) 149.81(3), C(1)-Fe-P(3) 176.78(6), C(1)-Fe-C(22) 87.62(10), P(1)-Fe-C(22) 100.48(8), P(2)-Fe-C(22) 97.86(8), P(3)-Fe-C(22) 95.60(8), Fe-C(22)-O(22) 177.1(2).

quantitative conversion after 7 d. The synthesis of 2a' was more conveniently carried out by heating a toluene solution of 2a at 80 °C for 12 h, although a small amount of precipitate formed due to the decomposition of the iron species. Nevertheless, 2a'was isolated in 83% yield after an appropriate workup procedure (see Experimental Section). The hydride resonance of 2a' (in THF- $d_8$ ) was found at -12.66 ppm as a triplet of doublets ( $J_{P-H}$ = 66.0 and 28.8 Hz), which is substantially upfield-shifted compared to that of 2a (-9.58 ppm). The chemical shift is consistent with a *trans* arrangement of the hydride and PMe<sub>3</sub> in 2a', because the less *trans*-influencing PMe<sub>3</sub> should induce a shorter Fe-H bond and, hence, more shielding from the iron center. In principle, the magnitude of heteronuclear <sup>31</sup>P-<sup>1</sup>H coupling constants  $({}^{2}J_{P-M-H})$  can also provide valuable information about the molecular structure, although it is very sensitive to the nature of the metal center. Field and co-workers have shown that in complexes  $RuRH(PP_3)$  [PP<sub>3</sub> = P(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P- $(CH_3)_2$ ; R = H, Cl, and various alkenyl groups], the magnitude of  ${}^{2}J_{P-M-H(trans)} > {}^{2}J_{P-M-H(cis)}$ , whereas for the analogous FeRH-(PP<sub>3</sub>) complexes,  ${}^{2}J_{P-M-H(cis)} > {}^{2}J_{P-M-H(trans)}$ .<sup>23</sup> The latter results are in agreement with our structural assignment of **2a**', as the *cis* coupling constant  ${}^{2}J_{\text{PMe3-Fe-H}}$  in **2a** (52.0 Hz) is larger than the *trans* coupling constant  ${}^{2}J_{\text{PMe3-Fe-H}}$  in **2a**' (28.8 Hz). The IR spectra of the two isomers revealed a significant difference in the CO stretching frequencies, with the band of 2a' being 25 cm<sup>-1</sup> lower. The red shift could be attributed to a shorter Fe–CO bond distance in 2a', which would allow a more effective  $\pi$ -back-donation from the iron center. Attempts to validate this hypothesis by growing X-ray quality crystals of 2a' were fruitless; however, the fact that the pincer aromatic ring has a weaker trans effect than the hydride does support a shorter Fe-CO bond in 2a'. Moreover, the electron repulsion between an occupied iron d orbital and a filled  $\pi$  orbital of the pincer aromatic ring should also result in substantially more



Figure 5. ORTEP drawing of  $[2,6-({}^{i}Pr_{2}PO)_{2}C_{6}H_{3}]Fe(H)(CO)_{2}(3a)$ at the 50% probability level. Selected bond lengths (Å) and angles (deg): Fe(2)-H 1.44(2), Fe(2)-C(1B) 1.995(2), Fe(2)-P(1B) 2.1843(6), Fe(2)-P(2B) 2.1885(6), Fe(2)-C(22B) 1.794(2), Fe(2)-C(23B) 1.772(2), C(22B)-O(22B) 1.147(3), C(23B)-O(23B) 1.150(3), C(1B)-Fe(2)-P(1B) 80.15(7), C(1B)-Fe(2)-P(2B) 80.03(7), P-(1B)-Fe(2)-P(2B) 158.16(3), C(1B)-Fe(2)-C(22B) 92.04(9), C(1B)-Fe(2)-C(23B) 168.81(10), Fe(2)-C(22B)-O(22B) 178.8(2), Fe(2)-C(23B)-O(23B) 177.8(2).

back-donation into the  $\pi^*$  orbital of CO in 2a' (in a push-and-pull manner).



The geometric isomerization of 2a is reminiscent of Milstein's iridium PCP-pincer system, where, upon heating, the cis-dihydride complex is converted to the more stable trans-dihydride complex (eq 4).<sup>24</sup> The thermodynamic driving force for that process as well as the isomerization reaction in eq 3 is probably the reduced  $p_{\pi}-d_{\pi}$  repulsion (when the CO  $\pi^*$  orbital is aligned with these orbitals), as described above. A computational study of the iridium system with a truncated pincer ligand has supported a trigonal twist mechanism for the isomerization reaction shown in eq 4.25 Consistent with this nondissociative mechanism, the isomerization of 2a was not inhibited by added PMe<sub>3</sub> (see the Supporting Information). When the reaction was performed under 1 atm of CO, in addition to the expected 2a', a doubly CO-substituted hydride complex formed as the minor product (vide infra). However, the percentage conversion of 2a was not affected, suggesting that CO does not inhibit the isomerization either. While these results appear to agree with the trigonal twist mechanism, alternative pathways initiated by the reductive elimination of the Ar-H bond, the dissociation of the pincer

phosphorus arm, and irreversible dissociation of CO or PMe<sub>3</sub> cannot be ruled out.



At 80 °C in toluene and *in the presence of CO*, the substitution of the remaining PMe<sub>3</sub> of 2a occurred, resulting in clean formation of the dicarbonyl iron hydride 3a after 3 d (eq 5). Key spectroscopic evidence for this compound included a hydride resonance at -9.61 ppm as a triplet ( ${}^{2}J_{P-H} = 52.4$  Hz, in THF- $d_8$ ) in the <sup>1</sup>H NMR, two CO resonances at 213.1 ppm (triplet,  ${}^{2}J_{P-C} = 13.8 \text{ Hz}$ ) and 214.7 ppm (triplet,  ${}^{2}J_{P-C} = 11.1 \text{ Hz}$ ) in the  ${}^{13}C{}^{1}H$  NMR, and two strong CO stretching frequencies (1993 and 1946  $\text{cm}^{-1}$ ) in the IR. Single crystals of 3a were obtained from the recrystallization of the complex in methanol, and the X-ray studies revealed two independent molecules in the crystalline lattice with different orientations of the 'Pr groups (only one molecule is shown in Figure 5). In relation to the hydride ligand, the *trans* Fe-C bond [1.794(2) Å]is longer than the cis Fe-C bond [1.772(2) Å], once again reflecting the fact that the hydride exerts a greater trans effect than the aryl ring. The trans CO bond distance [1.147(3) Å] is shorter than the cis one [1.150(3) Å], which is probably due to less  $\pi$ -back-donation from the iron center.<sup>26</sup>



Catalytic Studies. One conceivable catalytic application of transition metal hydride complexes is for the reduction of carbonyl functionalities.<sup>4,15,27</sup> Our previous study of nickel hydride complexes containing similar POCOP-pincer ligands has shown that they are effective catalysts for the hydrosilylation of aldehydes.<sup>15a</sup> On the basis of the observed stoichiometric reactions, we have proposed a two-step mechanism involving the insertion of an aldehyde into a Ni-H bond followed by the reaction of the resulting nickel alkoxide species with a silane to regenerate the nickel hydride. Recently there has been considerable interest in developing iron-catalyzed hydrosilylation of aldehydes and ketones.<sup>28,29</sup> Although these catalytic systems have not been subjected to thorough mechanistic investigations, iron hydride species are quite likely to participate in the catalytic cycles. We were thus curious to see whether the iron hydride complexes reported here would catalyze similar reactions. We found that in the presence of 1 mol % of 1a the hydrosilylation of PhCHO with  $(EtO)_3SiH$  in THF- $d_8$  at  $50 \,^{\circ}\text{C}$  (eq 6) produced (EtO)<sub>3</sub>SiOCH<sub>2</sub>Ph quantitatively within 1 h (entry 2, Table 1). Interestingly, a similar reaction catalyzed by an imido-molybdenum hydride complex has been reported to yield a mixture of (EtO)<sub>3</sub>SiOCH<sub>2</sub>Ph, (EtO)<sub>2</sub>Si(OCH<sub>2</sub>Ph)<sub>2</sub>, and  $(EtO)Si(OCH_2Ph)_{3.30}^{30}$  Compared to 1a, other iron pincer hydride complexes proved to be less reactive catalysts

PhCHO + H
$$\stackrel{|}{-}$$
Si $\stackrel{-}{-}$  $\underbrace{1 \text{ mol\% [Fe]}}_{\text{THF}-d_8, 50 \circ \text{C}}$ PhCH<sub>2</sub>OSi $\stackrel{-}{-}$ (6)

 Table 1. Catalytic Activity of Iron Hydride Complexes in the

 Hydrosilylation of PhCHO<sup>a</sup>

entry	[Fe]	silane	time (h)	conversion $(\%)^b$
1	no catalyst	(EtO) <sub>3</sub> SiH	48	0
2	1a	(EtO) <sub>3</sub> SiH	1	>99
3	1b	(EtO) <sub>3</sub> SiH	4	>99
4	2a	(EtO) <sub>3</sub> SiH	68	>99
5	2a'	(EtO) <sub>3</sub> SiH	96	92
6	3a	(EtO) <sub>3</sub> SiH	48	6
7	1a	PhSiH <sub>3</sub>	1	>99
8	no catalyst	PhSiH <sub>3</sub>	48	0
9	1a	Ph <sub>2</sub> SiH <sub>2</sub>	2.5	>99
10	no catalyst	Ph <sub>2</sub> SiH <sub>2</sub>	48	0
11	1a	Et <sub>3</sub> SiH	24	0

<sup>*a*</sup> Reaction conditions: PhCHO (0.50 mmol), silane (0.55 mmol), and iron hydride complex (5.0  $\mu$ mol) in 0.50 mL of THF-*d*<sub>8</sub> at 50 °C. <sup>*b*</sup> Determined by <sup>1</sup>H NMR.

(entries 3–6). For complexes with an identical pincer ligand, the catalytic activity followed the decreasing order of 1a > 2a > 2a' > 3a. In addition to (EtO)<sub>3</sub>SiH, PhSiH<sub>3</sub> and Ph<sub>2</sub>SiH<sub>2</sub> were suitable reagents for the hydrosilylation of PhCHO (entries 7 and 9), although more than one hydrosilylation product were obtained in both cases due to multiple Si–H bonds in the silanes. On the other hand, the catalytic reaction with Et<sub>3</sub>SiH did not proceed at all (entry 11). To confirm that the reactions were catalyzed by iron, control experiments were performed, and there were no significant hydrosilylation products observed (entries 1, 8, and 10).

To further extend the utility of our iron catalysts, we explored the catalytic hydrosilylation of aldehydes bearing different functionalities (eq 7). With 1 mol % of **1a** as the catalyst and (EtO)<sub>3</sub>SiH as the reductant, F-, Me-, MeO-, and Me<sub>2</sub>N-substituted benzaldehydes (entries 2–7, Table 2) were reduced to the corresponding alcohols in good yields following basic hydrolysis of the initial products. Electron-donating groups appear to make the hydrosilylation reactions sluggish (entries 3–5); however, there is almost no difference in terms of the required reaction time for PhCHO and a benzaldehyde with an electron-withdrawing group at the *para*-position (entry 2). Other aromatic aldehydes such as 2-naphthaldehyde (entry 8) and 2-furaldehyde (entry 9) are viable substrates for our catalytic system. For an aldehyde containing both C=O and C=C bonds, only the C=O bond was reduced (entry 10).

Various ketones were also tested under our hydrosilylation conditions (eq 8 and Table 3). In general, they are less reactive than the aldehydes; for many ketone substrates, a higher temperature of 80 °C was required to ensure full conversions. Substituent effect on the hydrosilylation rate could potentially provide some key mechanistic insights. Unfortunately, in this case there are no obvious trends, as both electron-withdrawing groups (entry 2) and electron-donating groups (entry 3) render the ketones less reactive than the unsubstituted one (entry 1). Functional groups such as MeO (entry 3), NH<sub>2</sub> (entry 4), and pyridyl group (entry 7) are tolerated under the catalytic

$$\begin{array}{c} \text{RCHO} + \text{ (EtO)}_{3}\text{SiH} \xrightarrow{1 \text{ mol\% [1a]}} & 10\% \text{ NaOH} \\ \text{(1.1 equiv)} & \text{THF} & \text{MeOH, 50 °C} \end{array} \\ \end{array} \xrightarrow{\text{RCH2OH (7)}} \\ \end{array}$$

Table 2. Catalytic Hydrosilylation of Aldehydes with 1a<sup>a</sup>

entry	substrate	temperature	time	isolated yield
1	СНО	50 °C	1.5 h	91%
2	СНО	50 °C	1.5 h	91%
3	СНО	65 °C	2.5 h	90%
4	СНО	65 °C	3 h	82%
5	MeoN CHO	65 °C	3 h	85%
6	CHO F	50 °C	3.5 h	92%
7	СНО	65 °C	1 h	88%
8	СНО	65 °C	3 h	82%
9	СНО	50 °C	2 h	84%
10	СНО	50 °C	36 h	80%

<sup>*a*</sup> Reaction conditions: RCHO (2.0 mmol), (EtO)<sub>3</sub>SiH (2.2 mmol), and 1a (0.020 mmol) in 2.0 mL of THF. All the aldehydes were fully converted to the corresponding silyl ethers (monitored by TLC and GC).

conditions. Aliphatic ketones (entry 6) can also be reduced, but bulky ketones such as 2',4',6'-trimethylacetophenone (entry 9) resist the hydrosilylation.

Mechanistic Investigations. The catalytic cycles for transition metal catalyzed hydrosilylation of aldehydes and ketones may involve the insertion of the carbonyl group into a metal-hydrogen bond.  $^{15a,29,31}$  To explore this mechanistic scenario, we treated a solution of 1a in THF- $d_8$  with 1 equiv of PhCHO and heated the mixture to 50 °C. No appreciable reaction was observed even after 2 d, suggesting that C=O insertion is unlikely to happen under the catalytic conditions. No H/D exchange between 1a and PhCDO at the same temperature (monitored for 24 h) also ruled out the possibility of C=O insertion being reversible and thermodynamically uphill. Likewise, there was no observable reaction between 1a and  $(EtO)_3SiH$  in THF- $d_8$  when heated at 50 °C for 24 h. A very recent study by Nikonov and co-workers uses a deuteriumlabeled silane to probe whether or not the metal hydride moiety truly participates in the reduction.<sup>32</sup> Such an approach works only if the deuterium-labeled silane does not undergo fast H/D exchange with the metal hydride. The commercially available  $Ph_2SiD_2$  fits this criterion, as there is no H/D exchange between 1a and  $Ph_2SiD_2$  at 50 °C (within 8 h). Additionally, as shown in Table 1 (entry 9), the use of  $Ph_2SiD_2$  is still relevant to the catalytic reactions. A stoichiometric reaction of PhCDO,

Table 3. Catalytic Hydrosilylation of Ketones with 1a<sup>a</sup>



<sup>*a*</sup> Reaction conditions: RCOR' (2.0 mmol), (EtO)<sub>3</sub>SiH (2.2 mmol), and **1a** (0.020 mmol) in 2.0 mL of THF (for reactions at 50 °C) or toluene (for reactions at 80 °C). <sup>*b*</sup> For reactions that did not go to completion within 2 d at 80 °C, NMR conversions are given in parentheses.

 $Ph_2SiD_{24}$  and Ia (1:1:1) in THF- $d_8$  at 50 °C for 10 h produced a mixture of Ph<sub>2</sub>SiD(OCD<sub>2</sub>Ph) and Ph<sub>2</sub>Si(OCD<sub>2</sub>Ph)<sub>2</sub> in a 4:1 ratio with no deuterium incorporation into 1a. This result implies that the hydride ligand is intact during the catalytic cycle. The hydrosilylation reactions reported here are more likely to proceed via the dissociation of  $PMe_3$  (or CO in the case of 3a), thereby creating a vacant coordination site at the iron center to activate either the silane or the carbonyl substrate. The relative catalytic reactivity of different iron hydride complexes seems to support this mechanistic hypothesis, considering the fact that our best catalyst, 1a, contains the most labile ligand. Additional evidence comes from the effect of added PMe<sub>3</sub> on the reaction time needed for the catalytic hydrosilylation reaction. When the concentrations of substrates and catalyst 1a were kept the same in two experiments,<sup>33</sup> the reaction without added PMe<sub>3</sub> required 70 min to reach completion, while the one with added  $PMe_3$  (10 equiv with respect to 1a) took 4.5 h to complete, confirming that PMe<sub>3</sub> inhibits the catalysis. At the moment, the mechanistic details after the dissociation of PMe<sub>3</sub> remain unclear to us. Possible catalytic cycles are illustrated in Scheme 2. The open coordination site left by PMe<sub>3</sub> dissociation may be occupied by a silane to generate a  $\eta^2$ -silane  $\sigma$ -adduct,<sup>34</sup> and the subsequent reaction with the carbonyl group would complete the catalytic cycle (in blue). Such a mechanism has been proposed in hydrosilylation reactions catalyzed by high-valent rhenium oxo complexes.<sup>35</sup> Alternatively, as suggested by a recent report,<sup>30</sup> perhaps the carbonyl substrate is activated first to form an  $\eta^1$ - or  $\eta^2$ -carbonyl species,<sup>36</sup> followed by the reduction with the silane (in red). Distinguishing these two mechanistic pathways requires detailed kinetic studies, which are ongoing in our laboratories.

#### CONCLUDING REMARKS

When using a transition metal hydride complex to catalyze a reduction reaction, one cannot intuitively assume that the hydride ligand will directly participate in the reaction. In this paper, we have prepared a new class of iron pincer hydride complexes. These well-defined iron species are competent catalysts for the hydrosilylation of aldehydes and ketones. Mechanistic studies have ruled out the possibility of C=O insertion into the iron-hydrogen bond. However, the hydride ligand is not merely a spectator. As demonstrated in the ligand substitution reactions, the hydride ligand exerts a strong *trans* influence that facilitates the ligand dissociation and creates an open coordination site for substrate activation.

## EXPERIMENTAL SECTION

**General Comments.** All the organometallic compounds were prepared and handled under an argon atmosphere using standard glovebox and Schlenk techniques. Dry and oxygen-free solvents (THF, pentane, diethyl ether, and toluene) were collected from an Innovative Technology solvent purification system and used throughout the experiments. Methanol was degassed by bubbling argon through it for 15 min and then dried over molecular sieves. Tetrahydrofuran-*d*<sub>8</sub> (99.5% D, packed in sealed ampules) was purchased from Cambridge Isotope Laboratories, Inc. and used without further purification. Benzene-*d*<sub>6</sub> was distilled from Na and benzophenone under an argon atmosphere. 1,3-(<sup>i</sup>Pr<sub>2</sub>PO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>,<sup>14g</sup> 1,3-(Ph<sub>2</sub>PO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>,<sup>14b</sup> and 1,3-(<sup>t</sup>Bu<sub>2</sub>PO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub><sup>14d</sup> were prepared as described in the literature. All the aldehydes were freshly distilled or purified by recrystallization.

**Preparation of Fe(PMe<sub>3</sub>)**<sub>4</sub>. Fe(PMe<sub>3</sub>)<sub>4</sub> was prepared according to a slightly modified procedure from the one described by Karsch.<sup>37</sup> A mixture of anhydrous FeCl<sub>2</sub> (1.0 g, 7.9 mmol) and Mg turnings (1.5 g, 61.7 mmol) was vigorously stirred in a Schlenk flask under vacuum for at least 1 h while being heated with a heat gun. Once the flask was cooled to room temperature, a 1.0 M solution of PMe<sub>3</sub> in THF (39.3 mL, 39.3 mmol) was added. The resulting mixture was stirred for 1 h at room temperature as its color changed from green to dark yellow. The volatiles were removed under vacuum, and the remaining solid was treated with 30 mL of pentane. After filtration, removal of pentane from the filtrate under vacuum produced Fe(PMe<sub>3</sub>)<sub>4</sub> as a yellow solid (2.38 g, 84% yield), which was used for the subsequent synthesis without further purification.

Synthesis of  $[2,6-({}^{i}Pr_{2}PO)_{2}C_{6}H_{3}]Fe(H)(PMe_{3})_{2}$  (1a). At  $-78 \, ^{\circ}C$ , 1,3- $({}^{i}Pr_{2}PO)_{2}C_{6}H_{4}$  (618 mg, 1.8 mmol) and Fe(PMe\_{3})\_{4} (650 mg, 1.8 mmol) were mixed in 30 mL of THF. The resulting mixture was slowly warmed to room temperature and stirred for an additional 3 h, at which point the color of the solution changed from yellow to dark brown. The volatiles were removed under vacuum, and the yellowish residue was extracted with diethyl ether (20 mL × 2). Removal of the solvent from the combined etherate solutions under vacuum yielded the crude product, which was washed with methanol (5 mL × 3) and dried under vacuum to produce a yellow powder (667 mg, 67% yield). X-ray quality crystals of 1a were obtained from the recrystallization of the hydride complex in THF at  $-30 \, ^{\circ}C$ .  ${}^{1}H$  NMR (400 MHz, THF- $d_{8}$ ,  $\delta$ ): -14.87 (tdd,  $J_{P-H} = 78.4$ , 47.6, and 22.0 Hz, FeH, 1H), 0.92 (d,  $J_{P-H} = 5.6$  Hz, PMe<sub>3</sub>, 9H), 0.95–0.98



#### Scheme 2. Potential Catalytic Cycles of the Hydrosilylation Reactions Catalyzed by 1a<sup>a</sup>

<sup>*a*</sup> The square indicates the vacant coordination site.

(m, CHCH<sub>3</sub>, 6H), 1.12–1.17 (m, CHCH<sub>3</sub>, 6H), 1.33–1.37 (m, CHCH<sub>3</sub>, 6H), 1.38–1.42 (m, CHCH<sub>3</sub>, 6H), 1.44 (d,  $J_{P-H} = 6.0$  Hz,  $PMe_3$ , 9H), 2.29–2.33 (m, CHCH<sub>3</sub>, 2H), 2.55–2.62 (m, CHCH<sub>3</sub>, 2H), 6.17 (d,  $J_{H-H} = 7.6$  Hz, Ar, 2H), 6.48 (t,  $J_{H-H} = 7.6$  Hz, Ar, 1H).  ${}^{13}C{}^{1}H$  NMR (101 MHz, THF- $d_8$ ,  $\delta$ ): 18.6 (s, CHCH<sub>3</sub>), 18.9 (s, CHCH<sub>3</sub>), 19.0 (t,  $J_{P-C} = 2.0$  Hz, CHCH<sub>3</sub>), 19.6 (s, CHCH<sub>3</sub>), 35.2 (td,  $J_{P-C} = 14.1$  and 9.0 Hz, CHCH<sub>3</sub>), 35.6 (s, CHCH<sub>3</sub>), 102.9 (td,  $J_{P-C} = 3.3$  and 3.3 Hz, Ar), 122.7 (d,  $J_{P-C} = 3.2$  Hz, Ar), 150.0–150.3 (m, Ar), 164.5 (td,  $J_{P-C} = 9.8$  and 4.3 Hz, Ar).  ${}^{31}P{}^{1}H{}$  NMR (162 MHz, THF- $d_8$ ,  $\delta$ ): 6.6 (dt,  $J_{P-P} = 42.1$  and 27.5 Hz, PMe<sub>3</sub>, 1P), 13.7 (dt,  $J_{P-P} = 42.1$  and 16.2 Hz, PMe<sub>3</sub>, 1P), 221.0 (dd,  $J_{P-P} = 27.5$  and 16.2 Hz,  $OP^{i}Pr_{2}$ , 2P). Anal. Calcd for C<sub>24</sub>H<sub>50</sub>FeO<sub>2</sub>P<sub>4</sub>: C, 52.37; H, 9.16. Found: C, 52.29; H, 9.09.

**[2,6-(Ph<sub>2</sub>PO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]Fe(H)(PMe<sub>3</sub>)<sub>2</sub> (1b).** This was prepared in 69% yield by a procedure similar to that used for 1a. <sup>1</sup>H NMR (400 MHz, THF- $d_8$ ,  $\delta$ ): -13.61 (tdd,  $J_{P-H}$  = 59.6, 54.0, and 19.9 Hz, Fe*H*, 1H), 0.51 (d,  $J_{P-H}$  = 5.6 Hz, PMe<sub>3</sub>, 9H), 1.14 (d,  $J_{P-H}$  = 6.0 Hz, PMe<sub>3</sub>, 9H), 6.41 (d,  $J_{H-H}$  = 7.6 Hz, Ar, 2H), 6.63 (t,  $J_{H-H}$  = 7.6 Hz, Ar, 1H), 7.16–7.19 (m, Ar, 6H), 7.47–7.52 (m, Ar, 10H), 7.97–7.99 (m, Ar, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, THF- $d_8$ ,  $\delta$ ): 21.0 (d,  $J_{P-C}$  = 20.9 Hz, PMe<sub>3</sub>), 27.7 (d,  $J_{P-C}$  = 21.1 Hz, PMe<sub>3</sub>), 103.8 (td,  $J_{P-C}$  = 5.3 and 2.2 Hz, Ar), 123.0 (d,  $J_{P-C}$  = 2.3 Hz, Ar), 127.6 (t,  $J_{P-C}$  = 3.9 Hz, Ar), 128.5 (t,  $J_{P-C}$  = 4.0 Hz, Ar), 129.4 (s, Ar), 130.6 (s, Ar), 131.9 (t,  $J_{P-C}$  = 5.4 Hz, Ar), 133.3 (t,  $J_{P-C}$  = 6.6 Hz, Ar), 135.0 (t,  $J_{P-C}$  = 13.3 Hz, Ar), 142.7 (t,  $J_{P-C}$  = 14.1 Hz, Ar), 149.9–150.3 (m, Ar), 163.8–164.0 (m, Ar). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, THF- $d_8$ ,  $\delta$ ): 3.9 (dt,  $J_{P-P}$  = 31.3 and 31.3 Hz, PMe<sub>3</sub>, 1P), 4.6 (dt,  $J_{P-P}$  = 31.3 and 20.6 Hz, PMe<sub>3</sub>, 1P), 198.7 (dd,  $J_{P-P}$  = 31.3 and 20.6 Hz, OPPh<sub>2</sub>, 2P). Anal. Calcd for C<sub>36</sub>H<sub>42</sub>FeO<sub>2</sub>P<sub>4</sub>: C, 62.99; H, 6.17. Found: C, 62.70; H, 6.17.

Attempted Synthesis of  $[2,6-({}^{t}Bu_{2}PO)_{2}C_{6}H_{3}]Fe(H)(PMe_{3})_{2}$ (1c). The reaction of 1,3-( ${}^{t}Bu_{2}PO)_{2}C_{6}H_{4}$  (200 mg, 0.50 mmol) with Fe(PMe<sub>3</sub>)<sub>4</sub> (180 mg, 0.50 mmol) was carried out under the same conditions as those used for the synthesis of 1a. The  ${}^{31}P\{{}^{1}H\}$  NMR spectrum of the isolated material (a sticky oil) in  $C_6D_6$  showed predominantly unreacted phosphinite ligand, and the <sup>1</sup>H NMR spectrum contained a triplet of doublets at -14.20 ppm (<sup>2</sup> $J_{P-H} = 72.0$  and 29.6 Hz), which constituted less than 5% of the isolated material.

Synthesis of [2,6-(<sup>i</sup>Pr<sub>2</sub>PO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]Fe(H)(PMe<sub>3</sub>)(CO) (2a). Under a carbon monoxide atmosphere ( $\sim$ 1 atm), a solution of 1a (840 mg, 1.53 mmol) in 25 mL of THF was stirred at room temperature for 24 h. The resulting solution was filtered through a short pad of Celite, and the solvent was removed under vacuum. The residue was washed with methanol  $(3 \text{ mL} \times 2)$  and dried under vacuum to produce a pale yellow solid (750 mg, 98% yield). X-ray quality crystals of 2a were obtained from the recrystallization of the hydride complex in toluene/methanol. <sup>1</sup>H NMR (400 MHz, THF- $d_8$ ,  $\delta$ ): -9.58 (td,  $J_{\rm P-H}$  = 62.4 and 52.0 Hz, FeH, 1H), 1.01-1.05 (m, CH<sub>3</sub>, 6H), 1.08-1.14 (m, CH<sub>3</sub>, 6H), 1.34-1.41 (m, CH<sub>3</sub>, 12H), 1.43 (d,  $J_{P-H} = 7.6$  Hz, PMe<sub>3</sub>, 9H), 2.30-2.38 (m, CH, 2H), 2.41-2.52 (m, CH, 2H), 6.23 (d,  $J_{H-H} =$ 7.6 Hz, Ar, 2H), 6.54 (t,  $J_{H-H}$  = 7.6 Hz, Ar, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, THF- $d_8$ ,  $\delta$ ): 17.7 (s, CH<sub>3</sub>), 18.0 (t,  $J_{P-C}$  = 2.7 Hz, CH<sub>3</sub>), 18.8 (t,  $J_{P-C} = 2.3 \text{ Hz}, CH_3$ , 25.8 (d,  $J_{P-C} = 24.4 \text{ Hz}, PMe_3$ ), 33.6 (t,  $J_{P-C} = 13.2$ Hz, CH<sub>3</sub>), 33.7 (t,  $J_{P-C}$  = 8.6 Hz, CH<sub>3</sub>), 103.4 (t,  $J_{P-C}$  = 5.2 Hz, Ar), 124.0 (s, Ar), 139.5–140.0 (m, Ar), 164.5 (t,  $J_{P-C} = 8.5$  Hz, Ar), 216.7–217.1 (m, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, THF- $d_8$ ,  $\delta$ ): 10.7 (t,  $J_{P-P} = 14.9 \text{ Hz}, PMe_3, 1P), 227.7 (d, J_{P-P} = 14.9 \text{ Hz}, OP'Pr_2, 2P). IR (in$ toluene):  $\nu_{CO} = 1928 \text{ cm}^{-1}$ . Anal. Calcd for  $C_{22}H_{41}FeO_3P_3$ : C, 52.60; H, 8.23. Found: C, 52.98; H, 8.36.

**Displacement of PMe<sub>3</sub> from 1b by CO.** In a J. Young valve NMR tube, a solution of **1b** (9.6 mg, 14  $\mu$ mol) in ~0.5 mL of THF- $d_8$  was degassed using one freeze—pump—thaw cycle and then mixed with 1 atm of CO. The progress of the reaction was monitored by both <sup>1</sup>H NMR and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. After 4 d, approximately 2% of **1b** (based on the <sup>1</sup>H NMR integration of the hydride resonances) was converted to **2b**, which showed a hydride resonance at -8.57 ppm (td,  ${}^2J_{P-H} = 55.2$  and 50.4 Hz). The sealed NMR tube was then heated with a 60 °C oil bath, and the reaction was periodically monitored by NMR.

After 3 d, a new hydride species **2b**' grew in (24% NMR conversion) with concomitant disappearance of **2b**. Selected <sup>1</sup>H NMR data (400 MHz, THF- $d_8$ ,  $\delta$ ) of **2b**': -11.20 (td, <sup>2</sup> $J_{P-H}$  = 66.8 and 28.8 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR data (162 MHz, THF- $d_8$ ,  $\delta$ ) of **2b**': 3.03 (t,  $J_{P-P}$  = 30.1 Hz, PMe<sub>3</sub>, 1P), 188.87 (d,  $J_{P-P}$  = 30.1 Hz, OP<sup>i</sup>Pr<sub>2</sub>, 2P).

Synthesis of [2,6-(<sup>i</sup>Pr<sub>2</sub>PO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]Fe(H)(CO)(PMe<sub>3</sub>) (2a'). Under an argon atmosphere, a solution of 2a (600 mg, 1.2 mmol) in 20 mL of toluene was heated at 80 °C for 12 h, during which time a small amount of precipitate was formed. The reaction mixture was filtered through a pad of Celite, and the solvent was removed under vacuum. The product was further purified by washing with methanol  $(3 \text{ mL} \times 2)$ and isolated as a pale gray crystalline solid (500 mg, 83% yield). <sup>1</sup>H NMR (400 MHz, THF- $d_8$ ,  $\delta$ ): -12.66 (td,  $J_{P-H}$  = 66.0 and 28.8 Hz, FeH, 1H),  $0.85 - 0.90 (m, CH_3, 6H), 1.06 (d, J_{P-H} = 6.4 Hz, PMe_3, 9H), 1.08 - 1.14$ (m, CH<sub>3</sub>, 6H), 1.39–1.47 (m, CH<sub>3</sub>, 12H), 2.54–2.64 (m, CH, 4H), 6.27 (d,  $J_{H-H}$  = 7.6 Hz, Ar, 2H), 6.58 (t,  $J_{H-H}$  = 7.6 Hz, Ar, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, THF- $d_8$ ,  $\delta$ ): 16.9 (t,  $J_{P-C} = 2.7$  Hz,  $CH_3$ ), 17.6 (s, CH<sub>3</sub>), 18.1 (t,  $J_{P-C}$  = 4.7 Hz, CH<sub>3</sub>), 18.8 (t,  $J_{P-C}$  = 5.3 Hz, CH<sub>3</sub>), 20.7 (d,  $J_{P-C}$  = 21.9 Hz, PMe<sub>3</sub>), 30.3 (td,  $J_{P-C}$  = 14.9 and 8.8 Hz, CH), 36.1 (td,  $J_{P-C}$  = 7.5 and 2.9 Hz, CH), 103.8–104.0 (m, Ar), 124.7 (d,  $J_{P-C}$  = 3.3 Hz, Ar), 145.6–146.2 (m, Ar), 164.5 (td,  $J_{P-C}$  = 10.4 and 4.7 Hz, *Ar*), 218.6–219.6 (m, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, THF- $d_8$ ,  $\delta$ ): 7.2  $(t, J_{P-P} = 29.6 \text{ Hz}, PMe_3, 1P), 227.2 (d, J_{P-P} = 29.6 \text{ Hz}, OP^{i}Pr_2, 2P). \text{ IR}$ (in toluene):  $v_{CO}$  = 1903 cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>41</sub>FeO<sub>3</sub>P<sub>3</sub>: C, 52.60; H, 8.23. Found: C, 52.65; H, 8.29.

Effect of Added PMe<sub>3</sub> or CO on the Isomerization of 2a. In a glovebox under an argon atmosphere, a solution of 2a (30 mg, 0.060 mmol) in 1.5 mL of THF- $d_8$  was evenly divided into three portions and placed in three J. Young valve NMR tubes. The first sample was degassed using one freeze–pump–thaw cycle and then mixed with 1 atm of CO. To the second sample tube, 5 equiv of PMe<sub>3</sub> (10.3  $\mu$ L, 0.10 mmol) was added. All three NMR tubes were then sealed and heated with a 60 °C oil bath. The progress of the isomerization was monitored by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, and the conversions were calculated from the integrations of the phosphorus resonances. A plot of NMR conversions as a function of time is provided in the Supporting Information.

Synthesis of [2,6-(<sup>i</sup>Pr<sub>2</sub>PO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]Fe(H)(CO)<sub>2</sub> (3a). Under a carbon monoxide atmosphere ( $\sim 1$  atm), a solution of 1a (1.10 g, 2.0 mmol) in 30 mL of toluene was stirred at room temperature for 1 d and then heated with an 80 °C oil bath for 3 d. The solution was subsequently pumped to dryness, and the residue was extracted with 20 mL of toluene. After filtration, the toluene solution was concentrated under vacuum and the crude product was subjected to recrystallization from methanol, resulting in colorless crystals that were suitable for X-ray diffraction studies (460 mg, 51% yield). <sup>1</sup>H NMR (400 MHz, THF- $d_{8}$ ,  $\delta$ ): -9.61 (t,  $J_{P-H}$  = 52.4 Hz, FeH, 1H), 1.03-1.08 (m, CH<sub>3</sub>), 6H), 1.12-1.18 (m, CH<sub>3</sub>, 6H), 1.36-1.45 (m, CH<sub>3</sub>, 12H), 2.44-2.53  $(m, CH, 2H), 2.57-2.67 (m, CH, 2H), 6.35 (d, J_{H-H} = 8.0 Hz, Ar, 2H),$ 6.67 (t,  $J_{H-H} = 8.0 \text{ Hz}, Ar, 1\text{H}$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, THF- $d_8, \delta$ ):  $17.2 (t, J_{P-C} = 3.3 Hz, CH_3), 17.3 (s, CH_3), 17.7 (s, CH_3), 17.9 (s, C$ 33.4 (t,  $J_{P-C}$  = 14.8 Hz, CH), 35.0 (t,  $J_{P-C}$  = 11.5 Hz, CH), 104.8 (t,  $J_{P-C} = 5.6 \text{ Hz}, Ar$ , 125.7 (s, Ar), 136.3 (t,  $J_{P-C} = 17.8 \text{ Hz}, Ar$ ), 164.4 (t,  $J_{P-C} = 8.9 \text{ Hz}, Ar$ , 213.1 (t,  $J_{P-C} = 13.8 \text{ Hz}, CO$ ), 214.7 (t,  $J_{P-C} = 11.1$ Hz, CO).  ${}^{31}P{}^{1}H$  NMR (162 MHz, THF- $d_{8}$ ,  $\delta$ ): 230.5 (s). IR (in toluene):  $v_{CO} = 1993$ , 1946 cm<sup>-1</sup>. Anal. Calcd for  $C_{20}H_{32}FeO_4P_2$ : C, 52.88; H, 7.10. Found: C, 53.12; H, 7.03.

Hydrosilylation of PhCHO Catalyzed by Various Iron Hydride Complexes. In a J. Young valve NMR tube, PhCHO (51  $\mu$ L, 0.50 mmol) and an iron hydride catalyst (5.0  $\mu$ mol, 1 mol %) were dissolved in 0.50 mL of THF- $d_8$ , followed by the addition of a silane (0.55 mmol). The NMR tube was sealed and placed in a 50 °C oil bath. The progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy, and the results are summarized in Table 1.

Table 4. Crystal Data Collection and Refinement Parameters

	1a	2a	3a
empirical formula	C <sub>24</sub> H <sub>50</sub> O <sub>2</sub> P <sub>4</sub> Fe	C <sub>22</sub> H <sub>41</sub> O <sub>3</sub> P <sub>3</sub> Fe	C <sub>20</sub> H <sub>32</sub> O <sub>4</sub> P <sub>2</sub> Fe
fw	550.37	502.31	454.25
temp, K	150(2)	150(2)	150(2)
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\overline{1}$
a, Å	10.3557(2)	10.6189(1)	10.7596(2)
<i>b,</i> Å	15.3040(2)	14.7715(2)	14.0546(3)
<i>c,</i> Å	18.1959(3)	15.9611(2)	14.9506(3)
α, deg	90	90	82.846(1)
$\beta$ , deg	93.710(1)	91.729(1)	87.478(1)
γ, deg	90	90	89.989(1)
volume, Å <sup>3</sup>	2877.71(8)	2502.47(5)	2241.05(8)
Ζ	4	4	4
$d_{\rm calc}$ , g/cm <sup>3</sup>	1.270	1.333	1.346
<i>λ,</i> Å	1.54178	1.54178	1.54178
$\mu$ , mm <sup>-1</sup>	6.438	6.802	6.924
no. of data collected	24 417	21 071	18 941
no. of unique data, $R_{\rm int}$	5056, 0.0454	4436, 0.0486	7692, 0.0360
goodness-of-fit on $F^2$	1.047	1.040	1.029
R1, wR2 $(I > 2\sigma(I))$	0.0347, 0.0888	0.0356, 0.0907	0.0338, 0.0871
R1, wR2 (all data)	0.0425, 0.0938	0.0423, 0.0951	0.0388, 0.0913

Effect of Added PMe<sub>3</sub> on the Hydrosilylation of PhCHO with (EtO)<sub>3</sub>SiH Catalyzed by 1a. To a solution of 1a (6.0 mg, 0.011 mmol) in 1.30 mL of THF- $d_8$  was added PhCHO (111  $\mu$ L, 1.1 mmol) and (EtO)<sub>3</sub>SiH (221  $\mu$ L, 1.2 mmol). The resulting mixture was evenly divided into two portions and placed in two J. Young valve NMR tubes. To one of them was added PMe<sub>3</sub> (5.6  $\mu$ L, 0.054 mmol), and then both NMR tubes were placed in a 50 °C oil bath. The progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy.

General Procedure for the Catalytic Hydrosilylation of Aldehydes. To a 25 mL Schlenk tube containing a solution of 1a (11 mg, 0.02 mmol) in 2 mL of THF were added an aldehyde (2.0 mmol) and (EtO)<sub>3</sub>SiH (406  $\mu$ L, 2.2 mmol). The reaction mixture was stirred at 50 or 65 °C until there was no aldehyde left (monitored by TLC and GC-MS). The reaction was then quenched by MeOH (1 mL) and a 10% aqueous solution of NaOH (~5 mL) with vigorous stirring at 50 °C for about 2 d. The organic product was extracted with Et<sub>2</sub>O (10 mL × 3), dried over anhydrous MgSO<sub>4</sub>, and concentrated under vacuum. The alcohol product was further purified using flash column chromatography (eluted with 5–30% ethyl acetate in hexanes). The <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H}</sup> NMR spectra of the primary alcohol products are provided in the Supporting Information.

General Procedure for the Catalytic Hydrosilylation of Ketones. Ketones were reduced following a similar procedure to the one used for aldehydes except that toluene was used as the solvent for the reactions at 80 °C. The <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the secondary alcohol products are provided in the Supporting Information.

**X-ray Structure Determinations.** Crystal data collection and refinement parameters are summarized in Table 4. Intensity data were collected at 150 K on a Bruker SMART6000 CCD diffractometer using graphite-monochromated Cu K $\alpha$  radiation,  $\lambda = 1.54178$  Å. The data frames were processed using the program SAINT. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multiscan technique. The structures were solved by a combination of direct methods in SHELXTL and the difference Fourier technique and refined by full-matrix least-squares procedures. Non-hydrogen atoms were refined with anisotropic

displacement parameters. Each hydride was located directly from the difference map and the position refined. The remaining H-atoms were either located or calculated and subsequently treated with a riding model. Compound **3a** crystallized as two independent molecules in the crystalline lattice with different orientations of the <sup>i</sup>Pr groups.

# ASSOCIATED CONTENT

**Supporting Information.** X-ray crystallographic data in CIF format, experimental details on the effect of added PMe<sub>3</sub> or CO on the isomerization of **2a**, and characterization (<sup>1</sup>H NMR and  ${}^{13}C{}^{1}H$  NMR data) of the alcohol products. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

Corresponding Author

\*E-mail: hairong.guan@uc.edu.

#### ACKNOWLEDGMENT

We thank the National Science Foundation (CHE-0952083) and the donors of the American Chemical Society Petroleum Research Fund (49646-DNI3) for generous support of this research, Prof. Hongjian Sun (Shandong University, China) for helpful suggestions on the synthesis of  $Fe(PMe_3)_4$ , and Prof. Mu-Hyun Baik (Indiana University) and Prof. Seth Brown (University of Notre Dame) for stimulating discussions. P.B. is grateful to the University of Cincinnati University Research Council for a graduate student research fellowship. X-ray data were collected on a Bruker SMART6000 diffractometer, which was funded through an NSF-MRI grant (CHE-0215950).

#### REFERENCES

(1) Nakazawa, H.; Itazaki, M. Top. Organomet. Chem. 2011, 33, 27-81.

(2) For representative studies of nitrogenase models, see: (a) Smith,
J. M.; Lachicotte, R. J.; Holland, P. L. J. Am. Chem. Soc. 2003,
125, 15752–15753. (b) Brown, S. D.; Peters, J. C. J. Am. Chem. Soc.
2004, 126, 4538–4539. (c) Sadique, A. R.; Gregory, E. A.; Brennessel,
W. W.; Holland, P. L. J. Am. Chem. Soc. 2007, 129, 8112–8121. (d) Yu,
Y.; Sadique, A. R.; Smith, J. M.; Dugan, T. R.; Cowley, R. E.; Brennessel,
W. W.; Flaschenriem, C. J.; Bill, E.; Cundari, T. R.; Holland, P. L. J. Am. Chem. Soc. 2008, 130, 6624–6638.

(3) For recent reviews on hydrogenase models, see: (a) Tard, C.; Pickett, C. J. *Chem. Rev.* **2009**, *109*, 2245–2274. (b) Gloaguen, F.; Rauchfuss, T. B. *Chem. Soc. Rev.* **2009**, *38*, 100–108. (c) Barton, B. E.; Olsen, M. T.; Rauchfuss, T. B. *Curr. Opin. Biotechnol.* **2010**, *21*, 292–297.

(4) (a) Bolm, C.; Legros, J.; Le Paih, J.; Zani, L. *Chem. Rev.* 2004, 104, 6217–6254.(b) *Iron Catalysis in Organic Chemistry*; Plietker, B., Ed.; Wiley-VCH: Weinheim, 2008. (c) Morris, R. H. *Chem. Soc. Rev.* 2009, 38, 2282–2291. (d) Junge, K.; Schröder, K.; Beller, M. *Chem. Commun.* 2011, 47, 4849–4859.

(5) (a) Almeida, S. S. P.; Duarte, M. T.; Ribeiro, L. M. D.; Gormley, F.; Galvão, A. M.; Fraústo Da Silva, J. J. R.; Pombeiro, A. J. L. J. Organomet. Chem. 1996, 524, 63–66. (b) Field, L. D.; Messerle, B. A.; Smernik, R. J.; Hambley, T. W.; Turner, P. Inorg. Chem. 1997, 36, 2884–2892. (c) Field, L. D.; Messerle, B. A.; Smernik, R. J. Inorg. Chem. 1997, 36, 5984–5990. (d) Albertin, G.; Antoniutti, S.; Bortoluzzi, M. Inorg. Chem. 2004, 43, 1328–1335. (e) Franke, O.; Wiesler, B. E.; Lehnert, N.; Peters, G.; Burger, P.; Tuczek, F. Z. Anorg. Allg. Chem. 2006, 632, 1247–1256. (f) Thomas, C. M.; Peters, J. C. Angew. Chem., Int. Ed. 2006, 45, 776–780. (g) Gilbertson, J. D.; Szymczak, N. K.; Crossland, J. L.; Miller, W. K.; Lyon, D. K.; Foxman, B. M.; Davis, J.; Tyler, D. R. Inorg. Chem. 2007, 46, 1205–1214. (h) Thoreson, K. A.; Follett, A. D.;

McNeill, K. Inorg. Chem. 2010, 49, 3942–3949. (i) Field, L. D.; Guest, R. W.; Turner, P. Inorg. Chem. 2010, 49, 9086–9093.

(6) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Frediani, P.; Bohanna, C.; Esteruelas, M. A.; Oro, L. A. Organometallics 1992, 11, 138–145.
(b) Bianchini, C.; Farnetti, E.; Graziani, M.; Peruzzini, M.; Polo, A. Organometallics 1993, 12, 3753–3761. (c) Daida, E. J.; Peters, J. C. Inorg. Chem. 2004, 43, 7474–7485. (d) Casey, C. P.; Guan, H. J. Am. Chem. Soc. 2007, 129, 5816–5817. (e) Casey, C. P.; Guan, H. J. Am. Chem. Soc. 2009, 131, 2499–2507. (f) Coleman, M. G.; Brown, A. N.; Bolton, B. A.; Guan, H. Adv. Synth. Catal. 2010, 352, 967–970. (g) Federsel, C.; Boddien, A.; Jackstell, R.; Jennerjahn, R.; Dyson, P. J.; Scopelliti, R.; Laurenczy, G.; Beller, M. Angew. Chem., Int. Ed. 2010, 49, 9777–9780. (h) Zhou, S.; Fleischer, S.; Junge, K.; Beller, M. Angew. Chem., Int. Ed. 2011, 50, 5120–5124. (i) von der Höh, A.; Berkessel, A. ChemCatChem 2011, 3, 861–867.

(7) (a) Gossage, R. A.; van de Kuil, L. A.; van Koten, G. Acc. Chem. Res.
1998, 31, 423–431. (b) Albrecht, M.; van Koten, G. Angew. Chem., Int. Ed. 2001, 40, 3750–3781. (c) Singleton, J. T. Tetrahedron 2003, 59, 1837–1857. (d) van der Boom, M. E.; Milstein, D. Chem. Rev. 2003, 103, 1759–1792. (e) Liang, L.-C. Coord. Chem. Rev. 2006, 250, 1152–1177. (f) Nishiyama, H. Chem. Soc. Rev. 2007, 36, 1133–1141.(g) The Chemistry of Pincer Compounds; Morales-Morales, D.; Jensen, C. M., Eds.; Elsevier: Amsterdam, 2007. (h) Choi, J.; MacArthur, A. H. R.; Brookhart, M.; Goldman, A. S. Chem. Rev. 2011, 111, 1761–1779. (i) Selander, N.; Szabó, K. J. Chem. Rev. 2011, 111, 2048–2076.

(8) (a) Enthaler, S.; Junge, K.; Beller, M. Angew. Chem., Int. Ed. 2008, 47, 3317–3321. (b) Gaillard, S.; Renaud, J.-L. ChemSusChem 2008, 1, 505–509.

(9) For representative examples of iron complexes with bis-(imino)pyridine ligands, see: (a) Small, B. L.; Brookhart, M.; Bennett, A. M. A. J. Am. Chem. Soc. **1998**, 120, 4049–4050. (b) Small, B. L.; Brookhart, M. J. Am. Chem. Soc. **1998**, 120, 7143–7144. (c) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. Chem. Commun. **1998**, 849–850. (d) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. J. Am. Chem. Soc. **1999**, 121, 8728–8740. For a recent review, see: (e) Gibson, V. C.; Redshaw, C.; Solan, G. A. Chem. Rev. **2007**, 107, 1745–1776.

(10) For iron complexes with bis(phosphino)pyridine ligands, see:
(a) Dahlhoff, W. V.; Nelson, S. M. J. Chem. Soc. A 1971, 2184–2190.
(b) Giannoccaro, P.; Vasapollo, G.; Nobile, C. F.; Sacco, A. Inorg. Chim. Acta 1982, 61, 69–75.
(c) Zhang, J.; Gandelman, M.; Herrman, D.; Leitus, G.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. Inorg. Chim. Acta 2006, 359, 1955–1960.
(d) Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. Inorg. Chem. 2006, 45, 7252–7260.
(e) Pelczar, E. M.; Emge, T. J.; Krogh-Jespersen, K.; Goldman, A. S. Organometallics 2008, 27, 5759–5767.
(f) Langer, R.; Leitus, G.; Ben-David, Y.; Milstein, D. Angew. Chem., Int. Ed. 2011, 50, 2120–2124.

(11) For iron complexes with other neutral pincer-type ligands, see: (a) Benito-Garagorri, D.; Becker, E.; Wiedermann, J.; Lackner, W.; Pollak, M.; Mereiter, K.; Kisala, J.; Kirchner, K. Organometallics 2006, 25, 1900–1913. (b) Benito-Garagorri, D.; Wiedermann, J.; Pollak, M.; Mereiter, K.; Kirchner, K. Organometallics 2007, 26, 217–222. (c) Benito-Garagorri, D.; Puchberger, M.; Mereiter, K.; Kirchner, K. Angew. Chem., Int. Ed. 2008, 47, 9142-9145. (d) Benito-Garagorri, D.; Alves, L. G.; Puchberger, M.; Mereiter, K.; Veiros, L. F.; Calhorda, M. J.; Carvalho, M. D.; Ferreira, L. P.; Godinho, M.; Kirchner, K. Organometallics 2009, 28, 6902-6914. (e) Benito-Garagorri, D.; Alves, L. G.; Veiros, L. F.; Standfest-Hauser, C. M.; Tanaka, S.; Mereiter, K.; Kirchner, K. Organometallics 2010, 29, 4932-4942. (f) Alves, L. G.; Dazinger, G.; Veiros, L. F.; Kirchner, K. Eur. J. Inorg. Chem. 2010, 3160-3166. (g) Danopoulos, A. A.; Tsoureas, N.; Wright, J. A.; Light, M. E. Organometallics 2004, 23, 166-168. (h) Danopoulos, A. A.; Wright, J. A.; Motherwell., W. B. Chem. Commun. 2005, 784-786. (i) Danopoulos, A. A.; Pugh, D.; Smith, H.; Sassmannshausen, J. Chem.-Eur. J. 2009, 15, 5491-5502. (j) Pugh, D.; Wells, N. J.; Evans, D. J.;

Danopoulos, A. A. *Dalton Trans.* **2009**, 7189–7195. (k) Nakajima, Y.; Nakao, Y.; Sakaki, S.; Tamada, Y.; Ono, T.; Ozawa, F. *J. Am. Chem. Soc.* **2010**, *132*, 9934–9936.

(12) (a) Creaser, C. S.; Kaska, W. C. Inorg. Chim. Acta 1978, 30, L325–L326. (b) Fryzuk, M. D.; Leznoff, D. B.; Ma, E. S. F.; Rettig, S. J.; Young, V. G., Jr. Organometallics 1998, 17, 2313–2323. (c) Contel, M.; Stol, M.; Casado, M. A.; van Klink, G. P. M.; Ellis, D. D.; Spek, A. L.; van Koten, G. Organometallics 2002, 21, 4556–4559. (d) Ingleson, M. J.; Fullmer, B. C.; Buschhorn, D. T.; Fan, H.; Pink, M.; Huffman, J. C.; Caulton, K. G. Inorg. Chem. 2008, 47, 407–409. (e) Adhikari, D.; Basuli, F.; Fan, H.; Huffman, J. C.; Pink, M.; Mindiola, D. J. Inorg. Chem. 2008, 47, 4439–4441. (f) Buschhorn, D.; Pink, M.; Fan, H.; Caulton, K. G. Inorg. Chem. 2008, 47, 5129–5135. (g) Walstrom, A. N.; Fullmer, B. C.; Fan, H.; Pink, M.; Buschhorn, D. T.; Caulton, K. G. Inorg. Chem. 2008, 47, 9002–9009. (h) Weintrob, E. C.; Tofan, D.; Bercaw, J. E. Inorg. Chem. 2009, 48, 3808–3813. (i) Xu, G.; Sun, H.; Li, X. Organometallics 2009, 28, 6090–6095.

(13) Jansen, A.; Pitter, S. Monatsh. Chem. 1999, 130, 783-794.

(14) (a) Morales-Morales, D.; Grause, C.; Kasaoka, K.; Redón, R.; Cramer, R. E.; Jensen, C. M. Inorg. Chim. Acta 2000, 300-302, 958-963. (b) Bedford, R. B.; Draper, S. M.; Scully, P. N.; Welch, S. L. New J. Chem. 2000, 24, 745-747. (c) Hunks, W. J; Jennings, M. C.; Puddephatt, R. J. Inorg. Chem. 2000, 39, 2699-2702. (d) Göttker-Schnetmann, I.; White, P.; Brookhart, M. J. Am. Chem. Soc. 2004, 126, 1804-1811. (e) Morales-Morales, D.; Redón, R.; Yung, C.; Jensen, C. M. Inorg. Chim. Acta 2004, 357, 2953-2956. (f) Pandarus, V.; Zargarian, D. Chem. Commun. 2007, 978-980. (g) Pandarus, V.; Zargarian, D. Organometallics 2007, 26, 4321–4334. (h) Naghipour, A.; Sabounchei, S. J.; Morales-Morales, D.; Canseco-González, D.; Jensen, C. M. Polyhedron 2007, 26, 1445-1448. (i) Olsson, D.; Arunachalampillai, A.; Wendt, O. F. Dalton Trans. 2007, 5427-5433. (j) Pandarus, V.; Castonguay, A.; Zargarian, D. Dalton Trans. 2008, 4756–4761. (k) Castonguay, A.; Spasyuk, D. M.; Madern, N.; Beauchamp, A. L.; Zargarian, D. Organometallics 2009, 28, 2134-2141. (1) Solano-Prado, M. A.; Estudiante-Negrete, F.; Morales-Morales, D. Polyhedron 2010, 29, 592-600. (m) Lefevre, X.; Durieux, G.; Lesturgez, S.; Zargarian, D. J. Mol. Catal. A: Chem. 2011, 335, 1-7. (n) Lefevre, X.; Spasyuk, D. M.; Zargarian, D. J. Organomet. Chem. 2011, 696, 864-870.

(15) (a) Chakraborty, S.; Krause, J. A.; Guan, H. Organometallics
2009, 28, 582–586. (b) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. J. Am. Chem. Soc. 2010, 132, 8872–8873. (c) Chakraborty, S.; Guan, H. Dalton Trans. 2010, 39, 7427–7436. (d) Huang, F.; Zhang, C.; Jiang, J.; Wang, Z.-X.; Guan, H. Inorg. Chem. 2011, 50, 3816–3825.
(e) Chakraborty, S.; Patel, Y. J.; Krause, J. A.; Guan, H. Polyhedron 2011, doi:10.1016/j.poly.2011.04.030.

(16) (a) Gómez-Benítez, V.; Baldovino-Pantaleón, O.; Herrera-Á lvarez, C.; Toscano, R. A.; Morales-Morales, D. *Tetrahedron Lett.* **2006**, 47, 5059–5062. (b) Zhang, J.; Medley, C. M.; Krause, J. A.; Guan, H. *Organometallics* **2010**, 29, 6393–6401.

(17) Hebden, T. J., St.; John, A. J.; Gusev, D. G.; Kaminsky, W.; Goldberg, K. I.; Heinekey, D. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 1873–1876.

(18) (a) Kulkarni, A. A.; Daugulis, O. Synthesis 2009, 24, 4087–4109.
(b) Albrecht, M. Chem. Rev. 2010, 110, 576–623.

(19) In some cases the "directing" groups provide the thermodynamic driving force rather than the kinetic preference for the C–H bond activation. For examples, see: Zhang, X.; Kanzelberger, M.; Emge, T. J.; Goldman, A. S. J. Am. Chem. Soc. **2004**, *126*, 13192–13193.

(20) (a) Klein, H.-F.; Camadanli, S.; Beck, R.; Leukel, D.; Flörke, U. Angew. Chem., Int. Ed. **2005**, 44, 975–977. (b) Camadanli, S.; Beck, R.; Flörke, U.; Klein, H.-F. Organometallics **2009**, 28, 2300–2310.

(21) The analogous iron hydride complexes have been proposed as the key intermediates in catalytic formation of aldimines through the insertion of isonitriles into benzene C–H bonds. For details, see: Jones, W. D.; Foster, G. P.; Putinas, J. M. J. Am. Chem. Soc. **1987**, *109*, 5047–5048.

(22) The signs of the coupling constants are not specified in this paper.

(23) Bampos, N.; Field, L. D.; Messerle, B. A. Organometallics 1993, 12, 2529–2535.

(24) Rybtchinski, B.; Ben-David, Y.; Milstein, D. Organometallics 1997, 16, 3786-3793.

(25) Li, S.; Hall, M. B. Organometallics 1999, 18, 5682-5687.

(26) An alternative explanation involves more polarization of the *trans* CO ligand than the *cis* CO. For discussions pertaining to the electrostatic effect of transition metal complex fragments on the polarization of carbonyl ligands, see: (a) Goldman, A. S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1996**, *118*, 12159–12166. (b) Zhu, K.; Achord, P. D.; Zhang, X.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2004**, *126*, 13044–13053.

(27) (a) Recent Advances in Hydride Chemistry; Peruzzini, M.; Poli, R., Eds.; Elsevier: Amsterdam, 2001. (b) Clapham, S. E.; Hadzovic, A.; Morris, R. H. Coord. Chem. Rev. 2004, 248, 2201–2237. (c) Conley, B. L.; Pennington-Boggio, M. K.; Boz, E.; Williams, T. J. Chem. Rev. 2010, 110, 2294–2312.

(28) (a) Nishiyama, H.; Furuta, A. Chem. Commun. 2007, 760-762. (b) Furuta, A.; Nishiyama, H. Tetrahedron Lett. 2008, 49, 110-113. (c) Inagaki, T.; Phong, L. T.; Furuta, A.; Ito, J.; Nishiyama, H. Chem.-Eur. J. 2010, 16, 3090-3096. (d) Hosokawa, S.; Ito, J.; Nishiyama, H. Organometallics 2010, 29, 5773-5775. (e) Shaikh, N. S.; Junge, K.; Beller, M. Org. Lett. 2007, 9, 5429-5432. (f) Shaikh, N. S.; Enthaler, S.; Junge, K.; Beller, M. Angew. Chem., Int. Ed. 2008, 47, 2497-2501. (g) Addis, D.; Shaikh, N.; Zhou, S.; Das, S.; Junge, K.; Beller, M. Chem. Asian J. 2010, 5, 1687-1691. (h) Tondreau, A. M.; Lobkovsky, E.; Chirik, P. J. Org. Lett. 2008, 10, 2789-2792. (i) Tondreau, A. M.; Darmon, J. M.; Wile, B. M.; Floyd, S. K.; Lobkovsky, E.; Chirik, P. J. Organometallics 2009, 28, 3928-3940. (j) Langlotz, B. K.; Wadepohl, H.; Gade, L. H. Angew. Chem., Int. Ed. 2008, 47, 4670-4674. (k) Kandepi, V. V. K. M.; Cardoso, J. M. S.; Peris, E.; Royo, B. Organometallics 2010, 29, 2777-2782. (1) Yang, J.; Tilley, T. D. Angew. Chem., Int. Ed. 2010, 49, 10186-10188. (m) Muraoka, T.; Shimizu, Y.; Kobayashi, H.; Ueno, K.; Ogino, H. Organometallics 2010, 29, 5423-5426. (n) Jiang, F.; Bézier, D.; Sortais, J.-B.; Darcel, C. Adv. Synth. Catal. 2011, 353, 239–244. (o) Misal Castro, L. C.; Bézier, D.; Sortais, J.-B.; Darcel, C. Adv. Synth. Catal. 2011, 353, 1279-1284.

(29) For a review on iron-catalyzed hydrosilylation reactions, see: Zhang, M.; Zhang, A. *Appl. Organomet. Chem.* **2010**, *24*, 751–757.

(30) Peterson, E.; Khalimon, A. Y.; Simionescu, R.; Kuzmina, L. G.; Howard., J. A. K.; Nikonov, G. I. *J. Am. Chem. Soc.* **2009**, *131*, 908–909.

(31) (a) Díez-González, S.; Nolan, S. P. Acc. Chem. Res. **2008**, *41*, 349–358. (b) Tran, B. L.; Pink, M.; Mindiola, D. J. Organometallics **2009**, 28, 2234–2243.

(32) Shirobokov, O. G.; Kuzmina, L. G.; Nikonov, G. I. J. Am. Chem. Soc. 2011, 133, 6487–6489.

(33) [PhCHO] = 0.85 M, [(EtO)<sub>3</sub>SiH] = 0.92 M, [1a] = 0.0085 M, in THF- $d_8$  at 50 °C.

(34) (a) Corey, J. Y.; Braddock-Wilking, J. Chem. Rev. **1999**, 99, 175–292. (b) Corey, J. Y. Chem. Rev. **2011**, 111, 863–1071.

(35) (a) Ison, E. A.; Trivedi, E. R.; Corbin, R. A.; Abu-Omar, M. M.
J. Am. Chem. Soc. 2005, 127, 15374–15375. (b) Du, G.; Abu-Omar,
M. M. Organometallics 2006, 25, 4920–4923. (c) Du, G.; Fanwick, P. E.;
Abu-Omar, M. M. J. Am. Chem. Soc. 2007, 129, 5180–5187.

(36) (a) Huang, Y.-H.; Gladysz, J. A. J. Chem. Educ. 1988, 65, 298–303. (b) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. Angew. Chem., Int. Ed. Engl. 1990, 29, 256–272.

(37) Karsch, H. H. Chem. Ber. 1977, 110, 2699-2711.