ORGANOMETALLICS

Activation of Dihydrogen and Silanes by Cationic Iron Bis(phosphinite) Pincer Complexes

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Supporting Information

ABSTRACT: Treatment of iron POCOP-pincer hydride complexes cis- $[2,6-(^{i}Pr_2PO)_2C_6H_3]$ Fe(H)(PMe_3)₂ (1-H), $[2,6-(^{i}Pr_2PO)_2C_6H_3]$ -Fe(H)(PMe_3)(CO) (2-H, trans H/CO; 2'-H, cis H/CO), and cis- $[2,6-(^{i}Pr_2PO)_2C_6H_3]$ Fe(H)(CO)₂ (3-H) with HBF₄·Et₂O in CD₃CN/ THF- d_8 results in a rapid evolution of H₂. Except for the reaction of 1-H, which leads to decomposition of the pincer structure, all other hydrides are converted cleanly to acetonitrile-trapped cationic complexes. Protonation of these hydrides with the weaker acids CF₃CO₂H and HCO₂H establishes the basicity order of 1-H > 2-H > 2'-H > 3-H, with 3-H bearing the least basic hydride ligand. An alternative method of abstracting hydride by $[Ph_3C]^+[BF_4]^-$ gives complicated products; the reaction of 2-H generates two pincer products, $[HPMe_3]^+[BF_4]^-$ and Gomberg's dimer, which supports a



single electron transfer pathway. Cationic complexes $\{[2,6-({}^{i}Pr_{2}PO)_{2}C_{6}H_{3}]Fe(CO)(PMe_{3})(CH_{3}CN)\}^{+}[BF_{4}]^{-}$ (2⁺-BF₄, trans CO/CH₃CN) and cis- $\{[2,6-({}^{i}Pr_{2}PO)_{2}C_{6}H_{3}]Fe(CO)_{2}(CH_{3}CN)\}^{+}[BF_{4}]^{-}$ (3⁺-BF₄) are prepared from protonation of 2-H (or 2'-H) and 3-H with HBF₄:Et₂O, respectively. Both compounds react with H₂ with the aid of ${}^{i}Pr_{2}NEt$ to yield neutral hydride complexes and $[{}^{i}Pr_{2}N(H)Et]^{+}[BF_{4}]^{-}$. In addition, they catalyze the hydrosilylation of benzaldehyde and acetophenone with (EtO)₃SiH and show higher catalytic activity than the neutral hydrides 2-H/2'-H and 3-H. The mechanism for the formation of 2⁺-BF₄ and the X-ray structure of 2⁺-BF₄ are also described.

INTRODUCTION

Transition metal catalyzed reduction of polar bonds is an essential process in fine or commodity chemical synthesis.¹ The efficiency of a catalytic system is sometimes directly linked to how effectively the metal can activate the reducing agents (e.g., H_2 , silanes, and boranes). Among various activation strategies,^{2–4} the use of cationic complexes has resulted in tremendous success for a myriad of reduction processes,⁵ particularly hydrosilylation reactions.⁶⁻¹¹ A generalized (and simplified) mechanism that features a cationic catalyst is illustrated in Scheme 1 using a ketone as a representative substrate. When cationic and coordinatively unsaturated, the metal center often has a good binding affinity for H-E (E = H, SiR₃), resulting in a σ -complex and/or the oxidative addition product. Forming the latter is usually less favorable for a cationic species due to little back-donation from an electrophilic metal to the H–E σ^* orbital. Nevertheless, the subsequent stepwise, outersphere transfer of E⁺ and H⁻ to the ketone substrate completes the catalytic cycle.

Hydrogenation reactions following this mechanism are best known as ionic hydrogenation, which has been thoroughly reviewed by Bullock.¹² In terms of reduction with silanes, cationic iridium bis(phosphinite) pincer (also known as POCOP-pincer) complexes have shown remarkable activity for catalytic hydrosilylation of compounds bearing C–O or C=O bonds.¹⁰ Mechanistic studies have supported catalytic Scheme 1. Catalytic Reduction of a Ketone with a Cationic Complex



cycles with general features of Scheme $1.^{13,14}$ This type of mechanism has also been proposed for hydrosilylation reactions catalyzed by $[CpW(CO)_2(IMes)]^+[B(C_6F_5)_4]^{-,6a}$ cationic Re(V) oxo complexes,⁷ and $[CpRu(P^iPr_3)(CH_3CN)_2]^{+,9b,c,e}$

We have reported that iron hydride complexes with a POCOPpincer ligand (Figure 1) are effective catalysts for the hydrosilylation of aldehydes/ketones¹⁵ and the dehydrogenation of

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Figure 1. Iron hydride complexes with a POCOP-pincer ligand.

ammonia borane.¹⁶ Our mechanistic analyses have suggested that the hydride ligand remains intact during catalysis, but helps facilitate the dissociation of the *trans* ligand L' for substrate binding. Wei and co-workers have recently studied our hydrosilylation system computationally.¹⁷ Their DFT calculations have pointed out that the pathway with the lowest kinetic barrier begins with ligand substitution by a carbonyl substrate followed by C==O insertion into the Fe–H bond. Such a mechanism is, however, inconsistent with our observation that the reaction of PhCDO, Ph₂SiD₂, and **1-H** generates Ph₂SiD-(OCD₂Ph) and Ph₂Si(OCD₂Ph)₂ with no deuterium incorporated into **1-H**.

In this work, we remove the hydride ligand of these iron pincer complexes via protonation reactions. The resulting cationic compounds are still active catalysts for the hydrosilylation of benzaldehyde and acetophenone. In fact, they are more reactive than the parent neutral hydride complexes. We also describe stoichiometric activation of H_2 by the cationic pincer complexes in the presence of an externally added base.

RESULTS AND DISCUSSION

Abstraction of the Hydride Ligand. Our initial strategy to remove the hydride ligand from iron was to treat the complexes in Figure 1 with $[Ph_3C]^+[BF_4]^-$. Mixing 1-H with $[Ph_{3}C]^{+}[BF_{4}]^{-}$ in $CD_{2}Cl_{2}$ led to the rapid disappearance of the hydride species as confirmed by ¹H NMR; however, the ³¹P{¹H} NMR spectrum displayed two resonances, one at 40.5 ppm (major) and the other at -13.0 ppm (minor). These chemical shifts are indicative of a breakdown of the pincer framework.¹⁸ The reaction of **2-H** with $[Ph_3C]^+[BF_4]^-$ in CD₂Cl₂ resulted in a complicated mixture featuring very broad ¹H NMR resonances. Fortunately, the same reaction carried out in a coordinating solvent, CD₃CN, was much more informative due to well-resolved NMR peaks. The spectra recorded at 1 h revealed three pincer complexes: the unreacted 2-H, acetonitriletrapped complex 2^+ -BF₄ (vide infra), and the third iron complex assigned as bis(acetonitrile) complex 4^+ -BF₄ (eq 1).



The mass spectrum of the reaction mixture showed ions 2^+ (m/z 542) and 4^+ (m/z 507) as well as their expected fragmentations. 4^+ -BF₄ was assigned as a *cis*-bis(acetonitrile) complex based on the observation of two sets of methine resonances; the more symmetric *trans* isomer should have one set of methine resonances. The ¹H NMR spectrum also showed the formation of Gomberg's dimer S^{19} and [HPMe₃]⁺[BF₄]⁻.

The presence of **5** is a strong indication of single electron transfer (SET) from **2-H** to $[Ph_3C]^+[BF_4]^-$, resulting in $[2-H]^{+\bullet}$ and the trityl radical (which dimerizes to give **5**). Radical cations of this type are known to be acidic enough to protonate their original hydride complexes²⁰ and in this case PMe₃ as well.

To avoid the complications associated with SET, we resorted to Brønsted acids to remove the hydride ligand.²¹ The success of such a process is obviously dependent on the strength of the acid used. Table 1 summarizes the protonation results using

Table 1. Extent of Protonation of Iron Hydrides by Different Acids^a

entry	acid	1-H	2-H	2'-H	3-H
1	$HBF_4 \cdot Et_2O$	>99% ^b	>99%	>99%	>99%
2	CF ₃ CO ₂ H	>99% ^b	>99%	34%	0% ^c
3	HCO ₂ H	31% ^b	5%	0% ^c	0% ^c

^{*a*}Conditions: hydride (10 μ mol) and acid (10 μ mol) mixed in CD₃CN/THF- d_8 (1:1, ~0.5 mL total) at -30 °C and then warmed to RT (for HBF₄·Et₂O) or at RT (for CF₃CO₂H and HCO₂H) until the equilibrium was reached. ^{*b*}Decomposition of the pincer complex was observed. ^{*c*}Reaction was monitored for 48 h.

acids with varying pK_a values, which provide a qualitative sense of the basicity of the iron hydride complexes. The protonation reactions were carried out in $CD_3CN/THF-d_8$ (1:1) and monitored by NMR spectroscopy. The role of CD₃CN was to intercept any coordinatively unsaturated species prior to decomposition, and THF- d_8 was added to improve solubility. Reactions of the iron hydrides with 1 equiv of HBF₄·Et₂O ($pK_a = 0.1$ in $CH_3CN^{22,23}$) were fast at -30 °C, resulting in a rapid loss of H₂. Within a few minutes, the color of the solutions turned to bright yellow. The change in color was more vivid in the cases of 2-H, 2'-H, and 3-H, as they are either pale yellow (2-H) or almost colorless (2'-H and 3-H). The ¹H NMR spectra confirmed the disappearance of the hydride resonance but with no evidence for a dihydrogen or dihydride species. Unlike the other hydride complexes, the reaction of 1-H led to extensive decomposition and the formation of HPMe₃⁺. Evidently, HBF₄·Et₂O protonates not only the hydride ligand but also PMe₃; hence it causes the collapse of the pincer scaffold. While all the hydrides described in this study are fully protonated by HBF₄. Et₂O (entry 1), using weaker acids differentiates the basicity of these complexes. When CF_3CO_2H (pK_a = 12.7 in $CH_3CN^{22,23}$) was added to the solution of 1-H or 2-H at room temperature, the hydride resonance disappeared within a few minutes (entry 2). On the other hand, only 34% of 2'-H was protonated under similar conditions, and no protonation reaction was observed for 3-H. Using an even weaker acid $(HCO_2H)^{24}$ resulted in 31% of 1-H being protonated (entry 3). Analogous to the reactions with HBF4·Et2O and CF3CO2H, substantial decomposition was observed in this case. Treatment of 2-H with HCO₂H converted merely 5% of 2-H, while 2'-H and 3-H did not undergo protonation at all.

The aforementioned protonation data suggest that the relative basicity of the iron hydride complexes follows a decreasing order of 1-H > 2-H > 2'-H > 3-H. The kinetic site for the protonation should be the hydride ligand, as demonstrated in related systems.²⁵ However, no dihydrogen complexes were observed, suggesting that the dihydrogen molecule is weakly bound to iron and readily displaced by CD₃CN. The relative basicity of the iron hydride complexes is consistent with the order of electron density at the iron center.

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A more electron-rich iron center is likely to induce more negative charge on the hydride ligand, thus making the protonation more readily. The presence of the electron-donating PMe₃ ligand makes the Fe-H more basic; thus the bis-PMe₃ complex 1-H is most readily protonated. As the PMe₃ ligand is substituted by a π -accepting CO ligand, the electron density at the metal is reduced and the basicity decreases. Complexes 2-H and 2'-H have identical supporting ligands, but 2-H is more basic than 2'-H, likely due to its hydride being disposed at the opposite side of the stronger *trans*-influencing ligand CO.

Synthesis of Cationic Iron Pincer Complexes. Because HBF_4 · Et_2O readily protonates all the iron hydrides, it was chosen as the acid to synthesize the targeted cationic pincer complexes. In the presence of CH_3CN as a coordinating solvent, the reactions of 2-H (eq 2) and 3-H (eq 3) with HBF_4 ·



Et₂O led to CH₃CN-trapped complexes 2⁺-BF₄ and 3⁺-BF₄, respectively. The ³¹P{¹H} spectrum of 2⁺-BF₄ reveals a triplet at -0.2 ppm for PMe₃ and a doublet at 206.4 ppm for the phosphinite ligand. The magnitude of the ³¹P-³¹P coupling constant for 2⁺-BF₄ (16.5 Hz) is comparable to that for 2-H (14.9 Hz), implying that these two complexes have the same spatial arrangement for PMe₃ and the pincer ligand. For comparison, 2'-H, in which PMe₃ and the *ipso* carbon are *cis* to each other, gives a much larger ³¹P-³¹P coupling constant of 29.6 Hz. In the case of 3⁺-BF₄, two ¹³C resonances (205.5 and 210.5 ppm) appear in the region for a carbonyl group, which is consistent with a *C_s* symmetry structure bearing two *cis* CO ligands. As expected, ¹H NMR of 3⁺-BF₄ shows two sets of multiplets for the methine hydrogens of the isopropyl groups.

The structure of 2^+ -BF₄ was more unambiguously established by X-ray crystallography. As shown in Figure 2, CH₃CN is located trans to the carbonyl group and the PMe3 ligand remains trans to the ipso carbon. Structural comparison between 2^+ -BF₄ and 2-H (Table 2) reveals some noticeable differences in bond lengths and angles. Compared to 2-H, all the Fe-P bonds of 2^+ -BF₄ are elongated by 0.06-0.10 Å. Although the $\text{Fe}-\text{C}_{ipso}$ distance is almost identical, the Fe-C22bond is shortened by 0.04 Å, reflecting a decreasing trans influence changing from H⁻ to CH₃CN. Interestingly, 2⁺-BF₄ has a wider P1-Fe-P2 angle than 2-H [156.83(2) vs 149.81(3) Å], which is mainly due to how the pincer ligand distorts from a perfect meridional geometry. The chelating rings of POCOP-pincer systems bearing an aromatic backbone are flat in general,²⁶ but the iron pincer complexes are substantially less planar for the core structure, perhaps due to a



Figure 2. ORTEP drawing of $\{[2,6-(^{i}Pr_2PO)_2C_6H_3]Fe(CO)(PMe_3)-(CH_3CN)\}^+[BF_4]^- (2^+-BF_4)$ at the 50% probability level. For clarity, the counterion BF_4^- is not shown.

Table 2. Selected Bond Lengths	(Å)	and	Angles	(deg)	for
Complexes 2 ⁺ -BF ₄ and 2-H					

			2^+-BF_4			$2 - H^a$	
	Fe-C(1)		2.001(2)		2	2.013(2)	
	Fe-P(1)		2.2594(7)		2	2.2002(6)
	Fe-P(2)		2.2854(7)		2	2.1888(7)
	Fe-P(3)		2.2888(7)		2	2.2198(6)
	Fe-C(22)		1.731(2)		1	.774(2)	
	C(22)-O(22)		1.155(3)		1	.157(3)	
	C(1)-Fe-P(1)		79.23(6)		7	79.43(7)	
	C(1)-Fe-P(2)		78.06(6)		7	7.58(7)	
	C(1)-Fe-P(3)		177.86(6)		1	76.78(6)
	P(1)-Fe- $P(2)$		156.83(2)		1	49.81(3)
	P(2)-Fe-P(3)		102.18(3)		1	02.04(2)
	P(1)-Fe-P(3)		100.68(3)		ç	9.81(2)	
	C(2)-O(1)-P(1)		113.75(13)		1	13.08(1	3)
	C(6)-O(2)-P(2)		112.48(13)		1	10.23(1	4)
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^aThe crystal structure of **2-H** was reported earlier by us (see ref 15).



Figure 3. Distortion of the pincer ligand in 2⁺-BF₄ and 2-H.

more crowded octahedral geometry about iron.²⁷ In 2^+ -BF₄, the pincer ligand adopts an asymmetric bend conformation (Figure 3) with the phosphorus atoms being displaced +0.4950 and -0.2988 Å out of the least-squares plane defined by the C1, O1, O2, and Fe.²⁸ In contrast, **2-H** has a "gull wing"

Scheme 2. Protonation of 2-H and 2'-H Involving Square-Pyramidal Intermediates



Scheme 3. Protonation of 2-H and 2'-H Involving a Distorted Trigonal-Bipyramidal Intermediate



conformation²⁶ to take advantage of the small size of the hydride ligand, resulting in the phosphorus atoms deviating from the C1–O1–O2–Fe plane by +0.5135 and +0.2161 Å.²⁹

Although 1-H reacts with HBF_4 ·Et₂O, attempts to isolate the corresponding cationic complex failed even when the protonation reaction was carried out at low temperatures. Switching the acid to CF_3COOH did not improve the synthesis. The purification was hampered by the formation of $HPMe_3^+$, free diphosphinite ligand, and other decomposition products.

The reaction of 2'-H with HBF₄·Et₂O, on the other hand, cleanly afforded one pincer-ligated complex, which was obtained in 84% yield after workup. The ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR and IR data and crystal structure determination of the isolated compound match well with those of 2^+ -BF₄, suggesting that PMe₃ and CO swap their positions during the reaction. A mechanism consistent with this result is outlined in Scheme 2. Upon protonation of the hydride and loss of H_2 , the square-pyramidal intermediate A' would rapidly isomerize to A so that the two strongly trans-influencing ligands (CO and aryl group) avoid being trans to each other. Trapping of the predominant intermediate A with CH_3CN produces 2^+ -BF₄. A similar mechanism has been proposed by Kirchner for the carbonylation of $Fe(PNP)(X)_2(CO)$ (PNP = aminophosphinebased pincer ligands³⁰) facilitated by AgBF₄.³¹ In that study, regardless of which geometric isomer (cis or trans) was used, abstraction of halide from Fe(PNP)(X)₂(CO) provided the same 16-electron intermediate, $[Fe(PNP)(X)(CO)]^+$, which is analogous to A with CO occupying the apical position of the square pyramid. Trapping of $[Fe(PNP)(X)(CO)]^+$ by CO gave *trans*- $[Fe(PNP)(X)(CO)_2]^+$ exclusively.

Although we cannot rule out the possibility of isomerization of a kinetically trapped product $2'^{+}$ -BF₄ to 2^{+} -BF₄ (shaded in gray in Scheme 2), such a mechanism seems less likely. We have previously shown that geometric isomerization of 18-electron iron POCOP-pincer complexes places CO *trans* to the pincer aromatic ring.¹⁵ Similar observations have been made by others in *cis*-to-*trans* isomerization of (PCP)Ir-(H)₂CO³² and (PNP)Fe(X)₂CO.³³ DFT calculations carried out by Hall on the iridium system have suggested that the isomerization process is driven by a delocalized interaction between the π orbitals of CO, the d_{π} orbital of Ir, and the π orbitals of the pincer aromatic ring in the *trans* isomer.³⁴ Therefore, we had anticipated that $2'^{+}$ -BF₄ would be thermodynamically more stable than 2^{+} -BF₄.

Protonation of 2-H and 2'-H could converge to a Y-shaped, distorted trigonal-bipyramidal intermediate B (Scheme 3), and the subsequent coordination of CH₃CN to the iron center of B might selectively give 2⁺-BF₄. This mechanism is also disfavored because the Y-structure generally requires the ligand *trans* to the acute angle (in this case, the angle formed by CO and PMe₃) to be a weak σ -donor and a good π -donor.³⁵ Ligands that fit this criterion are usually halides, amides, and alkoxides. Although B is less likely to be a ground-state structure, it could be the transition state for the interconversion between A and A'.

Activation of Dihydrogen. Protonation of the neutral iron pincer hydrides to yield the cationic complexes is, in principle, a reversible process. Having a base with an appropriate $pK_{\rm b}$ value, the cationic dihydrogen intermediate can be reverted back to the neutral hydride, thereby activating H₂ in a heterolytic (H^+/H^-) fashion. The protonation results shown in Table 1 imply that the pK_{a} value for the conjugate acid of 2-H should fall in between the values for CF3CO2H and HCO2H, and therefore a typical amine should be able to assist with H₂ activation. Indeed when a mixture of 2⁺-BF₄ and ⁱPr₂NEt (Hünig's base) in CH_2Cl_2 was exposed to H_{21} the color of the solution changed from yellow to almost colorless, suggesting the consumption of 2⁺-BF₄. Within 2.5 h at room temperature, 2⁺-BF₄ was fully converted to 2-H and 2'-H along with the protonated base, $[{}^{i}Pr_{2}N(H)Et]^{+}[BF_{4}]^{-}$ (eq 4). From the ${}^{31}P{}^{1}H$ NMR spectrum, the ratio between 2-H and 2'-H was determined to be 3:2, which did not change with time.



The formation of **2-H** and **2'-H** must be a kinetically controlled process, as the latter has been previously shown to be the thermodynamically more stable isomer.¹⁵ We speculate that following the dissociation of CH_3CN from **2⁺-BF**₄, intermediate **A** is configurationally stable enough to allow H_2 to coordinate from the site *trans* to CO (Scheme 4). The resulting dihydrogen complex **C** undergoes intermolecular deprotonation by ⁱPr₂NEt to give rise to **2-H**. Meanwhile, **C** also proceeds with *intramolecular* deprotonation by PMe₃ with concomitant migration of CO to the opposite side of the aryl

group. Such a pathway involving intramolecular heterolysis of H_2 with the elimination of $[HPMe_3]^+$ may look unusual but is precedented. Tyler and co-workers have shown that *trans*-Fe(diphosphine)₂Cl₂ reacts with H_2 in water to give *trans*- $[Fe(diphosphine)_2(H)(H_2)]^+Cl^-$ along with some protonated diphosphine ligand.³⁶ In our case, a coordinatively unsaturated intermediate **D** is generated and reacts with free PMe₃ (available via proton transfer from $[HPMe_3]^+$ to iPr_2NEt), thus explaining the formation of **2'-H**.



Activation of H₂ with 3^+ -**B**F₄ is significantly more sluggish (eq 5). The reaction at room temperature was incomplete even after 11 days, with 91% of 3^+ -**B**F₄ being converted to 3-**H**. Presumably, the dissociation of CH₃CN from 3^+ -**B**F₄ is much slower than from 2^+ -**B**F₄. Since CF₃CO₂H failed to protonate 3-**H** (Table 1), the less acidic [ⁱPr₂N(H)Et]⁺[BF₄]⁻ is not likely to protonate 3-**H** either, suggesting that the equilibrium in eq 5 lies predominantly to the right.

To activate H_2 in a catalytic fashion, hydrogenation of benzaldehyde was attempted in the presence of 1 mol % of 2^+ -BF₄ under ~1 atm of H_2 pressure. The limited solubility of 2^+ -BF₄ in commonly used organic solvents such as THF, diethyl ether, and toluene presented a minor technical challenge. Although it is highly soluble in CHCl₃ and CH₂Cl₂, these solvents can cause decomposition of hydride intermediates (especially if heated) and therefore are not suitable for the catalytic study. Given these factors, chlorobenzene- d_5 was chosen as the solvent so that the reaction could be conveniently monitored by NMR. Unfortunately, at 70 °C, no hydrogenation of benzaldehyde was observed at 24 h (eq 6). The ¹H NMR spectrum revealed a very

PhCHO + H₂
$$\xrightarrow{1 \text{ mol}\% 2^+ \cdot \mathbf{BF}_4}$$
 PhCH₂OH (6)
(~1 atm) C₆D₅Cl, 70 °C
24 h

Scheme 4. Proposed Pathways Leading to the Formation of Both 2-H and 2'-H



small amount of hydride species at -9.47 ppm (a multiplet), and the ${}^{31}P{}^{1}H$ NMR spectrum showed substantial decomposition of the pincer complex. Because the stoichiometric activation of H₂ by 3^+ -BF₄ was much slower, catalytic hydrogenation with this particular cationic complex was not pursued.

Catalytic Hydrosilylation Reactions. Better success was achieved when the cationic complexes were employed to catalyze the hydrosilylation of carbonyl groups. As shown in Table 3, hydrosilylation of benzaldehyde (eq 7) catalyzed by

Table 3. Catalytic Hydrosilylation of Benzaldehyde^a

entry	catalyst	time (h)	yield $(\%)^b$	catalyst remaining $(\%)^c$
1	2^+-BF_4	24	>99	8
2	2-H	24	15	95
3	2′-H	24	0	>99
4	3^+ -BF ₄	48	10	0
5	3-H	48	0	>99

^{*a*}Conditions: iron catalyst (4.8 μ mol), PhCHO (0.48 mmol), (EtO)₃SiH (0.52 mmol), and hexamethylbenzene (26.5 μ mol, internal standard) in 0.5 mL of C₆D₅Cl. ^{*b*}Calculated by ¹H NMR. ^{*c*}Calculated by ³¹P{¹H} NMR.

PhCHO + (EtO)₃SiH
$$\frac{1 \text{ mol}\% [\text{Fe}]}{C_6 D_5 \text{Cl}, 50 \text{ °C}}$$
 PhCH₂O-[Si] (7)

2⁺-BF₄ at 50 °C went to completion in 24 h (entry 1), whereas the reaction catalyzed by the corresponding neutral iron hydride **2-H** gave hydrosilylation products³⁷ in 15% yield over the same period of time (entry 2). In contrast, **2'-H** did not catalyze this reaction at all (entry 3). Cationic complex **3⁺-BF**₄ was not an efficient catalyst either; only 10% yield was obtained after 48 h (entry 4). However, it is still a better catalyst than **3-H**, which showed no catalytic activity (entry 5).

Overall, the cationic complexes are better catalysts than the analogous neutral hydride complexes, but only 2^+ -BF₄ shows a drastic improvement. To further understand the catalytic reactivity of these complexes, the percentage of remaining catalyst at the end of the reaction was measured by ³¹P{¹H} NMR spectroscopy (the rightmost column of Table 3). In the case of 2^+ -BF₄, only 8% of the catalyst was present at the end of the reaction (entry 1). The bulk of the catalyst was converted to 2-H, 2'-H, and a small quantity of unidentified species. As expected from our previous study,¹⁵ 5% of 2-H was isomerized to 2'-H (entry 2). For 3⁺-BF₄, the cationic species was converted to 3-H quantitatively within 4 h, and hydrosilylated products were obtained in 10% yield (entry 4). Once 3⁺-BF₄ was fully converted to 3-H, the catalytic reaction ceased, which is consistent with the observation of no catalytic activity for 3-H (entry 5).

Acetophenone was also subjected to the hydrosilylation conditions using either the cationic or the neutral iron complexes as the catalysts, although the temperature had to be raised to 80 $^{\circ}$ C (eq 8). In terms of the relative catalytic

$$Ph \xrightarrow{O}_{CH_3} + (EtO)_3SiH \xrightarrow{1 \text{ mol\% [Fe]}}_{C_6H_5CI, 80 \text{ °C}} Ph \xrightarrow{O}_{H} (8)$$

activity (Table 4), the general trend is similar to that observed in the benzaldehyde reduction. For instance, after 48 h, 79% of the acetophenone was converted to hydrosilylation products³⁸

Table 4. Catalytic Hydrosilylation of Acetophenone^a

entry	catalyst	time (h)	conversion $(\%)^b$
1	2^+-BF_4	48	79
2	2-H	48	54
3	3^+ -BF ₄	48	63
4	3-H	48	56

^{*a*}Conditions: iron catalyst (9.5 μ mol), PhCOCH₃ (0.95 mmol), and (EtO)₃SiH (1.05 mmol) in 1 mL of C₆H₅Cl. ^{*b*}Calculated by ¹H NMR.

when 2^+ -BF₄ was used as the catalyst (entry 1), whereas 54% conversion was obtained for the reaction catalyzed by 2-H (entry 2). Complex 3^+ -BF₄ (entry 3) showed a marginally better efficiency than 3-H (entry 4), which is in agreement with the results for the hydrosilylation of benzaldehyde. It is interesting to note that for the acetophenone reaction the catalytic activity of 3-H is comparable to that of 2-H. For the hydrosilylation of the aldehyde mentioned above, 2-H is a better catalyst than 3-H (Table 3, entries 2 and 5). We hypothesize that at 80 °C the lower activity of 3-H is offset by its higher thermal stability.

CONCLUSION

As part of our efforts to develop catalytic processes using cationic iron POCOP-pincer complexes, we have studied the protonation of four iron hydride complexes with various Brønsted acids and established the basicity order of 1-H > 2-H > $2^\prime\text{-}H$ > 3-H. We have also observed a SET pathway for the reaction between 2-H and $[Ph_3C]^+[BF_4]^-$, which results in a complicated mixture of products, making $[Ph_3C]^+[BF_4]^$ unsuitable for the synthesis of the desired cationic complexes. Instead, we have used HBF₄·Et₂O to successfully remove the hydride ligand from 2-H/2'-H and 3-H to yield 2^+ -BF₄ and 3^+ -BF₄, respectively. Synthesis of an analogous cationic complex from 1-H remains challenging due to the facile protonation of PMe₃. With two new cationic iron complexes in hand, we have investigated their reactivity for the activation of small molecules such as H₂ and silanes. In the presence of an external base, ⁱPr₂NEt, both 2^+ -BF₄ and 3^+ -BF₄ can cleave H₂ in a heterolytic manner, resulting in neutral hydride complexes and $[{}^{i}Pr_{2}N(H)Et]^{+}[BF_{4}]^{-}$. Although $2^{+}-BF_{4}$ is not a viable catalyst for the hydrogenation of benzaldehyde (under 1 atm of H₂ pressure), 2^+ -BF₄ and 3^+ -BF₄ are effective in catalyzing the hydrosilylation of benzaldehyde and acetophenone and demonstrating improved activity over the corresponding neutral hydride complexes.

In our previous work on hydrosilylation reactions catalyzed by 1-H,¹⁵ deuterium-labeling experiments showed that the hydride was intact during the catalytic reaction, thus only playing the role of promoting ligand dissociation. The DFT calculations by Wei et al., however, supported a mechanism involving the delivery of the hydride to the C=O group.¹⁷ The current cationic iron system is likely to operate via the mechanism shown in Scheme 1, which is analogous to what we have proposed for the neutral hydride system. The difference is that the silane complex in this case is cationic, resulting in more favorable silvlium transfer to the carbonyl substrates. Explaining the discrepancy between the experimental data and DFT calculations for the neutral hydride catalysts would require additional investigations. Nevertheless, through this study, we have further confirmed that for the Fe-POCOP system the hydride ligand is not necessarily needed for catalytic hydrosilvlation reactions.

EXPERIMENTAL SECTION

General Comments. All the organometallic compounds were prepared and handled under an argon atmosphere using standard Schlenk and inert-atmosphere box techniques. Dry and oxygen-free solvents were collected from an Innovative Technology solvent purification system and used throughout all experiments. Deuterated NMR solvents (CD₃CN, CDCl₃, and C₆D₅Cl) were purchased from Cambridge Isotope Laboratories, Inc., kept under an argon atmosphere, and used without further purification. ¹H, ¹³C{¹H}, and $^{31}\text{P}\{^1\hat{H}\}$ NMR spectra were recorded on a Bruker Avance-400 MHz spectrometer. Chemical shift values in ¹H and ¹³C{¹H} NMR spectra were referenced internally to the residual solvent resonances. ${}^{31}P{}^{1}H{}$ spectra were referenced externally to 85% H₃PO₄ (0 ppm). Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a Smart Orbit diamond attenuated total reflectance (ATR) accessory. The mass spectrum of the reaction in eq 1 was obtained by injecting the reaction mixture (in CH₃CN) into a Micromass Q-TOF-2 mass spectrometer at a flow rate of 4 μ L/min. Complexes 1-H, 2-H, 2'-H, and 3-H were prepared as described in the literature.15

Reaction of 2-H with [Ph₃C]⁺[BF₄]⁻. In a J. Young NMR tube, 2-H (6.0 mg, 12 μ mol) was mixed with ~0.5 mL of CD₃CN. The hydride complex was not fully dissolved, but turned into a clear solution upon further mixing with $[Ph_3C]^+[BF_4]^-$ (3.9 mg, 12 μ mol). After 1 h, the ³¹P{¹H} NMR spectrum showed a mixture of **2-H** (45% of total pincer complexes), 2⁺-BF₄ (30%), 4⁺-BF₄ (25%), and [HPMe₃]⁺[BF₄]^{-.39} ³¹P{¹H} NMR (162 MHz, δ): -2.1 (s, [HPMe₃]⁺), 0.15 (t, ²J_{PP} = 17.2 Hz, PMe₃ of 2⁺-BF₄), 11.5 (t, ${}^{2}J_{PP}$ = 16.6 Hz, PMe₃ of 2-H), 197.0 (s, OPⁱPr₂ of 4⁺-BF₄), 207.3 (d, ${}^{2}J_{PP}$ = 17.2 Hz, OPⁱPr₂ of 2⁺-BF₄), 231.9 (d, ${}^{2}J_{PP}$ = 16.6 Hz, OPⁱPr₂ of 2-H). The ¹H NMR spectrum showed 5⁴⁰ in addition to the products mentioned above. Selected ¹H NMR data of **2-H** (400 MHz, δ): -9.41 (td, ${}^{2}J_{PH}$ = 62.8 and 50.4 Hz, FeH), 0.96-1.02 (m, CH(CH₃)₂), 1.05-1.12 (m, CH(CH₃)₂), 1.41 (d, ${}^{2}J_{PH} = 7.2$ Hz, PCH₃), 2.30–2.39 (m, CH(CH₃)₂), 2.43– 2.55 (m, CH(CH₃)₂), 6.25 (d, ${}^{3}J_{HH}$ = 7.6 Hz, ArH), 6.60 (t, ${}^{3}J_{HH}$ = 7.6 Hz, ArH). Selected ¹H NMR data of 2⁺-BF₄: 1.67 (d, ${}^{2}J_{PH}$ = 8.4 Hz, PCH₃), 2.67–2.78 (m, CH(CH₃)₂), 6.67 (d, ${}^{3}J_{HH} = 8.0$ Hz, ArH), 7.02 (t, ${}^{3}J_{HH} = 8.0$ Hz, ArH). Selected ${}^{1}H$ NMR data of 4⁺-BF₄: 2.88–2.95 (m, CH(CH₃)₂), 2.96–3.05 (m, CH(CH₃)₂), 6.51 (d, ${}^{3}J_{HH} = 8.0$ Hz, ArH), 6.87 (t, ${}^{3}J_{HH} = 8.0$ Hz, ArH). Selected ${}^{1}H$ NMR data of 5: 5.18–5.24 (m, Ph₃CCH), 5.97 (dd, ${}^{3}J_{HH} = 10.8$ and 4.0 Hz, Ph₃CCHCH), 6.16 (dd, ${}^{3}J_{HH} = 10.8$ Hz, ${}^{4}J_{HH} = 2.4$ Hz, Ph₂C=CCH). ¹H NMR data of [HPMe₃]⁺[BF₄]⁻: 1.79 (dd, ${}^{2}J_{PH} = 2.4$ Hz, Ph₂C=CCH). 15.6 Hz, ${}^{3}J_{HH} = 5.6$ Hz, $[HP(CH_{3})_{3}]^{+}$), 6.06 (dm, ${}^{1}J_{PH} = 508$ Hz, ${}^{3}J_{\text{HH}} = 5.6 \text{ Hz}, [HP(CH_{3})_{3}]^{+}$). TOF-MS (ES+) data of the reaction mixture (in CH₃CN, m/z): M⁺ of 2⁺ calcd for C₂₄H₄₃NO₃P₃Fe 542.1805, found 542.2819; [M - CH₃CN]⁺ of 2⁺ calcd for $C_{22}H_{40}O_{3}P_{3}Fe$ 501.1540, found 501.2165; $[M-CH_{3}CN-CO]^{+}$ of 2^+ calcd for C₂₁H₄₀O₂P₃Fe 473.1591, found 473.2400; M⁺ of 4⁺ calcd for C₂₃H₃₇N₂O₃P₂Fe 507.1629, found 507.2582; [M - CH₃CN]⁺ of 4^+ calcd for $C_{21}H_{34}NO_3P_2Fe$ 466.1364, found 466.2246.

Procedures for the Protonation Reactions. In a J. Young NMR tube, an iron hydride complex (10 μ mol) was dissolved in ~0.5 mL of CD₃CN/THF- d_8 (1:1). The resulting solution was cooled to -30 °C, followed by the addition of HBF₄·Et₂O (10 μ mol) and then slowly warmed to room temperature. For the experiments involving CF₃CO₂H or HCO₂H, the acid (10 μ mol) was added at room temperature. The progress of the reaction was monitored by ¹H NMR and ³¹P NMR spectroscopy until it reached equilibrium or for 48 h (for the reaction of **3-H** with CF₃CO₂H and the reactions of **2'-H** and **3-H** with HCO₂H). Protonation of **1-H** with CF₃CO₂H and HCO₂H was also attempted by starting the reaction at -30 °C first; however, the results were the same with a significant amount of decomposition products observed.

Synthesis of { $[2,6-({}^{i}Pr_2PO)_2C_6H_3]Fe(CO)(PMe_3)(CH_3CN)$ }-[BF₄]⁻ (2⁺-BF₄). A solution of 2-H (100 mg, 0.20 mmol) in THF/ CH₃CN (1 mL each) was cooled to -30 °C, followed by the addition of HBF₄·Et₂O (28 μ L, 0.20 mmol) at this temperature. The reaction mixture was then slowly warmed to room temperature while gas evolution was observed. The resulting bright yellow solution was passed through a short pad of Celite, and the solvent was removed under vacuum to produce a crystalline solid (107 mg, 85% yield). ¹H NMR (400 MHz, CDCl₃, δ): 1.29–1.41 (m, CH(CH₃)₂, 24H), 1.73 (d, ²J_{PH} = 8.4 Hz, PMe₃, 9H), 2.38 (s, NCCH₃, 3H), 2.68–2.79 (m, CH, 4H), 6.66 (d, ³J_{HH} = 8.0 Hz, ArH, 2H), 6.99 (t, ³J_{IHH} = 8.0 Hz, ArH, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 4.9 (s, CH₃CN), 18.0 (s, CH₃), 18.1 (s, CH₃), 18.5 (s, CH₃), 18.6 (s, CH₃), 21.1 (d, ¹J_{PC} = 26.4 Hz, PMe₃), 31.3 (t, ¹J_{PC} = 7.2 Hz, CH), 32.2 (t, ¹J_{PC} = 10.4 Hz, CH), 106.7 (t, ³J_{PC} = 4.7 Hz, ArC), 128.1 (s, ArC), 132.9 (s, CH₃CN), 134.4–135.0 (m, ArC), 164.0 (t, ²J_{PC} = 6.5 Hz, ArC), 216.3-216.5 (m, CO). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): -0.2 (t, ²J_{PP} = 16.5 Hz, PMe₃, 1P), 206.4 (d, ²J_{PP} = 16.5 Hz, OPⁱPr₂, 2P). ATR-IR (solid): ν_{CO} = 1946 cm⁻¹. Anal. Calcd for C₂₄H₄₃NO₃P₃FeBF₄: C, 45.82; H, 6.89; N, 2.23. Found: C, 45.83; H, 6.85; N, 2.38.

Synthesis of *cis*-{[2,6-(ⁱPr₂PO)₂C₆H₃]Fe(CO)₂(CH₃CN)}⁺[BF₄]⁻ (**3**⁺-BF₄). This compound was prepared in 82% yield by a procedure similar to that used for 2⁺-BF₄. ¹H NMR (400 MHz, CDCl₃, δ): 1.30– 1.54 (m, CH(CH₃)₂, 24H), 2.42 (s, NCCH₃, 3H), 2.74–2.84 (m, CH, 2H), 2.89–2.98 (m, CH, 2H), 6.75 (d, ²J_{HH} = 8.0 Hz, ArH, 2H), 7.10 (t, ²J_{HH} = 8.0 Hz, ArH, 1H). ¹³C{¹H} NMR (101 MHz, CDCl₃, δ): 4.7 (s, CH₃CN), 16.7 (s, CH₃), 17.1 (t, ²J_{PC} = 2.0 Hz, CH₃), 17.3 (s, CH₃), 18.6 (t, ²J_{PC} = 2.4 Hz, CH₃), 29.2 (t, ¹J_{PC} = 12.9 Hz, CH), 30.7 (t, ¹J_{PC} = 10.6 Hz, CH), 108.1 (t, ³J_{PC} = 5.5 Hz, ArC), 129.8 (s, ArC), 131.9 (t, ²J_{PC} = 12.6 Hz, ArC), 132.8 (s, CH₃CN), 164.5 (t, ²J_{PC} = 7.1 Hz, ArC), 205.5 (t, ²J_{PC} = 8.3 Hz, CO), 210.5 (t, ²J_{PC} = 27.2 Hz, CO). ³¹P{¹H} NMR (162 MHz, CDCl₃, δ): 206.9 (s). ATR-IR (solid): ν_{CO} = 2046 and 1989 cm⁻¹. Anal. Calcd for C₂₂H₃₄NO₄P₂FeBF₄: C, 45.47; H, 5.90; N, 2.41. Found: C, 45.41; H, 5.75; N, 2.56.

X-ray Structure Determination. Single crystals of 2⁺-BF₄ were grown from a saturated solution in THF/CH₃CN (or CH₂Cl₂) at -30 °C. Crystal data collection and refinement parameters are summarized in Table S1. Intensity data were collected at 150 K on a Bruker APEX-II CCD detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to $\lambda = 0.77490$ Å. The data frames were collected using the program APEX2 and processed using the program SAINT, a routine within APEX2. The data were corrected for absorption and beam corrections based on the multiscan technique as implemented in SADABS. The structure was solved by a combination of direct methods SHELXTL v6.14 and the difference Fourier technique and refined by full-matrix least-squares on F^2 . Non-hydrogen atoms were refined with anisotropic displacement parameters. The BF4⁻ anion is disordered; a reasonable twocomponent disorder model is given (major occupancy = 0.67). The H atom positions were calculated and treated with a riding model in subsequent refinements. The isotropic displacement parameters for the H atoms were defined as aU_{eq} (a = 1.5 for methyl and 1.2 for all others) of the adjacent atom.

Attempted Hydrogenation of Benzaldehyde. In a J. Young NMR tube, 2⁺-BF₄ (3.0 mg, 4.8 µmol) was mixed with 0.5 mL of C₆D₅Cl, followed by the addition of benzaldehyde (49 µL, 0.48 mmol) and hexamethylbenzene (4.3 mg, 26.5 µmol, internal standard). The reaction mixture was frozen by liquid nitrogen, after which the headspace of the NMR tube was evacuated and then exposed to a hydrogen atmosphere (1 atm). The frozen sample was thawed at room temperature before the NMR tube was disconnected from the hydrogen source. The reaction mixture was heated by an oil bath at 70 °C, and the progress of the reaction was monitored by ¹H and ³¹P{¹H} NMR spectroscopy.

General Procedure for Catalytic Hydrosilylation of Benzaldehyde. In a typical experiment, an iron catalyst (4.8 μ mol, 1 mol %) and 0.5 mL of C₆D₅Cl were mixed in a J. Young NMR tube. To this solution, benzaldehyde (49 μ L, 0.48 mmol), triethoxysilane (96 μ L, 0.52 mmol), and hexamethylbenzene (4.3 mg, 26.5 μ mol, internal standard) were added at once. The reaction mixture was heated by an oil bath at 50 °C, and the progress of the reaction was monitored by ¹H and ³¹P{¹H} NMR spectroscopy. The combined yield for the

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hydrosilylation products was calculated by comparing the integration of $PhCH_2O$ methylene resonances¹⁵ with that of the internal standard. The percentage of the remaining iron catalyst was calculated from ³¹P NMR integrations of the iron catalysts and other iron species (without a standard).

General Procedure for Catalytic Hydrosilylation of Acetophenone. In a typical experiment, an iron catalyst (9.5 μ mol, 1 mol %) was dissolved in 1 mL of C₆H₅Cl. To this solution, acetophenone (111 μ L, 0.95 mmol) and triethoxysilane (194 μ L, 1.05 mmol) were added. The reaction mixture was heated by an oil bath at 80 °C for 48 h. After cooling to room temperature, an aliquot was withdrawn from the mixture, diluted with CDCl₃, and then subjected to ¹H NMR analysis. No byproducts were observed for any of the reactions with acetophenone. The percentage conversion of acetophenone was calculated based on the integrations of PhCH(OSiR₃)CH₃ and PhCOCH₃.¹⁵

ASSOCIATED CONTENT

S Supporting Information

Complete details of the crystallographic study (PDF and CIF), characterization data for 2^+ -BF₄ and 3^+ -BF₄, and representative NMR spectra of the catalytic reaction. 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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(37) Multiple hydrosilylation products were observed for the reactions described in Table 3 (entries 1, 2, and 4). This is due to the redistribution of PhCH₂O and EtO groups on silicon.

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