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Hydrosilylation of Diene Derivatives Catalyzed by Fe-Iminobipyridine Complexes Aiming at Syntheses of Organosilane Compounds Containing a Terminal Olefin Portion

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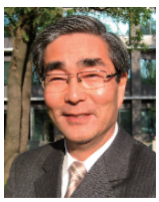

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Abstract

The catalytic ability of Fe-iminobipyridine complexes ((BPI)$FeBr_2$, BPI = iminobipyridine) for hydrosilylation of both a non-conjugated diene and a conjugated diene was investigated aiming at the production of organosilane compounds bearing a terminal olefin portion. Steric effects of (BPI)$FeBr_2$ were controlled by the substituents at the terminal pyridine ring (R^1), the imino carbon (R^2), and the imino nitrogen (Ar) of the BPI ligand. As regards a non-conjugated diene, hydrosilylation of 1,7-octadiene with diphenylsilane (Ph_2SiH_2) produced a mixture of mono- and di-hydrosilylated compounds. To obtain the mono-hydrosilylated compound preferably in the 1:1 reaction of non-conjugated diene and silane, the substituent effect of the BPI ligand was investigated. As a result, larger steric hindrance of (BPI)$FeBr_2$ based on substituents slowed the hydrosilylation, instead the selectivity of the mono-hydrosilylated compound was substantially improved. The 6′-Me group on a terminal pyridine was most effective. Finally, production of the mono-hydrosilylated compound from 1,7-octadiene and Ph_2SiH_2 reached 77% yield and 0.94 selectivity. In the case of a conjugated diene, (BPI)$FeBr_2$ with any substituents selectively generated 1,4-hydrosilylated compound in hydrosilylation of 2,3-dimethyl-1,3-butadiene with Ph_2SiH_2. In this case, higher steric hindrance of (BPI)$FeBr_2$ simply decreased the yield of the product.

Keywords: Hydrosilylation catalyst | Fe complex | Hydrosilylation of diene

1. Introduction

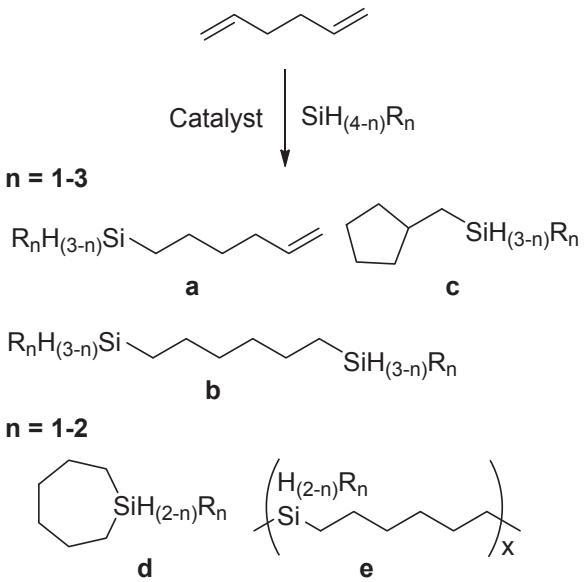
Organosilane compounds and materials have attracted a great deal of interest because of their versatile and excellent properties. For example, a silane coupling agent often modifies surface properties of solid materials, and assists the linkage between the solid surfaces and functional organics leading to new composites in not only industrial application but also dentistry.[1–3] Creation of a simple and convenient synthesis of organosilane compounds bearing functional groups may contribute to the development of a wide range of research fields and applications.

Hydrosilylation of olefin is a widely-used and atom-economical methodology to obtain organosilane compounds on the basis of the generation of a Si-C bond. Pt catalysts[4–6] such as Speier's[4] and Karstedt's[5] are generally used for hydrosilylation, despite the rarity of Pt. In order not to depend on the use of precious metals, alternative catalysts composed of earth-abundant metals, such as Fe,[7–14] Co,[10,11,15–22] and Ni,[23,24] have been significantly developed. Especially, Fe catalysts have drawn considerable attention because of an absolute advantage in earth abundance.

One recent interest in this research field is the creation of a practical catalytic system to obtain organosilane compounds in hydrosilylation reaction of olefins with a functional group. Several hydrosilylation reactions in which a functional group in the olefin remains intact have been reported: chemoselective hydrosilylation of olefin bearing halogeno,[10,14,17,20,21,24] hydroxy,[19,21] carbonyl,[9,19,20] epoxy,[8,11,19,20,22,24,25] amino,[14,16,20,24] and thioether[26] groups. In contrast, the application of hydrosilylation for the preparation of organosilanes bearing a C=C double bond portion is limited. If only one C=C double bond in a diene derivative is hydrosilylated, the desired organosilane would be produced.

Hydrosilylation of internal olefins catalyzed by a transition metal complex is generally rare. Although several examples have been reported, iron complexes showing such activity have been little reported. Moreover, silane compounds having an olefin portion in a terminal position are more useful as a silane coupling agent than those in an internal position. Therefore, we sought a reaction system in which an Fe complex catalyzes mono hydrosilylation of terminal dienes to yield organosilanes bearing an olefin portion in the terminal position. Terminal diene derivatives can be classified into non-conjugated dienes and conjugated ones. A non-conjugated diene which has two alkenyl groups at both ends (α, ω-non-conjugated diene) possibly affords several products by hydrosilylation. For example, there are several reports for hydrosilylation of 1,5-hexadiene which produces the mono-hydrosilylated compound (**a**), the di-hydrosilylated (**b**), cyclized products (**c** and **d**), and polymer (**e**) (Scheme 1).[27] Cyclized compounds (**c** and **d**) were often obtained from 1,5-hexadiene.[27–29] Dienes longer than 1,5-hexadiene would not be suitable for the cyclization except 4,4-substiduted-1,6-heptadiene and 4,4,5,5-substiduted-1,7-octadiene.[30] Mono-hydrosilylated compound undergoes polymerization through intermolecular hydrosilylation except using tertiary silane derivatives as substrates.[28] Similarly, oligohydrosiloxane derivatives which have multiple Si-H bonds often form inorganic/organic hybrid polymers (polyorganosiloxane).[31] Mono- and di-hydrosilylated compounds are obtained from any reaction conditions and any chain length. However, the selective mono hydrosilylation of α, ω-non-conjugated diene has been rarely reported.

As regards conjugated dienes, butadiene derivatives can be converted to organosilane compounds having a terminal olefin portion through 1,2-additon of silane. However, 1,4-hydrosilylation commonly takes place on butadiene derivatives.[15,23,25,32,33] Although there have been three reports about selective 1,2-hydrosilylation of dienes to date,[34,35] only a Pt catalyst succeeded in 1,2-hydrosilylation of butadiene derivatives.[34]



Scheme 1. Possible products obtained from hydrosilylation of 1,5-hexadiene.

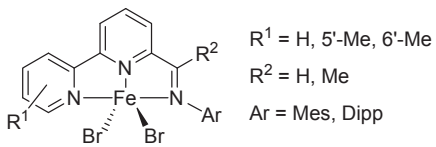


Figure 1. Molecular structure of (BPI)$FeBr_2$.

Table 1. Abbreviations of (BPI)$FeBr_2$ in this study

	R^1	R^2	Ar	Reference
$\mathbf{1_{HM}}$	H	H	Mes	13
$\mathbf{1_{MM}}$	H	Me	Mes	14
$\mathbf{1_{HD}}$	H	H	Dipp	13
$\mathbf{1_{MD}}$	H	Me	Dipp	14
$\mathbf{2_{HM}}$	5′-Me	H	Mes	This work
$\mathbf{2_{MM}}$	5′-Me	Me	Mes	This work
$\mathbf{2_{HD}}$	5′-Me	H	Dipp	This work
$\mathbf{2_{MD}}$	5′-Me	Me	Dipp	This work
$\mathbf{3_{HM}}$	6′-Me	H	Mes	13
$\mathbf{3_{MM}}$	6′-Me	Me	Mes	This work
$\mathbf{3_{HD}}$	6′-Me	H	Dipp	13
$\mathbf{3_{MD}}$	6′-Me	Me	Dipp	This work

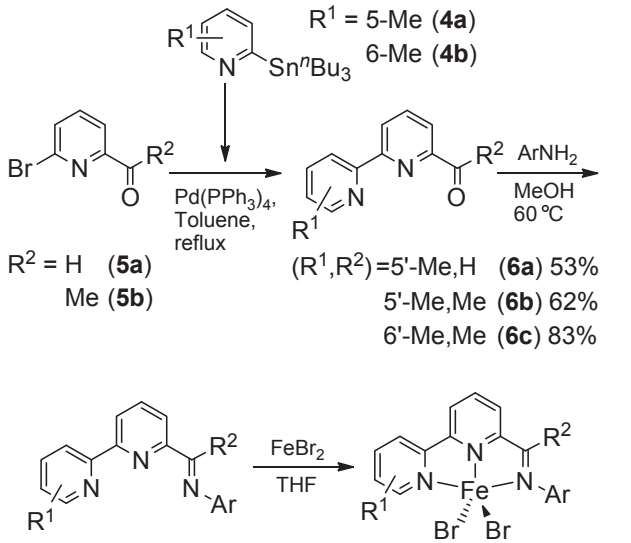
Our group developed Fe complexes aiming at hydrosilylation.[12–14,36] Recently, we found that Fe-iminobipyridine complexes ((BPI)$FeBr_2$, BPI = iminobipyridine, Figure 1 and Table 1) were good pre-catalysts for olefin hydrosilylation.[13,14] These complexes were activated by $NaBHEt_3$, leading to extremely high catalytic ability for hydrosilylation. It was also reported that steric effects around a catalytic Fe center can be controlled by the introduction of substituents at the terminal pyridine ring (R^1), the imino carbon (R^2), and the imino nitrogen (Ar).[14] Best turnover number (TON), 42,000, was recorded in $\mathbf{1_{MM}}$ catalyzed reaction between 1-octene and diphenylsilane (Ph_2SiH_2).[14] To our knowledge, this TON is the highest among Fe catalysts reported so far.

In this paper, we attempted to apply the series of (BPI)$FeBr_2$ to hydrosilylation of both linear non-conjugated and conjugated dienes with the hope that one unsaturated bond of diene is used for hydrosilylation and the other unsaturated part remains unreacted in the catalytic system. Substituent effect of R^1, R^2, and Ar in BPI (Figure 1) on hydrosilylation selectivity was investigated.

2. Results and Discussion

Preparation of Iminobipyridine Derivatives Bearing 5′-Me and 6′-Me Group and Their Fe Complexes. Fe-iminobipyridine complexes, (BPI)$FeBr_2$, used in this paper are shown in Figure 1, which consist of a combination of three substituents at the terminal pyridine ring (R^1), the imino carbon (R^2), and the imino nitrogen (Ar). The abbreviations of them are summarized in Table 1. Complexes **1**, **2**, and **3** represent (BPI)$FeBr_2$ with H, 5′-Me, and 6′-Me groups on the terminal pyridine, respectively. First and second suffixes of each number represent R^2 and Ar, where **H** and **M** at R^2, **M** and **D** at Ar indicate a hydrogen atom, Me, Mes, and Dipp groups, respectively (Mes = 2,4,6-trimethylphenyl, Dipp = 2,6-diisopropylphenyl).

Synthetic routes of new ligands in this paper are similar to those of aldimine type iminobipyridine ligands (R^2 = H) reported to date (Scheme 2).[13] Stille coupling between **4a** and **5a** or **5b**, **4b** and **5b** afforded bipyridine derivatives bearing a carbonyl group, **6a**, **6b**, and **6c**, respectively. Imino bond formation was performed by the condensation reaction between formyl- or acetylbipyridine derivatives (**6a**, **6b**, or **6c**) and $ArNH_2$ (Ar = Mes, Dipp) to give corresponding BPI ligands



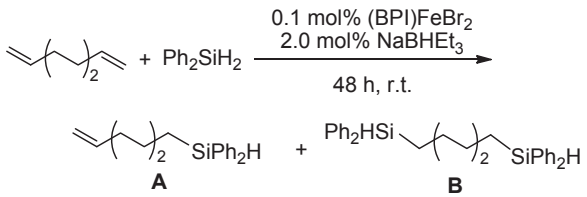
Scheme 2. Synthetic route of (BPI)$FeBr_2$.

(**7a–f**). Finally, 1:1 reaction between $FeBr_2$ and the BPI ligand in THF under N_2 resulted in the formation of the precipitate of pure (BPI)$FeBr_2$. BPI ligands and their precursors were characterized by NMR, DART mass, and elemental analysis. The iron complexes were characterized by FAB mass and elemental analysis. NMR measurements of all iron complexes were difficult due to their poor solubility in common solvents. These iron complexes can be easily handled under ambient conditions prior to the formation of the active species induced by $NaBHEt_3$ reduction.

Hydrosilylation of a Non-Conjugated Diene. Among (BPI)$FeBr_2$, $\mathbf{1_{HM}}$ has the simplest ligand with the smallest steric hindrance. Therefore, we firstly employed $\mathbf{1_{HM}}$ as a catalyst for non-conjugated diene hydrosilylation.

1,7-octadiene was employed as a substrate, since longer diene is suitable because it may not form cyclization products. Similarly, with respect to silane source, we selected diphenylsilane (Ph_2SiH_2), since SiH_4, phenylsilane ($PhSiH_3$) and hydrosiloxane derivatives are used as polymer production.[28,31] Thus, the catalytic ability and product selectivity of (BPI)$FeBr_2$ was evaluated by the reaction between 1,7-octadiene and Ph_2SiH_2 (Scheme 3).

Hydrosilylation of a diene was conducted according to the previous report of (BPI)$FeBr_2$ catalysts.[14] To a mixture of 1,7-octadiene and Ph_2SiH_2 without any other solvent 0.1 mol % $\mathbf{1_{HM}}$ was added and then 2.0 mol % $NaBHEt_3$ was added to initiate hydrosilylation. The mono-hydrosilylated compound (**A**) and the di-hydrosilylated one (**B**) were obtained as products, and cyclic silanes and polymer were not detected at all. Table 2 shows the yield and selectivity of products of hydrosilylation in various molar ratios of 1,7-octadiene and Ph_2SiH_2. TON indicates turnover number of hydrosilylation based on the Fe complex; the production of the mono-hydrosilylated compound (**A**) counts once, and that of the di-hydrosilylated



Scheme 3. Hydrosilylation of 1,7-octadiene with Ph_2SiH_2 catalyzed by (BPI)$FeBr_2$.

Table 2. Hydrosilylation catalyzed by $\mathbf{1_{HM}}$ in the various ratio of 1,7-octadiene and Ph_2SiH_2[a]

Entry	[Octadiene]: [Ph_2SiH_2]	Yield[b,c] (TON)[b,d]		Selectivity[e]
		A	**B**	
1	1:1	74% (740)	21% (420)	0.78
2	2:1	78% (780)	17% (340)	0.82
2	3:1	88% (880)	3% (60)	0.97
3	5:1	86% (860)	1% (20)	0.99

[a]Reaction conditions: Neat, r.t., 48 h, under N_2, 0.1 mol % $\mathbf{1_{HM}}$, 2.0 mol % $NaBHEt_3$. [b]Determined by HPLC. [c]The yields are based on the initial concentration of Ph_2SiH_2. [d]TONs are based on the initial concentration of the Fe complex. [e]Selectivity = [**A**]/[Total yield].

Table 3. Hydrosilylation between 1,7-octadiene and Ph_2SiH_2 catalyzed by R^2 substituted (BPI)$FeBr_2$ (R^2 = H or Me)[a]

Entry	Cat.	Yield[b,c] (TON)[b,d]		Total yield	Selectivity[e]
		A	B		
1	$\mathbf{1_{HM}}$	74% (740)	21% (420)	95%	0.78
2	$\mathbf{1_{MM}}$	73% (730)	16% (320)	89%	0.82
3	$\mathbf{1_{HD}}$	72% (720)	20% (400)	92%	0.78
4	$\mathbf{1_{MD}}$	69% (690)	17% (340)	86%	0.80

[a]Reaction conditions: Neat, r.t., 48 h, under N_2, [1,7-octadiene]: [Ph_2SiH_2] = 1:1, 0.1 mol % (BPI)$FeBr_2$, 2.0 mol % $NaBHEt_3$. [b]Determined by HPLC. [c]The yields are based on the initial concentration of Ph_2SiH_2. [d]TONs are based on the initial concentration of the Fe complex. [e]Selectivity = [**A**]/[Total yield].

Table 4. Hydrosilylation of 1,7-octadiene with Ph_2SiH_2 catalyzed by R^1 substituted (BPI)$FeBr_2$ (R^1 = 5′-Me or 6′-Me)[a]

Entry	Cat.	Yield[b,c] (TON)[b,d]		Total yields	Selectivity[e]
		A	B		
1	$\mathbf{2_{HM}}$	77% (770)	17% (340)	94%	0.82
2	$\mathbf{2_{MM}}$	71% (710)	12% (240)	83%	0.86
3	$\mathbf{2_{HD}}$	67% (670)	19% (380)	86%	0.78
4	$\mathbf{2_{MD}}$	65% (650)	18% (360)	83%	0.78
5	$\mathbf{3_{HM}}$	65% (650)	9% (180)	71%	0.97
6	$\mathbf{3_{MM}}$	64% (640)	8% (160)	72%	0.89
7	$\mathbf{3_{HD}}$	69% (690)	12% (240)	81%	0.85
8	$\mathbf{3_{MD}}$	66% (660)	5% (100)	71%	0.93

[a]Reaction conditions: Neat, r.t., 48 h, under N_2, [1,7-octadiene]: [Ph_2SiH_2] = 1:1, 0.1 mol % (BPI)$FeBr_2$, 2.0 mol % $NaBHEt_3$. [b]Determined by HPLC. [c]The yields are based on the initial concentration of Ph_2SiH_2. [d]TONs are based on the initial concentration of the Fe complex. [e]Selectivity = [**A**]/[Total yield].

compound (**B**) counts twice. And the selectivity of **A** is defined as yield(**A**)/total yield.

With increase of the content of diene, the selectivity of **A** increased. It was reported that a Pt catalyst selectively generated the mono-hydrosilylated compound in the reaction of 1,5-hexadiene with 2-fold $SiHCl_3$ with 90% yield and 0.90 selectivity.[37] $\mathbf{1_{HM}}$ exhibited similar performance in the catalytic reaction between 1,7-octadiene and Ph_2SiH_2. However, in this case, more than three molar equivalents of diene were required to effectively suppress the generation of the di-hydrosilylated compound (**B**). From the viewpoint of atom economical strategy, excess diene was wasteful. Thus, we tried to improve the catalytic system.

Substituents Effect of (BPI)$FeBr_2$ on Catalytic Hydrosilylation of a Non-Conjugated Diene. At first, the substituent effect of R^2 on the yield and selectivity of hydrosilylation of 1,7-octadiene was examined in the 1:1 mixture of diene and silane (Table 3). $\mathbf{1_{HM}}$ showed the highest total yield (95%, Entry 1 in Table 3). Introduction of a Me group at R^2 slightly reduced the total yields of the product (Entries 2, 4 in Table 3) both in the Ar = Mes and Dipp system, while the selectivity of the mono-hydrosilylated compound increased with decrease of total yield. Di-hydrosilylated compound is generated from the mono-silylated one which has more steric hindrance than the original substrate, 1,7-octadiene. This steric effect was enhanced by the introduction of a Me group at R^2. As a substituent at R^2 may not have a direct effect on the catalytic center of (BPI)$FeBr_2$, introduction of R^2 results in small decrease in yield and increase of selectivity.

To increase the steric effect in the vicinity of the Fe center, a Me group was introduced at the 5′- or 6′-positon of the terminal pyridine of (BPI)$FeBr_2$ (R^1 = 5′-Me or 6′-Me). Catalytic abilities of 5′- and 6′-substituted Fe complexes are summarized in Table 4.

In the case of 5′-subsituted complexes with/without a Me group at R^2 ($\mathbf{2_{HM}}$–$\mathbf{2_{MD}}$ in Table 1), total yields and selectivity (Table 4 Entries 1–4) were quite similar to those of non-substituted complexes (R^1 = H, Table 3).

On the other hand, the introduction of 6′-Me group at R^1 significantly decreased total yield of hydrosilylated compounds, which resulted from the steric barrier to the approach of the substrates (Entries 5–8), since the 6′-Me group directly covers the coordination site of Fe for the substrate binding. On the contrary, the selectivity of the mono-hydrosilylated compound (**A**) increased with decrease of total yield. $\mathbf{3_{HM}}$ and $\mathbf{3_{MD}}$ showed good selectivity of the mono-hydrosilylated product (0.97 and 0.93) and even lower yield (71%). These facts indicate that the low yield with high selectivity originates from slower production of the di-hydrosilylated compound (**B**) than that of the mono-hydrosilylated one (**A**), i.e., the difference of the production rate between **A** and **B** is subject to the selectivity. Moreover, it is worth noting that the production of **B** never starts without enough concentration of **A** in the reaction mixture.

Reaction Time and Temperature Dependence on Catalytic Hydrosilylation of a Non-Conjugated Diene. The aforementioned findings suggested longer reaction time by using $\mathbf{3_{HM}}$ and $\mathbf{3_{MD}}$ as catalysts to make total yields higher and selectivity lower. Time dependence on the product yield and selectivity of hydrosilylation of 1,7-octadiene catalyzed by $\mathbf{3_{HM}}$ and $\mathbf{3_{MD}}$ was examined, and the results are shown in Table 5. Those of $\mathbf{1_{HM}}$ are also shown for comparison.

In the all cases, the elongation of reaction time increased total yields and decreased selectivity (Table 5), since the time elongation also increased the yield of the di-hydrosilylated compound (**B**). Catalytic hydrosilylation by $\mathbf{3_{HM}}$ and $\mathbf{3_{MD}}$ was quite slow compared to that by $\mathbf{1_{HM}}$. The reaction catalyzed by $\mathbf{3_{HM}}$ kept high selectivity during the reaction. However, the total yield by $\mathbf{3_{HM}}$ leveled off around 80%. The best result was obtained from the reaction using $\mathbf{3_{MD}}$. Total yield by $\mathbf{3_{MD}}$ increased up to 89% at 168 h with good selectivity (0.87). In this case, the yield of **A** hit a peak at 72 h and slightly decreased after 72 h with gradual increase of **B**.

In order to improve the yield and selectivity, the hydrosilylation catalyzed by $\mathbf{1_{HM}}$, $\mathbf{3_{HM}}$, and $\mathbf{3_{MD}}$ at higher temperature was conducted. Table 6 showed the results of hydrosilylation of 1,7-octadiene with Ph_2SiH_2 at 120 °C. Total yield by $\mathbf{1_{HM}}$ substantially got worse compared to that at r.t., while the selectivity was improved. Although hydrosilylation by $\mathbf{3_{HM}}$ maintained 0.95 selectivity even at 120 °C, total yield at 48 h

Table 5. Time dependence of hydrosilylation of 1,7-octadiene with Ph_2SiH_2 catalyzed by $\mathbf{1_{HM}}$, $\mathbf{3_{HM}}$, and $\mathbf{3_{MD}}$ at room temperature[a]

Entry	Cat.	Time (h)	Yield[b,c] (TON)[b,d]		Total yield	Selectivity[e]
			A	**B**		
1	$\mathbf{1_{HM}}$	1	38% (380)	10% (200)	48%	0.79
2	$\mathbf{1_{HM}}$	48	74% (740)	21% (420)	95%	0.78
3	$\mathbf{3_{HM}}$	1	15% (300)	0.9% (18)	16%	0.95
4	$\mathbf{3_{HM}}$	48	69% (540)	4% (80)	71%	0.95
5	$\mathbf{3_{HM}}$	72	74% (740)	5% (100)	79%	0.93
6	$\mathbf{3_{HM}}$	168	75% (750)	7% (140)	82%	0.91
7	$\mathbf{3_{MD}}$	1	11% (110)	0.6% (60)	12%	0.95
8	$\mathbf{3_{MD}}$	48	66% (390)	5% (100)	71%	0.93
9	$\mathbf{3_{MD}}$	72	78% (780)	7% (140)	85%	0.92
10	$\mathbf{3_{MD}}$	168	77% (720)	12% (240)	89%	0.87

[a]Reaction conditions: Neat, r.t., under N_2, [1,7-octadiene]:[Ph_2SiH_2] = 1:1, 0.1 mol % (BPI)$FeBr_2$, 2.0 mol % $NaBHEt_3$. [b]Determined by HPLC. [c]The yields are based on the initial concentration of Ph_2SiH_2. [d]TONs are based on the initial concentration of the Fe complexes. [e]Selectivity = [**A**]/[Total yield].

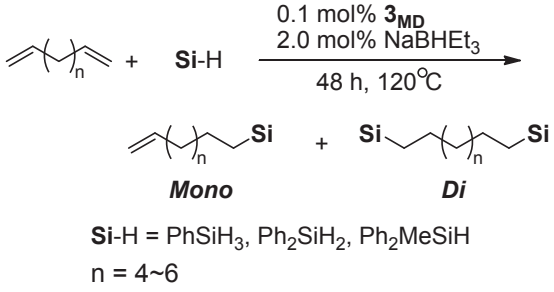
Table 6. Hydrosilylation of 1,7-octadiene with Ph_2SiH_2 catalyzed by $\mathbf{1_{HM}}$, $\mathbf{3_{HM}}$, and $\mathbf{3_{MD}}$ at 120 °C[a]

Entry	Cat.	Time	Yield[b,c] (TON)[b,d]		Total yield	Selectivity[e]
			A	**B**		
1	$\mathbf{1_{HM}}$	48	69% (690)	11% (220)	80%	0.86
2	$\mathbf{3_{HM}}$	48	54% (540)	3% (8)	57%	0.95
3	$\mathbf{3_{MD}}$	48	77% (770)	5% (100)	82%	0.94

[a]Reaction conditions: Neat, 120 °C, under N_2, [1,7-octadiene]:[Ph_2SiH_2] = 1:1, 0.1 mol % (BPI)$FeBr_2$, 2.0 mol % $NaBHEt_3$. [b]Determined by HPLC. [c]The yields are based on the initial concentration of Ph_2SiH_2. [d]TONs are based on the initial concentration of the Fe complexes. [e]Selectivity = [**A**]/[Total yield].

was lowered from 71% to 57% by the elevation of the reaction temperature. In contrast, the total yield (82%) and selectivity (0.94) by $\mathbf{3_{MD}}$ were improved at higher temperature. This difference apparently originates from the thermal stability of the active species of Fe complexes; unstable active species of $\mathbf{1_{HM}}$ and $\mathbf{3_{HM}}$ decomposed at higher temperature, and stable that of $\mathbf{3_{MD}}$ led to the better yield and selectivity. Among (BPI)$FeBr_2$ in this study, $\mathbf{3_{MD}}$ has the bulkiest ligand. Therefore, the active site of the catalytically active species derived from $\mathbf{3_{MD}}$ has tolerance against decomposition at higher temperature, leading to thermal stability of the active species and concomitantly longer reaction time. Bulkiness of the ligand would contribute to not only the selectivity for mono-hydrosilylated compound but also the thermal stability of the catalyst.

Thus, the best yield and selectivity for mono-hydrosilylated compound (**A**) were accomplished in the reaction conditions exhibited by Entry 3 in Table 6, 77% yield of **A** with 0.94 selectivity.



Scheme 4. Hydrosilylation of various non-conjugated dienes and silanes at catalyzed by $\mathbf{3_{MD}}$ at 120 °C.

Table 7. Hydrosilylation of various non-conjugated dienes and silanes catalyzed by $\mathbf{3_{MD}}$ at 120 °C[a]

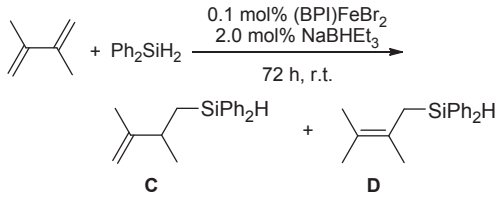
Entry	Chain Length (n)	**Si**-H	Yield[b,c] (TON)[b,d]		Total yield	Selectivity[e]
			Mono	***Di***		
1	4	$PhSiH_3$	57% (570)	38% (760)	95%	0.60
2	4	Ph_2MeSiH	N.D.	N.D.	—	—
3	5	Ph_2SiH_2	35% (350)	3% (6)	38%	0.92
4	6	Ph_2SiH_2	28% (280)	2% (4)	30%	0.93

[a]Reaction conditions: Neat, 120 °C, under N_2, [diene]:[**Si**-H] = 1:1, 0.1 mol % $\mathbf{3_{MD}}$, 2.0 mol % $NaBHEt_3$. [b]Determined by HPLC. [c]The yields are based on the initial concentration of Ph_2SiH_2. [d]TONs are based on the initial concentration of the Fe complexes. [e]Selectivity = [***Mono***]/[Total yield].

Hydrosilylation by Using Primary and Tertiary Silanes and Terminal Dienes with Longer Chain Length. As mentioned above, the steric hindrance of an iminobipyridine ligand greatly affected the selectivity for mono-hydrosilylated compound by the hydrosilylation of a diene. Next, we examined hydrosilylation by using primary and tertiary silanes and terminal dienes with longer chain length. $\mathbf{3_{MD}}$ was selected as a catalyst, since it showed best performance for the selective production of the mono-hydrosilylated compound at 120 °C (Entry 3 in Table 6). $PhSiH_3$ and Ph_2MeSiH were employed as primary and tertiary silane substrates. Hydrosilylation of 1,7-octadiene (n = 4 in Scheme 4) with them are summarized in Table 7 (Entry 1 and 2).

Total yield of the hydrosilylated compounds from the reaction between 1,7-octadiene (n = 4) with $PhSiH_3$ was quite high (95%), but it consisted of 57% of mono-hydrosilylated compound (***Mono***) and 38% of di-hydrosilylated compound (***Di***) Therefore, the selectivity of ***Mono*** was quite low (0.60). In the reaction of 1,7-octadiene with Ph_2MeSiH, no products were detected. It was already reported that hydrosilylation of an olefin with a tertiary silane by (BPI)$FeBr_2$ hardly proceeded.[13,14] Less catalytic activity of (BPI)$FeBr_2$ for a tertiary silane in this study was well consistent with previous reports.

Hydrosilylation of dienes longer than 1,7-octadiene were also carried out to elucidate the influence of the chain length of the diene. Hydrosilylation of 1,8-nonadiene (n = 5 in Scheme 4) and Ph_2SiH_2 afforded 35% of mono-hydrosilylated compound (***Mono***) and 2% of di-hydrosilylated one (***Di***) (Entry 3 in Table 7). 1,9-decadiene (n = 6 in Scheme 4) was



Scheme 5. Hydrosilylation of 2,3-dimethyl-1,3-butadiene with Ph_2SiH_2 catalyzed by (BPI)$FeBr_2$.

Table 8. Catalytic hydrosilylation of 2,3-dimethyl-1,3-butadiene with Ph_2SiH_2 using (BPI)$FeBr_2$ as catalysts[a]

Entry	Cat.	Yield[b,c] of **D** (TON)[b,d]
1	$\mathbf{1_{HM}}$	88% (880)
2	$\mathbf{1_{MM}}$	67% (670)
3	$\mathbf{1_{HD}}$	92% (920)
4	$\mathbf{1_{MD}}$	64% (640)
5	$\mathbf{2_{HM}}$	84% (840)
6	$\mathbf{2_{MM}}$	33% (330)
7	$\mathbf{2_{HD}}$	80% (800)
8	$\mathbf{2_{MD}}$	23% (230)
9	$\mathbf{3_{HM}}$	30% (300)
10	$\mathbf{3_{MM}}$	21% (210)
11	$\mathbf{3_{HD}}$	39% (390)
12	$\mathbf{3_{MD}}$	26% (260)

[a]Reaction conditions: Neat, r.t., 72 h, under N_2, [2,3-dimethyl-1,3-butadiene]: [Ph_2SiH_2] = 1:1, 0.1 mol % (BPI)$FeBr_2$, 2.0 mol % $NaBHEt_3$. [b]Determined by HPLC. [c]The yields are based on the initial concentration of Ph_2SiH_2. [d]TONs are based on the initial concentration of the Fe complexes.

also selected as a substrate, which produced ***Mono*** compound and ***Di*** compound with 28% and 2% yield, respectively, in the same reaction conditions (Entry 4 in Table 7). Total yields of both reactions (n = 5 and 6) were quite low (38% and 30% for n = 5 and n = 6, respectively), though the selectivity of both reactions (0.92 and 0.93 for n = 5 and n = 6) was similar to the reaction between 1,7-octadiene and Ph_2SiH_2 (0.94, Entry 3 in Table 6).

These results indicate that steric hindrance of substrates also drastically affects the yield and selectivity, similar to that of an iminobipyridine ligand; bulky substrate increases the selectivity for mono-hydrosilylated compound and decreases the yield.

Hydrosilylation of a Conjugated Diene. For the hydrosilylation of a conjugated diene, the reactions of 2,3-dimethyl-1,3-butadiene with Ph_2SiH_2 were employed (Scheme 5). Although possible products were 1,2-hydrosilylated compound (**C**) and 1,4-hydrosilylated one (**D**), (BPI)$FeBr_2$ generated only the 1,4-addition product in all cases (Table 8).

Among (BPI)$FeBr_2$ complexes, $\mathbf{1_{HD}}$ was most active for hydrosilylation of 2,3-dimethyl-1,3-butadiene (92%). Introduction of a Me group at R^2 largely decreased the product yield (even number Entries in Table 8), especially, by using the Fe complex with R^1 = 5′-Me, the yields were reduced to one-third or less of those by non-substituted complexes at R^1 (Entries 6 and 8 in Table 7). Similarly, the steric effect of 6′-Me group at R^1 on catalytic hydrosilylation was tremendously large; the product yields obtained from $\mathbf{3_{HM}}$–$\mathbf{3_{MD}}$ catalysis dramatically decreased (Entries 9–12 in Table 7). It is suggested that 1,4-

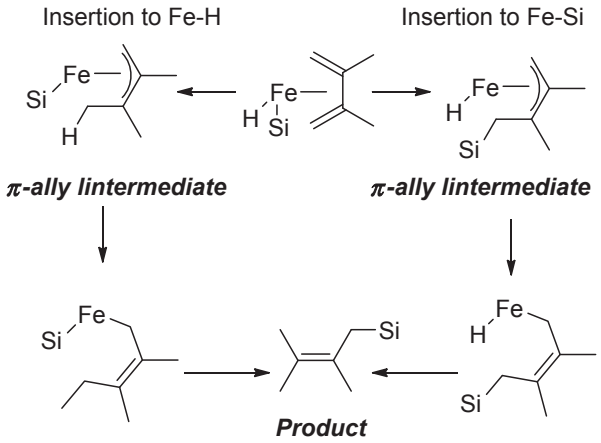


Figure 2. Suggested mechanism of 1,4-hydrosilylated compound production by hydrosilylation of a butadiene derivative.

hydrosilylation proceeds through the intermediate of the π-allyl complex (Figure 2).[33,34] There are two possible pathways to form π-allyl complexes via diene insertion to Fe-Si or Fe-H (Figure 2). It remains unclear whether the reaction proceeds via diene insertion to Fe-Si or Fe-H. However both intermediates have similar steric hindrance around Fe. Thus, to form the π-allyl intermediates, large space is required in the vicinity of the Fe center. Therefore the steric hindrance of the BPI ligand is more effective on conjugated diene activation than that on non-conjugated diene.

3. Conclusion

In order to obtain an organosilane compound bearing a terminal olefin portion, we tried hydrosilylation of a non-conjugated diene and a conjugated diene using Fe-iminobipyridine complexes ((BPI)$FeBr_2$) as catalysts. Upon the hydrosilylation of a non-conjugated diene, $\mathbf{1_{HM}}$ produced both the mono-hydrosilylated compound and the di-hydrosilylated one by the reaction between 1,7-octadiene and Ph_2SiH_2. For the selective production of the desired compound (the mono-hydrosilylated compound) by $\mathbf{1_{HM}}$ catalysis, more than three molar equivalents of 1,7-octadiene were required. To decrease excess diene in this reaction, the effect of substituents of (BPI)$FeBr_2$ on hydorosilylation of 1,7-octadiene was investigated. Steric hindrance of the BPI ligand based on three substituents (R^1, R^2, and Ar) slowed the reaction, instead it improved the selectivity of a desired compound. Particularly, 6′-Me group on the terminal pyridine of BPI was most effective, since it covers the Fe center directly. Yield and selectivity for the mono-hydrosilylated compound in the reaction between 1,7-octadiene and Ph_2SiH_2 reached 77% and 0.94, respectively. Selectivity of the mono-hydrosilylated compound is kinetically controlled, therefore steric effect of the BPI ligand is advantageous to improve the selectivity. Similarly, steric hindrance of substrates also affected the selectivity of the mono-hydrosilylated compound. However, large steric hindrance of both an iminobipyridine ligand and substrates decrease the yield of hydrosilylation product. Thus, in order to obtain various mono-hydrosilylated compounds from dienes selectively, the steric effect of an iminobipyridine ligand should be

adjusted for substrates. On the other hand, upon the application of (BPI)$FeBr_2$ to hydrosilylation of a conjugated diene (2,3-dimethyl-1,3-butadiene), 1,4-hydrosilylatied compound was selectively formed. In this case, the steric effect based on three substituents simply decreased the yield of a product. Although 1,2-hydrosilylated compound would be a desired product in this study, production of it was not observed at all. Selective 1,2-hydrosilylation is quite rare, and there have been only three reports so far.[34,35] Only one report of them succeeded in the formation of an organosilane compound bearing a terminal olefin portion by 1,2-hydrosilylation of 1,3-butadiene.[34] To obtain a target compound in this study through the hydrosilylation of conjugated diene derivatives, further improvement and strategy of catalytic system should be required.

4. Experimental

Instruments. ^1H and $^{13}C\{^1H\}$ NMR were recorded on a JEOL JMN-AL400. The residual peaks of the solvent were used as an internal standard of the chemical shifts. HPLC analyses were performed with a Shimadzu Prominence UFLC (LC-20 series) equipped with an ODS column (Cosmosil 5C18-MS-II (250 × 4.6 mm)), column oven, and UV detector. Acetonitrile (100%) was used as carrier phase of which flow rate was 1.0 mL/min. Column temperature was kept at 40 °C during analyses. Products were detected by the absorption at 199 nm. Quantification of the products was performed using calibration curves prepared by the plot of peak area vs concentration of authentic samples.

Materials. Fe-iminobipyridine complexes, $\mathbf{2_{HM}}$, $\mathbf{2_{MM}}$, $\mathbf{2_{HD}}$, $\mathbf{2_{MD}}$, $\mathbf{3_{HM}}$, and $\mathbf{3_{HD}}$ were prepared according to previous reports.[13,14] 5-Methyl-2-tributylstannyl-pyridine (**4a**), 6-methyl-2-tributylstannyl-pyridine (**4b**), and 6-bromopyridine-2-carboaldehyde (**5a**) were also prepared according to the literature.[12,13] Super dehydrated grade hexane, THF, and toluene were purchased from Kanto Chemical Co. Inc. and used as solvents. All other chemicals were purchased from commercial sources and used as received.

[5′-Methyl-2,2′-bipyridine]-6-carboxaldehyde (6a). **4a** (37.1 g, 97.1 mmol), **5a** (18.0 g, 96.8 mmol), and $Pd(PPh_3)_4$ (5.59 g, 4.84 mmol) were dissolved in toluene (180 mL) under N_2, and the solution was heated at reflux for 12 h. After cooling to room temperature, 6 M HClaq (230 mL) and $CHCl_3$ were added. The water phase was neutralized with 10 M NaOHaq (150 mL) and ice-cooling, resulting in a white precipitate of crude **6a**. The crude product was extracted with three 300 mL portions of $CHCl_3$, and purified by silica gel column chromatography eluted with AcOEt. 10.2 g of **6a** was obtained as a white powder (51.5 mmol, 53%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.42 (s, 3H, PyCH_3), 7.68 (d, 1H, $J = 8.0$, *Py*), 7.96 (m, 2H, *Py*), 8.44 (d, 1H, $J = 8.1$, *Py*), 8.53 (s, 1H, 6′-H, *Py*), 8.62 (dd, 1H, $J = 6.8$, 1.7 Hz, *Py*), 10.16 (s, 1H, O=C*H*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 18.57 (Py*C*H_3), 120.93, 121.22, 124.99, 134.31, 137.71, 137.96, 149.92, 152.38, 152.59, 156.95 (*Py*), 193.92 (O=*C*H). Anal. Calcd for $C_{12}H_{10}N_2O$: C, 71.71; H, 5.09; N, 14.13. Found: C, 72.51; H, 5.19; N, 14.02. HRMS (DART): $[M + H]^+$ Calcd. for $C_{12}H_{11}N_2O$: 199.0871; Found: 199.0873.

1-[5′-Methyl-2,2′-bipyridine-6-yl]ethanone (6b). This compound was prepared by the same procedure with **6a** from **4a** (37.1 g, 97.1 mmol), **5b** (19.3 g, 96.5 mmol), and $Pd(PPh_3)_4$ (5.61 g, 4.86 mmol) in toluene (205 mL). **6b** was obtained as a brown solid (12.7 g, 59.8 mmol, 62%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.41 (s, 3H, PyCH_3), 2.83 (s, 3H, O=CCH_3), 7.65 (dd, 1H, $J = 8.1$, 2.1 Hz, *Py*), 7.93 (td, 1H, $J = 7.8$, 0.67 Hz, *Py*), 8.02 (m, 1H, *Py*), 8.41 (d, 1H, $J = 8.1$ Hz, *Py*), 8.51 (m, 1H, *Py*), 8.57 (m, 1H, *Py*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 18.55 (Py*C*H_3), 25.89 (O=C*C*H_3), 120.78, 121.21, 124.09, 134.08, 137.67, 137.83, 149.71, 152.88, 152.94, 155.55 (*Py*), 200.42 (O=*C*CH_3). Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.56; H, 6.20; N, 12.78. HRMS (DART): $[M + H]^+$ Calcd. for $C_{13}H_{13}N_2O$: 213.10279; Found: 213.10149.

1-[6′-Methyl-2,2′-bipyridine-6-yl]ethanone (6c). This compound was prepared by the same procedure with **6a** from **4b** (45.0 g, 118 mmol), **5b** (21.4 g, 107 mmol), and $Pd(PPh_3)_4$ (6.38 g, 5.52 mmol) in toluene (214 mL). **6c** was obtained as a white powder (18.9 g, 88.8 mmol, 83%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.65 (s, 3H, PyCH_3), 2.84 (s, 3H, O=CCH_3), 7.21 (m, 1H, *Py*), 7.74 (m, 1H, *Py*), 7.94 (m, 1H, *Py*), 8.04 (d, 1H, $J = 7.7$ Hz, *Py*), 8.32 (d, 1H, $J = 7.8$ Hz, *Py*), 8.65 (d, 1H, $J = 7.8$ Hz, *Py*). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 24.66 (Py*C*H_3), 25.80 (O=C*C*H_3), 118.12, 121.26, 123.73, 124.35, 137.17, 137.70, 152.89, 154.71, 155.69, 158.03 (Py), 200.38 (O=*C*CH_3). Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.46; H, 6.20; N, 12.93. HRMS (DART): $[M + H]^+$ Calcd. for $C_{13}H_{13}N_2O$: 213.10279; Found: 213.10125.

***N*-([5′-Methyl-2,2′-bipyridin-6-yl]methylene)-2,4,6-trimethylbenzenamine (7a).** 2,4,6-trimethylaniline (2.42 mL, 15.1 mmol) and **6a** (3.0 g, 15.1 mmol) were dissolved in MeOH (30.0 mL) and stirred at 60 °C for 3 days. Cooling the reaction mixture to room temperature resulted in the precipitation of a yellow solid. The yellow solid of **7a** was filtered and washed with two 10 mL portions of MeOH, then dried in vacuo (4.23 g, 13.4 mmol, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.16 (s, 6H, *o*-CH_3, PhCH_3), 2.30 (s, 3H, *p*-CH_3, PhCH_3), 2.41 (s, 3H, PyCH_3), 6.91 (s, 2H, *m*-H, *Ph*), 7.64 (dd, 1H, $J = 8.0$, 1.8 Hz, *Py*), 7.94 (t, 1H, $J = 7.8$ Hz, *Py*), 8.29 (dd, 1H, $J = 7.8$, 0.85 Hz, *Py*), 8.37 (d, 1H, $J = 8.1$ Hz, *Py*), 8.42 (s, 1H, N=C*H*), 8.47 (dd, 1H, $J = 7.8$, 0.85 Hz, *Py*), 8.53 (d, 1H, $J = 1.8$ Hz, *Py*). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$): δ (ppm) 18.43, 18.57, 20.93 (Ar*C*H_3), 120.72, 120.90, 122.43, 126.96, 128.91, 133.47, 133.85, 137.63, 137.66, 148.15, 149.85, 153.32, 154.17, 156.27, 164.17 (N=*C*H, *Ar*, and *Py*). Anal. Calcd for $C_{21}H_{21}N_3$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.83; H, 6.86; N, 13.31. HRMS (DART): $[M + H]^+$ Calcd. for $C_{21}H_{22}N_3$: 316.1814; Found: 316.1816.

***N*-(1-[5′-Methyl-2,2′-bipyridin-6-yl]ethylidene)-2,4,6-trimethylbenzenamine (7b).** 2,4,6-trimethylaniline (2.42 mL, 15.1 mmol) and **6b** (3.0 g, 14.1 mmol) were dissolved in MeOH (30.0 mL), and finally 10 drops of HCOOH was added. The mixture was stirred at 60 °C for 3 days. Cooling the reaction mixture to room temperature resulted in the precipitation of a yellow solid. The yellow solid of **7b** was filtered and washed with two 10 mL portions of MeOH, then dried in vacuo (3.43 g, 10.4 mmol, 74%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.02 (s, 6H, *o*-CH_3, PhCH_3), 2.28 (s, 3H, N=CCH_3 or *p*-CH_3, PhCH_3), 2.30 (s, 3H, N=CCH_3 or *p*-CH_3, PhCH_3), 2.41 (s, 3H,

PyCH_3), 6.90 (s, 2H, *m*-H, *Ph*), 7.64 (bd, 1H, $J = 8.0$ Hz, *Py*), 7.91 (t, 1H, $J = 7.8$ Hz, *Py*), 8.36 (bd, 1H, $J = 7.8$ Hz, *Py*), 8.43 (d, 1H, $J = 8.0$ Hz, *Py*), 8.48 (bd, 1H, $J = 7.8$ Hz, *Py*), 8.52 (s, 1H, 6′-H, *Py*). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$): δ (ppm) 16.65 (N=C*C*H$_3$), 18.05, 18.57, 20.90 (Ar*C*H$_3$), 120.76, 120.96, 121.75, 125.46, 128.68, 132.28, 133.66, 137.44, 137.57, 146.47, 149.75, 153.70, 155.12, 155.83, 167.76 (N=*C*CH$_3$ and *Ar*). Anal. Calcd for $C_{22}H_{23}N_3$: C, 80.21; H, 7.03; N, 12.76. Found: C, 80.20; H, 7.10; N, 12.73. HRMS (DART): $[M + H]^+$ Calcd. for $C_{22}H_{24}N_3$: 330.1970; Found: 330.1965.

***N*-([5′-Methyl-2,2′-bipyridin-6-yl]methylene)-2,6-diisopropylbenzenamine (7c).** 2,6-diisopropylaniline (3.17 mL, 15.1 mmol) and **6a** (3.0 g, 15.1 mmol) were dissolved in MeOH (30.0 mL) and stirred at 60 °C for 3 days. Cooling the reaction mixture to room temperature resulted in the precipitation of a yellow solid. The yellow solid of **7c** was filtered and washed with two 10 mL portions of MeOH, then dried in vacuo (4.86 g, 13.6 mmol, 90%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.20 (d, 12H, $J = 6.9$ Hz, PhCH(CH_3)$_2$), 2.41 (s, 3H, PyCH_3), 3.01 (sept, 2H, $J = 6.9$ Hz, PhC*H*(CH$_3$)$_2$), 7.11–7.21 (m, 3H, *Ph*), 7.64 (dd, 1H, $J = 8.0$, 2.0 Hz, *Py*), 7.96 (t, 1H, $J = 7.8$ Hz, *Py*), 8.29 (dd, 1H, $J = 7.8$, 0.92 Hz, *Py*), 8.39 (m, 2H, N=C*H* and *Py*), 8.49 (dd, 1H, $J = 7.8$, 0.92 Hz, *Py*), 8.54 (m, 1H, 6′-H, *Py*). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$): δ (ppm) 18.58, 23.61, 28.14 (Py*C*H$_3$ and *o*-^{i}Pr, Ph ^{i}*Pr*), 120.88, 120.98, 122.54, 123.20, 124.56, 133.90, 137.39, 137.70, 137.73, 148.72, 149.77, 153.25, 154.04, 156.29, 163.65 (N=*C*H and *Ar*). Anal. Calcd for $C_{24}H_{27}N_3$: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.38; H, 7.75; N, 11.78. HRMS (DART): $[M + H]^+$ Calcd. for $C_{24}H_{28}N_3$: 358.2283; Found: 358.2284.

***N*-(1-[5′-Methyl-2,2′-bipyridin-6-yl]ethylidene)-2,6-diisopropylbenzenamine (7d).** 2,6-diisopropylaniline (3.04 mL, 14.5 mmol) and **6b** (3.08 g, 14.5 mmol) were dissolved in MeOH (25.0 mL), and finally 20 drops of HCOOH were added. The mixture was stirred at 60 °C for 7 days. Cooling the reaction mixture to room temperature resulted in the precipitation of a white solid. The white solid of **7d** was filtered and washed with two 10 mL portions of MeOH, then dried in vacuo (3.83 g, 10.3 mmol, 71%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.19 (d, 12H, $J = 6.9$ Hz, PhCH(CH_3)$_2$), 2.35 (s, 3H, N=CCH_3), 2.42 (s, 3H, PyCH_3), 2.81 (sept, 2H, $J = 6.9$ Hz, PhC*H*(CH$_3$)$_2$), 7.13 (dd, 1H, $J = 8.4$, 6.7 Hz, *p*-H, *Ph*), 7.20 (d, 2H, $J = 7.2$ Hz, *m*-H, *Ph*), 7.66 (bd, 1H, $J = 8.0$ Hz, *Py*), 7.94 (t, 1H, $J = 7.8$ Hz, *Py*), 8.40 (d, 1H, $J = 7.8$ Hz, *Py*), 8.47 (d, 1H, $J = 8.1$ Hz, *Py*), 8.51–8.57 (m, 2H, *Py*). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$): δ (ppm) 17.43, 18.59, 23.11, 23.41, 28.44 (N=C*C*H$_3$, Py*C*H$_3$ and *o*-^{i}Pr, Ph ^{i}*Pr*), 120.85, 121.07, 121.85, 123.15, 123.69, 133.75, 135.98, 137.53, 137.74, 146.72, 149.63, 153.59, 155.03, 155.73, 167.26 (N=*C*CH$_3$ and *Ar*). Anal. Calcd for $C_{25}H_{29}N_3$: C, 80.82; H, 7.87; N, 11.31. Found: C, 80.85; H, 7.89; N, 11.28. HRMS (DART): $[M + H]^+$ Calcd. for $C_{25}H_{30}N_3$: 372.24397; Found: 372.24340.

***N*-(1-[6′-Methyl-2,2′-bipyridin-6-yl]ethylidene)-2,4,6-trimethylbenzenamine (7e).** 2,4,6-trimethylaniline (2.03 mL, 14.1 mmol) and **6c** (3.0 g, 14.1 mmol) were dissolved in MeOH (25.0 mL), and finally 20 drops of HCOOH were added. The mixture was stirred at 60 °C for 7 days. The solvent was evaporated, and the residue was purified by Kugelrohr distillation (200 °C, 120 pa). **7e** was obtained as a yellow solid (2.97 g, 9.02 mmol, 64%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.03 (s, 6H, *o*-CH$_3$, PhCH_3), 2.30 (s, 3H, N=CCH_3 or *p*-CH$_3$, PhCH_3), 2.31 (s, 3H, N=CCH_3 or *p*-CH$_3$, PhCH_3), 2.68 (s, 3H, PyCH_3), 6.91 (s, 2H, *m*-H, *Ph*), 7.20 (d, 1H, $J = 7.6$ Hz, *Py*), 7.74 (t, 1H, $J = 7.8$ Hz, *Py*), 7.92 (t, 1H, $J = 7.8$ Hz, *Py*), 8.36 (d, 1H, $J = 7.9$ Hz, *Py*), 8.39 (d, 1H, $J = 7.8$ Hz, *Py*), 8.59 (d, 1H, $J = 7.8$ Hz, *Py*). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$): δ (ppm) 16.38 (N=C*C*H$_3$), 18.08, 20.92, 24.73 (Ar*C*H$_3$), 118.33, 121.22, 122.25, 123.62, 125.49, 128.70, 132.33, 137.40, 137.45, 146.40, 155.02, 155.45, 155.82, 158.01, 167.84 (N=*C*CH$_3$ and *Ar*). Anal. Calcd for $C_{22}H_{23}N_3$: C, 80.21; H, 7.04; N, 12.76. Found: C, 80.31; H, 7.05; N, 12.82. HRMS (DART): $[M + H]^+$ Calcd. for $C_{22}H_{24}N_3$: 330.19702; Found: 330.19666.

***N*-(1-[6′-Methyl-2,2′-bipyridin-6-yl]ethylidene)-2,6-diisopropylbenzenamine (7f).** 2,6-diisopropylaniline (3.04 mL, 14.5 mmol) and **6b** (3.08 g, 14.5 mmol) were dissolved in MeOH (25.0 mL), and finally 20 drops of HCOOH were added. The mixture was stirred at 60 °C for 7 days. Cooling the reaction mixture to room temperature resulted in the precipitation of a white solid. The white solid of **7d** was filtered and washed with two 10 mL portions of MeOH, then dried in vacuo (3.83 g, 10.3 mmol, 71%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.17 (d, 12H, $J = 6.9$ Hz, PhCH(CH_3)$_2$), 2.33 (s, 3H, N=CCH_3), 2.66 (s, 3H, PyCH_3), 2.79 (sept, 2H, $J = 6.9$ Hz, PhC*H*(CH$_3$)$_2$), 7.11 (dd, 1H, $J = 8.5$, 6.6 Hz, *p*-H, *Ph*), 7.19 (m, 3H, *Py* and *m*-H, *Ph*), 7.73 (t, 1H, $J = 7.8$ Hz, *Py*), 7.93 (t, 1H, $J = 7.8$ Hz, *Py*), 8.35 (d, 1H, $J = 7.8$ Hz, *Py*), 8.38 (d, 1H, $J = 7.8$ Hz, *Py*), 8.56 (d, 1H, $J = 7.8$ Hz, *Py*). $^{13}C\{^1H\}$ NMR (100.4 MHz, $CDCl_3$): δ (ppm) 17.41, 23.09, 23.38, 24.85, 28.40 (N=C*C*H$_3$, Py*C*H$_3$ and *o*-^{i}Pr, Ph ^{i}*Pr*), 118.19, 121.12, 122.10, 123.12, 123.53, 123.64, 136.00, 137.18, 137.46, 146.71, 155.31, 155.57, 155.71, 158.08, 167.33 (N=*C*CH$_3$ and *Ar*). Anal. Calcd for $C_{25}H_{29}N_3$: C, 80.82; H, 7.87; N, 11.31. Found: C, 80.77; H, 7.99; N, 11.30. HRMS (DART): $[M + H]^+$ Calcd. for $C_{25}H_{30}N_3$: 372.24397; Found: 372.24431.

***N*-([5′-Methyl-2,2′-bipyridin-6-yl]methylene)-2,4,6-trimethylbenzenamine Iron (II) Bromide ($\mathbf{2_{HM}}$).** 731 mg of **7a** (2.32 mmol) were dissolved in THF (25 mL) under N_2. After the addition of $FeBr_2$ (500 mg, 2.32 mmol) to the solution, a precipitate appeared. The mixture was stirred for 12 h. The resulting precipitate was collected by filtration, and washed with THF (5 mL × 3) and hexane (5 mL × 3), then dried in vacuo. $\mathbf{2_{HM}}$ was obtained as dark brown powder (1.16 g, 2.18 mmol, 94%). Anal. Calcd for $C_{21}H_{21}Br_2FeN_3$: C, 47.49; H, 3.99; N, 7.91. Found: C, 47.74; H, 4.40; N, 7.19. HRMS(FAB): $[M - Br]^+$ Calcd. for $C_{22}H_{23}BrFeN_3$: 450.0268; Found: 450.0277.

***N*-(1-[5′-Methyl-2,2′-bipyridin-6-yl]ethylidene)-2,4,6-trimethylbenzenamine Iron (II) Bromide ($\mathbf{2_{MM}}$).** $\mathbf{2_{MM}}$ was obtained from the reaction between **7b** (764 mg, 2.32 mmol) and $FeBr_2$ (500 mg, 2.32 mmol) according to the procedure of $\mathbf{2_{HM}}$.

Brownish gray powder, Yield: 1.23 g (2.27 mmol, 98%). Anal. Calcd for $C_{22}H_{23}Br_2FeN_3 \cdot C_4H_8O$ (M + THF): C, 49.60; H, 4.68; N, 7.23. Found: C, 49.94; H, 4.92; N, 6.94. HRMS(FAB): $[M - Br]^+$ Calcd. for $C_{22}H_{23}BrFeN_3$: 464.0425; Found: 464.0442.

***N*-([5′-Methyl-2,2′-bipyridin-6-yl]methylene)-2,6-diisopropylbenzenamine Iron (II) Bromide ($\mathbf{2_{HD}}$).** $\mathbf{2_{HD}}$ was obtained from the reaction between **7c** (500 mg, 1.40 mmol) and $FeBr_2$ (308 mg, 1.40 mmol) according to the procedure of $\mathbf{2_{HM}}$.

Greenish gray powder, Yield: 721 mg (1.26 mmol, 90%). Anal. Calcd for $C_{24}H_{27}Br_2FeN_3 \cdot 0.5H_2O$ ($M + 0.5H_2O$): C, 49.52; H, 4.85; N, 7.22. Found: C, 49.73; H, 4.72; N, 7.44. HRMS(FAB): $[M - Br]^+$ Calcd. for $C_{24}H_{27}BrFeN_3$: 492.0738; Found: 492.0740.

***N*-(1-[5′-Methyl-2,2′-bipyridin-6-yl]ethylidene)-2,6-diisopropylbenzenamine Iron (II) Bromide ($\mathbf{2_{MD}}$).** $\mathbf{2_{MD}}$ was obtained from the reaction between **7d** (500 mg, 1.35 mmol) and $FeBr_2$ (296 mg, 1.35 mmol) according to the procedure of $\mathbf{2_{HM}}$.

Blue powder, Yield: 561 mg (0.96 mmol, 71%). Anal. Calcd for $C_{25}H_{29}Br_2FeN_3 \cdot H_2O$ ($M + H_2O$): C, 49.62; H, 5.16; N, 6.94. Found: C, 49.78; H, 4.90; N, 6.93. HRMS(FAB): $[M - Br]^+$ Calcd. for $C_{25}H_{29}BrFeN_3$: 506.0894; Found: 506.0881.

***N*-(1-[6′-Methyl-2,2′-bipyridin-6-yl]ethylidene)-2,4,6-trimethylbenzenamine Iron (II) Bromide ($\mathbf{3_{MM}}$).** $\mathbf{3_{MM}}$ was obtained from the reaction between **7e** (500 mg, 1.56 mmol) and $FeBr_2$ (334 mg, 1.56 mmol) according to the procedure of $\mathbf{2_{HM}}$.

Gray powder, Yield: 786 mg (1.44 mmol, 95%). Anal. Calcd for $C_{22}H_{23}Br_2FeN_3 \cdot (0.5C_4H_8O)$ ($M + 0.5$THF): C, 49.6; H, 4.68; N, 7.23. Found: C, 49.29; H, 4.75; N, 7.05. HRMS(FAB): $[M - Br]^+$ Calcd. for $C_{22}H_{23}BrFeN_3$: 464.0425; Found: 464.0441.

***N*-(1-[6′-Methyl-2,2′-bipyridin-6-yl]ethylidene)-2,4,6-trimethylbenzenamine Iron (II) Bromide ($\mathbf{3_{MD}}$).** $\mathbf{3_{MD}}$ was obtained from the reaction between **7f** (861 mg, 2.32 mmol) and $FeBr_2$ (500 mg, 2.32 mmol) according to the procedure of $\mathbf{2_{HM}}$.

Gray powder, Yield: 1.21 g (2.06 mmol, 89%). Anal. Calcd for $C_{25}H_{29}Br_2FeN_3 \cdot H_2O$ ($M + H_2O$): C, 49.62; H, 5.16; N, 6.94. Found: C, 49.64; H, 5.00; N, 6.99. HRMS(FAB): $[M - Br]^+$ Calcd. for $C_{25}H_{29}BrFeN_3$: 506.0894; Found: 506.0870.47.49.

Typical Procedure for the Catalytic Hydrosilylation of Olefins with Silanes. (BPI)$FeBr_2$ (0.0057 mmol) was placed in a Schlenk tube in air at room temperature. Next, the air in the Schlenk tube was replaced with nitrogen. 1,7-octadiene (0.86 mL, 5.6 mmol) and diphenylsilane (1.1 mL, 5.6 mmol) were placed in the Schlenk tube. Amount of 1,7-octadiene was increased as appropriate. Sodium triethylborohydride ($NaBHEt_3$) (1.0 M in toluene, 115 µL, 0.115 mmol) was then added to the suspension to start the reaction. The solution was stirred at room temperature or 120 °C. The reaction was stopped by exposure to air at appropriate time. The reaction mixture was subjected to HPLC analysis to determine the yield and TON.

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Supporting Information

^{1}H NMR and $^{13}C\{^1H\}$ spectra of **6a–c**, **7a–7f**, and products of hydrosilylation (**A**, **B**, and **D**). This material is available on http://dx.doi.org/10.1246/bcsj.20180197.

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