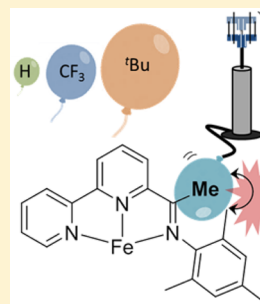# Hydrosilylation of Olefins Catalyzed by Iron Complexes Bearing Ketimine-Type Iminobipyridine Ligands

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ABSTRACT: A series of NNN-pincer iron complexes bearing ketimine-type iminobipyridene (BPI) ligands were prepared. These iron complexes were effective catalysts for the hydrosilylation of olefins using primary, secondary, and tertiary silanes. The effect of the substituents on the imino carbon on the catalytic activity was examined, and it was found that an appropriate combination of the imino carbon and imino nitrogen substituents led to complexes with quite high catalytic activity: the turnover number achieved was up to 42000. These iron catalytic systems provide a low-cost and promising alternative to currently employed precious metal systems for the hydrosilylation of olefins.

■ INTRODUCTION

Catalytic hydrosilylation of olefins is one of the most straightforward and atom-economical methods to synthesize organosilanes, which are versatile and indispensable compounds.[1] Platinum catalysts such as Karstedt's and Speier's catalysts are known to be very effective for olefin hydrosilylation.[2] However, platinum is a precious metal. Therefore, the development of base-metal catalysts for the hydrosilylation reaction of olefins is one of the most important and urgent topics of research.

As iron is a typical base metal, many iron complexes have been investigated for the hydrosilylation of olefins, and several effective iron complexes have been reported. It is generally important to select an appropriate ligand that suitably coordinates to the transition metal in order to render a highly active homogeneous catalyst.[3] To date, published work shows that Fe[4−11] and Co[12] complexes, bearing pincer-type ligands, are effective hydrosilylation catalysts.

Chirik and co-workers showed that the NNN pincer-type ligand 2,6-diiminopyridine (PDI) was a good ligand for the iron-catalyzed hyrosilylation of olefins. The nitrogen complex (PDI)Fe(N₂)₂ exhibited higher hydrosilylation catalytic activity in comparison to any iron catalyst reported so far.[4] However, it was found to be very unstable toward air and moisture. Chirik's group reported that the corresponding dialkyl complex, (PDI)FeR₂, was more robust and maintained high catalytic activity. However, high temperatures were required to activate this catalyst. Iron complexes bearing NNN and PNN pincer-type ligands have been reported to be good hydrosilylation catalysts (Figure 1).[4−9] Our group and Chirik's group reported that iron complexes bearing the NNN pincer-type ligand terpyridine, (terpy)FeX₂, effectively catalyzed the hydrosilylation of olefins.[4c,5] It should be noted that the bulkiness of PDI and terpy substituents situated near the iron active site greatly affected the catalytic activity: the bulkiness of the substituents on the imino nitrogens of PDI and that on the 5-,
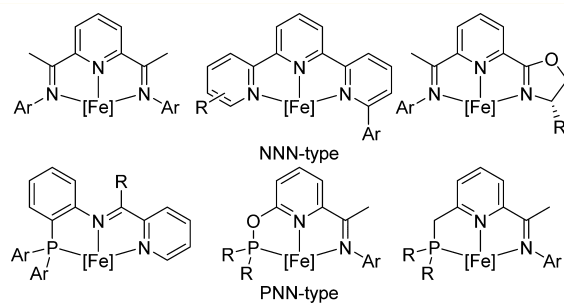

Figure 1. Iron complexes bearing NNN and PNN pincer-type ligands.

6-, 5′-, and 6′-positions of terpy played a crucial role in the catalytic activity.

Other notable examples of NNN pincer-type iron complexes showing catalytic activity for olefin hydrosilylation have been reported by the research groups of Lu[6] and Thomas.[7] Moreover, Walter and Huang reported that iron complexes bearing PNN pincer-type ligands were also effective catalysts for the hydrosilylation of olefins.[8] These iron complexes exhibited functional group tolerance toward reactive functionalities, such as ketones, esters, and amides.

We recently reported that the NNN pincer-type ligand 6-imino-2,2′-bipyridine (BPI) was an appropriate ligand for Fe. The iron complexes (BPI)FeBr₂ exhibited high catalytic activity for the hydrosilylation of olefins.[10] NaBHEt₃ was required as a cocatalyst in this system to activate the iron complex. In these iminobipyridine iron complexes, the three substituents, R′ (the substituent at the 6′-position of the bipyridine unit), R (the substituent on the imino carbon), and Ar (the substituent on the imino nitrogen), are expected to affect the catalytic activity. Complexes with R = H and R = hydrocarbon are denoted as aldimine- and ketimine-type iminobipyridine complexes,

respectively (Figure 2). In a previous study,[10] we examined the effect of the substituents (R′ and Ar) on the aldimine-type
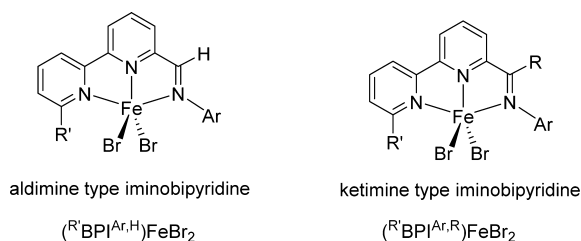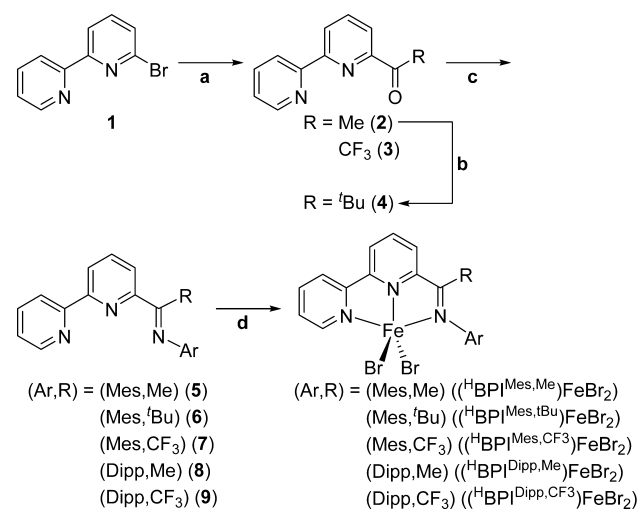

Figure 2. Iron complexes bearing aldimine- and ketimine-type iminobipyridines.

complex (BPI)FeBr$_2$ on the catalytic activity; we found that an appropriate balance between substituents was important in designing better catalysts. A high turnover number (TON) of 12038 was reported for the hydrosilylation of 1-octene with diphenylsilane (Ph$_2$SiH$_2$). We surmised that the steric and/or electronic balance between the two substituents, that on the imino carbon and that on the imino nitrogen, was responsible for the catalytic activity. In this paper, we report the synthesis of iron complexes bearing ketimine-type iminobipyridine ligands and examine their catalytic activity on the hydrosilylation of olefins.

■ RESULTS AND DISCUSSION

Preparation of Ketimine-Type Iminobipyridine Derivatives and Their Iron Complexes. The reaction sequences for the preparation of the iron complexes bearing an iminobipyridine derivative and two Br atoms are shown in Scheme 1. In this paper, the (^{H}BPI^{Ar,R})FeBr$_2$ (Ar = Mes (2,4,6-Me$_3$C$_6$H$_2$), Dipp (2,6-^{i}Pr$_2$C$_6$H$_3$); R = Me, ^{t}Bu, CF$_3$) convention is used to describe the iron complexes, where H, Ar, and R stand for a substituent at the 6′-position of the bipyridine unit,

Scheme 1. Synthetic Routes of Iron Complexes with Ketimine-Type Iminobipyridine Ligands[a]

(Ar,R) = (Mes,Me) (5)
 (Mes,^{t}Bu) (6)
 (Mes,CF$_3$) (7)
 (Dipp,Me) (8)
 (Dipp,CF$_3$) (9)

(Ar,R) = (Mes,Me) ((^{H}BPI^{Mes,Me})FeBr$_2$)
 (Mes,^{t}Bu) ((^{H}BPI^{Mes,tBu})FeBr$_2$)
 (Mes,CF$_3$) ((^{H}BPI^{Mes,CF3})FeBr$_2$)
 (Dipp,Me) ((^{H}BPI^{Dipp,Me})FeBr$_2$)
 (Dipp,CF$_3$) ((^{H}BPI^{Dipp,CF3})FeBr$_2$)

[a]Conditions: (a) *n*-BuLi, Me$_2$NC(O)R (R = Me, CF$_3$), in THF/hexane/ether, at −78 °C (54−89% yield); (b) NaH, MeI, in THF, at 0 °C (79% yield); (c) ArNH$_2$ (Ar = Mes, Dipp), H$^+$ cat. (5, 8, formic acid; 6, 7, 9, *p*-toluenesulfonic acid monohydrate), in MeOH (5, 8) or toluene (6, 7, 9), at reflux temperature (43−88% yield); (d) anhydrous FeBr$_2$, in THF, at room temperature (56−99% yield).

that on the imino nitrogen, and that on the imino carbon, respectively. 1-[2,2′-Bipyridin-6-yl]ethanone derivatives **2** and **3** were obtained by treating 6-bromo-2,2′-bipyridine (**1**) with ^{n}BuLi, followed by the addition of the corresponding *N,N*-dimethylacetamide derivatives (Me$_2$NC(O)R: R = Me, CF$_3$) (Scheme 1a). 2,2-Dimethyl-1-[2,2′-bipyridin-6-yl]-1-propanone (**4**) was prepared by methylation of **2** (Scheme 1b). Next, the iminobipyridine derivatives **5**−**9** were obtained by the condensation between **2**, **3**, or **4** and the corresponding amines (Scheme 1c). As the iminobipyridine derivative **6** was found to be unstable, it was used without isolation. Finally, these iminobipyridine derivatives were treated with iron(II) bromide (FeBr$_2$) in THF to give the corresponding iron complexes ((^{H}BPI^{Ar,R})FeBr$_2$) (Scheme 1d). The iron complexes and their precursors shown in Scheme 1 were characterized by NMR and/or elemental analysis.

Hydrosilylation of 1-Octene with Primary, Secondary, and Tertiary Hydrosilanes Catalyzed by (^{H}BPI^{Ar,R})FeBr$_2$. (^{H}BPI^{Ar,R})FeBr$_2$ (0.01 mol % based on the concentration of the hydrosilane added later) was placed in a Schlenk tube. Then, the air in the tube was replaced with nitrogen, and silane and 1-octene (1:2 molar ratio) were added. Finally, NaBHEt$_3$ (0.2 mol %) was added to the suspension with stirring at room temperature, and a homogeneous solution was obtained within a few minutes. This process was exothermic. The solution was stirred without any temperature control for 24 h, and the reaction mixture was subsequently exposed to air. The resulting solution was analyzed by HPLC to determine the yields of the hydrosilylated product(s).

In order to compare the catalytic activity of our iminobipyridine iron complexes with that of Karstedt's catalyst, we also examined the hydrosilylation reaction catalyzed by Karstedt's catalyst under the same reaction conditions. The results are summarized in Table 1. In all cases, selective anti-Markovnikov addition occurred and only 1-octyl-substituted silanes were formed; 2-octyl-substituented silanes or any other isomers were not detected.

TON (turnover number) was used to evaluate the catalytic activity. Some of the iron complexes were active enough to produce not only the monoalkylated silane but also the dialkylated silane. For example, when (^{H}BPI^{Mes,Me})FeBr$_2$ was used (Table 1, entry 2), the iron catalyst first converted PhSiH$_3$ to Ph(octyl)SiH$_2$ and this monoalkylated product reacted with further 1-octene, under the catalytic conditions, to give the dialkylated product Ph(octyl)$_2$SiH; the final yields were 56% and 26% for mono- and dialkylated products, respectively. The TON of this reaction was 5610 for Ph(octyl)SiH$_2$ and 2640 for Ph(octyl)$_2$SiH. In order to produce Ph(octyl)$_2$SiH, the hydrosilylation reaction occurs twice. Therefore, the overall hydrosilylation catalytic activity for (^{H}BPI^{Mes,Me})FeBr$_2$ is estimated to be 10890 (= 5610 + 2 × 2640), which is denoted as "total TON" in this paper.

When (^{H}BPI^{Mes,R})FeBr$_2$ was used as the hydrosilylation catalyst with the primary silane PhSiH$_3$, the following features were found (Table 1, entries 1−4): (i) the iron complexes with R = CH$_3$, CF$_3$ produced not only monoalkylated silane but also dialkylated silane and showed very high catalytic activity (total TON = 10890 and 12360, respectively) and (ii) the iron complexes with R = H, ^{t}Bu produced mainly monoalkylated silane (the yield of dialkylated silane was only 1%), and the total TONs decreased, 2300 (R = H) and 1640 (R = ^{t}Bu), in comparison to those of the iron complexes with R = CH$_3$, CF$_3$. For the hydrosilylation reactions with the secondary silane

Table 1. Hydrosilylation of 1-Octene Catalyzed by (BPI)FeBr$_2$ and Karstedt's Catalyst[a]

$$\text{silane} \;+\; 2\text{ eq}\; \text{1-octene} \xrightarrow[\text{r.t., 24 h}]{\substack{\text{Fe complex cat.}\\ \text{NaBHEt}_3\text{ cat.}}} \text{hydrosilylated product}$$

entry	Fe complex	amt of Fe complex (mol %)[b]	silane	product (yield (%), TON)[c]		total TON[d]
1	(^{H}BPI^{Mes,H})FeBr$_2$	0.01	PhSiH$_3$	Ph(octyl)SiH$_2$ (21, 2140)	Ph(octyl)$_2$SiH (1, 80)	2300
2	(^{H}BPI^{Mes,Me})FeBr$_2$			Ph(octyl)SiH$_2$ (56, 5610)	Ph(octyl)$_2$SiH (26, 2640)	10890
3	(^{H}BPI^{Mes,tBu})FeBr$_2$			Ph(octyl)SiH$_2$ (15, 1480)	Ph(octyl)$_2$SiH (1, 80)	1640
4	(^{H}BPI^{Mes,CF3})FeBr$_2$			Ph(octyl)SiH$_2$ (67, 6660)	Ph(octyl)$_2$SiH (29, 2850)	12360
5	(^{H}BPI^{Dipp,H})FeBr$_2$			Ph(octyl)SiH$_2$ (65, 6460)	Ph(octyl)$_2$SiH (31, 3110)	12680
6	(^{H}BPI^{Dipp,Me})FeBr$_2$			Ph(octyl)SiH$_2$ (60, 5950)	Ph(octyl)$_2$SiH (8, 750)	7450
7	(^{H}BPI^{Dipp,CF3})FeBr$_2$			Ph(octyl)SiH$_2$ (63, 6330)	Ph(octyl)$_2$SiH (7, 680)	7690
8	Karstedt's catalyst			Ph(octyl)SiH$_2$ (3, 260)	Ph(octyl)$_2$SiH (0, 0)	260
9	(^{H}BPI^{Mes,H})FeBr$_2$	0.01	Ph$_2$SiH$_2$	Ph$_2$(octyl)SiH (65, 6480)	Ph$_2$(octyl)$_2$Si (0, 0)	6480
10	(^{H}BPI^{Mes,Me})FeBr$_2$			Ph$_2$(octyl)SiH (31, 3120)	Ph$_2$(octyl)$_2$Si (65, 6460)	16040
11	(^{H}BPI^{Mes,tBu})FeBr$_2$			Ph$_2$(octyl)SiH (42, 4190)	Ph$_2$(octyl)$_2$Si (0, 0)	4190
12	(^{H}BPI^{Mes,CF3})FeBr$_2$			Ph$_2$(octyl)SiH (54, 5370)	Ph$_2$(octyl)$_2$Si (45, 4490)	14350
13	(^{H}BPI^{Dipp,H})FeBr$_2$			Ph$_2$(octyl)SiH (94, 9380)	Ph$_2$(octyl)$_2$Si (1, 70)	9520
14	(^{H}BPI^{Dipp,Me})FeBr$_2$			Ph$_2$(octyl)SiH (71, 7100)	Ph$_2$(octyl)$_2$Si (7, 710)	8520
15	(^{H}BPI^{Dipp,CF3})FeBr$_2$			Ph$_2$(octyl)SiH (75, 7530)	Ph$_2$(octyl)$_2$Si (1, 110)	7750
16	Karstedt's catalyst			Ph$_2$(octyl)SiH (92, 9210)	Ph$_2$(octyl)$_2$Si (0, 0)	9210
17	(^{H}BPI^{Mes,H})FeBr$_2$	0.1	Ph$_2$MeSiH	Ph$_2$Me(octyl)Si (74, 741)		741
18	(^{H}BPI^{Mes,Me})FeBr$_2$			Ph$_2$Me(octyl)Si (80, 795)		795
19	(^{H}BPI^{Mes,tBu})FeBr$_2$			Ph$_2$Me(octyl)Si (13, 132)		132
20	(^{H}BPI^{Mes,CF3})FeBr$_2$			Ph$_2$Me(octyl)Si (65, 645)		645
21	(^{H}BPI^{Dipp,H})FeBr$_2$			Ph$_2$Me(octyl)Si (49, 494)		494
22	(^{H}BPI^{Dipp,Me})FeBr$_2$			Ph$_2$Me(octyl)Si (62, 621)		621
23	(^{H}BPI^{Dipp,CF3})FeBr$_2$			Ph$_2$Me(octyl)Si (1, 7)		7
24	Karstedt's catalyst			Ph$_2$Me(octyl)Si (93, 928)		928

[a]Reaction conditions: Neat, room temperature, 24 h, Schlenk tube, [silane]:[1-octene] = 1:2, [Fe complex]:[NaBHEt$_3$] = 1:20. [b]mol % = [Fe complex]/[silane] × 100. [c]Determined by HPLC. The values are based on the initial concentration of hydrosilane. [d]Total TON = TON of single-alkylated product + 2 × (TON of double-alkylated product).
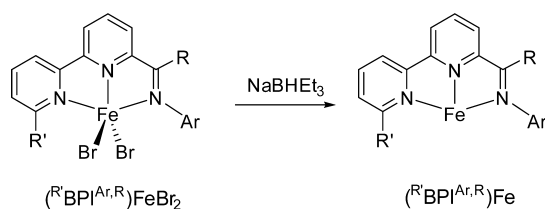
Ph$_2$SiH$_2$ (Table 1, entries 9−12), the catalytic activities were greater than that with the primary silane PhSiH$_3$ for all of the iron complexes screened: total TON = 10890−16040 (R = Me), 12360−14350 (R = CF$_3$), 2300−6480 (R = H), 1640−4190 (R = ^{t}Bu). The tendencies observed for PhSiH$_3$ (i and ii) were also observed for Ph$_2$SiH$_2$. It should be noted that the catalytic activities of iron complexes bearing either an electron-donating (Me) or an electron-withdrawing substituent (CF$_3$) are greater than those of the iron complexes with H on the imino carbon. These results suggest that the catalytic activity is mainly controlled by steric and not by electronic effects of the substituent on the imino carbon. The bulkiness of the substituent on the imino nitrogen also affects the catalytic activity. (^{H}BPI^{Dipp,H})FeBr$_2$ showed greater activity than (^{H}BPI^{Dipp,Me})FeBr$_2$ and (^{H}BPI^{Dipp,CF3})FeBr$_2$ (Table 1, entries 5−7 and 13−15). This is the opposite of the tendency observed for (^{H}BPI^{Mes,R})FeBr$_2$, implying that the combination of substituents on the imino carbon and imino nitrogen is important. One more point that needs our attention is the distribution of mono- and dialkylated products. The distribution obtained with PhSiH$_3$ catalyzed by (^{H}BPI^{Mes,Me})FeBr$_2$ and (^{H}BPI^{Mes,CF3})FeBr$_2$ is similar to that obtained by (^{H}BPI^{Dipp,H})-FeBr$_2$. In contrast, the distribution obtained with Ph$_2$SiH$_2$ catalyzed by (^{H}BPI^{Mes,Me})FeBr$_2$ and (^{H}BPI^{Mes,CF3})FeBr$_2$ is different from that by (^{H}BPI^{Dipp,H})FeBr$_2$. This seems to be an effect of the steric combination of the substituents on the imino

carbon and imino nitrogen. The tertiary silane Ph$_2$MeSiH also gave a hydrosilylation product, but the catalytic activities were low in comparison to those with primary and secondary silanes (Table 1, entries 17−23).

When Karstedt's catalyst was used under the same reaction conditions (Table 1, entries 8, 16, and 24), only monoalkylated product was formed with all silanes. In comparison to Karstedt's catalyst, the catalytic activity of our iron complexes is slightly lower with the tertiary silane but much greater with the primary and secondary silanes.

Effect of the Substituent on the Imino Carbon on Catalytic Activity. We previously reported that iminobipyridine derivatives ($^{R'}$BPI^{Ar,R}) were appropriate ligands for iron and their complexes, after suitable activation, exhibit high hydrosilylation catalytic activity.[10] The dibromoiron complex ($^{R'}$BPI^{Ar,R})FeBr$_2$ was inactive and only after treatment with NaBHEt$_3$ did the resulting system show catalytic activity. Therefore, we proposed that ($^{R'}$BPI^{Ar,R})Fe, formed from ($^{R'}$BPI^{Ar,R})FeBr$_2$ and NaBHEt$_3$ via ($^{R'}$BPI^{Ar,R})Fe(H)$_2$, was the real active species (Scheme 2).[10] The effect of the substituents (R' and Ar) on the catalytic activity was examined, and it was found that the bulkiness of R' and Ar had a dominant effect because of their proximity to the iron active site. How does the substituent on the imino carbon (R), being far from the active site, affect the catalytic activity? In this case, both electronic and steric effects had to be considered.

Scheme 2. Iron Complexes with an Iminobipyridine Derivative Ligand

which leaves the iron active site open for the substrate to approach.

Therefore, the catalytic activity of $(^HBPI^{Mes,H})Fe$ is lower than those of $(^HBPI^{Mes,Me})Fe$ and $(^HBPI^{Mes,CF3})Fe$. The structural orientation in $(^HBPI^{Dipp,R})Fe$ is different from that of $(^HBPI^{Mes,R})Fe$. The torsion angle in $(^HBPI^{Dipp,H})Fe$ is about 50°, the Dipp ring adopts an upright position, and the i-Pr group in the Dipp does not block the active iron site. This is presumably the reason for the high TON value for $(^HBPI^{Dipp,H})FeBr_2$. Therefore, the substituent (R) on the imino carbon may control the orientation of the aromatic (Ar) ring on the imino nitrogen. If R = H and Ar = Mes, the Mes ring adopts a coplanar orientation and blocks the approach of the substrate to the active iron site, whereas if R = CH_3, CF_3, ^tBu and Ar = Mes, Dipp or if R = H and Ar = Dipp, the Ar ring takes an upright position, leaving open the active iron site, resulting in high catalytic activity to the same extent for R = CH_3, CF_3.

Hydrosilylation of Functionalized Olefins. It is known that transition-metal catalysts are susceptible to catalyst poisons such as Cl-, N-, or S-containing compounds. We next examined the hydrosilylation of several functionalized olefins with Ph_2SiH_2 catalyzed by $(^HBPI^{Mes,Me})FeBr_2$. The results of this study, together with those for $(^HBPI^{Dipp,H})FeBr_2$ from our previous work,[10] are summarized in Table 3. 6-Chloro-1-hexene and N,N-dimethylallylamine were converted into the corresponding hydrosilylated products in the presence of 0.1 mol % of $(^HBPI^{Mes,Me})FeBr_2$ (Table 3, entries 1 and 4). The yield of hydrosilylated N,N-dimethylallylamine increased when 1.0 mol % of $(^HBPI^{Mes,Me})FeBr_2$ was used (Table 3, entry 3). The catalytic activities for Cl- and N-containing olefins were greater for $(^HBPI^{Mes,Me})FeBr_2$ than for $(^HBPI^{Dipp,H})FeBr_2$. In contrast, hydrosilylation of allyl phenyl sulfide did not occur, presumably caused by the coordination of the sulfur of the substrate to the catalytically active iron species, which reduces or destroys the catalytic activity (Table 3, entries 6 and 7). Vinylpentamethyldisiloxane was converted to the corresponding monoalkylated silane by $(^HBPI^{Mes,Me})FeBr_2$ (Table 3, entry 8).

Hydrosilylation of 1-Octene with Various Hydrosilanes Catalyzed by $(^HBPI^{Mes,Me})FeBr_2$. We then investigated the influence of various hydrosilanes on the hydrosilylation of 1-octene in the presence of $(^HBPI^{Mes,Me})FeBr_2$. The results are summarized in Table 4 and include some results from Table 1. When 0.1 mol % of $(^HBPI^{Mes,Me})FeBr_2$ was used, $PhSiH_3$, Ph_2SiH_2, and $PhMeSiH_2$ were completely converted into the corresponding dialkylated silanes (Table 4, entries 1, 3, and 5). In contrast, both, mono- and dialkylated silanes were formed when the amount of catalyst was reduced from 0.1 to

The order of the electron-donating ability of the substituent on the imino carbon is $CF_3 \ll H < Me < ^tBu$.[15] The observed catalytic activities (shown in Table 1) did not match this order. For example, the catalytic activity with $PhSiH_3$ for $(^HBPI^{Mes,Me})FeBr_2$ (bearing an electron-donating group) is similar to that for $(^HBPI^{Mes,CF3})FeBr_2$ (bearing an electron-withdrawing group) (Table 1, entries 2 and 4) and much greater than that of $(^HBPI^{Mes,H})FeBr_2$ (Table 1, entry 1).

To understand the effect of the substituent on the imino carbon on the catalytic activity, the proposed active spices $(^HBPI^{Ar,R})Fe$ were subjected to density functional theory (DFT) studies.[13] All calculations were performed under B3LYP[14−16]/ SDD[17] (Fe), 6-31G(d,p) (C, H, N, F) level using Gaussian 09 software. The natural bond orbital (NBO) analysis data[18] are given in Table 2. The atomic natural charges on the iron atom in $(^HBPI^{Ar,R})Fe$ ranged from 0.42 to 0.48, except in $(^HBPI^{Mes,H})Fe$, and did not significantly change with the variation of the substituent on the imino carbon. The HOMO and LUMO energy levels do not seem to explain the observed order of reactivity.

The optimized structures and HOMO and LUMO of $(^HBPI^{Mes,H})Fe$ and $(^HBPI^{Mes,Me})Fe$ are depicted in Figure 3. The most notorious difference is the orientation of the Mes ring. The iminobipyridine unit and the Mes ring are coplanar in $(^HBPI^{Mes,H})Fe$, with a torsion angle of 0.0° between the rings (Table 2). This is probably due to the extension of the π system. In contrast, the BPI unit and the Mes ring are orthogonal in $(^HBPI^{Mes,Me})Fe$ (torsion angle 88.8°, Table 2). This is due to the steric repulsion between the Mes group on the imino nitrogen and the Me group on the imino carbon. The torsion angles in $(^HBPI^{Mes,tBu})Fe$ and $(^HBPI^{Mes,CF3})Fe$ are 85.3 and 87.2°, respectively (Table 2). When there is no steric repulsion (R = H), the Mes ring adopts a coplanar orientation in order to extend the π conjugation. In such an orientation a Me group on the Mes is brought toward the vacant site of the Fe and blocks the iron active site. If there is steric repulsion between R and Ar, the aryl ring adopts an upright position,

Table 2. NBO Atomic Charges (q_{Fe}, HOMO, and LUMO) and Torsion Angles

	$(^HBPI^{Mes,R})Fe$				$(^HBPI^{Dipp,R})Fe$		
	R = H	R = Me	R = ^tBu	R = CF_3	R = H	R = Me	R = CF_3
σ_m[a]	0.00	−0.07	−0.10	0.43	0.00	−0.07	0.43
σ_p[a]	0.00	−0.17	−0.20	0.54	0.00	−0.17	0.54
q_{Fe}[b]	(0.19)	0.44	0.43	0.46	0.42	0.47	0.48
HOMO (eV)[b]	−3.52	−3.49	−3.63	−3.94	−3.58	−3.63	−4.00
LUMO (eV)[b]	−1.69	−1.44	−1.45	−2.26	−1.38	−1.47	−2.28
Δ (eV)[b]	1.83	2.17	2.18	1.67	2.20	2.16	1.72
torsion angle (deg)[b,c]	0.0	88.8	85.3	87.2	49.7	89.9	88.5

[a]Hammett substituent constants. [b]B3RYP (SDD/Fe; 6-31G(d,p)/C, H, N, F). [c]Torsion angle of iminobipyridine unit and aryl ring on the imino nitrogen.
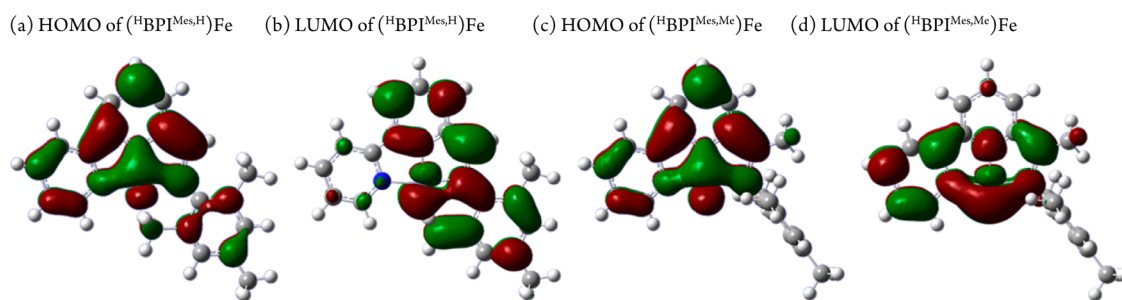
(a) HOMO of $(^{H}BPI^{Mes,H})Fe$ (b) LUMO of $(^{H}BPI^{Mes,H})Fe$ (c) HOMO of $(^{H}BPI^{Mes,Me})Fe$ (d) LUMO of $(^{H}BPI^{Mes,Me})Fe$

Figure 3. HOMO and LUMO of $(^{H}BPI^{Mes,R})Fe$ (R = H, Me).

Table 3. Hydrosilylation of Functionalized Olefins Catalyzed by $(^{H}BPI^{Mes,Me})FeBr_2$ and $(^{H}BPI^{Dipp,H})FeBr_2$[a]

Ph_2SiH_2 + 2 eq olefin $\xrightarrow[\text{r.t., 24 h}]{\text{Fe complex cat.}\ \text{NaBHEt}_3\ \text{cat.}}$ hydrosilylated product

entry	Fe complex	mol%[b]	olefin	product	yield (TON)[c]
1	$(^{H}BPI^{Mes,Me})FeBr_2$	0.1	(allyl-Cl chain)	HPh_2Si(chain)Cl	67% (665)
2	$(^{H}BPI^{Dipp,H})FeBr_2$	0.1			34% (338)
3	$(^{H}BPI^{Mes,Me})FeBr_2$	1.0	(allyl amine)	HPh_2Si(chain)N	94% (94)
4		0.1			19% (193)
5	$(^{H}BPI^{Dipp,H})FeBr_2$	0.1			3% (33)
6	$(^{H}BPI^{Mes,Me})FeBr_2$	1.0	(allyl-S-Ph)	HPh_2Si(chain)S-Ph	0% (0)
7	$(^{H}BPI^{Dipp,H})FeBr_2$	1.0			0% (0)
8	$(^{H}BPI^{Mes,Me})FeBr_2$	0.1	(vinyl-Si-O-Si)	(Si-O-Si product) HPh_2Si	81% (809)

[a]Reaction conditions: neat, room temperature, 24 h, Schlenk tube, [silane]:[olefin] = 1:2, [Fe complex]:[NaBHEt$_3$] = 1:20. [b]mol % = [Fe complex]/[silane] × 100. [c]Isolated yield. The values are based on the initial concentration of hydrosilane.

0.01 mol % (Table 4, entries 2, 4, and 6). With Et$_2$SiH$_2$, both mono- and dialkylated silanes were formed even in the presence of 0.1 mol % of iron complex (Table 4, entry 7). While no reaction occurred with Ph$_3$SiH (Table 4, entry 8), other tertiary silanes, such as Ph$_2$MeSiH, PhMe$_2$SiH, and Et$_3$SiH, were converted into monoalkylated silanes (Table 4, entries 9, 11, and 13). It should be noted that our catalytic system could convert Ph$_2$MeSiH and PhMe$_2$SiH into the corresponding hydrosilylated products in 80% and 95% yields, respectively, despite the fact that hydrosilylation of olefins with tertiary silanes is known to be difficult. These reactions occurred in the presence of only 0.01 mol % of iron complex (Table 4, entries 10 and 12). The hydrosilylation reactions with silanes bearing siloxyl groups, such as (Me$_3$SiO)Me$_2$SiH and (Me$_3$SiO)$_2$MeSiH, proceeded smoothly in the presence of 0.1 mol % of iron complex (Table 4, entries 14 and 15). When (HMe$_2$Si)$_2$O was used, both monoalkylated silane and dialkylated silane were formed (Table 4, entry 16), though Me$_2$(octyl)SiOSiMe$_2$H could not be isolated because of the difficulty in removing an impurity.

Effect of the Iron Catalyst Concentration on the Catalytic Activity. Table 1 shows that $(^{H}BPI^{Mes,Me})FeBr_2$ has a relatively high catalytic activity for primary, secondary, and tertiary hydrosilanes in comparison to other iron catalysts and especially for Ph$_2$SiH$_2$, for which the highest TON was observed. Therefore, we examined the effect of reducing the amount of $(^{H}BPI^{Mes,Me})FeBr_2$ on the TON. Thus, reactions of

Ph$_2$SiH$_2$ with 1-octene were performed in the presence of 0.01, 0.003, 0.002, and 0.001 mol % of $(^{H}BPI^{Mes,Me})FeBr_2$.

Ph$_2$SiH$_2$ and 1-octene in a 1:2 molar ratio and 0.01 mol % of $(^{H}BPI^{Mes,Me})FeBr_2$ were placed in a Schlenk tube. NaBHEt$_3$ (0.2 mol %) was added to the suspension with stirring at room temperature, which resulted in the formation of a homogeneous solution within 5 min. The solution was stirred without any temperature control for 10 min and then separated into several portions. An appropriate amount of a mixture of Ph$_2$SiH$_2$ and 1-octene, in a 1:2 molar ratio, was added to each portion to dilute the contents of the iron species to 0.003, 0.002, and 0.001 mol %. The resulting solutions were stirred for 24 h, and the yields of hydrosilylated products were determined by HPLC. In all cases, the monoalkylated silane was exclusively formed. The TONs were 18000, 34000, and 42000 for iron catalyst concentrations of 0.003, 0.002, and 0.001 mol %, respectively. To our knowledge, a TON value of 42000 is the highest reported value in an iron complex catalyzed olefin hydrosilylation.

■ CONCLUSION

We have prepared a series of ketimine-type iminobipyridine iron complexes. When these iron complexes are activated by NaBHEt$_3$, they exhibit high catalytic activities for the hydrosilylation of terminal olefins with primary, secondary, and tertiary silanes. The iron catalyst converts primary or secondary silanes into not only monoalkylated silanes but also dialkylated silanes. The alkylation of silanes by olefin hydrosilylation is assumed to proceed stepwise: i.e., the monoalkylated product forms first, followed by formation of the dialkylated product. Therefore, controlling each reaction rate is important for the selective formation of these alkylated silanes and can be achieved by changing the amount of the iron catalyst. These iron complexes can be handled under ambient conditions prior to the formation of the active species.

■ EXPERIMENTAL SECTION

All reactions were carried out under a nitrogen atmosphere using Schlenk techniques. Hexane, toluene, diethyl ether, and THF were distilled from sodium and benzophenone prior to use and stored under nitrogen. 2-Tributylstannylpyridine, $(^{H}BPI^{Mes,H})FeBr_2$, and $(^{H}BPI^{Dipp,H})FeBr_2$ were synthesized according to literature methods.[10] All other chemicals were purchased from commercial sources. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a JEOL JNM-AL 400 spectrometer. The residual peaks of the solvent were used as an internal standard. NMR measurements of all iron complexes were difficult due to their poor solubility in common solvents. IR spectra were recorded on a JASCO FTIR-6200 spectrometer. GC-MS measurements were conducted on a Shimadzu gas chromatograph linked to a QP-2010 Plus mass spectrometer.

Table 4. Hydrosilylation of 1-Octene with Various Silanes Catalyzed by (^{H}BPI^{Mes,Me})FeBr$_2$[a]

$$\text{silane} + 2 \text{ eq } 1\text{-octene} \xrightarrow[\text{r.t., 24 h}]{\begin{array}{c}(^{H}\text{BPI}^{Mes,Me})\text{FeBr}_2 \text{ cat.}\\ \text{NaBHEt}_3 \text{ cat.}\end{array}} \text{hydrosilylated product}$$

entry	silane	amt of silane (mol %)[b]	product (yield (%), TON)[c]		total TON[d]
1	PhSiH$_3$	0.1	Ph(octyl)SiH$_2$ (0, 0)	Ph(octyl)$_2$SiH (93, 930)	1860
2		0.01	Ph(octyl)SiH$_2$ (56, 5610)	Ph(octyl)$_2$SiH (26, 2640)	10890
3	Ph$_2$SiH$_2$	0.1	Ph$_2$(octyl)SiH (0, 0)	Ph$_2$(octyl)$_2$Si (91, 909)	1818
4		0.01	Ph$_2$(octyl)SiH (31, 3120)	Ph$_2$(octyl)$_2$Si (65, 6460)	16040
5	PhMeSiH$_2$	0.1	PhMe(octyl)SiH (0, 0)	PhMe(octyl)$_2$Si (70, 703)	1406
6		0.01	PhMe(octyl)SiH (64, 6350)	PhMe(octyl)$_2$Si (0.5, 50)	6450
7[e]	Et$_2$SiH$_2$	0.1	Et$_2$(octyl)SiH (68, 675)	Et$_2$(octyl)$_2$Si (26, 257)	1189
8	Ph$_3$SiH	0.1	Ph$_3$(octyl)Si (0, 0)		0
9	Ph$_2$MeSiH	0.1	Ph$_2$Me(octyl)Si (80, 795)		795
10		0.01	Ph$_2$Me(octyl)Si (45, 4520)		4520
11	PhMe$_2$SiH	0.1	PhMe$_2$(octyl)Si (95, 951)		951
12		0.01	PhMe$_2$(octyl)Si (39, 3870)		3870
13[e]	Et$_3$SiH	0.1	Et$_3$(octyl)Si (10, 102)		102
14[e]	(Me$_3$SiO)Me$_2$SiH	0.1	(Me$_3$SiO)Me$_2$(octyl)Si (74, 739)		739
15[e]	(Me$_3$SiO)$_2$MeSiH	0.1	(Me$_3$SiO)$_2$Me(octyl)Si (79, 791)		791
16[e]	(HMe$_2$Si)$_2$O	0.1	Me$_2$(octyl)SiOSiMe$_2$H (−, −)	(Me$_2$(octyl)Si)$_2$O (46, 457)	

[a]Reaction conditions: neat, room temperature, 24 h, Schlenk tube, [silane]:[olefin] = 1:2, [Fe complex]:[NaBHEt$_3$] = 1:20. [b]mol % = [Fe complex]/[silane] × 100. [c]Determined by HPLC. The values are based on the initial concentration of hydrosilane. [d]Total TON = TON of single-alkylated product + 2 × (TON of double-alkylated product). [e]Isolated yield.

HPLC analyses were performed on a Shimadzu Prominence UFLC (LC-20 series) chromatograph using a Cosmosil 5C18-MS-II column (250 × 4.6 mm). The instrument was set to an injection volume of 5 μL. Acetonitrile (100%) was used as the carrier phase with a flow rate of 1.0 mL/min. The column temperature was kept at 40 °C. Quantification was performed using the calibration curves of peak area versus concentration, covering the relevant concentration range, using pure hydrosilylation products. The reaction mixture was exposed to air, diluted to the appropriate concentration (within the calibration range), and analyzed by HPLC.

6-Bromo-2,2′-bipyridine (1). A mixture of 2,6-dibromopyridine (74.0 g, 312 mmol), 2-tributylstannylpyridine (115 g, 312 mmol), and Pd(PPh$_3$)$_4$ (18.5 g, 16.0 mmol) in toluene (120 mL) was refluxed overnight. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure. The crude product was brined in CHCl$_3$ (630 mL) and 6 M HCl aqueous solution (630 mL). The aqueous layer was washed with CHCl$_3$ (630 mL × 2), and the aqueous layer was added dropwise to a 10 M NaOH aqueous solution (420 mL) at 0 °C. Part of the product crystallized out of the solution and was collected by filtration. The product in the filtrate was extracted with CHCl$_3$ (630 mL). The crude product collected from the filtration was combined and dissolved in the extracted CHCl$_3$ and dried over anhydrous Na$_2$SO$_4$. After the solvent was removed under reduced pressure, the resulting solid was purified by column chromatography (silica, AcOEt/hexane 1/9). The target product was obtained as a white powder in 62% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.32 (dd, 1H, $^3J_{HH}$ = 4.8 and 7.6 Hz), 7.48 (d, 1H, $^3J_{HH}$ = 7.8 Hz), 7.66 (t, 1H, $^3J_{HH}$ = 7.8 Hz), 7.81 (td, 1H, $^3J_{HH}$ = 7.9 Hz and $^4J_{HH}$ = 1.5), 8.37 (d, 1H, $^3J_{HH}$ = 7.7 Hz), 8.49 (d, 1H, $^3J_{HH}$ = 8.2 Hz), 8.66 (bd, 1H,

$^3J_{HH}$ = 4.4 Hz). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ (ppm) 119.84, 121.62, 124.40, 128.12, 137.15, 139.36, 141.72, 149.34, 154.61, 157.46. GC-MS (EI): 236 (44), 234 (46), 155 (100).

1-[2,2′-Bipyridin-6-yl]ethanone (2). The compound was prepared according to the published procedure with some modifications.[19] ^{n}BuLi (2.65 M in hexane, 26.5 mL, 70.2 mmol) was added dropwise to a solution of **1** (15.0 g, 63.8 mmol) in a mixture of ether (45 mL), hexane (23 mL), and THF (23 mL) for 30 min at −78 °C. After the mixture was stirred for a further 30 min at −78 °C, N,N-dimethylacetamide (12.0 mL, 128 mmol) was slowly added over 1 min at −78 °C. The mixture was cooled to below −80 °C and then warmed to room temperature. The reaction mixture was quenched with H$_2$O (45 mL) and then extracted with AcOEt (90 mL × 5). The organic fractions were combined and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure. The crude product was purified by washing with hexane or by Kugelrohr distillation (140 °C, 170 Pa). The target product was obtained as a brown powder in 89% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 2.84 (s, 3H), 7.36 (bt, 1H, $^3J_{HH}$ = 5.9 Hz), 7.87 (bt, 1H, $^3J_{HH}$ = 8.1 Hz), 7.96 (t, 1H, $^3J_{HH}$ = 7.8 Hz), 8.05 (d, 1H, $^3J_{HH}$ = 7.6 Hz), 8.53 (d, 1H, $^3J_{HH}$ = 8.0 Hz), 8.62 (d, 1H, $^3J_{HH}$ = 7.9 Hz), 8.70 (bd, 1H, $^3J_{HH}$ = 4.0 Hz). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ (ppm) 25.86, 121.26, 121.59, 124.26, 124.42, 137.13, 137.95, 149.38, 153.10, 155.53, 155.56, 200.41. GC-MS (EI): 198 (60), 170 (51), 155 (100).

2,2,2-Trifluoro-1-[2,2′-bipyridin-6-yl]ethanone (3). The compound was prepared according to the published procedure with some modifications.[19] ^{n}BuLi (2.65 M in hexane, 14.0 mL, 35.2 mmol) was added dropwise to a solution of **1** (7.52 g, 32.0 mmol) in a mixture of ether (23 mL), hexane (12 mL), and THF (12 mL) for 30 min at −78

°C. After the mixture was stirred for a further 30 min at −78 °C, 2,2,2-trifluoro-*N,N*-dimethylacetamide (7.2 mL, 64.0 mmol) was slowly added over 1 min at −78 °C. The mixture was cooled to below −80 °C, and then the reaction mixture was warmed to room temperature. The reaction mixture was quenched with H_2O (75 mL) and then extracted with AcOEt (150 mL × 5). The organic fractions were combined and dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by Kugelrohr distillation (120 °C, 140 Pa). The target product was obtained as a brownish white powder in 54% yield. The product was contaminated with traces of an unknown impurity. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.38 (m, 1H), 7.87 (qd, 1H, $^5J_{HF}$ = 1.6 and $^3J_{HH}$ = 7.8 Hz), 8.05 (t, 1H, $^3J_{HH}$ = 7.8 Hz), 8.17 (dd, 1H, $^3J_{HH}$ = 0.9 and 7.8 Hz), 8.54 (bd, 1H, $^3J_{HH}$ = 7.8 Hz), 8.71 (bt, 1H, $^3J_{HH}$ = 5.8 Hz), 8.77 (dd, 1H, $^3J_{HH}$ = 0.7 and 8.2 Hz). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ (ppm) 92.20 (q, $^2J_{CF}$ = 32.59 Hz), 121.66, 124.72, 124.77, 125.98, 137.39, 138.28, 147.92, 149.31, 154.56, 156.22, 180.78 (q, $^2J_{CF}$ = 34.05 Hz). GC-MS (EI): 252 (36), 183 (20), 155 (100).

2,2-Dimethyl-1-[2,2′-bipyridin-6-yl]-1-propanone (4). The compound was prepared according to the published procedure with some modifications.[20] To a suspension of sodium hydride (7.80 g, 195 mmol) in THF (550 mL) below 0 °C was added a solution of **2** (4.29 g, 21.7 mmol) in THF (43.0 mL) dropwise. The reaction mixture was warmed to room temperature and stirred for 3 h before recooling to 0 °C. Iodomethane (13.5 mL, 217 mmol) was added dropwise, and the reaction mixture was stirred at room temperature overnight. Excess sodium hydride was quenched with H_2O (70.0 mL) and AcOEt (70.0 mL). The organic fraction was collected and dried over Na_2SO_4. The solvent was removed under reduced pressure. NMR examination of the crude product showed that it was a mixture of tri- and dialkylated ketones. This crude material was resubjected to the initial reaction conditions, first by dropwise addition to a suspension of sodium hydride (7.80 g, 195 mmol) in THF (550 mL) below 0 °C and then, after stirring at room temperature, iodomethane (13.5 mL, 217 mmol) was added and stirring was continued overnight. The reaction mixture was quenched following the workup described above, to furnish the trialkylated ketone. The crude product was purified by Kugelrohr distillation (150 °C, 180 Pa). The target product was obtained as a yellow oil in 79% yield. The product was contaminated with traces of an unknown impurity. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 1.55 (s, 9H), 7.34 (dd, 1H, $^3J_{HH}$ = 4.9 and 7.3 Hz), 7.86 (m, 1H), 7.93 (m, 2H), 8.41 (d, 1H, $^3J_{HH}$ = 8.2 Hz), 8.56 (dd, 1H, $^3J_{HH}$ = 2.8 and 6.4 Hz), 8.69 (d, 1H, $^3J_{HH}$ = 5.1 Hz). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ (ppm) 27.83, 40.29, 121.17, 123.31, 123.83, 124.10, 137.16, 137.92, 149.36, 149.17, 153.94, 154.41, 155.81 (q, $^2J_{CF}$ = 34.05 Hz). GC-MS (EI): 212 (17), 197 (9), 156 (100).

N-(1-[2,2′-Bipyridin-6-yl]ethylidene)-2,4,6-trimethylbenzenamine (5). The compound was prepared according to the published procedure with some modifications.[19] A mixture of 2,4,6-trimethylaniline (1.45 mL, 10.1 mmol), **2** (2.00 g, 10.1 mmol), and formic acid (5 drops) in MeOH (20.0 mL) was heated to reflux temperature. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure. The resulting oil was purified by Kugelrohr distillation (240 °C, 140 Pa). The desired product was obtained as a yellow oil in 71% yield. The product was contaminated with traces of an unknown impurity. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 2.04 (s, 6H), 2.31 (s, 6H), 6.92 (s, 2H), 7.33 (m, 1H), 7.84 (m, 1H), 7.94 (t, 1H, $^3J_{HH}$ = 7.8 Hz), 8.42 (d, 1H, $^3J_{HH}$ = 7.8 Hz), 8.55 (t, 2H, $^3J_{HH}$ = 8.2 Hz), 8.71 (m, 1H). ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$): δ (ppm) 16.58, 17.98, 20.84, 121.16, 121.26, 122.02, 123.88, 125.38, 128.66, 132.25, 136.96, 137.45, 146.42, 149.27, 154.94, 155.87, 156.15, 167.61. GC-MS (EI): 315 (33), 300 (100).

N-(2,2-Dimethyl-[2,2′-bipyridin-6-yl]propylidene)-2,4,6-trimethylbenzenamine (6). The compound was prepared according to the published procedure with some modifications.[20] A mixture of 2,4,6-trimethylaniline (0.89 mL, 6.24 mmol), **4** (1.00 g, 4.16 mmol), and *p*-toluenesulfonic acid monohydrate (41.0 mg, 0.21 mmol) in toluene (20.0 mL) was heated to reflux temperature (Dean–Stark trap). After the mixture was cooled to room temperature, the solvent was removed under reduced pressure. The resulting oil was purified by

Kugelrohr distillation (240 °C, 170 Pa). The desired product was obtained as a yellow powder in 43% yield. The product was contaminated with traces of an unknown impurity. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 1.42 (s, 9H), 2.06 (s, 6H), 2.08 (s, 3H), 6.56 (s, 2H), 6.76 (d, 1H, $^3J_{HH}$ = 7.4 Hz), 7.30 (m, 1H), 7.52 (t, 1H, $^3J_{HH}$ = 8.1 Hz), 7.82 (m, 1H), 8.21 (d, 1H, $^3J_{HH}$ = 7.9 Hz), 8.40 (d, 1H, $^3J_{HH}$ = 7.9 Hz), 8.64 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ (ppm) 18.39, 20.72, 29.13, 40.52, 119.69, 121.17, 121.55, 123.89, 125.48, 128.26, 131.60, 136.30, 137.10, 149.18, 155.93, 156.09 (two signals of aromatic carbons were not assignable due to coincident signals). GC-MS (EI): 300 (100).

N-(2,2,2-Trifluoro-[2,2′-bipyridin-6-yl]ethylidene)-2,4,6-trimethylbenzenamine (7). The compound was prepared according to the published procedure with some modifications.[21] A mixture of 2,4,6-trimethylaniline (0.43 mL, 3.03 mmol), **3** (0.64 g, 2.53 mmol), and *p*-toluenesulfonic acid monohydrate (14.6 mg, 0.08 mmol) in toluene (6.4 mL) was heated to reflux temperature (Dean–Stark trap). After the mixture was cooled to room temperature, the solvent was removed under reduced pressure. The resulting oil was purified by Kugelrohr distillation (200 °C, 200 Pa). The desired product was obtained as a yellow powder in 79% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 1.98 (s, 6H), 2.21 (s, 3H), 6.76 (s, 2H), 7.12 (d, 1H, $^3J_{HH}$ = 7.6 Hz), 7.31 (m, 1H), 7.74 (m, 2H), 8.07 (d, 1H, $^3J_{HH}$ = 8.1 Hz), 8.40 (d, 1H, $^3J_{HH}$ = 8.0 Hz), 8.63 (br, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ (ppm) 17.91, 20.82, 121.28, 121.77, 122.20, 123.10, 124.32, 124.48, 128.84, 133.61, 137.07, 137.49, 143.48, 147.92, 149.14, 155.18, 156.17 (One signal was not assignable due to coincident signal). Anal. Calcd for $C_{21}H_{18}F_3N_3$: C, 68.28; H, 4.91; N, 11.38. Found: C, 68.16; H, 5.00; N, 11.42. GC-MS (EI): 349 (37), 329 (18), 310 (16), 300 (100).

N-(1-[2,2′-Bipyridin-6-yl]ethylidene)-2,6-diisopropylbenzenamine (8). The compound was prepared according to the published procedure with some modifications.[19] A mixture of 2,6-diisopropylaniline (2.11 mL, 10.1 mmol), **2** (2.00 g, 10.1 mmol), and formic acid (5 drops) in MeOH (20.0 mL) was heated to reflux temperature. After the mixture was cooled to room temperature, the yellow solid was collected by filtration and washed with MeOH (10.0 mL × 2). The target product was obtained as a yellow powder in 88% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 1.16 (d, 12H, $^3J_{HH}$ = 6.8 Hz), 2.33 (s, 3H), 2.79 (sept, 2H, $^3J_{HH}$ = 6.6 Hz), 7.11 (m, 1H), 7.18 (m, 2H), 7.34 (m, 1H), 7.85 (m, 1H), 7.95 (t, 1H, $^3J_{HH}$ = 7.9 Hz), 8.40 (bd, 1H, $^3J_{HH}$ = 7.3 Hz), 8.55 (bt, 2H, $^3J_{HH}$ = 7.9 Hz), 8.71 (bd, 1H, $^3J_{HH}$ = 4.4 Hz). ^{13}C{^{1}H} NMR (100.4 MHz, CDCl$_3$): δ (ppm) 17.67, 23.07, 23.36, 28.42, 121.22, 121.32, 122.07, 123.67, 123.94, 135.97, 137.02, 137.54, 146.69, 149.33, 155.04, 155.80, 156.21, 167.19. Anal. Calcd for $C_{24}H_{27}N_3$: C, 80.63; H, 7.61; N, 11.75. Found: C, 81.02; H, 7.70; N, 11.71. GC-MS (EI): 357 (20), 342 (67), 300 (19), 202 (72), 183 (27), 170 (22), 157 (100).

N-(2,2,2-Trifluoro-[2,2′-bipyridin-6-yl]ethylidene)-2,6-diisopropylbenzenamine (9). The compound was prepared according to the published procedure with some modifications.[21] A mixture of 2,6-diisopropylaniline (0.85 mL, 4.03 mmol), **3** (1.02 g, 4.03 mmol), and *p*-toluenesulfonic acid monohydrate (23.3 mg, 0.12 mmol) in toluene (10.2 mL) was heated to reflux temperature (Dean–Stark trap). After the mixture was cooled to room temperature, the solvent was removed under reduced pressure. The resulting oil was purified by Kugelrohr distillation (210 °C, 140 Pa). The desired product was obtained as a yellow oil in 55% yield. The product was contaminated with traces of an unknown impurity. ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 1.18 (d, 12H, $^3J_{HH}$ = 6.8 Hz), 2.78 (sept, 2H, $^3J_{HH}$ = 6.4 Hz), 7.10 (m, 3H), 7.17 (d, 1H, $^3J_{HH}$ = 6.7 Hz), 7.29 (t, 1H, $^3J_{HH}$ = 6.2 Hz), 7.72 (t, 2H, $^3J_{HH}$ = 6.7 Hz), 7.87 (d, 1H, $^3J_{HH}$ = 7.1 Hz), 8.40 (d, 1H, $^3J_{HH}$ = 7.6 Hz), 8.62 (br, 1H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ (ppm) 22.36, 28.45, 121.92, 122.31, 123.43, 123.78, 124.33, 124.77, 134.57, 137.00, 137.46, 143.73, 147.06, 149.09, 153.45 (q, $^2J_{CF}$ = 33.01 Hz), 155.08, 156.06 (one signal was not assignable due to coincident signal). GC-MS (EI): 411 (11), 368 (10), 342 (100).

N-(1-[2,2′-Bipyridin-6-yl]ethylidene)-2,4,6-trimethylbenzenamine Iron(II) Bromide ((^{H}BPI^{Mes,Me})FeBr$_2$). FeBr$_2$ (anhydrous) (1.98 g, 6.26 mmol) was added to a solution of **5** (1.38 g, 6.26 mmol)

in THF (100 mL) at room temperature with vigorous stirring. The precipitate that formed during the reaction was collected by filtration, washed three times with THF (10 mL), and dried in vacuo. $(^HBPI^{Mes,Me})FeBr_2$ was obtained as a brownish purple powder in 99% yield. Anal. Calcd for $C_{42}H_{44}Br_4Fe_2N_6O$ (2M + H_2O): C, 46.70; H, 4.11; N, 7.78. Found: C, 47.12; H, 4.22; N, 7.37. HRMS (FAB): calcd for $C_{21}H_{21}FeN_3$ $[M - 2Br]^+$, 371.1085; found, 371.1084.

N-**(2,2-Dimethyl-[2,2′-bipyridin-6-yl]propylidene)-2,4,6-trimethylbenzenamine Iron(II) Bromide (($^HBPI^{Mes,tBu}$)FeBr₂).** This complex was prepared as a bluish purple powder in 56% yield following the procedure above for $(^HBPI^{Mes,Me})FeBr_2$. Anal. Calcd for $C_{240}H_{270}Br_{22}Fe_{11}N_{30}$ (10M + $FeBr_2$): C, 48.47; H, 4.58; N, 7.07. Found: C, 48.46; H, 4.73; N, 7.10. HRMS (FAB): calcd for $C_{24}H_{27}FeN_3$ $[M - 2Br]^+$, 413.1554; found, 413.1550.

N-**(2,2,2-Trifluoro-[2,2′-bipyridin-6-yl]ethylidene)-2,4,6-trimethylbenzenamine Iron(II) Bromide (($^HBPI^{Mes,CF3}$)FeBr₂).** This complex was prepared as a brown powder in 88% yield following the procedure above for $(^HBPI^{Mes,Me})FeBr_2$. Anal. Calcd for $C_{48}H_{50}Br_4F_6Fe_2N_6$ (2M + hexane): C, 45.89; H, 4.01; N, 6.69. Found: C, 45.81; H, 4.00; N, 6.51. HRMS (FAB): calcd for $C_{21}H_{18}F_3FeN_3$ $[M - 2Br]^+$, 425.0802; found, 425.0801.

N-**(1-[2,2′-Bipyridin-6-yl]ethylidene)-2,6-diisopropylbenzenamine Iron(II) Bromide (($^HBPI^{Dipp,Me}$)FeBr₂).** This complex was prepared as a red-purple powder in 83% yield following the procedure above for $(^HBPI^{Mes,Me})FeBr_2$. Anal. Calcd for $C_{24}H_{27}Br_2FeN_3$: C, 50.29; H, 4.75; N, 7.33. Found: C, 49.99; H, 4.82; N, 7.20. HRMS (FAB): calcd for $C_{24}H_{27}FeN_3$ $[M - 2Br]^+$, 413.1554; found, 413.1562.

N-**(2,2,2-Trifluoro-[2,2′-bipyridin-6-yl]ethylidene)-2,6-diisopropylbenzenamine Iron(II) Bromide (($^HBPI^{Dipp,CF3}$)FeBr₂).** This complex was prepared as an emerald green powder in 56% yield following the procedure above for $(^HBPI^{Mes,Me})FeBr_2$. Anal. Calcd for $C_{24}H_{24}Br_2F_3FeN_3$: C, 45.97; H, 3.96; N, 6.70. Found: C, 45.91; H, 3.97; N, 6.72. HRMS (FAB): calcd for $C_{24}H_{24}F_3FeN_3$ $[M - 2Br]^+$, 467.1272; found, 467.1255.

Typical Procedure for the Catalytic Hydrosilylation of Olefins with Silanes. $(^HBPI^{Mes,H})FeBr_2$ (3.0 mg, 0.0058 mmol) was placed in a Schlenk tube in air at room temperature. Next, the air in the Schlenk tube was replaced with nitrogen. 1-Octene (18 mL, 120 mmol) and phenylsilane (7.2 mL, 58 mmol) were placed in the Schlenk tube. Sodium triethylborohydride (1.0 M in toluene, 120 μL, 0.12 mmol) was then added to the suspension at room temperature, leading to the formation of a homogeneous dark brown solution within several minutes. The evolution of heat from the reaction suggested an exothermic reaction. The solution was stirred without any temperature control for 24 h and eventually exposed to air. The reaction mixture was subjected to HPLC analysis to determine the TON.

DFT Calculations. All calculations were performed using the Gaussian 09 program.[13] The geometry of $(^HBPI^{Ar,R})Fe$ was optimized by the DFT method with the B3LYP functional.[14−16] For the Fe atom, an SDD basis set was used with the corresponding ECPs.[17] The usual 6-31G(d,p) basis sets were used for the other atoms.[16] Frequency calculations, at the same level, were performed on optimized structures to ensure that minima exhibit only a positive frequency. The molecular structures were drawn using the GaussView version 4.1.2. program. NBO analysis[18] was performed to investigate the Fe−N and/or Fe−C interactions in $(^HBPI^{Ar,R})Fe$.

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Notes

The authors declare no competing financial interest.

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