Articles

Base-Promoted Silicon−Hydrogen Bond Activation of Silanes by Iridium(III) Porphyrin Complexes

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Iridium(III) porphyrin silyls were synthesized in moderate to high yields conveniently from the reactions of iridium(III) porphyrin carbonyl chloride and methyl with silanes, via silicon−hydrogen bond activation (SiHA) in solvent-free conditions and nonpolar solvents. Base was found to promote the SiHA reactions. Specifically, K_3PO_4 accelerated the SiHA with iridium porphyrin carbonyl chloride, while KOAc promoted the SiHA by iridium porphyrin methyl. Mechanistic experiments suggested that iridium(III) porphyrin carbonyl chloride initially formed iridium porphyin cation, which then reacted with silanes likely via heterolysis to give iridium porphyrin hydride. Iridium porphyrin hydride further reacted with silanes to yield iridium porphyrin silyls. On the other hand, iridium(III) porphyrin methyl and silyls underwent either oxidative addition or σ-bond metathesis to form the products. In the presence of base, a pentacoordinated silicon hydride species likely formed and reacted with iridium porphyrin methyl to form iridium porphyrin anion, which could further react with silanes to yield iridium porphyrin hydride after protonation. Ir(ttp)H finally reacted with excess silanes to give iridium porphyrin silyl complexes.

Introduction

Silicon−hydrogen bond activation (SiHA) is an important process for both catalytic applications in organic synthesis[1–3] and the synthesis of transition metal silyls.[4] Recently, silicon−hydrogen bond activation has been utilized for the catalytic functionalization of hydrocarbons by transition metal complexes, and transition metal silyls are proposed as the intermediates.[2,3] The preparation of transition metal silyls from the reactions of metal halides with silanes has been extensively utilized.[5]

The silicon−hydrogen bond activation with the late high-valent transition metal such as rhodium(III) or iridium(III) complexes is interesting.[5–7] So far, the mechanistic possibilities of silicon−hydrogen bond activation by these late transition metal complexes can be heterolysis,[8,9] oxidative addition,[7,10,11] or σ-bond metathesis.[12,13] One key supporting evidence for the oxidative addition is the isolation of an iridium(V) silyl intermediate, which has been characterized by X-ray diffraction.[7,11]

Our group has reported that silicon−hydrogen bonds activation by rhodium(III) porphyrins (por) can provide a facile synthetic route to rhodium silyl complexes.[8] We have reported that rhodium(III) porphyrin halides and methyls reacted with silanes to give high yields of rhodium porphyrin silyls via silicon−hydrogen bond activation in solvent-free conditions. Rh(por)Cl was proposed to undergo ionization into $Rh(por)^+Cl^-$, which then underwent silylation to yield rhodium porphyrin silyls. On the other hand, Rh(por)Me reacted with silanes via either oxidative addition or σ-bond metathesis (Scheme 1). These reactions are mechanistically puzzling since cis-interaction on the same face of a porphyrin by the methyl group and silane could be sterically very demanding.

To broaden the synthetic scope and to gain further mechanistic understanding of these metalloporphyrin-based SiHA, we have explored the SiHA chemistry with high-valent iridium(III) porphyrins. In addition, the base-promoted SiHA was discovered. Herein, we now report the successful results of these studies.

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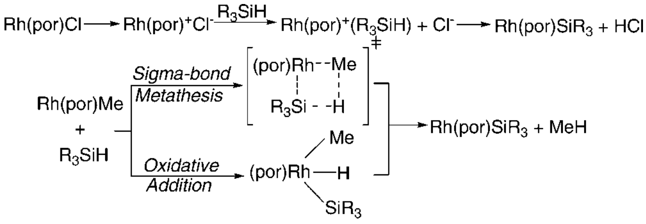
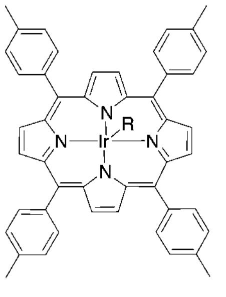
Scheme 1. Mechanism of SiHA of Silanes with Rh(ttp)Cl or Rh(ttp)Me





ttp = 5, 10, 15, 20-tetratolylporphyrinato
R = Cl(CO), Me or $SiR_1R_2R_3$

Figure 1. Structures of iridium porphyrin complexes.

Table 1. Temperature Optimization of SiHA

entry	temp (°C)	time	% **2b**[a]
1	120	9 days	trace
2	140	6 days	10
3	200	4.5 h	6
4	200	4 days	84

[a] Average yield of duplicate experiments.

Results and Discussion

Optimization in Solvent-Free Conditions. Initially, Ir(ttp)-Cl(CO) **1a** (Figure 1) reacted with $HSiEt_3$ **2a** in solvent-free conditions at 120 °C (Table 1, entry 1). However, only a trace amount of Ir(ttp)$SiEt_3$ **2b** was obtained even after 9 days, while Ir(ttp)H **1d** was observed as the major product according to the ^1H NMR analysis of the crude reaction mixture. When the reaction temperature was increased to 200 °C, after 4.5 h, Ir(ttp)H was generated as the major product together with Ir(ttp)$SiEt_3$ **2b** isolated in a low yield of 6% (Table 1, entry 3). After 4 days, Ir(ttp)$SiEt_3$ **2b** was isolated in 84% yield (Table 1, entry 4). Therefore, the temperature of 200 °C was employed for subsequent studies.

When the optimized solvent-free conditions at 200 °C were applied to the reactions of Ir(ttp)Cl(CO) **1a** with various silanes, moderate to good yields of iridium porphyrin silyl complexes were obtained (eq 1, Table 2). Ir(ttp)Cl(CO) **1a** dissolved in alkyl-substituted silanes only upon heating, but dissolved in aromatic silanes even at room temperature.

The yields of the products depended on the steric hindrance of silanes.[8] Cone angles obtained from phosphines have been used as a measure of steric hindrance, and cone angles of silanes are identical to the corresponding phosphines[14] [H_3SiPh (101°), $HSi(OEt)_3$ (109°), H_2SiPh_2 (128°), $HSiEt_3$ (132°), $HSiPr_3$ (132°), $HSiPh_2Me$ (136°)].[15] In general, more bulky silanes with larger cone angles reacted with slower rates and gave lower yields. No SiHA product was found when Ir(ttp)Cl(CO) **1a** reacted with the more hindered $HSiPr_3$ or $HSi^{t}BuMe_2$. However, the rate of SiHA was also dependent on the solubility of Ir(ttp)Cl(CO) **1a** in silane. A better solvent, such as $H_2SiPhMe$ or $HSiPhMe_2$, gave a faster rate (Table 2, entries 5 and 7), while a poor solvent such as $HSiEt_3$ gave a slower rate (Table 2, entry 1).

Table 2. Solvent-Free SiHA of Silanes by Ir(ttp)Cl(CO)

$$\mathrm{Ir(ttp)Cl(CO)} + \mathrm{HSiR_1R_2R_3} \xrightarrow[\text{time}]{\mathrm{N_2},\ \text{temp}} \mathrm{Ir(ttp)SiR_1R_2R_3} \quad (1)$$

entry	$HSiR_3$	temp (°C)	time	product (% yield)[b]
1	$HSiEt_3$, **2a**	200	4 days	Ir(ttp)$SiEt_3$ **2b** (84)
2	$HSi(OEt)_3$ **3a**	200	6 h	Ir(ttp)$Si(OEt)_3$ **3b** (54)
3	$HSiBnMe_2$ **4a**	200	1 day	Ir(ttp)$SiBnMe_2$ **4b** (78)
4	H_3SiPh **5a**	140	5 h	Ir(ttp)$SiPhH_2$ **5b** (90)
5	$H_2SiPhMe$ **6a**	200	0.5 h	Ir(ttp)SiPhMeH **6b** (34)
6	H_2SiPh_2 **7a**	140	2 days	Ir(ttp)$SiPh_2H$ **7b** (68)
7[a]	$HSiPh_2Me$ **8a**	200	6 h	Ir(ttp)$SiPh_2Me$ **8b** (42)

[a] 30% yield of Ir(ttp)SiPhMeH **6b** was also generated according to ^1H NMR analysis of the crude reaction mixture. [b] Average yield of duplicate experiments.

Iridium porphyrin silyls are thermally stable when the silyl group is trisubstituted. However, the monosubstituted Ir(ttp-)$SiPhH_2$ **5b** decomposed at 200 °C even in a nitrogen atmosphere. Therefore, the reaction of Ir(ttp)Cl(CO) **1a** and H_3SiPh **5a** was carried out at a lower temperature of 140 °C (Table 2, entry 4). Ir(ttp)$SiPhH_2$ **5b** and Ir(ttp)SiPhMeH **6b** could not be purified by column chromatography on alumina or recrystallization from CH_2Cl_2/MeOH. However, these two complexes could be purified simply by washing off the impurities with methanol under N_2.

For $HSiPh_2Me$ **8a** only, besides the SiHA reaction, silicon−carbon bond activation (SiCA) was also observed. When **8a** reacted with Ir(ttp)Cl(CO) **1a** at 200 °C, according to ^1H NMR analysis, Ir(ttp)H[16,17] initially formed. Then both the SiHA product **8b** and SiCA product **6b** were generated slowly and simultaneously in the ratio of 1.00 to 1.16 with the slow disappearance of Ir(ttp)H.[18] In addition, Ir(ttp)H also reacted with $HSiPh_2Me$ to generate both **8b** and **6b** at 200 °C in about 1.00 to 0.71 ratio,[18] which suggested that Ir(ttp)H was the intermediate for the parallel formation of both **8b** and **6b** in the reaction of **1a** and **8a** at 200 °C.

Base-Promoted SiHA with Ir(ttp)Cl(CO). Yamanoi and his co-worker reported that a base, especially K_3PO_4, can promote catalysis of a SiHA reaction.[3] Our group also found that 2,6-dimethylpyridine can increase the rate of SiHA of Rh(ttp)X (X = Cl and OTf) and $HSiEt_3$.[8] We therefore examined the possibility of base-promoted SiHA.

Table 3 and eq 2 show the successful results of base-promoted SiHA reaction of Ir(ttp)Cl(CO) **1a** and $HSiEt_3$ **2a** in solvent-free conditions. Addition of 5 equiv of K_3PO_4 enhanced the reaction rate and yield slightly (Table 3, entries 3 and 2), while addition of 10 equiv of K_3PO_4 enhanced the reaction rate and yield remarkably even at a lower temperature of 140 °C (Table 3, entry 4). However, the addition of 20 equiv of K_3PO_4 decreased the reaction yield slightly (Table 3, entry 5), and this may be due to the decomposition of intermediates or the occurrence of a side reaction caused by excess base. The optimal amount of K_3PO_4 was therefore found to be 10 equiv.

We further screened other salts with anions of different basicity and nucleophilicity in the reaction of Ir(ttp)Cl(CO) and $HSiEt_3$. The pK_a values for conjugated acids have been used to

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(18) See the Supporting Information for details.

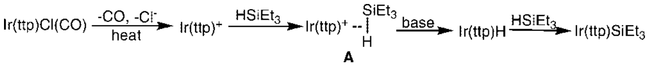
Table 3. Base-Promoted SiHA of $HSiEt_3$ in Solvent-Free Conditions

$$\text{Ir(ttp)Cl(CO)} + \text{HSiEt}_3 \xrightarrow[\text{temp, time}]{\text{base, N}_2} \underset{\textbf{2b}}{\text{Ir(ttp)SiEt}_3} \quad (2)$$

entry	base	equiv	temp (°C)	time (days)	% **2b**[a]
1	none	0	200	4	84
2	none	0	140	6	10
3	K_3PO_4	5	140	1	46
4	K_3PO_4	10	140	1	88
5	K_3PO_4	20	140	1	80
6	K_2CO_3	10	140	1	16
7	KOH	10	140	1	37
8	KF	10	140	5	50
9	CsCl	10	140	6	4
10	KI	10	140	5	14
11	KOAc	10	140	5	12

[a] Average yield of duplicate experiments.

Scheme 2. Mechanism of Base-Promoted SiHA of Ir(ttp)Cl(CO) with $HSiEt_3$



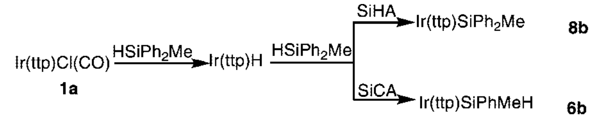
$$\underset{\textbf{1c}}{\text{Ir(ttp)(BF}_4\text{)(CO)}} + \text{HSiEt}_3 \xrightarrow[\text{1 d}]{\text{N}_2\text{, 200 °C}} \underset{\textbf{2b}\ 61\%}{\text{Ir(ttp)SiEt}_3} \quad (3)$$

$$\text{Ir(ttp)H} + \text{HSiEt}_3 \xrightarrow[\text{2d}]{\text{N}_2\text{, 140 °C}} \underset{\textbf{2b}\ 92\%}{\text{Ir(ttp)SiEt}_3} \quad (4)$$

compare the basicities of anions [H_2O (15.7) > H_3PO_4 (12.32) > H_2CO_3 (10.3) > HOAc (4.76) > HF (3.17) > HCl (−8.0) > HI (<−9.0)].[19] In general, a stronger base can promote SiHA of silane effectively (Table 3, entries 4 and 7). However, a very strong base such as KOH gave lower product yield, which was likely due to base-promoted decomposition of either the intermediate or the product. Since $Ir(ttp)SiEt_3$ in the presence of KOH (10 equiv) remained stable at 200 °C in benzene-d_6 for 3 days, an intermediate was likely decomposed by a strong base. One possible route is the conversion of the weakly basic Ir(ttp)H intermediate into $Ir(ttp)^-$, which further undergoes thermal decomposition.[20]

Mechanistic Studies. Scheme 2 illustrates the proposed mechanism for the SiHA. Initially, Ir(ttp)Cl(CO) ionizes into $Ir(ttp)^+Cl^-$ upon heating. This step is supported by the rate-enhanced reaction with $Ir(ttp)(BF_4)(CO)$[21] **1c** bearing a more labile anion. At 200 °C, Ir(ttp)Cl(CO) required 4 days to give $Ir(ttp)SiEt_3$ in 84% yield (Table 2, entry 1). $Ir(ttp)(BF_4)(CO)$ only took 1 day to complete the reaction to produce 61% yield of **2b** (eq 3). The slightly lower yield may be caused by the lower stability of **1c** at high temperature.[21] Then $Ir(ttp)^+$ forms a silane complex **A**, which reacts to give the observed intermediate Ir(ttp)H together with Et_3SiCl presumably. Further reaction of Ir(ttp)H with excess silane produces the iridium porphyrin silyl product. In the presence of a strong base (K_3PO_4, KOH, KF), Ir(ttp)H is formed more rapidly by the facile attack on the silicon atom in the iridium−silane complex by a base. The intermediate Ir(ttp)H then reacts with excess silane to yield $Ir(ttp)SiEt_3$. Indeed, when the reaction mixture of Ir(ttp)Cl(CO) **1a** and 100 equiv of $HSiEt_3$ **2a** with the addition of K_3PO_4 in benzene-d_6 was heated for 1.5 h at 140 °C in a sealed NMR tube, Ir(ttp)H was observed first without any $Ir(ttp)SiEt_3$.[18] Therefore, the base-promoted SiHA is due to the accelerated formation of the Ir(ttp)H intermediate. Furthermore, in an independent experiment, Ir(ttp)H reacted with $HSiEt_3$ to give 92% yield of $Ir(ttp)SiEt_3$ at 140 °C after 2 days (eq 4).

Scheme 3. Mechanism of SiHA and SiCA of Ir(ttp)Cl(CO) and $HSiPh_2Me$



$$\underset{\textbf{8b}}{\text{Ir(ttp)SiPh}_2\text{Me}} + \text{HSiPh}_2\text{Me} \xrightarrow[\text{2d}]{\text{N}_2\text{, 200°C}} \underset{\textbf{8b}\ 33\%}{\text{Ir(ttp)SiPh}_2\text{Me}} + \underset{\textbf{6b}\ 31\%}{\text{Ir(ttp)SiPhMeH}} \quad (5)$$

$$\underset{\textbf{6b}}{\text{Ir(ttp)SiPhMeH}} + \text{HSiPh}_2\text{Me} \xrightarrow[\text{2d}]{\text{N}_2\text{, 200°C}} \underset{\textbf{8b}\ 40\%}{\text{Ir(ttp)SiPh}_2\text{Me}} + \underset{\textbf{6b}\ 46\%}{\text{Ir(ttp)SiPhMeH}} \quad (6)$$

Table 4. SiHA of Silanes by Ir(ttp)Cl(CO)

$$\text{Ir(ttp)Cl(CO)} + \underset{\text{100 equiv}}{\text{HSiR}_3} \xrightarrow[\text{solvent, time}]{\text{200 °C, N}_2} \text{Ir(ttp)SiR}_3 \quad (7)$$

entry	silane	solvent	time	product (% yield)[a]
1	$HSiEt_3$ **2a**	benzene	9 days	$Ir(ttp)SiEt_3$ **2b** (58)
2	$HSiEt_3$ **2a**	cyclohexane	9 days	$Ir(ttp)SiEt_3$ **2b** (60)
3	$His(OEt)_3$ **3a**	benzene	6 h	$Ir(ttp)Si(OEt)_3$ **3b** (85)
4	$His(OEt)_3$ **3a**	cyclohexane	12 h	$Ir(ttp)Si(OEt)_3$ **3b** (88)

[a] Average yield of duplicate experiments.

Scheme 3 illustrates the proposed mechanism for the reaction of Ir(ttp)Cl(CO) with $HSiPh_2Me$ with SiHA, SiCA, and silyl exchange reactions. Ir(ttp)Cl(CO) reacts with $HSiPh_2Me$ to give Ir(ttp)H initially, which then reacts with excess $HSiPh_2Me$ to yield both SiHA product **8b** and SiCA product **6b** concurrently. We do not know the details of the SiCA, as iridium porphyrin silyls could undergo slower reactions (2 days) to give **6b** or **8b** in $HSiPh_2Me$ solvent to give a mixture of **8b** and **6b** (eqs 5 and 6).

SiHA in Solvents. We have reported that the SiHA of silanes with rhodium porphyrin complexes should be carried out in solvent-free conditions due to the competitive activation of solvent, such as benzene and dichloromethane.[8] However, iridium porphyrin complexes appeared to be less reactive toward solvents. So the SiHA reaction was carried out in a nonpolar solvent, such as benzene or cyclohexane.

Table 4 and eq 7 show the results of SiHA of silanes by Ir(ttp)Cl(CO) **1a** in benzene and cyclohexane. For $HSiEt_3$ **2a**, the reaction rate was slower than that in neat solvent-free conditions, as expected by the lower concentration of **2a** used (Table 4, entries 1 and 2 vs Table 2, entry 1). The lower yielding reaction of **2b** is likely due to the lower reactivity of **2a**. However, a higher yield was obtained for $HSi(OEt)_3$ **3a** even in a solvent (Table 4, entries 3 and 4 vs Table 2, entry 2). The faster rate and higher yield may be due to the better solubility of Ir(ttp)Cl(CO) in solvent and the higher reactivity of $HSi(OEt)_3$. Therefore, benzene and cyclohexane were both suitable solvents for this reaction. Ir(ttp)Cl(CO) **1a** also underwent rate-enhanced SiHA in benzene in the presence of K_3PO_4 (eq 8).

$$\text{Ir(ttp)Cl(CO)} + \underset{\text{100 equiv}}{\text{HSiEt}_3} \xrightarrow[\text{N}_2\text{, dark, 140 °C, 3 days}]{\text{10 equivK}_3\text{PO}_4\text{, benzene}} \underset{\textbf{2b}\ 92\%}{\text{Ir(ttp)SiEt}_3} \ (8)$$

SiHA with Ir(ttp)Me. The SiHA by more electron-rich Ir(ttp)Me **1b** bearing a nondissociating methyl group was also successful (Table 5, eq 9). In solvent-free conditions, **1b** reacted with $HSiEt_3$ **2a** to give 83% yield of $Ir(ttp)SiEt_3$ **2b** at 200 °C after 5 days (Table 5, entry 2). However, **1b** reacted with $HSi(OEt)_3$ **3a** only to produce 16% yield of $Ir(ttp)Si(OEt)_3$ **3b**

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Table 5. Silicon−Hydrogen Bond Activation by Ir(ttp)Me

$$\mathrm{Ir(ttp)Me + HSiR_3 \xrightarrow{N_2,\ temp,\ time} Ir(ttp)SiR_3} \quad (9)$$

entry	$HSiR_3$	temp (°C)	time (days)	product (% yield)[b]
1	$HSi(OEt)_3$, **3a**	200	7	$Ir(ttp)Si(OEt)_3$ **3b** (16)
2	$HSiEt_3$, **2a**	200	5	$Ir(ttp)SiEt_3$ **2b** (83)
3	$HSiEt_3$, **2a**	150	8	$Ir(ttp)SiEt_3$ **2b** (12)
4[a]	$HSiEt_3$, **2a**	200	7	$Ir(ttp)SiEt_3$ **2b** (10)
5[a]	$HSi(OEt)_3$, **3a**	200	4	$Ir(ttp)Si(OEt)_3$ **3b** (8)

[a] In benzene solvent, Ir(ttp)Me:silane = 1:100. [b] Average yield of duplicate experiments.

Table 6. Base-Promoted SiHA of $HSiEt_3$ by Ir(ttp)Me in Solvent-Free Conditions

$$\mathrm{Ir(ttp)Me + HSiEt_3 \xrightarrow[N_2,\ 150^{o}C,\ 8d]{10\ equiv\ base} Ir(ttp)SiEt_3} \quad (10)$$

entry	base	% **2b**	entry	base	% **2b**[a]
1	none	12	5	KF	15
2	K_3PO_4	44	6	CsCl	6
3	K_2CO_3	14	7	KI	9
4	KOH	trace	8	KOAc	60

[a] Average yield of duplicate experiments.

(Table 5, entry 1). The lower yield was attributed to the poor reactivity and selectivity, since most Ir(ttp)Me remained and Ir(ttp)Et generated via carbon−oxygen bond activation reaction was also observed. At 150 °C, a poor yield of **2b** was produced (Table 5, entry 3). When the reaction was carried out in benzene solvent, a higher reaction temperature of 200 °C was required, but still poor product yields were observed (Table 5, entries 4 and 5).

Base-Promoted SiHA with Ir(ttp)Me. To further enhance the SiHA by Ir(ttp)Me, the base effect on SiHA was examined. Table 6 and eq 10 list the results of the base-promoted SiHA by Ir(ttp)Me. We were delighted to find that the addition of K_3PO_4 or KOAc gave higher product yields (Table 6, entries 2 and 8), although KOH and CsCl proved to be detrimental.

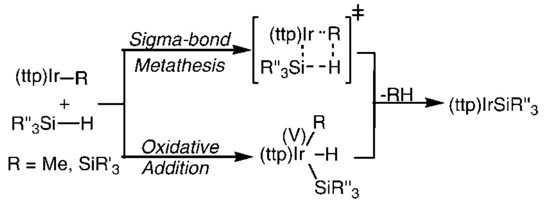
SiHA with Iridium Porphyrin Silyls. The SiHA reaction was also observed with the electron-rich $Ir(ttp)SiEt_3$ and $Ir(ttp)SiBnMe_2$ complexes. $Ir(ttp)SiBnMe_2$ **4b** reacted with $HSiEt_3$ **2a** at 200 °C in 4 days to give 20% of $Ir(ttp)SiEt_3$ **2b** and 71% of **4b** was recovered, while $Ir(ttp)SiEt_3$ **2b** reacted with $HSiBnMe_2$ to give 82% of $Ir(ttp)SiBnMe_2$ **4b** after 2 days, and **2b** was completely consumed (eqs 11 and 12). The higher conversion of $Ir(ttp)SiEt_3$ into **4b** (eq 12) is likely due to the preferred formation of a less hindered $Ir(ttp)SiBnMe_2$ complex.

$$\mathrm{Ir(ttp)SiBnMe_2 + HSiEt_3 \xrightarrow[4\ d]{N_2,\ 200^{o}C} \underset{\mathbf{2b}\ 20\%}{Ir(ttp)SiEt_3} + HSiBnMe_2} \quad (11)$$

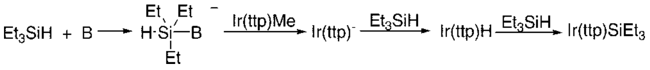
$$\mathrm{Ir(ttp)SiEt_3 + HSiBnMe_2 \xrightarrow[2\ d]{N_2,\ 200^{o}C} \underset{\mathbf{4b}\ 82\%}{Ir(ttp)SiBnMe_2} + HSiEt_3} \quad (12)$$

Mechanism of SiHA with Ir(ttp)Me and $Ir(ttp)SiR_3$. Scheme 4 shows the proposed reaction pathways for the reaction of Ir(ttp)Me or $Ir(ttp)SiR_3$ with silanes without the addition of base. Oxidative addition can occur via the formation of an Ir(V) intermediate since an Ir(V) intermediate in SiHA has been reported by Bergman and co-workers.[11] Alternatively, σ-bond metathesis or σ-complex-assisted metathesis[13] via a four-centered transition state is also possible. The distinction between oxidative addition and σ-bond metathesis has been attempted by theoretical methods since it is experimentally difficult.[22] A dissociative mechanism via homolysis of Ir(ttp)Me is unlikely since the Ir−Me bond is stronger than the Rh−Me bond, which is about 58 kcal/mol[23] and will require a very long reaction time. An alternative dissociative mechanism via heterolytic cleavage of Ir−Me is not probable since Ir^-/Me^+ or Ir^+/Me^- ion pairs are unstable and the energetic requirement would be expected to be even much higher than that of homolysis.[21]

Scheme 4. Mechanism of SiHA of Ir(ttp)Me and $Ir(ttp)SiR_3$ with Silanes



Scheme 5. Mechanism of SiHA of Ir(ttp)Me and Silane with Base



While we do not understand very well the mechanism of the base-promoted SiHA by Ir(ttp)Me, we speculate in Scheme 5 that a base (B = $K_2PO_4^-$ and OAc^-) can attack Et_3SiH to form a pentavalent BEt_3SiH^-,[21] which is more reactive to convert Ir(ttp)Me into $Ir(ttp)^-$. Then rapid proton abstraction of $Ir(ttp)^-$ with Et_3SiH or other proton source forms Ir(ttp)H, which subsequently undergoes facile SiHA with Et_3SiH to produce $Ir(ttp)SiEt_3$. Indeed, Ir(ttp)H was observed by ^1H NMR spectroscopy when the reactions were run only in the presence of base, such as K_3PO_4 or KOAc, while no Ir(ttp)H was found without the addition of base. This proposed mechanism further accounts for the effect of base strength. In the presence of weak base, such as CsCl or KI, the formation of BEt_3SiH^- is disfavored. On the other hand, in the presence of very strong base, such as KOH, $Ir(ttp)^-$ is formed rapidly, but undergoes facile competitive decomposition, and only a trace amount of $Ir(ttp)SiEt_3$ is observed.

X-ray Structure. The structures of $Ir(ttp)Si(OEt)_3$ (**3b**) and $Ir(ttp)SiBnMe_2$ (**4b**) were confirmed by single-crystal X-ray diffraction studies and are shown in Figures 2 and 3 (30% thermal ellipsoids). Crystals were grown from CH_2Cl_2/MeOH solution. Details of data collection and processing parameters are given in Table 7. Tables 8 and 9 list selected bond lengths and angles for **3b** and **4b**, respectively.

From Figures 2 and 3 and Table 8, the coordination sphere of the iridium atom of $Ir(ttp)Si(OEt)_3$ **3b** forms a triclinic geometry with the four porphyrinato nitrogen atoms occupying the basal sites, while the silicon atom resides at the axial site. The mean bond length of Ir−N bonds is 2.030 Å, which is longer than the reported five-coordinated organorhodium(III) porphyrin (2.013 Å for $Rh(tmp)SiPh_2Me$).[8] The Ir−Si length is 2.277 Å, which is slightly shorter than that of reported Rh−Si (2.329 Å for $Rh(tmp)SiPh_2Me$, 2.305 Å for $Rh(tpp)SiMe_3$ and

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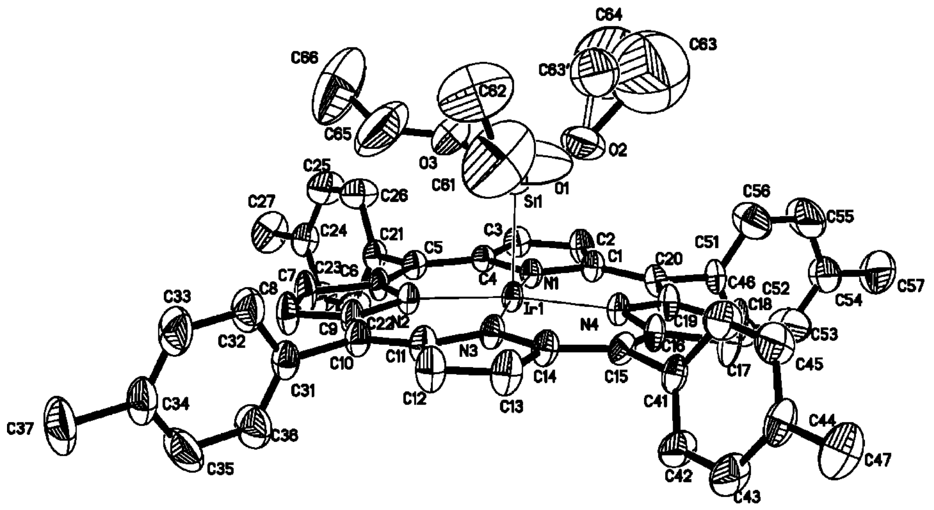

Figure 2. Molecular structure of Ir(ttp)Si(OEt)$_3$ (30% thermal ellipsoids).

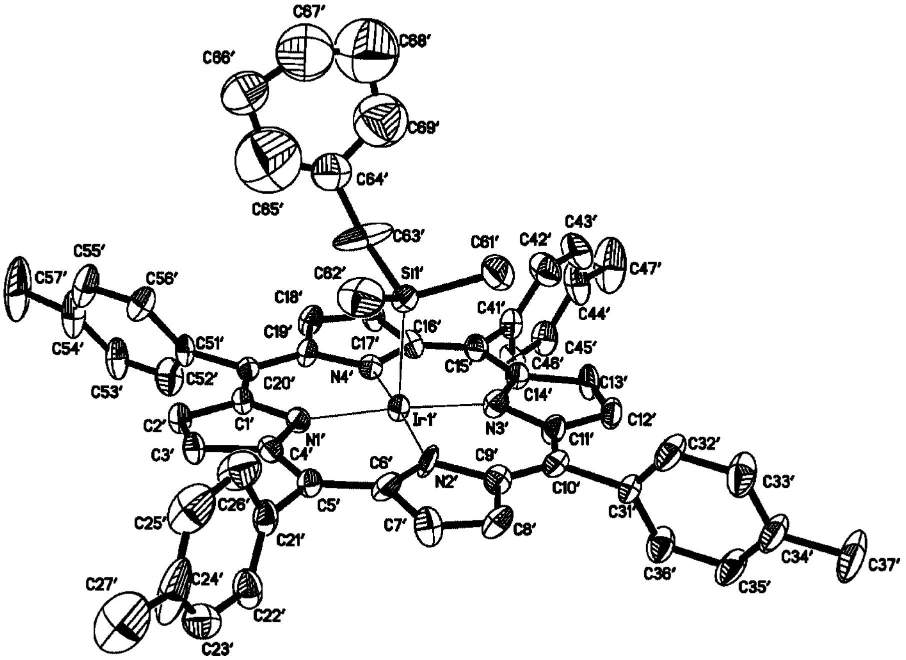

Figure 3. Molecular structure of Ir(ttp)SiBnMe$_2$ (30% thermal ellipsoids).

2.32 Å for Rh(oep)SiEt$_3$).[8,25] It is also shorter than that of Ir−Si in iridium complexes.[26] The Ir atom lies almost at the center of the mean plane of the porphyrin ring. The Ir−Si bond length of Ir(ttp)SiBnMe$_2$ **4b** is 2.328 Å, which is longer than that of Ir(ttp)Si(OEt)$_3$ **3b**. The Ir atom is also located at the center of the mean plane of the porphyrin ring.

Conclusion

We have discovered that iridium porphyrin silyl complexes were synthesized from the reactions of iridium(III) porphyrin carbonyl chloride and methyl with silanes via silicon−hydrogen bond activation in both solvent and solvent-free conditions. SiHA reactions were promoted by basic additives. K$_3$PO$_4$ facilitated the SiHA of silane by Ir(ttp)Cl(CO) most efficiently, while KOAc acceleratd the SiHA with Ir(ttp)Me best. Preliminary mechanistic experiments suggested that iridium porphyrin carbonyl chloride initially formed iridium porphyrin cation, which then reacted with silanes to generate iridium porphyrin hydride. Ir(ttp)H further reacted with excess silane via silicon−hydrogen bond activation reaction to yield iridium porphyrin silyls. On the other hand, the silicon−hydrogen bond activation reaction of silanes by iridium(III) porphyrin methyl and silyls likely underwent oxidative addition or σ-bond metathesis. In the presence of base, an anionic pentacoordinated silicon hydride species likely formed, which would further react with iridium porphyrin methyl to generate iridium porphyrin

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Table 7. Crystal Data for Ir(ttp)Si(OEt)$_3$ and Ir(ttp)SiBnMe$_2$

	3b	4b
empirical formula	$C_{54}H_{51}IrN_4O_3Si$	$C_{57}H_{49}IrN_4Si \cdot 1/4CH_2Cl_2$
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
fw	1024.28	1031.52
a (Å)	11.743 (6)	13.780 (2)
b (Å)	12.886 (6)	51.702 (9)
c (Å)	16.755 (8)	15.311 (3)
α (deg)	83.320 (10)	90
β (deg)	84.748 (9)	97.874 (4)
γ (deg)	85.872 (10)	90
Z	2	8
D_{calc} (mg/m^3)	1.359	1.268
absorp coeff (mm^{-1})	2.736	2.555
V (Å^3)	2503 (2)	10806 (3)
F(000)	1036	4164
cryst size (mm)	0.50 × 0.40 × 0.30	0.50 × 0.40 × 0.30
no. of reflns collcd	13 356	57 969
absorp corr	SADABS	SADABS
max. and min. transmn	1.0000 and 0.480014	1.0000 and 0.500568
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	8740/16/577	19 016/156/1216
goodness-of-fit on F^2	1.072	1.138
final $R_1{}^a/wR_2{}^b$ [$I > 2\sigma(I)$]	0.0545/0.1436	0.0986/0.2632
final $R_1{}^a/wR_2{}^b$ (all data)	0.0677/0.1555	0.1371/0.2851
$w_1/w_2{}^c$	0.1018/0.8042	0.1040/232.8366

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] Weighting scheme $w^{-1} = \sigma^2(F_o^2) + (w_1P)^2 + w_2P$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 8. Selected Bond Lengths and Angles of Ir(ttp)Si(OEt)$_3$

Bond Lengths (Å)			
Ir(1)−N(1)	2.040 (6)	Ir(1)−N(2)	2.022 (6)
Ir(1)−N(3)	2.029 (6)	Ir(1)−N(4)	2.029 (6)
Ir(1)−Si(1)	2.277 (3)	Si(1)−O(1)	1.552 (11)
Si(1)−O(2)	1.616 (9)	Si(1)−O(3)	1.604 (10)
Bond Angles (deg)			
N(1)−Ir(1)−Si(1)	90.88 (19)	N(2)−Ir(1)−Si(1)	95.1 (2)
N(3)−Ir(1)−Si(1)	94.3 (2)	N(4)−Ir(1)−Si(1)	92.9 (2)
O(1)−Si(1)−Ir(1)	112.7 (5)	O(2)−Si(1)−Ir(1)	109.6 (3)
O(3)−Si(1)−Ir(1)	113.3 (4)	O(1)−Si(1)−O(2)	103.9 (8)
O(1)−Si(1)−O(3)	113.6 (8)	O(3)−Si(1)−O(2)	102.7 (6)

Table 9. Selected Bond Lengths and Angles of Ir(ttp)SiBnMe$_2$

Bond Lengths (Å)			
Ir(1)−N(1)	2.036 (12)	Ir(1)−N(2)	2.026 (14)
Ir(1)−N(3)	2.025 (13)	Ir(1)−N(4)	2.030 (13)
Ir(1)−Si(1)	2.328 (5)	Si(1)−C(61)	1.865 (2)
Si(1)−C(62)	1.852 (6)	Si(1)−C(63)	1.85 (3)
Bond Angles (deg)			
N(1)−Ir(1)−Si(1)	93.5 (4)	N(2)−Ir(1)−Si(1)	92.3 (5)
N(3)−Ir(1)−Si(1)	92.7 (4)	N(4)−Ir(1)−Si(1)	91.6 (4)
C(61)−Si(1)−Ir(1)	110.4 (8)	C(62)−Si(1)−Ir(1)	110.8 (9)
C(63)−Si(1)−Ir(1)	110.2 (8)	C(61)−Si(1)−C(62)	106.6 (14)
C(61)−Si(1)−C(63)	109.4 (15)	C(63)−Si(1)−C(62)	109.8 (14)

anion. Ir(ttp)H was produced after protonation and finally reacted with excess silane to give iridium porphyrin silyl complexes.

Experimental Section

Unless otherwise noted, all chemicals were obtained from commercial suppliers and used before purification. Hexane for chromatography was distilled from anhydrous calcium chloride. Thin-layer chromatography was performed on precoated alumina plates for analysis of reaction mixture. All reactions were carried out in a Teflon screw-head stoppered tube in N_2 in the absence of light by aluminum foil wrapping. The purification of iridium silyl complexes was carried out by flash column chromatography in air using aluminum (90 active neutral, 70−230 mesh). All reactions were run in duplicate, and the yields obtained were average yields. Samples for microanalysis were recrystallized from CH_2Cl_2/MeOH and were then dried at 40−60 °C under vacuum (0.005 mmHg) for 3 days. Ir(ttp)Cl(CO)[16] **1a**, Ir(ttp)Me[16,17] **1b**, Ir(ttp)(BF$_4$)(CO)[21] **1c**, and Ir(ttp)H[16,17] **1d** were prepared according to the literature.

^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz). Chemical shifts were reported with reference to the residual solvent protons in $CDCl_3$ (δ 7.26 ppm) as the internal standard. Chemical shifts (δ) were reported in parts per million (ppm) downfield from TMS. Coupling constants (*J*) are reported in hertz (Hz). ^{13}C NMR spectra were recorded on a Bruker DPX 300 (75 MHz) spectrometer and referenced to $CDCl_3$ (δ 77.1 ppm) spectra. High-resolution mass spectra (HRMS) were performed on a Thermofinnign MAT 95 XL in FAB (using 3-nitrobenzyl alcohol (NBA) matrix and CH_2Cl_2 as the solvent) and ESI model (MeOH/CH_2Cl_2, 1:1, as the solvent).

Reactions of Ir(ttp)Cl(CO) 1a with Silanes. General Procedure. The reaction of Ir(ttp)Cl(CO) **1a** with triethylsilane (**2a**) is described as a typical example. Triethylsilane (1.1 mL, 500 equiv) was added to Ir(ttp)Cl(CO) (12.5 mg, 0.014 mmol), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 200 °C for 4 days in N_2. The crude product was purified by column chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)SiEt$_3$ **2b** (11.5 mg, 0.0118 mmol, 84%) was produced. $R_f = 0.52$ (hexane/CH_2Cl_2 = 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ −3.22 (q, 6 H, $J = 7.8$ Hz), −1.25 (t, 9 H, $J = 7.8$ Hz), 2.68 (s, 12 H), 7.50 (d, 8 H, $J = 8.4$ Hz), 7.96 (t, 8 H, $J = 6.0$ Hz), 8.51 (s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 0.1, 5.3, 21.7, 29.9, 124.8, 127.6, 127.7, 131.3, 133.4, 133.8, 137.3, 138.8, 143.8. HRMS (FAB): calcd for $(C_{54}H_{51}N_4SiIr)^+$ *m/z* 976.3507; found *m/z* 976.3526. Anal. Calcd for $C_{54}H_{51}N_4SiIr$: C, 66.43; H, 5.26; N, 5.74. Found: C, 66.43; H, 5.24; N, 5.64.

Reaction between Ir(ttp)Cl(CO) 1a and Triethylsilane (2a). Triethylsilane (1.0 mL, 500 equiv) and Ir(ttp)Cl(CO) (11.2 mg, 0.012 mmol) were heated at 120 °C for 9 days. Only trace amount of Ir(ttp)SiEt$_3$ **2b** was observed according to ^{1}H NMR.

Reaction between Ir(ttp)Cl(CO) 1a and Triethylsilane (2a). Triethylsilane (1.0 mL, 500 equiv) and Ir(ttp)Cl(CO) (11.2 mg, 0.012 mmol) were heated at 200 °C for 4.5 h. A purple solid of

Ir(ttp)SiEt$_3$ **2b** (0.7 mg, 0.0007 mmol, 6%) was obtained after column chromatography.

Reaction between Ir(ttp)Cl(CO) 1a and Triethylsilane (2a). Triethylsilane (1.2 mL, 500 equiv) and Ir(ttp)Cl(CO) (14.1 mg, 0.015 mmol) were heated at 140 °C for 6 days under N$_2$. A purple solid of Ir(ttp)SiEt$_3$ **2b** (1.5 mg, 0.0015 mmol, 10%) was obtained after column chromatography.

Reaction between Ir(ttp)Cl(CO) 1a and Triethoxysilane (3a). Triethoxyslane (1.3 mL, 500 equiv) and Ir(ttp)Cl(CO) (13.3 mg, 0.014 mmol) were heated at 200 °C for 6 h under N$_2$. A purple solid of Ir(ttp)Si(OEt)$_3$ **3b** (7.7 mg, 0.0076 mmol, 54%) was obtained after column chromatography. $R_f = 0.28$ (hexane/CH$_2$Cl$_2$ = 5:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ −0.22 (t, 9 H, $J = 6.9$ Hz), 0.91 (q, 6 H, $J = 6.9$ Hz), 2.68 (s, 12 H), 7.50 (d, 8 H, $J = 8.1$ Hz), 7.99 (d, 8 H, $J = 8.1$ Hz), 8.58 (s, 8 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 17.3, 21.8, 55.1, 124.3, 127.7, 127.8, 131.2, 133.9, 137.4, 139.2, 143.6. HRMS (FAB): calcd for $(C_{54}H_{51}N_4SiIr)^+$ *m/z* 1024.3354; found *m/z* 1024.2260. Anal. Calcd for $C_{54}H_{51}N_4O_3SiIr$: C, 63.32; H, 5.02; N, 5.47. Found: C, 63.15; H, 4.98; N, 5.38.

Reaction between Ir(ttp)Cl(CO) 1a and Benzyldimethylsilane (4a). Benzyldimethylsilane (1.2 mL, 500 equiv) and Ir(ttp)-Cl(CO) (13.6 mg, 0.015 mmol) were heated at 200 °C for 1 day under N$_2$. A purple solid of Ir(ttp)SiBnMe$_2$ **4b** (11.8 mg, 0.0117 mmol, 78%) was obtained after column chromatography. $R_f = 0.55$ (hexane/CH$_2$Cl$_2$ = 5:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ −3.83 (s, 6 H), −2.21 (s, 2 H), 2.69 (s, 12 H), 5.32 (t, 2 H, $J = 3.6$ Hz), 6.47 (t, 3 H, $J = 3.6$ Hz), 7.50 (t, 8 H, $J = 7.2$ Hz), 7.96 (d, 4 H, $J = 7.5$ Hz), 8.04 (d, 4 H, $J = 7.5$ Hz), 8.58 (s, 8 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ −7.3, 21.7, 21.1, 123.2, 125.2, 127.5, 128.1, 128.2, 131.8, 133.9, 134.3, 137.9, 139.2, 144.0. HRMS (FAB): calcd for $(C_{57}H_{49}N_4SiIr)^+$ *m/z* 1010.3350; found *m/z* 1010.3340. Anal. Calcd for $C_{54}H_{51}N_4O_3SiIr$: C, 67.76; H, 4.89; N, 5.54. Found: C, 67.65; H, 4.948; N, 5.41.

Reaction between Ir(ttp)Cl(CO) 1a and Phenylsilane (5a). Phenylsilane (1.0 mL, 500 equiv) and Ir(ttp)Cl(CO) (15.6 mg, 0.017 mmol) were heated at 140 °C for 5 h under N$_2$. A dark brown solid of Ir(ttp)SiH$_2$Ph **5b** (14.8 mg, 0.0153 mmol, 90%) was obtained when the reaction mixture was washed by MeOH. ^{1}H NMR (CDCl$_3$, 300 MHz): δ −2.16 (s, 2 H, $^1J_{Si-H} = 202.8$ Hz), 2.69 (s, 12 H), 4.33 (d, 2 H, $J = 6.3$ Hz), 6.37 (t, 2 H, $J = 6.3$ Hz), 6.76 (t, 1 H, $J = 6.3$ Hz), 7.51 (d, 8 H, $J = 7.5$ Hz), 7.88 (d, 4 H, $J = 7.2$ Hz), 8.00 (d, 4 H, $J = 7.2$ Hz), 8.53 (s, 8 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 21.7, 124.2, 126.1, 127.5, 127.6, 131.3, 131.4, 133.6, 133.9, 137.3, 138.7, 143.0. HRMS (FAB): calcd for $(C_{54}H_{43}N_4SiIr)^+$ *m/z* 968.2881; found *m/z* 968.2872.

Reaction between Ir(ttp)Cl(CO) 1a and Phenylmethylsilane (6a). Phenylmethylsilane (0.8 mL, 500 equiv) and Ir(ttp)Cl(CO) (11.2 mg, 0.012 mmol) were heated at 200 °C for 0.5 h under N$_2$. A purple solid of Ir(ttp)SiPhMeH **6b** (4.0 mg, 0.0041 mmol, 34%) was obtained when the reaction mixture was washed by MeOH. $R_f = 0.46$ (hexane/CH$_2$Cl$_2$ = 5:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ −3.45 (d, 3 H, $J = 3.3$ Hz), −2.24 (q, 1 H, $J = 3.3$ Hz, $^1J_{Si-H} = 200.1$ Hz), 2.68 (s, 12 H), 4.34 (d, 2 H, $J = 6.9$ Hz), 6.40 (t, 2 H, $J = 7.5$ Hz), 6.78 (t, 1 H, $J = 7.4$ Hz), 7.53 (t, 8 H, $J = 5.7$ Hz), 7.86 (d, 4 H, $J = 8.4$ Hz), 7.98 (d, 4 H, $J = 8.4$ Hz), 8.49 (s, 8 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ −9.8, 21.8, 124.5, 126.2, 127.5, 127.7, 127.8, 130.6, 131.4, 133.7, 134.0, 137.4, 138.9, 143.3. HRMS (FAB): calcd for $(C_{55}H_{45}N_4SiIr)^+$ *m/z* 982.3037; found *m/z* 982.3032.

Reaction between Ir(ttp)Cl(CO) 1a and Diphenylsilane (7a). Diphenylsilane (1.6 mL, 500 equiv) and Ir(ttp)Cl(CO) (16.0 mg, 0.017 mmol) were heated at 140 °C for 2 days under N$_2$. A purple solid of Ir(ttp)SiPh$_2$H **7b** (12.1 mg, 0.0116 mmol, 68%) was obtained after column chromatography. $R_f = 0.56$ (hexane/CH$_2$Cl$_2$ = 5:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ −1.76 (s, 1 H, $^1J_{Si-H} = 204.6$ Hz), 2.68 (s, 12 H), 4.50 (d, 4 H, $J = 7.5$ Hz), 6.39 (t, 4 H, $J = 7.5$ Hz), 6.75 (t, 2 H, $J = 7.5$ Hz), 7.48 (t, 8 H, $J = 7.5$ Hz), 7.72 (d, 4 H, $J = 7.5$ Hz), 7.95 (d, 4 H, $J = 7.5$ Hz), 8.45 (s, 8 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 21.8, 124.5, 126.2, 127.5, 127.7, 131.4, 132.0, 133.8, 134.0, 137.4, 138.9, 143.2. HRMS (FAB): calcd for $(C_{60}H_{47}N_4SiIr)^+$ *m/z* 1044.3194; found *m/z* 1044.3209. Anal. Calcd for $C_{60}H_{47}N_4SiIr$: C, 69.00; H, 4.54; N, 5.36. Found: C, 69.11; H, 4.54; N, 5.38.

Reaction between Ir(ttp)Cl(CO) 1a and Diphenylmethylsilane (8a). Diphenylmethylsilane (1.5 mL, 500 equiv) and Ir(ttp)-Cl(CO) (14.0 mg, 0.015 mmol) were heated at 200 °C for 6 h under N$_2$. A purple solid of Ir(ttp)SiPh$_2$Me **8b** (6.7 mg, 0.0063 mmol, 42%) was obtained after column chromatography. $R_f = 0.51$ (hexane/CH$_2$Cl$_2$ = 5:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ −3.07 (s, 3 H), 2.68 (s, 12 H), 4.61 (d, 4 H, $J = 7.2$ Hz), 6.46 (t, 4 H, $J = 7.5$ Hz), 6.77 (t, 2 H, $J = 7.2$ Hz), 7.46 (q, 8 H, $J = 7.5$ Hz), 7.78 (d, 4 H, $J = 7.8$ Hz), 7.89 (d, 4 H, $J = 7.8$ z), 8.42(s, 8 H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ −8.2, 21.8, 124.7, 126.1, 127.1, 127.6, 127.7, 131.4, 131.6, 133.6, 133.7, 133.9, 137.4, 138.9, 143.4. HRMS (FAB): calcd for $(C_{61}H_{49}N_4SiIr)^+$ *m/z* 1058.3350; found *m/z* 1058.3367. Anal. Calcd for $C_{54}H_{51}N_4O_3SiIr$: C, 69.22; H, 4.67; N, 5.29. Found: C, 69.21; H, 4.65; N, 5.03. Ir(ttp)SiPhMeH **6b** (4.4 mg, 0.0045 mmol, 30%) was also generated according to the ^{1}H NMR spectrum of the crude reaction mixture.

Reaction of Ir(ttp)Cl(CO) 1a and Diphenylmethylsilane (8a). Diphenylmethylsilane (1.4 mL, 500 equiv) was added to Ir(ttp)-Cl(CO) (13.4 mg, 0.014 mmol), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 200 °C under N$_2$. The reaction mixture was monitored by ^{1}H NMR spectroscopy by taking aliquots of the reaction mixture. After 1 day, the ratio of Ir(ttp)SiPh$_2$Me **8b** to Ir(ttp)SiPhMeH **6b** was about 1.00:1.16.

Reaction of Ir(ttp)Cl(CO) 1a with Silanes with Base Added. General Procedure. The reaction of Ir(ttp)Cl(CO) **1a** with triethylsilane (**2a**) with addition of K$_3$PO$_4$ is described as a typical example. Triethylsilane (1.1 mL, 500 equiv) was added to a mixture of Ir(ttp)Cl(CO) (12.6 mg, 0.014 mmol) and K$_3$PO$_4$ (29.7 mg, 0.140 mmol, 10 equiv), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 140 °C for 1 day under N$_2$. The crude product was purified by chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)SiEt$_3$ **2b** (12.0 mg, 0.0123 mmol, 88%) was produced.

Reaction of Ir(ttp)Cl(CO) 1a with Triethylsilane (2a) with K$_3$PO$_4$. Triethylsilane (1.3 mL, 500 equiv) was added to a mixture of Ir(ttp)Cl(CO) (14.8 mg, 0.016 mmol) and K$_3$PO$_4$ (17.0 mg, 0.080 mmol, 5 equiv). Then the mixture was heated at 140 °C for 1 day under N$_2$. A purple solid of Ir(ttp)SiEt$_3$ **2b** (7.2 mg, 0.0074 mmol, 46%) was obtained after column chromatography.

Reaction of Ir(ttp)Cl(CO) 1a with Triethylsilane (2a) with K$_3$PO$_4$. Triethylsilane (1.4 mL, 500 equiv) was added to a mixture of Ir(ttp)Cl(CO) (15.8 mg, 0.017 mmol) and K$_3$PO$_4$ (72.2 mg, 0.340 mmol, 20 equiv). Then the mixture was heated at 140 °C for 1 day under N$_2$. A purple solid of Ir(ttp)SiEt$_3$ **2b** (13.3 mg, 0.0136 mmol, 80%) was obtained after column chromatography.

Reaction of Ir(ttp)Cl(CO) 1a with Triethylsilane (2a) with K$_2$CO$_3$. Triethylsilane (1.0 mL, 500 equiv) was added to a mixture of Ir(ttp)Cl(CO) (12.2 mg, 0.013 mmol) and K$_2$CO$_3$ (18.0 mg, 0.130 mmol, 10 equiv). Then the mixture was heated at 140 °C for 1 day under N$_2$. A purple solid of Ir(ttp)SiEt$_3$ **2b** (2.0 mg, 0.0021 mmol, 16%) was obtained after column chromatography.

Reaction of Ir(ttp)Cl(CO) 1a with Triethylsilane (2a) with KOH. Triethylsilane (1.0 mL, 500 equiv) was added to a mixture of Ir(ttp)Cl(CO) (12.2 mg, 0.013 mmol) and KOH (7.3 mg, 0.130 mmol, 10 equiv). Then the mixture was heated at 140 °C for 1 day under N$_2$. A purple solid of Ir(ttp)SiEt$_3$ **2b** (4.7 mg, 0.0048 mmol, 37%) was obtained after column chromatography.

Reaction of Ir(ttp)Cl(CO) 1a with Triethylsilane (2a) with KF. Triethylsilane (1.3 mL, 500 equiv) was added to a mixture of Ir(ttp)Cl(CO) (15.3 mg, 0.017 mmol) and KF (9.9 mg, 0.170 mmol, 10 equiv). Then the mixture was heated at 140 °C for 5 days under

N_2. A purple solid of Ir(ttp)$SiEt_3$ **2b** (8.3 mg, 0.0085 mmol, 50%) was obtained after column chromatography.

Reaction of Ir(ttp)Cl(CO) 1a with Triethylsilane (2a) with CsCl. Triethylsilane (1.2 mL, 500 equiv) was added to a mixture of Ir(ttp)Cl(CO) (14.0 mg, 0.015 mmol) and CsCl (25.3 mg, 0.150 mmol, 10 equiv). Then the mixture was heated at 140 °C for 6 days under N_2. A purple solid of Ir(ttp)$SiEt_3$ **2b** (0.6 mg, 0.0006 mmol, 4%) was obtained after column chromatography.

Reaction of Ir(ttp)Cl(CO) 1a with Triethylsilane (2a) with KI. Triethylsilane (1.1 mL, 500 equiv) was added to a mixture of Ir(ttp)Cl(CO) (13.2 mg, 0.014 mmol) and KI (23.2 mg, 0.140 mmol, 10 equiv). Then the mixture was heated at 140 °C for 5 days under N_2. A purple solid of Ir(ttp)$SiEt_3$ **2b** (1.9 mg, 0.0020 mmol, 14%) was obtained after column chromatography.

Reaction of Ir(ttp)Cl(CO) 1a with Triethylsilane (2a) with KOAc. Triethylsilane (1.2 mL, 500 equiv) was added to a mixture of Ir(ttp)Cl(CO) (14.4 mg, 0.016 mmol) and KOAc (15.7 mg, 0.160 mmol, 10 equiv). Then the mixture was heated at 140 °C for 5 days under N_2. A purple solid of Ir(ttp)$SiEt_3$ **2b** (1.9 mg, 0.0019 mmol, 12%) was obtained after column chromatography.

Reactions of Ir(ttp)Cl(CO) 1a with Silanes in Solvent. General Procedure. The reaction of Ir(ttp)Cl(CO) **1a** with triethylsilane (**2a**) in benzene is described as a typical example. Triethylsilane (0.22 mL, 100 equiv) was added to Ir(ttp)Cl(CO) (12.9 mg, 0.014 mmol) in benzene (1.0 mL), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 200 °C for 9 days under N_2. The crude product was purified by chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)$SiEt_3$ **2b** (7.9 mg, 0.0081 mmol, 58%) was produced.

Reaction of Ir(ttp)Cl(CO) 1a with Triethylsilane 2a in Cyclohexane. Triethylsilane (0.22 mL, 100 equiv) was added to Ir(ttp)Cl(CO) (12.6 mg, 0.014 mmol) in cyclohexane (1.0 mL). Then the mixture was heated at 200 °C for 9 days under N_2. A purple solid of Ir(ttp)$SiEt_3$ **2b** (8.2 mg, 0.0084 mmol, 60%) was obtained after column chromatography.

Reaction of Ir(ttp)Cl(CO) 1a with Triethoxylsilane (3a) in Benzene. Triethoxylsilane (0.24 mL, 100 equiv) was added to Ir(ttp)Cl(CO) (12.2 mg, 0.013 mmol) in benzene (1.0 mL). Then the mixture was heated at 200 °C for 6 h under N_2. A purple solid of Ir(ttp)$Si(OEt)_3$ **3b** (11.3 mg, 0.0110 mmol, 85%) was obtained after column chromatography.

Reaction of Ir(ttp)Cl(CO) 1a with Triethoxylsilane (3a) in Cyclohexane. Triethoxylsilane (0.26 mL, 100 equiv) was added to Ir(ttp)Cl(CO) (12.9 mg, 0.014 mmol) in cyclohexane (1.0 mL). Then the mixture was heated at 200 °C for 12 h under N_2. A purple solid of Ir(ttp)$Si(OEt)_3$ **3b** (12.6 mg, 0.0123 mmol, 88%) was obtained after column chromatography.

Reaction of Ir(ttp)Cl(CO) 1a with Triethylsilane (2a) in Benzene with K_3PO_4 Added. Triethylsilane (0.26 mL, 100 equiv) was added to a mixture of Ir(ttp)Cl(CO) (14.4 mg, 0.016 mmol) and K_3PO_4 (34.0 mg, 0.160 mmol, 10 equiv) in benzene (1.0 mL), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 140 °C for 3 days under N_2. The crude product was purified by chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)$SiEt_3$ **2b** (14.6 mg, 0.015 mmol, 92%) was produced.

Reaction of Ir(ttp)Cl(CO) 1a with Triethylsilane (2a) in Benzene-*d*$_6$ with K_3PO_4 Added in a Sealed NMR Tube. Triethylsilane (90 μL, 100 equiv) was added to a mixture of Ir(ttp)Cl(CO) (5.4 mg, 0.006 mmol) and K_3PO_4 (12.3 mg, 0.058 mmol, 10 equiv) in benzene-*d*$_6$ (0.5 mL), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 140 °C in the presence of light under vacuum. When the reaction was traced by ^{1}H NMR, after 1.5 h, Ir(ttp)H was observed first without any Ir(ttp)$SiEt_3$.

Reaction of Ir(ttp)(BF_4)(CO) 1c and Triethylsilane (2a) Triethylsilane (1.0 mL, 500 equiv) was added to Ir(ttp)(BF_4)(CO) (12.8 mg, 0.013 mmol), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 200 °C for 1 day under N_2. The crude product was purified by chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)$SiEt_3$ **2b** (7.7 mg, 0.0079 mmol, 61%) was obtained.

Reaction of Ir(ttp)H 1d and Triethylsilane (2a). Triethylsilane (1.3 mL, 500 equiv) was added to Ir(ttp)H (14.0 mg, 0.016 mmol), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 140 °C for 2 days under N_2. The crude product was purified by chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)$SiEt_3$ **2b** (14.4 mg, 0.0147 mmol, 92%) was produced.

Reaction of Ir(ttp)H 1d and Diphenylmethylsilane (8a). Diphenylmethylsilane (1.0 mL, 500 equiv) was added to Ir(ttp)H (9.0 mg, 0.010 mmol), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 200 °C under N_2. The reaction mixture was monitored by ^{1}H NMR spectroscopy by taking aliquots of the reaction mixture. After 2 h, the ratio of Ir(ttp)$SiPh_2Me$ **8b** to Ir(ttp)SiPhMeH **6b** was about 1.00:0.71.

Reactions of Ir(ttp)Me 1b with Silanes. General Procedure. The reaction of Ir(ttp)Me **1b** with triethylsilane (**2a**) is described as a typical example. Triethylsilane (1.0 mL, 500 equiv) was added to Ir(ttp)Me (11.1 mg, 0.013 mmol), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 200 °C for 5 days under N_2. The crude product was purified by chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)$SiEt_3$ **2b** (10.5 mg, 0.0108 mmol, 83%) was obtained.

Reaction between Ir(ttp)Me 1b and Triethylsilane (2a). Triethylsilane (1.2 mL, 500 equiv) and Ir(ttp)Me (13.4 mg, 0.015 mmol) were heated at 150 °C for 8 days under N_2. A purple solid of Ir(ttp)$SiEt_3$ **2b** (1.8 mg, 0.0018 mmol, 12%) was obtained after column chromatography.

Reaction between Ir(ttp)Me 1b and Triethoxysilane (3a). Triethoxysilane (1.1 mL, 500 equiv) and Ir(ttp)Me (10.9 mg, 0.012 mmol) were heated at 200 °C for 7 days under N_2. A purple solid of Ir(ttp)$Si(OEt)_3$ **3b** (2.0 mg, 0.0019 mmol, 16%) was obtained after column chromatography.

Reactions of Ir(ttp)Me 1b with Silanes in Benzene. General Procedure. The reaction of Ir(ttp)Me **1b** with triethylsilane (**2a**) in benzene is described as a typical example. Triethylsilane (0.24 mL, 100 equiv) was added to Ir(ttp)Me (12.9 mg, 0.015 mmol) in benzene (1.0 mL), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 200 °C for 7 days under N_2. The crude product was purified by chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)$SiEt_3$ **2b** (1.5 mg, 0.0015 mmol, 10%) was produced.

Reaction of Ir(ttp)Me 1b with Triethoxylsilane (3a) in Benzene. Triethoxylsilane (0.26 mL, 100 equiv) was added to Ir(ttp)Me (11.9 mg, 0.014 mmol) in benzene (1.0 mL). Then the mixture was heated at 200 °C for 4 days under N_2. A purple solid of Ir(ttp)$Si(OEt)_3$ **3b** (1.1 mg, 0.0011 mmol, 8%) was obtained after column chromatography.

Reaction of Ir(ttp)Me 1b with Triethylsilane (2a) with Base Added. General Procedure. The reaction of Ir(ttp)Me **1b** with triethylsilane (**2a**) with addition of K_3PO_4 is described as a typical example. Triethylsilane (1.2 mL, 500 equiv) was added to a mixture of Ir(ttp)Me (13.1 mg, 0.015 mmol) and K_3PO_4 (31.8 mg, 0.150 mmol, 10 equiv), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 150 °C for 8 days under N_2. The crude product was purified by chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)$SiEt_3$ **2b** (6.4 mg, 0.0066 mmol, 44%) was produced.

Reaction of Ir(ttp)Me 1b with Triethylsilane (2a) with KOH. Triethylsilane (1.1 mL, 500 equiv) was added to a mixture of Ir(ttp)Me (12.3 mg, 0.014 mmol) and KOH (7.8 mg, 0.140 mmol, 10 equiv). Then the mixture was heated at 150 °C for 8 days under N_2. Only a trace amount of Ir(ttp)$SiEt_3$ **2b** was observed according to ^{1}H NMR.

Reaction of Ir(ttp)Me 1b with Triethylsilane (2a) with K_2CO_3. Triethylsilane (1.0 mL, 500 equiv) was added to a mixture of Ir(ttp)Me (11.8 mg, 0.013 mmol) and K_2CO_3 (18.0 mg, 0.130 mmol, 10 equiv). Then the mixture was heated at 150 °C for 8 days under N_2. A purple solid of Ir(ttp)$SiEt_3$ **2b** (1.8 mg, 0.0018 mmol, 14%) was produced.

Reaction of Ir(ttp)Me 1b with Triethylsilane (2a) with KF. Triethylsilane (1.2 mL, 500 equiv) was added to a mixture of Ir(ttp)Me (12.8 mg, 0.015 mmol) and KF (8.7 mg, 0.150 mmol, 10 equiv). Then the mixture was heated at 150 °C for 8 days under N_2. A purple solid of Ir(ttp)$SiEt_3$ **2b** (2.2 mg, 0.0023 mmol, 15%) was produced.

Reaction of Ir(ttp)Me 1b with Triethylsilane (2a) with CsCl. Triethylsilane (1.3 mL, 500 equiv) was added to a mixture of Ir(ttp)Me (14.1 mg, 0.016 mmol) and CsCl (26.9 mg, 0.160 mmol, 10 equiv). Then the mixture was heated at 150 °C for 8 days under N_2. A purple solid of Ir(ttp)$SiEt_3$ **2b** (0.9 mg, 0.0010 mmol, 6%) was produced.

Reaction of Ir(ttp)Me 1b with Triethylsilane (2a) with KI. Triethylsilane (1.1 mL, 500 equiv) was added to a mixture of Ir(ttp)Me (12.1 mg, 0.014 mmol) and KI (23.2 mg, 0.140 mmol, 10 equiv). Then the mixture was heated at 150 °C for 8 days under N_2. A purple solid of Ir(ttp)$SiEt_3$ **2b** (1.2 mg, 0.0013 mmol, 9%) was produced.

Reaction of Ir(ttp)Me 1b with Triethylsilane (2a) with KOAc. Triethylsilane (1.2 mL, 500 equiv) was added to a mixture of Ir(ttp)Me (13.3 mg, 0.015 mmol) and KOAc (14.7 mg, 0.150 mmol, 10 equiv). Then the mixture was heated at 150 °C for 8 days under N_2. A purple solid of Ir(ttp)$SiEt_3$ **2b** (8.8 mg, 0.0090 mmol, 60%) was produced.

Reaction of Ir(ttp)$SiPh_2Me$ (8b) with Diphenylmethylsilane (8a). Diphenylmethylsilane (1.2 mL, 500 equiv) was added to Ir(ttp)$SiPh_2Me$ (12.2 mg, 0.012 mmol), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 200 °C for 2 days under N_2. The crude product was purified by chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)$SiPh_2Me$ **8b** (4.2 mg, 0.0040 mmol, 33%) was obtained, and a 31% yield of Ir(ttp)SiPhMeH **6b** was produced according to ^{1}H NMR of the crude mixture.

Reaction of Ir(ttp)SiPhMeH (6b) with Diphenylmethylsilane (8a). Diphenylmethylsilane (1.5 mL, 500 equiv) was added to Ir(ttp)SiPhMeH (14.6 mg, 0.015 mmol), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 200 °C for 2 days under N_2. The crude product was purified by chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)$SiPh_2Me$ **8b** (6.4 mg, 0.0060 mmol, 40%) was produced, and 46% recovery yield of Ir(ttp)SiPhMeH **6b** was obtained according to ^{1}H NMR of the crude mixture.

Reaction of Ir(ttp)$SiEt_3$ 2b with Benzyldimethylsilane (4a). Benzyldimethylsilane (1.0 mL, 500 equiv) was added to Ir(ttp)$SiEt_3$ (12.2 mg, 0.012 mmol), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 200 °C for 2 days under N_2. The crude product was purified by chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)$SiBnMe_2$ **4b** (9.9 mg, 0.0098 mmol, 82%) was produced.

Reaction of Ir(ttp)$SiBnMe_2$ 4b with Triethylsilane (2a). Triethylsilane (1.2 mL, 500 equiv) was added to Ir(ttp)$SiBnMe_2$ (15.2 mg, 0.015 mmol), and the mixture was degassed by the freeze−pump−thaw method (3 cycles). Then the mixture was heated at 200 °C for 4 days under N_2, and **4b** was not consumed completely. The crude product was purified by chromatography on alumina eluting with hexane. A purple solid of Ir(ttp)$SiEt_3$ **2b** (2.9 mg, 0.0030 mmol, 20%) was produced, and Ir(ttp)$SiBnMe_2$ **4b** (10.8 mg, 0.0106 mmol, 71%) was recovered.

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Supporting Information Available: Crystallographic data for **3b** and **4b** and spectra for **5b** and **6b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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