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Facile Synthesis of Rhodium(III) Porphyrin Silyls by Silicon−Hydrogen Bond Activation with Rhodium(III) Porphyrin Halides and Methyls

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Rhodium(III) porphyrin silyls were synthesized in high yields conveniently from the reactions of rhodium(III) porphyrin halides and methyls with silanes, via silicon−hydrogen bond activation (SiHA) in solvent-free conditions. Preliminary mechanistic experiments suggested that rhodium(III) porphyrin chlorides initially formed cationic rhodium(III) species, which then underwent heterolysis to give the products. On the other hand, rhodium(III) porphyrin methyls underwent either oxidative addition or σ-bond metathesis to form the products.

Introduction

Transition metal silyl chemistry has grown immensely over the past decades, and research continues to prosper in this area.[1] Transition metal silyl complexes have been proposed to be vital in catalytic processes such as hydrosilylation,[2] silane polymerization,[3] and silylformylation.[4] Late-transition metal silyl complexes are usually electron-rich and display unique structural and bonding properties[5] such as metal silyl dπ back-bonding interactions.[1,6]

Our continuing interest in the chemistry of rhodium porphyrin,[7] in particular easily accessible rhodium porphyrin silyls,[8] has prompted us to develop a facile synthesis of rhodium porphyrin silyls.[8] Known synthetic methods for the preparation of rhodium porphyrin silyls have met with limitations. (1) The reactions of nucleophilic rhodium(I) porphyrin anions with trialkylsilyl chlorides require the use of less-friendly sodium amalgam.[8] (2) The one-electron oxidative additions of rhodium(II) porphyrins and related macrocycle metal−metal bonded dimers with Si−H bonds[9,10] demand the very inaccessible rhodium(II) porphyrin dimers. (3) The attempted reactions of the silyl anion, generated in HMPA, with rhodium porphyrin halides are not fruitful. The rapid undesirable reaction of the Me_3Si anion with HMPA gives a phosphoryl anion, which further reacts with cobalt(III) porphyrin chlorides to give cobalt porphyrin phosphoryls. This approach is likely not amenable to prepare rhodium porphyrin silyls.

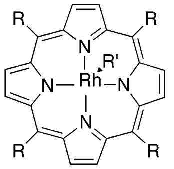

Figure 1. Structures of rhodium porphyrin complexes.

Reactions of hydrosilanes with rhodium porphyrin halides are in principle applicable to yield rhodium porphyrin silyls. This method has been applied in various organometallic complexes successfully[1] but not in rhodium porphyrins. We have adopted this method and discovered that rhodium(III) porphyrin halides and methyls reacted with silanes to give high yields of rhodium porphyrin silyls via silicon−hydrogen bond activation (SiHA) in solvent-free conditions. We now report our results on the synthesis and properties of rhodium porphyrin silyls as well as some mechanistic studies of the silicon−hydrogen bond activation by high-valent Rh(III) porphyrins.[12,13]

Results and Discussion

Optimization. Initially, when Rh(ttp)Cl (**1**) (Figure 1) was reacted with $HSiEt_3$ (**2a**) (100 equiv, 0.6 M) in benzene at 100 °C for 1 day, Rh(ttp)$SiEt_3$ (**2b**) was obtained with 52% yield (Table 1, entry 1). When the reaction temperature was increased to 200 °C, a lower yield of Rh(ttp)$SiEt_3$ (**2b**) was observed (Table 1, entry 2). Competitive activation of benzene to form an unstable intermediate likely occurred, as a rhodium porphyrin

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Table 1. Optimization of the Synthesis of Rh(ttp)SiEt$_3$, 2b

entry	solvent	equiv of Et$_3$SiH	temp (°C)	time (h)	% **2b**
1	benzene	100	100	24	52
2	benzene	100	200	24	18
3	solvent-free	250	150	1.5	51
4	solvent-free	250	200	1.5	81

Table 2. Si−H Activation of Silanes by Rh(por)X

entry	silane	Rh(por)X	time	product (% yield)
1	HSiEt$_3$, **2a**	Rh(ttp)Cl, **1a**	1.5 h	Rh(ttp)SiEt$_3$, **2b** (81)
2		Rh(tmp)Cl, **1b**	1 d	Rh(tmp)SiEt$_3$, **2c** (62)
3		Rh(tmp)I, **1c**	1 d	Rh(tmp)SiEt$_3$, **2c** (70)
4	HSi(OEt)$_3$, **4a**	Rh(tmp)Cl, **1b**	0.5 h	Rh(tmp)Si(OEt)$_3$, **4b** (62)
5		Rh(tmp)I, **1c**	0.5 h	Rh(tmp)Si(OEt)$_3$, **4b** (74)
6	HSiPr$_3$, **5a**	Rh(tmp)Cl, **1b**	1 d	Rh(tmp)SiPr$_3$, **5b** (51)
7		Rh(tmp)I, **1c**	1 d	Rh(tmp)SiPr$_3$, **5b** (45)
8	HSi^{i}Pr$_3$, **6a**	Rh(tmp)Cl, **1b**	2 d	Rh(tmp)Si^{i}Pr$_3$, **6b** (16)
9		Rh(tmp)I, **1c**	2 d	Rh(tmp)Si^{i}Pr$_3$, **6b** (23)
10	H$_2$SiPh$_2$, **7a**	Rh(ttp)Cl, **1a**	0.5 h	Rh(ttp)SiPh$_2$H, **7c** (72)
11		Rh(tmp)Cl, **1b**	0.5 h	Rh(tmp)SiPh$_2$H, **7b** (62)
12		Rh(tmp)I, **1c**	0.5 h	Rh(tmp)SiPh$_2$H, **7b** (56)
13	H$_3$SiPh, **8a**	Rh(tmp)Cl, **1b**	1 h	Rh(tmp)SiPhH$_2$, **8b** (82)
14		Rh(tmp)I **1c**	1 h	Rh(tmp)SiPhH$_2$, **8b** (75)
15	H$_2$SiPhMe, **9a**	Rh(tmp)Cl, **1b**	3 h	Rh(tmp)SiMePhH, **9b** (73)
16		Rh(tmp)I, **1c**	3 h	Rh(tmp)SiMePhH, **9b** (66)
17	HSiBnMe$_2$, **10a**	Rh(ttp)Cl, **1a**	1 h	Rh(ttp)SiBnMe$_2$, **10b** (88)
18		Rh(tmp)Cl, **1b**	1 h	Rh(tmp)SiBnMe$_2$, **10c** (91)
19		Rh(tmp)I, **1c**	6 h	Rh(tmp)SiBnMe$_2$, **11c** (77)
20	HSiPhMe$_2$, **11a**	Rh(ttp)Cl, **1a**	1 h	Rh(ttp)SiPhMe$_2$, **11b** (91)
21		Rh(tmp)Cl, **1b**	8 h	Rh(tmp)SiPhMe$_2$, **11c** (56)
22		Rh(tmp)I, **1c**	1 d	Rh(tmp)SiPhMe$_2$, **11c** (48)
23	HSiPh$_2$Me, **12a**	Rh(tmp)Cl, **1b**	0.5 h	Rh(tmp)SiPh$_2$Me, **12b** (61)
24	HSi^{t}BuMe$_2$, **13a**	Rh(tmp)Cl, **1b**	1 d	Rh(tmp)Si^{t}BuMe$_2$, **13b** (10)
25		Rh(tmp)I, **1c**	1 d	Rh(tmp)Si^{t}BuMe$_2$, **13b** (7)

triflate is known to react with arenes via electrophilic aromatic substitution at lower temperature[14] since no Rh(ttp)Ph was detected in the reaction mixture. When dichloromethane was used as the solvent, Rh(ttp)Cl reacted with HSiEt$_3$ (**2a**) (100 equiv, 0.6 M) at 100 °C for 2 days to give Rh(ttp)SiEt$_3$ (**2b**) and Rh(ttp)CH$_2$Cl (**3**). Both benzene and CH$_2$Cl$_2$ were not suitable solvents. Therefore, solvent-free conditions were employed (Table 1, entries 3, 4). Indeed, at 150 °C, **2b** was achieved in a reasonable yield of 51% in just 1.5 h. At 200 °C, a higher yield of 81% was also observed.

$$\mathrm{Rh(ttp)Cl} + \mathrm{HSiEt_3} \xrightarrow{\text{solvent}} \mathrm{Rh(ttp)SiEt_3} + \mathrm{Rh(ttp)CH_2Cl} \quad (1)$$

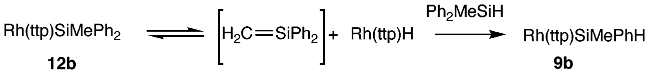
Synthetic Application. When the optimized solvent-free conditions at 200 °C were applied to the reactions of a variety of rhodium porphyrin chlorides and iodides with silanes, good yields of rhodium porphyrin silyls were generally obtained (eq 2, Table 2). Rh(por)X (X = Cl or I) dissolved in silanes only upon heating.

$$\mathrm{Rh(por)X} + \mathrm{HSiR_1R_2R_3} \rightarrow \mathrm{Rh(por)SiR_1R_2R_3} \quad (2)$$

The yields of the products depended on the steric hindrance of silanes. The cone angles of silanes are identical with the cone angles of phosphines[15] [Et$_3$SiH (132°), Pr$_3$SiH (132°), ^{i}Pr$_3$SiH (160°), SiH$_2$Ph$_2$ (128°), and HSiMe$_2$Ph (122°)][16] and have been used as a measure of steric hindrance. In general, more bulky silanes with larger cone angles reacted with slower rates and gave lower product yields. For example, the reactivity trend decreased with the increasing steric hindrance of silanes: HSiEt$_3$ (**2a**) > HSi^{i}Pr$_3$ (**6a**) > HSi^{t}BuMe$_2$ (**13a**) (Table 2, entries 3, 9, and 25). Sterically less hindered rhodium porphyrins of ttp reacted faster and gave higher yields than that of tmp (Table 2, entries 1 vs 2, 20 vs 21). No significant and systematic differences of halide effect in rates and yields were observed for Rh(tmp) X (X = Cl or I) (e.g., Table 2, entries 2 and 3, 8 and 9, 24 and 25).

For HSiPh$_2$Me (**12a**) only, the reaction time was important to achieve high product selectivity. When **12a** was reacted with Rh(ttp)Cl (**1a**) in 24 h at 200 °C, a nearly 1:1 mixture of Rh(ttp)SiPh$_2$Me (**12c**) (20%) and Rh(ttp)SiMePhH (**9c**) (18%) was obtained. Rh(tmp)Cl (**1b**) also gave **12b** (26%) and **9b** (28%) in 24 h. **9b** was a consecutive product, as **12b** also reacted with HSiPh$_2$Me to give **9b**. However, **9b** did not react with HSiPh$_2$Me to give **12b** at 200 °C in 2 days. Therefore, Rh(tmp)SiPhMeH is thermodynamically more stable than Rh(tmp)SiPh$_2$Me; presumably the latter is a secondary rather than a tertiary Rh-silyl complex. **12b** remained stable in benzene in the absence of HSiPh$_2$Me, so a highly reactive intermediate likely formed from **12b** and reacted rapidly with excess HSiPh$_2$Me to give **9b**. We propose that **12b** undergoes a β-hydride elimination to give Ph$_2$Si═CH$_2$ and Rh(tmp)H, which then reacts with HSiPh$_2$Me to give **9b** (Scheme 1).

Scheme 1



$$\underset{\mathbf{12b}}{\mathrm{Rh(ttp)SiMePh_2}} \rightleftharpoons \left[\mathrm{H_2C{=}SiPh_2}\right] + \mathrm{Rh(ttp)H} \xrightarrow{\mathrm{Ph_2MeSiH}} \underset{\mathbf{9b}}{\mathrm{Rh(ttp)SiMePhH}}$$

Table 3. Si−H Activation of Silanes by Rh(por)Me

entry	silane	Rh(por)Me	time	product (% yield)
1	HSiEt$_3$, **2a**	Rh(ttp)Me **1d**	1 h	Rh(ttp)SiEt$_3$, **2b** (86)
2		Rh(tmp)Me, **1e**	1 d	Rh(tmp)SiEt$_3$, **2c** (56)
3	HSi(OEt)$_3$, **4a**	Rh(ttp)Me, **1d**	1 h	Rh(ttp)Si(OEt)$_3$, **4c** (86)
4		Rh(tmp)Me, **1e**	0.5 h	Rh(tmp)Si(OEt)$_3$, **4b** (68)
5	H$_2$SiPh$_2$, **7a**	Rh(ttp)Me, **1d**	0.5 h	Rh(ttp)SiPh$_2$H, **7c** (67)
6	H$_2$SiPhMe, **9a**	Rh(ttp)Me, **1d**	3 h	Rh(ttp)SiMePhH, **9c** (68)
7	HSiBnMe$_2$, **10a**	Rh(ttp)Me, **1d**	3 h	Rh(ttp)SiBnMe$_2$, **10b** (68)
8	HSiPhMe$_2$, **11a**	Rh(ttp)Me, **1d**	6 h	Rh(ttp)SiPhMe$_2$, **11b** (79)
9	HSiPh$_2$Me, **12a**	Rh(ttp)Me, **1d**	0.5 h	Rh(ttp)SiPh$_2$Me, **12c** (78)

Besides rhodium porphyrin halides, rhodium porphyrin methyls reacted with silanes successfully to give rhodium porphryin silyls with comparable yields and rates (eq 3, Table 3). The metathesis reactions appear to be general and applicable to Rh(tmp)SiEt$_3$. In a silyl exchange reaction, Rh(tmp)SiEt$_3$ (**2c**) reacted with H$_2$SiPh$_2$ (**7a**) at 200 °C in 1 h to give 68% of Rh(tmp)SiPh$_2$H (**7b**) and presumably also Et$_3$SiH (eq 4).[17]

$$\mathrm{Rh(por)Me} + \mathrm{HSiR_1R_2R_3} \rightarrow \mathrm{Rh(por)SiR_1R_2R_3} \quad (3)$$

$$\mathrm{Rh(tmp)SiEt_3} + \mathrm{H_2SiPh_2} \xrightarrow[1\ \mathrm{h}]{200\ °\mathrm{C}} \underset{68\%}{\mathrm{Rh(tmp)SiPh_2H}} + \mathrm{Et_3SiH} \quad (4)$$

X-ray Structure. The structures of Rh(tmp)SiPh$_2$Me (**12b**) and Rh(tmp)SiPhMe$_2$ (**11c**) were confirmed by single-crystal X-ray diffraction studies and are shown in Figure 2 (30% thermal ellipsoids). Crystals were grown from dichloromethane/methanol solution. Details of data collection and processing parameters are given in Table 4.

From Figure 2 and Tables 4 and 5, the coordination sphere of the rhodium atom of Rh(tmp)SiPh$_2$Me (**12b**) forms a square pyramidal geometry with the four porphyrinato nitrogen atoms

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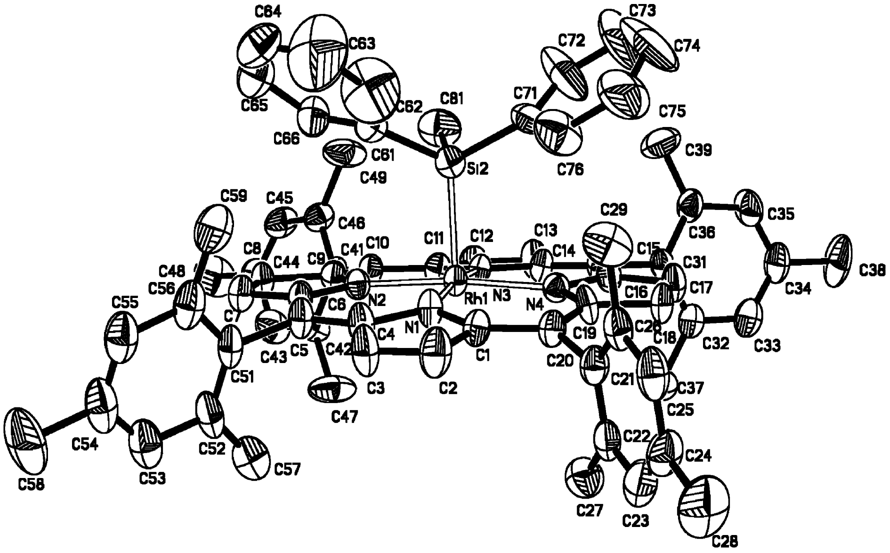

Figure 2. Molecular structure of Rh(tmp)SiPh$_2$Me, **12b**.

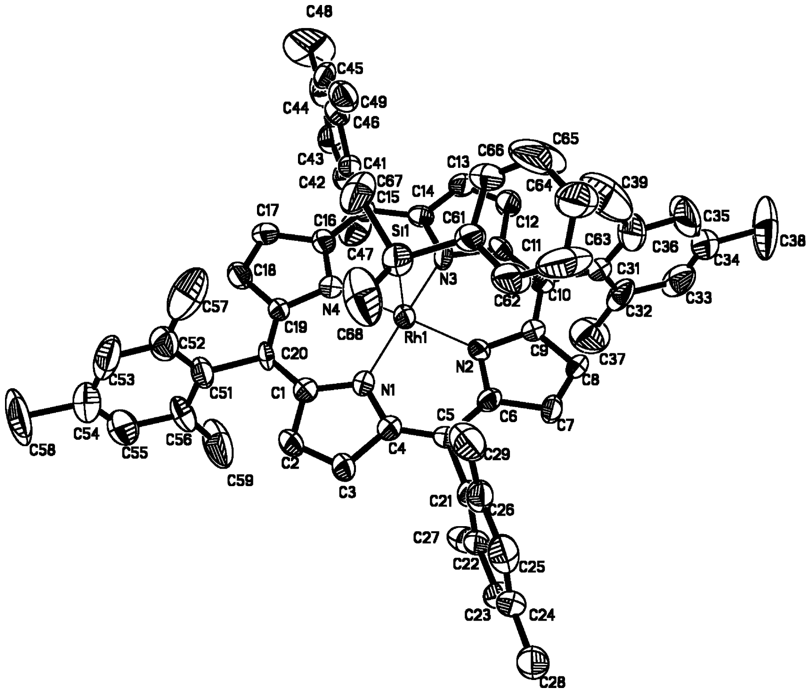

Figure 3. Molecular structure of Rh(tmp)SiPhMe$_2$, **11c**.

occupying the basal sites while the silicon atom of the diphenylmethyl group resides at the axial site. The mean bond length of the Rh−N bonds is 2.016 Å, which agrees with the reported five-coordinated organorhodium(III) porphyrin.[18] The Rh−Si length is 2.329 Å, which is longer than that of Rh(tpp)-SiMe$_3$ (Rh−Si = 2.305 Å)[8] and Rh(oep)SiEt$_3$ (Rh−Si = 2.305

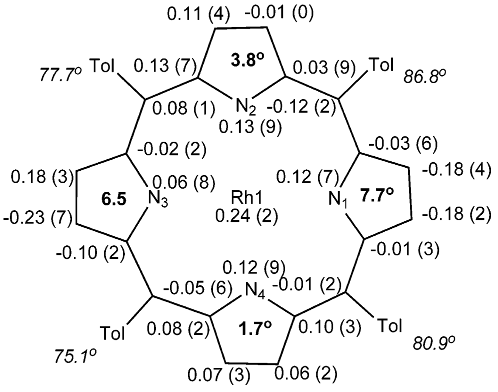

Figure 4. Displacement of the atoms of the Rh(tmp)SiPh$_2$Me (**12b**) porphyrin core.

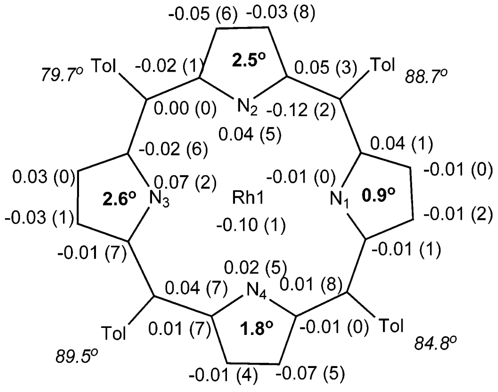

Figure 5. Displacement of the atoms of the Rh(tmp)SiPhMe$_2$ (**11c**)-porphyrin core.

Table 4. Crystal Data for Rh(tmp)SiPhMe$_2$ (11c) and Rh(tmp)SiPh$_2$Me (12b)

	11c	**12b**
empirical formula	$C_{64}H_{65}N_4RhSi$	$C_{69}H_{65}N_4RhSi$
cryst syst	tetragonal	orthorhombic
space group	$I4_1$	$Pna2_1$
fw	929.07	1081.25
a (Å)	28.4903(14)	21.854(4)
b (Å)	28.4903(14)	17.372(4)
c (Å)	14.7397(16)	14.901(3)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
Z	8	4
D_{calc} (g/cm^3)	1.152	1.270
absorp coeff	0.347	0.369
V (Å^3)	11964.2(15)	5657(2)
F(000)	4352	2264
cryst size (mm)	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.10
no. of reflns collected	42 238	15 052
absorp corr	SADABS	ABSCOR
max. and min. transmn	1.0000 and 0.388594	0.9641 and 0.8975
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	7891/0/569	8771/1/677
goodness-of-fit on F^2	0.960	1.105
final R indices [$I > 2\sigma(I)$]	R1 = 0.0949, wR2 = 0.2311	R1 = 0.0664, wR2 = 0.1418
abs struct param	0.29(7)	0.56(4)

Table 5. Selected Bond Lengths and Angles of Rh(tmp)SiPh$_2$Me, 12b

Bond Lengths (Å)			
Rh(1)−N(1)	2.021 (6)	Rh(1)−N(2)	2.011 (6)
Rh(1)−N(3)	2.003 (6)	Rh(1)−N(4)	2.017 (6)
Rh(1)−Si(2)	2.329 (3)	Si(2)−C(61)	1.855 (10)
Si (2)−C (71)	1.813 (11)	Si(2)−C(81)	1.922 (11)
Bond Angles (deg)			
Si(2)−Rh(1)−N(1)	99.0 (2)	Si(2)−Rh(1)−N(2)	91.05 (18)
Si(2)−Rh(1)−N(3)	89.24 (18)	Si(2)−Rh(1)−N(4)	95.05 (18)
Rh(1)−Si(2)−C(61)	115.3 (3)	Rh(1)−Si(2)−C(71)	115.7 (4)
Rh(1)−Si(2)−C(81)	108.3 (4)	C(61)−Si(2)−C(71)	112.7 (5)
C(61)−Si(2)−C(81)	100.9 (6)	C(81)−Si(2)−C(71)	101.7 (5)

Table 6. Selected Bond Lengths and Angles of Rh(tmp)SiPhMe$_2$, 11c

Bond Lengths (Å)			
Rh(1)−N(1)	2.036 (9)	Rh(1)−N(2)	2.001 (9)
Rh(1)−N(3)	2.009 (9)	Rh(1)−N(4)	2.027 (9)
Rh(1)−Si(1)	2.438 (5)	Si(1)−C(61)	1.833 (15)
Si (1)−C(67)	1.79 (2)	Si(1)−C(68)	1.79 (2)
Bond Angles (deg)			
Si(1)−Rh(1)−N(1)	90.7 (3)	Si(1)−Rh(1)−N(2)	92.2 (3)
Si(1)−Rh(1)−N(3)	93.1 (3)	Si(1)−Rh(1)−N(4)	91.7 (3)
Rh(1)−Si(1)−C(61)	113.5 (6)	Rh(1)−Si(1)−C(67)	111.8 (7)
Rh(1)−Si(1)−C(68)	114.7 (8)	C(61)−Si(1)−C(67)	106.3 (8)
C(61)−Si(2)−C(68)	102.9 (10)	C(67)−Si(1)−C(68)	106.9 (12)

Å),[10] owing to the steric hindrance of two phenyl rings. The porphyrin ring deviates slightly from planarity. The Rh atom is displaced 0.2417 Å from the mean plane of the porphyrin ring. The largest deviation relative to the mean plane of four pyrrole rings is at C_{12} (0.2371 Å), whereas N_2 lies approximately above the mean plane by about 0.1394 Å. The dihedral angles between the mesityl plane and the mean porphyrin plane are 86.8°, 80.9°, 75.1°, and 77.7°, respectively. The four mesityl groups are in a parallel arrangement. The dihedral angles between NC_4 pyrroles and the mean plane are 7.7°, 1.7°, 6.5°, and 3.8°, respectively.

The Rh−Si length of Rh(tmp)SiPhMe$_2$ (**11c**) is 2.438 Å and is longer than that of Rh(tpp)SiMe$_3$ (Rh−Si = 2.305 Å)[8] and Rh(tmp)SiPh$_2$Me (**12b**). The distances from Si to two methyl groups are the same (1.79 Å). The porphyrin ring deviates slightly from planarity. The Rh atom is displaced 0.1013 Å from the mean plane of the porphyrin ring. The individual NC_4 pyrrole rings are nearly planar. The largest deviation relative to the mean plane of the four pyrrole rings is at C_8 (0.0753 Å), whereas N_2 lies approximately above the mean plane by about 0.0456 Å. The dihedral angles between the mesityl plane and the mean porphyrin plane are 88.7°, 84.8°, 89.5°, and 79.7° respectively. The four mesityl groups are in a parallel arrangement. The dihedral angles between the NC_4 pyrroles and the mean plane are 0.9°, 2.5°, 2.6°, and 1.8° respectively.

Mechanism of Si−H Activation by Rh Porphyrin Halides. Scheme 2 illustrates a possible mechanism for the silicon−hydrogen bond activation. Rh(por)X initially undergoes ionization at high temperature to give a Rh(por) cation, which is then coordinated by a silane to give a silane complex **A**.[19] Coordination of the Si−H bond at an electrophilic rhodium center leads to a Si−H bond weakening. Subsequent activation of a silicon−hydrogen bond gives a rhodium porphyrin silyl. The detailed nature of this activation step could be a classical oxidative addition,[12,13] heterolysis,[20] or σ-bond metathesis.[21]

Supporting evidence for the intermediacy of the Rh(por) cation was obtained in two sets of experiments. First, Rh(ttp)-Cl reacted with trimethylsilylbenzene at 200 °C for 2 h under solvent-free conditions in a typical electrophilic aromatic substitution to give the *ipso*-substituted Rh(ttp)Ph in 21%. Even in a nonpolar solvent, ionization of Rh(por)Cl is still possible. Second, Rh(ttp)OTf[22] (**1f**) is much more reactive than Rh(ttp)-Cl toward Et$_3$SiH (Table 7). At 150 °C, Rh(ttp)Cl required 15 h to give Rh(ttp)SiEt$_3$ in 51% yield, while Rh(ttp)OTf only took 15 min to give a much higher yield of Rh(ttp)SiEt$_3$ at 78% (Table 7, entry 1 vs 3). A less coordinating OTf facilitates the formation of the Rh(ttp) cation.

We are less clear about the mechanism of the SiHA. Classical oxidative addition of a high-valent iridium(III) with a silane

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Scheme 2. Mechanism of SiHA of Silane with Rh(ttp)Cl, 1a

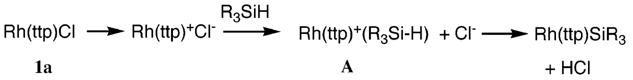

Table 7. Reaction of $HSiEt_3$ with Rh(ttp)X at 150 °C to Give $Rh(ttp)SiEt_3$, 2b

entry	Rh(ttp)X	time	% $Rh(ttp)SiEt_3$, **2b**
1	Rh(ttp)Cl, **1a**	15 h	51
2	Rh(ttp)Cl, **1a**	5 h	42[a]
3	Rh(ttp)(OTf), **1f**	15 min	78
4	Rh(ttp)(OTf), **1f**	15 min	25[a]

[a] 10 equiv of 2,6-dimethylpyridine added.

has been convincingly established through the isolation of an Ir(V) complex, further characterized by X-ray crystallography.[13] Rh(V) silyl complexes are known to form from the oxidative addition reactions of Rh(III) complexes with silanes.[23,24] In these SiHA, we were unable to detect any intermediate that would be highly unstable. We attempted to find out whether a heterolysis is operating by the study of base effect, as addition of a base was expected to facilitate the heterolysis.

Table 7 lists the results of the effect of added 2,6-dimethylpyridine. For Rh(ttp)Cl, a rate enhancement with a lower product yield was observed (Table 7, entries 1 and 2). However, for Rh(ttp)OTf, no rate enhancement and a much poorer product yield were found. We do not fully understand the difference of base effect in these complexes. At least for Rh(ttp)Cl, the Si−H activation was promoted by base.

Mechanism of Si−H Activation by Rh(ttp)R (R = methyl and silyl). The mechanism of silane activation with rhodium porphyrin methyls and silyls is unlikely a heterolysis. A typical rhodium porphyrin methyl bond falls at about 60 kcal/mol.[25] Even at 200 °C, homolysis or heterolysis in a nonpolar solvent is unlikely. Addition of pyridine in 10 equiv to the reaction mixture of $(EtO)_3SiH$ and Rh(tmp)Me produced little product even after 3 days, in contrast with 68% of $Rh(tmp)Si(OEt)_3$ formed in 30 min without addition of pyridine (Table 2, entry 4). The coordination of pyridine to Rh(tmp)Me completely shut down the activation. Unless an intermediate is observed, either oxidative addition or σ-bond metathesis remains a viable mechanistic option(s).

Conclusion

We have discovered a very facile synthetic approach to rhodium porphyrin silyl complexes from the reactions of Rh(III) porphyrin complexes of halides and methyls with silanes in solvent-free conditions. Preliminary mechanistic experiments suggested that rhodium porphyrin halides formed rhodium prophyrin cations and underwent base-promoted heterolysis in the silicon−hydrogen bond activation step. On the other hand, the mechanism of Si−H activation with Rh(ttp)Me likely operates through oxidative addition or σ-bond metathesis.

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. Benzonitrile was distilled from anhydrous P_2O_5. Thin-layer chromatography was performed on precoated silica gel 60 F_{254} plates for thin-layer analyses for reaction mixtures. For purification of rhodium complexes, flash column chromatography was used and carried out in air using silica gel. Samples for microanalyses were recrystallized from dichloromethane/methanol and were then dried at 50−60 °C in a vacuum (0.005 mmHg) for 2 days. Rh(ttp)Cl[26] (**1a**) and Rh(tmp)I[26] (**1c**) were prepared according to the literature.

^1H 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 7.24 ppm) or with tetramethylsilane (δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported in parts per million (ppm) in δ scale downfield from TMS. Coupling constants (J) are reported in hertz (Hz). Mass spectra were recorded on a Bruker APEX 47e FT-ICR mass spectrometer (FAB-MS and ESI-MS).

Preparation of (5,10,15,20-Tetramesitylporphyrinato)rhodium(III) Chloride [Rh(tmp)Cl] (1b).[26] H_2tmp (120 mg, 0.15 mmol) and $RhCl_3\cdot xH_2O$ (160 mg, 0.61 mmol) were refluxed in PhCN (10 mL) in air for 12 h. After removal of solvent under vacuum, the mixture was purified by column chromatography using CH_2Cl_2 as eluent. A purplish-red solid of **1b** (95 mg, 0.10 mmol, 65%) was obtained after recrystallization from CH_2Cl_2/MeOH. $R_f = 0.38$ (CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ 1.72 (s, 12 H), 2.03 (s, 12 H), 2.60(s, 12 H), 7.22 (s, 4 H), 7.27 (s, 4 H), 8.60 (s, 8 H). HRMS (EI): calcd for ($C_{56}H_{52}N_4ClRh^+$) m/z 918.2930; found m/z 918.2944. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.76, 22.18, 127.44, 128.20, 131.38, 131.82, 137.70, 138.60, 140.47, 142.17.

Reaction between [Rh(ttp)Cl] (1a) and Triethylsilane (2a) in Benzene. Rh(ttp)Cl[26] (10 mg, 0.012 mmol) and trimethylphenylsilane (193 μL, 100 equiv) were heated at 100 °C for 1 day under N_2 in the absence of light in benzene (2 mL). $Rh(ttp)SiEt_3$ (**2b**) (5.5 mg, 0.0062 mmol, 52%) was obtained after recrystallization from CH_2Cl_2/MeOH. $R_f = 0.68$ (hexane/CH_2Cl_2 = 2:1). ^1H NMR ($CDCl_3$, 300 MHz): δ −3.40 (q, 6 H, J = 7.8 Hz, 7.2 Hz), −1.35 (t, 9 H, J = 8.7 Hz), 2.68 (s, 12 H), 7.50 (d, 8 H, J = 8.1 Hz), 7.97−8.04 (t, 8 H, J = 7.8 Hz), 8.65 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 3.45, 5.87, 22.22, 123.46, 128.03, 128.12, 131.89, 134.21, 134.56, 137.83, 139.95, 144.33. HRMS (FAB): calcd for $(C_{54}H_{51}N_4SiRh)^+$ m/z 886.2933; found m/z 886.2948. Anal. Calcd for $C_{54}H_{51}N_4SiRh$: C, 73.12; H, 5.80; N, 6.31. Found: C, 73.20; H, 5.83; N, 6.22.

Reactions of [Rh(tmp)Cl] (1b) with Silanes. General Procedure. The reaction of Rh(tmp)Cl (**1b**) with triethylsilane (**2a**) is described as a typical example. Triethylsilane (0.5 mL) was added to Rh(tmp)Cl (10 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 for 1 day under N_2 in the absence of light. The crude product was purified by chromatography on silica gel eluting with hexane/CH_2Cl_2 (10:1) to hexane/CH_2Cl_2 (5:1). An orange solid of $Rh(tmp)SiEt_3$ (**2c**) (6.8 mg, 0.0068 mmol, 62%) was produced. $R_f = 0.34$ (hexane/CH_2Cl_2 = 5:1). ^1H NMR ($CDCl_3$, 300 MHz): δ −3.19 (q, 6 H, J = 8.1 Hz), −1.11 (t, 9 H, J = 7.8 Hz), 1.44 (s, 12 H), 2.33 (s, 12 H), 2.59 (s, 12 H), 6.95 (s, 4 H), 7.31 (s, 4 H), 8.41 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 4.79, 7.02, 21.91, 22.08, 23.07, 121.20, 128.50, 128.58, 131.20, 138.10, 138.99, 139.08, 140.60, 143.89. HRMS (FAB): calcd for $(C_{62}H_{67}N_4SiRh)^+$ m/z 998.4185; found m/z 998.4223. Anal. Calcd for $C_{62}H_{67}N_4SiRh$: C, 74.53; H, 6.76; N, 5.60. Found: C, 74.31; H, 6.38; N, 5.97.

Reaction between [Rh(tmp)Cl] (1b) and Triethoxysilane (4a). Triethoxysilane (0.5 mL) and Rh(tmp)Cl (10 mg, 0.011 mmol) were heated at 200 °C for 1 h under N_2 in the absence of light. An orange solid of $Rh(tmp)Si(OEt)_3$ (**4b**) (7.1 mg, 0.0068 mmol, 62%) was

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obtained. $R_f = 0.40$ (hexane/$CH_2Cl_2 = 5:1$). ^1H NMR ($CDCl_3$, 300 MHz): δ -0.28 (t, 9 H, $J = 6.9$ Hz), 0.98 (q, 6 H, $J = 6.9$ Hz), 1.57 (s, 12 H), 2.21 (s, 12 H), 2.60 (s, 12 H), 7.17 (s, 4 H), 7.30 (s, 4 H), 8.45 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 17.20, 22.10, 22.47, 31.60, 55.63, 120.92, 128.38, 130.99, 137.98, 139.20, 139.53, 140.39, 143.78. HRMS (FAB): calcd for $(C_{62}H_{67}N_4O_3SiRh)^+$ *m/z* 1046.4032; found *m/z* 1046.4046. Anal. Calcd for $C_{62}H_{67}N_4O_3SiRh$: C, 71.11; H, 6.45; N, 5.35. Found: C, 71.20; H, 6.48; N, 5.10.

Reaction between [Rh(tmp)Cl] (1b) and Tripropylsilane (5a). Tripropylsilane (0.5 mL) and Rh(tmp)Cl (10 mg, 0.011 mmol) were heated at 200 °C for 2 days under N_2 in the absence of light. An orange solid of Rh(tmp)$SiPr_3$ (**5b**) (5.8 mg, 0.006 mmol, 51%) was obtained. $R_f = 0.47$ (hexane/$CH_2Cl_2 = 5:1$). ^1H NMR ($CDCl_3$, 300 MHz): δ -3.15 (dt, 6 H, $J = 3.3$, 8.7 Hz), $-0.88-0.76$ (m, 6 H), -0.13 (t, 9 H, $J = 9.3$ Hz), 1.25 (s, 12 H), 2.39 (s, 12 H), 2.59 (s, 12 H), 7.13 (s, 4 H), 7.32 (s, 4 H), 8.41 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.86, 18.02, 21.89, 22.08, 23.72, 121.10, 128.52, 131.24, 138.09, 138.88, 139.13, 140.74, 143.95. HRMS (FAB): calcd for $(C_{65}H_{73}N_4SiRh)^+$ *m/z* 1040.4654; found *m/z* 1040.4707. Anal. Calcd for $C_{65}H_{73}N_4SiRh$: C, 74.97; H, 7.07; N, 5.38. Found: C, 74.56; H, 7.05; N, 5.24.

Reaction between [Rh(tmp)Cl] (1b) and Triisopropylsilane (6a). Triisopropylsilane (0.5 mL) and Rh(tmp)Cl (10 mg, 0.011 mmol) were heated at 200 °C for 2 days under N_2 in the absence of light. An orange solid of Rh(tmp)Si^iPr_3 (**6b**) (1.8 mg, 0.002 mmol, 16%) was obtained. $R_f = 0.50$ (hexane/$CH_2Cl_2 = 5:1$). ^1H NMR ($CDCl_3$, 300 MHz): δ -2.36 (heptet, 3 H, $J = 7.5$ Hz), -1.04 (d, 18 H, $J = 7.5$ Hz), 1.56 (s, 12 H), 2.53 (s, 12 H), 2.61 (s, 12 H), 7.06 (s, 4 H), 7.37 (s, 4 H), 8.41 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.88, 18.59, 21.66, 22.03, 23.49, 121.47, 128.49, 128.64, 131.73, 138.09, 138.64, 139.05, 140.90, 144.62. HRMS (FAB): calcd for $(C_{65}H_{73}N_4SiRh)^+$ *m/z* 1041.4732; found *m/z* 1041.4786. Anal. Calcd for $C_{65}H_{73}N_4SiRh$: C, 74.97; H, 7.07; N, 5.38. Found: C, 74.86; H, 6.54; N, 5.13.

Reaction between [Rh(tmp)Cl] (1b) and Diphenylsilane (7a). Diphenylsilane (0.5 mL) and Rh(tmp)Cl (10 mg, 0.011 mmol) were heated at 200 °C for 1 h under N_2 in the absence of light. An orange solid of Rh(tmp)$SiPh_2H$ (**7b**) (7.3 mg, 0.0068 mmol, 62%) was obtained. $R_f = 0.27$ (hexane/$CH_2Cl_2 = 5:1$). ^1H NMR ($CDCl_3$, 300 MHz): δ -0.73 (s, 1 H), 1.26 (s, 12 H), 1.84 (s, 12 H), 2.58 (s, 12 H), 4.41 (d, 4 H, $J = 7.5$ Hz), 6.16 (t, 4 H, $J = 7.5$ Hz), 7.14 (s, 4 H), 7.26 (s, 4 H), 8.43 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.38, 21.57, 22.15, 120.71, 126.38, 127.85, 130.90, 131.47, 136.18, 137.58, 138.36, 138.72, 139.31, 139.93, 143.21. HRMS (FAB): calcd for $(C_{68}H_{63}N_4SiRh)^+$ *m/z* 1066.3872; found *m/z* 1066.3869. Anal. Calcd for $C_{68}H_{63}N_4SiRh$: C, 76.53; H, 5.95; N, 5.25. Found: C, 76.20; H, 5.74; N, 5.10.

Reaction between [Rh(tmp)Cl] (1b) and Phenylsilane (8a). Phenylsilane (0.5 mL) and Rh(tmp)Cl (10 mg, 0.011 mmol) were heated at 200 °C for 1 h under N_2 in the absence of light. An orange solid of Rh(tmp)$SiPhH_2$ (**8b**) (8.9 mg, 0.009 mmol, 82%) was obtained. $R_f = 0.40$ (hexane/$CH_2Cl_2 = 5:1$). ^1H NMR ($CDCl_3$, 300 MHz): δ -1.20 (s, 2 H), 1.74 (s, 12 H), 1.84 (s, 12 H), 2.59 (s, 12 H), 4.29 (d, 2 H, $J = 7.5$ Hz), 6.15 (t, 2 H, $J = 7.5$ Hz), 6.53 (t, 1 H, $J = 7.5$ Hz), 7.14 (s, 4 H), 7.21 (s, 4 H), 8.45 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.08, 22.58, 54.10, 120.83, 126.82, 128.41, 131.30, 132.69, 138.14, 138.87, 139.53, 139.96, 143.39. HRMS (FAB): calcd for $(C_{62}H_{59}N_4SiRh)^+$ *m/z* 990.3506; found *m/z* 990.3559. Anal. Calcd for $C_{62}H_{59}N_4SiRh$: C, 75.13; H, 6.00; N, 5.65. Found: C, 74.63; H, 6.18; N, 5.17. IR (KBr, cm^{-1}): ν_{Si-H} 2304.

Reaction between [Rh(tmp)Cl] (1b) and Phenylmethylsilane (9a). Phenylmethylsilane (0.5 mL) and Rh(tmp)Cl (10 mg, 0.011 mmol) were heated at 200 °C for 3 h under N_2 in the absence of light. An orange solid of Rh(tmp)SiPhMeH (**9b**) (7.8 mg, 0.008 mmol, 73%) was obtained. $R_f = 0.40$ (hexane/$CH_2Cl_2 = 5:1$). ^1H NMR ($CDCl_3$, 300 MHz): δ -3.36 (d, 3 H, $J = 3.3$ Hz), -1.09 (d, 1 H, $^2J_{Rh-H} = 3$ Hz, $J_{Si-H} = 0.9$ Hz), 1.59 (s, 12 H), 1.98 (s, 12 H), 2.59 (s, 12 H), 4.41 (d, 2 H, $J = 6.6$ Hz), 6.24 (t, 2 H, $J = 7.6$ Hz), 6.58 (t, 1 H, $J = 7.5$ Hz), 7.17 (s, 4 H), 7.26 (s, 4 H), 8.43 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -3.30, 21.99, 22.10, 22.93, 120.93, 126.96, 128.43, 131.27, 131.96, 137.53, 138.11, 138.92, 139.26, 140.34, 143.47. HRMS (FAB): calcd for $(C_{63}H_{61}N_4SiRh)^+$ *m/z* 1004.3715; found *m/z* 1004.3677. Anal. Calcd for $C_{63}H_{61}N_4SiRh$: C, 75.28; H, 6.12; N, 5.57. Found: C, 74.75; H, 6.05; N, 5.50. IR (KBr, cm^{-1}): ν_{Si-H} 2304.

Reaction between [Rh(tmp)Cl] (1b) and Benzyldimethylsilane (10a). Benzyldimethylsilane (0.5 mL) and Rh(tmp)Cl (10 mg, 0.011 mmol) were heated at 200 °C for 1 h under N_2 in the absence of light. An orange solid of Rh(tmp)$SiBnMe_2$ (**10c**) (10.3 mg, 0.010 mmol, 91%) was obtained. $R_f = 0.30$ (hexane/$CH_2Cl_2 = 5:1$). ^1H NMR ($CDCl_3$, 300 MHz): δ -3.58 (s, 6 H), -2.04 (s, 2 H), 1.57 (s, 12 H), 2.31 (s, 12 H), 2.62 (s, 12 H), 5.26 (t, 2 H, $J = 6.0$ Hz), 6.43 (t, 3 H, $J = 3.0$ Hz), 6.97 (d, 1 H, $J = 7.2$ Hz), 7.21 (s, 4 H), 7.34 (s, 4 H), 8.50 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -2.64, 21.96, 22.101, 23.60, 25.67, 121.19, 123.47, 127.62, 128.57, 131.25, 138.20, 138.96, 140.59, 143.71. HRMS (FAB): calcd for $(C_{65}H_{65}N_4SiRh)^+$ *m/z* 1032.4028; found *m/z* 1032.4022. Anal. Calcd for $C_{65}H_{65}N_4SiRh$: C, 75.56; H, 6.34; N, 5.42. Found: C, 75.19; H, 6.28; N, 5.37.

Reaction between [Rh(tmp)Cl] (1b) and Dimethylphenylsilane (11a). Dimethylphenylsilane (0.5 mL) and Rh(tmp)Cl (10 mg, 0.011 mmol) were heated at 200 °C for 8 h under N_2 in the absence of light. An orange solid of Rh(tmp)$SiPhMe_2$ (**11c**) (6.2 mg, 0.006 mmol, 56%) was obtained. $R_f = 0.37$ (hexane/$CH_2Cl_2 = 5:1$). ^1H NMR ($CDCl_3$, 300 MHz): δ -3.22 (s, 6 H), 1.40 (s, 12 H), 2.14 (s, 12 H), 2.61 (s, 12 H), 4.48 (d, 2 H, $J = 6$ Hz), 6.30 (t, 2 H, $J = 9.2$ Hz), 6.60 (t, 1 H, $J = 9.0$ Hz), 7.13 (s, 4 H), 7.29 (s, 4 H), 8.41 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -0.68, 21.84, 22.07, 23.32, 121.16, 126.87, 128.03, 128.47, 131.29, 131.50, 138.10, 138.98, 140.70, 143.79. HRMS (FAB): calcd for $(C_{64}H_{63}N_4SiRh)^+$ *m/z* 1018.3872; found *m/z* 1018.3903. Anal. Calcd for $C_{64}H_{63}N_4SiRh$: C, 75.42; H, 6.23; N, 5.49. Found: C, 74.73; H, 6.13; N, 5.28.

Reaction between [Rh(tmp)Cl] (1b) and Diphenylmethylsilane (12a). Diphenylmethylsilane (0.5 mL) and Rh(tmp)Cl (10 mg, 0.011 mmol) were heated at 200 °C for 15 h under N_2 in the absence of light. An orange solid of Rh(tmp)$SiPh_2Me$ (**12b**) (2.8 mg, 0.003 mmol, 26%) was obtained with $R_f = 0.30$ (hexane/$CH_2Cl_2 = 5:1$). ^1H NMR ($CDCl_3$, 300 MHz): δ -2.80 (s, 3 H), 1.19 (s, 12 H), 2.08 (s, 12 H), 2.56 (s, 12 H), 4.53 (d, 4 H, $J = 7.6$ Hz), 6.26 (t, 4 H, $J = 7.5$ Hz), 6.55 (t, 2 H, $J = 7.5$ Hz), 7.07 (s, 4 H), 7.28 (s, 4 H), 8.40 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ -0.83, 21.70, 21.86, 23.15, 31.58, 121.53, 126.63, 127.46, 129.41, 131.29, 131.60, 132.58, 133.58, 138.03, 139.09, 140.63, 144.14. HRMS (FAB): calcd for $(C_{69}H_{65}N_4SiRh)^+$ *m/z* 1080.4028; found *m/z* 1080.3979. Anal. Calcd for $C_{69}H_{65}N_4SiRh$: C, 76.64; H, 6.06; N, 5.18. Found: C, 76.26; H, 6.02; N, 4.92. Rh(tmp)SiPhMeH (**9b**) (2.7 mg, 0.003 mmol, 28%) was also produced.

Reactions of [Rh(tmp)I] (1c) with Silanes. General Procedure. The reaction of Rh(tmp)I[27] with triethylsilane (**2a**) is described as a typical example. Triethylsilane (0.5 mL) was added to Rh(tmp)I (10 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 for 1 day under N_2 in the absence of light. The crude product was purified by chromatography on silica gel eluting with hexane/CH_2Cl_2 (10:1) to hexane/CH_2Cl_2 (5:1). An orange solid of Rh(tmp)$SiEt_3$ (**2c**) (6.0 mg, 0.005 mmol, 70%) was produced.

Reaction between [Rh(tmp)I] (1c) and Triethoxysilane (4a). Triethoxysilane (0.5 mL) and Rh(tmp)I (**1c**) (10 mg, 0.010 mmol) were heated at 200 °C for 1 h under N_2 in the absence of light. An

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orange solid of Rh(tmp)Si(OEt)$_3$ (**4b**) (7.6 mg, 0.007 mmol, 74%) was obtained.

Reaction between [Rh(tmp)I] (1c) and Tripropylsilane (5a). Tripropylsilane (0.5 mL) and Rh(tmp)I (10 mg, 0.010 mmol) were heated at 200 °C for 2 days under N$_2$ in the absence of light. An orange solid of Rh(tmp)SiPr$_3$ (**5b**) (4.6 mg, 0.004 mmol, 45%) was obtained.

Reaction between [Rh(tmp)I] (1c) and Triisopropylsilane (6a). Triisopropylsilane (0.5 mL) and Rh(tmp)I (10 mg, 0.010 mmol) were heated at 200 °C for 2 days under N$_2$ in the absence of light. An orange solid of Rh(tmp)Si^{i}Pr$_3$ (**6b**) (2.4 mg, 0.002 mmol, 23%) was obtained.

Reaction between [Rh(tmp)I] (1c) and Diphenylsilane (7a). Diphenylsilane (0.5 mL) and Rh(tmp)I (10 mg, 0.010 mmol) were heated at 200 °C for 1 h under N$_2$ in the absence of light. An orange solid of Rh(tmp)SiPh$_2$H (**7b**) (6 mg, 0.006 mmol, 56%) was obtained.

Reaction between [Rh(tmp)I] (1c) and Phenylsilane (8a). Phenylsilane (0.5 mL) and Rh(tmp)I (10 mg, 0.010 mmol) were heated at 200 °C for 1 h under N$_2$ in the absence of light. An orange solid of Rh(tmp)SiPhH$_2$ (**8b**) (7.3 mg, 0.007 mmol, 75%) was obtained.

Reaction between [Rh(tmp)I] (1c) and Phenylmethylsilane (9a). Phenylmethylsilane (0.5 mL) and Rh(tmp)I (10 mg, 0.010 mmol) were heated at 200 °C for 3 h under N$_2$ in the absence of light. An orange solid of Rh(tmp)SiPhMeH (**9b**) (6.5 mg, 0.006 mmol, 66%) was obtained.

Reaction between [Rh(tmp)I] (1c) and Benzyldimethylsilane (10a). Benzyldimethylsilane (0.5 mL) and Rh(tmp)I (10 mg, 0.010 mmol) were heated at 200 °C for 6 h under N$_2$ in the absence of light. An orange solid of Rh(tmp)SiBnMe$_2$ (**10c**) (7.8 mg, 0.007 mmol, 77%) was obtained.

Reaction between [Rh(tmp)I] (1c) and Dimethylphenylsilane (11a). Dimethylphenylsilane (0.5 mL) and Rh(tmp)I (10 mg, 0.010 mmol) were heated at 200 °C for 1 day under N$_2$ in the absence of light. The suspension slowly became transparent upon heating, and a red solution was finally formed. An orange solid of Rh(tmp)SiPhMe$_2$ (**11c**) (4.8 mg, 0.005 mmol, 48%) was obtained.

Reaction between [Rh(tmp)SiPh$_2$Me] (12b) and Diphenylmethylsilane (12a). Rh(tmp)SiPh$_2$Me (3 mg, 0.003 mmol) and diphenylmethylsilane (0.5 mL) were heated at 200 °C for 2 days under N$_2$ in the absence of light. After removing **12a**, the reaction mixture was subjected to NMR, which suggested that **12b** had completely converted to Rh(tmp)SiPhMeH (**9b**) (100% NMR yield).

Reaction between [Rh(tmp)SiPhMeH] (9b) and Diphenylmethylsilane (12a). Rh(tmp)SiPhMeH (**9b**) (3 mg, 0.003 mmol) and diphenylmethylsilane (**12a**) (0.5 mL) were heated at 200 °C for 3 days under N$_2$ in the absence of light. No Rh(tmp)SiPh$_2$Me (**12b**) signals were observed in the NMR spectrum.

Reaction of [Rh(ttp)Cl] (1a) with Triethylsilane (2a). Genaral Procedure. The reaction between triethylsilane and Rh(ttp)Cl is described as a typical example. Triethylsilane (0.5 mL) was added to Rh(ttp)Cl (10 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 1.5 h under N$_2$ in the absence of light. The crude product was purified by chromatography on silica gel eluting with hexane/CH$_2$Cl$_2$ (4:1) to hexane/CH$_2$Cl$_2$ (2:1). An orange solid of Rh(ttp)SiEt$_3$ (**2b**) (8.9 mg, 0.010 mmol, 81%) was obtained.

Reaction between [Rh(ttp)Cl] (1a) and Diphenylsilane (7a). Diphenylsilane (0.5 mL) and Rh(ttp)Cl (10 mg, 0.012 mmol) were heated at 200 °C for 0.5 h under N$_2$ in the absence of light. An orange solid of Rh(ttp)SiPh$_2$H (**7c**) (8.5 mg, 0.009 mmol, 72%) was obtained. R_f = 0.53 (hexane/CH$_2$Cl$_2$ = 2:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ −1.28 (d, 1 H, *J* = 2.8 Hz), 2.68 (s, 12 H), 4.31 (d, 4 H, *J* = 6.9 Hz), 6.35 (t, 4 H, *J* = 8.7 Hz), 6.71 (t, 2 H, *J* = 8.7 Hz), 7.48 (t, 8 H, *J* = 9.0 Hz), 7.73 (d, 4 H, *J* = 9.0 Hz), 7.97 (d,4 H, *J* = 9.0 Hz), 8.59 (s, 8 H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 22.22, 123.34, 126.53, 127.96, 128.02, 128.13, 128.45, 131.72, 131.98, 134.45, 134.55, 135.04, 137.74, 139.83, 143.82. HRMS (FAB): calcd for (C$_{60}$H$_{47}$N$_4$SiRh)$^+$ *m/z* 954.2620; found *m/z* 954.2650. Anal. Calcd for C$_{60}$H$_{47}$N$_4$SiRh: C, 75.46; H, 4.96; N, 5.86. Found: C, 75.69; H, 5.15; N, 5.56.

Reaction between [Rh(ttp)Cl] (1a) and Benzyldimethylsilane (10a). Benzyldimethylsilane (0.5 mL) and Rh(ttp)Cl (10 mg, 0.012 mmol) were heated at 200 °C for 1 h under N$_2$ in the absence of light. An orange solid of Rh(ttp)SiBnMe$_2$ (**10b**) (10.0 mg, 0.011 mmol, 88%) was obtained. R_f = 0.62 (hexane/CH$_2$Cl$_2$ = 2:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ −3.94 (s, 6 H), −2.47 (s, 2 H), 2.72 (s, 12 H), 5.30 (d, 2 H, *J* = 7.5 Hz), 6.47 (t, 3 H, *J* = 6.9 Hz), 7.53 (t, 8 H, *J* = 8.4 Hz), 7.80 (d, 4 H, *J* = 6.3 Hz), 8.10 (d, 4 H, *J* = 6.3 Hz), 8.73 (s, 8 H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ −4.45, 22.22, 24.42, 123.60, 127.65, 127.70, 128.06, 128.16, 128.81, 132.03, 134.20, 134.60, 137.93, 139.11, 139.86, 144.19. HRMS (FAB): calcd for (C$_{57}$H$_{49}$N$_4$SiRh)$^+$ *m/z* 920.2776; found *m/z* 920.2708. Anal. Calcd for C$_{57}$H$_{49}$N$_4$SiRh: C, 74.33; H, 5.36; N, 6.08. Found: C, 73.78; H, 5.36; N, 5.96.

Reaction between [Rh(ttp)Cl] (1a) and Dimethylphenylsilane (11a). Dimethylphenylsilane (0.5 mL) and Rh(ttp)Cl (10 mg, 0.012 mmol) were heated at 200 °C for 1 h under N$_2$ in the absence of light. An orange solid of Rh(ttp)SiPhMe$_2$ (**11b**) (10.2 mg, 0.011 mmol, 91%) was obtained. R_f = 0.58 (hexane/CH$_2$Cl$_2$ = 5:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ −3.54 (s, 6 H), 2.68 (s, 12 H), 4.22 (d, 2 H, *J* = 8.7 Hz), 6.41 (t, 2 H, *J* = 6.3 Hz), 6.75 (t, 1 H, *J* = 6.3 Hz), 7.49 (t, 8 H, *J* = 9.0 Hz), 7.92−8.01 (m, 8 H), 8.62 (s, 8 H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 0.00, 25.96, 35.33, 127.11, 130.09, 131.43, 131.72, 131.83, 134.18, 135.64, 138.24, 141.52, 143.68, 147.76. HRMS(FAB): calcd for (C$_{56}$H$_{47}$N$_4$SiRh)$^+$ *m/z* 906.2620; found *m/z* 906.2600. Anal. Calcd for C$_{56}$H$_{47}$N$_4$SiRh: C, 74.16; H, 5.22; N, 6.17. Found: C, 73.86; H, 5.02; N, 6.13.

Reaction between [Rh(ttp)Me] (1d) and Triethylsilane (2a). Genaral Procedure. The reaction between triethylsilane and Rh(ttp)Me[26] is described as a typical example. Triethylsilane (0.5 mL) was added to Rh(ttp)Me (10 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 h under N$_2$ in the absence of light. The crude product was purified by chromatography on silica gel eluting with hexane/CH$_2$Cl$_2$ (4:1) to hexane/CH$_2$Cl$_2$ (2:1). An orange solid of Rh(ttp)SiEt$_3$ (**2b**) (9.9 mg, 0.011 mmol, 86%) was obtained.

Reaction between [Rh(ttp)Me] (1d) and Triethoxysilane (4a). Triethoxysilane (0.5 mL) and Rh(ttp)Me (10 mg, 0.013 mmol) were heated at 200 °C for 1 h under N$_2$ in the absence of light. An orange solid of Rh(ttp)Si(OEt)$_3$ (**4c**) (10.4 mg, 0.011 mmol, 86%) was obtained. R_f = 0.52 (hexane/CH$_2$Cl$_2$ = 2:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ −0.28 (t, 9 H, *J* = 6.9 Hz), 0.77 (q, 6 H, J_1 = 6.9 Hz, J_2 = 7.2 Hz), 2.64 (s, 12 H), 7.51 (d, 8 H, *J* = 6.9 Hz), 7.99 (t, 8 H, *J* = 8.7 Hz), 8.70 (s, 8 H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 3.45, 5.87, 22.22, 123.46, 128.03, 128.12, 131.89, 134.21, 134.56, 137.83, 139.95, 144.33. HRMS (FAB): calcd for (C$_{54}$H$_{51}$N$_4$O$_3$SiRh)$^+$ *m/z* 934.2002; found *m/z* 934.2009. Anal. Calcd for C$_{54}$H$_{51}$N$_4$O$_3$SiRh: C, 69.37; H, 5.50; N, 5.99. Found: C, 69.35; H, 5.60; N, 5.95.

Reaction between [Rh(ttp)Me] (1d) Diphenylsilane (7a). Diphenylsilane (0.5 mL) and Rh(ttp)Me (10 mg, 0.013 mmol) were heated at 200 °C for 0.5 h under N$_2$ in the absence of light. An orange solid of Rh(ttp)SiPh$_2$H (**7c**) (8.2 mg, 0.008 mmol, 67%) was obtained.

Reaction between [Rh(ttp)Me] (1d) and Phenylmethylsilane (9a). Phenylmethylsilane (0.5 mL) and Rh(ttp)Me (10 mg, 0.013 mmol) were heated at 200 °C for 3 h under N$_2$ in the absence of light. An orange solid of Rh(ttp)SiPhMeH (**9c**) (7.7 mg, 0.0086 mmol, 68%) was obtained. R_f = 0.44 (hexane/CH$_2$Cl$_2$ = 2:1). ^{1}H NMR (CDCl$_3$, 300 MHz): δ −3.58 (d, 3 H, *J* = 3.3 Hz), −1.58

(d, 1 H, $J = 3.3$ Hz), 2.63 (s, 12 H), 4.13 (d, 2 H, $J = 6.9$ Hz), 6.36 (t, 2 H, $J = 6.3$ Hz), 6.74 (t, 1 H, $J = 7.5$ Hz), 7.87 (d, 8 H, $J = 6.9$ Hz), 8.01 (d, 4 H, $J = 6.9$ Hz), 8.05 (d, 4 H, $J = 6.9$ Hz), 8.63 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 0.69, 20.36, 31.59, 123.44, 126.37, 127.69, 128.06, 132.002, 134.37, 137.79, 139.87, 143.97. HRMS (FAB): calcd for $(C_{55}H_{45}N_4SiRh)^+$ m/z 892.3718; found m/z 892.3702. Anal. Calcd for $C_{55}H_{45}N_4SiRh$: C, 73.98; H, 5.08; N, 6.27. Found: C, 73.87; H, 4.99; N, 5.81. IR (KBr, cm^{-1}): ν_{Si-H} 1425.

Reaction between [Rh(ttp)Me] (1d) and Benzyldimethylsilane (10a). Benzyldimethylsilane (0.5 mL) and Rh(ttp)Me (10 mg, 0.013 mmol) were heated at 200 °C for 0.5 h under N_2 in the absence of light. An orange solid of Rh(ttp)SiBnMe$_2$ (**10b**) (9.6 mg, 0.010 mmol, 88%) was obtained.

Reaction between [Rh(ttp)Me] (1d) and Dimethylphenylsilane (11a). Dimethylphenylsilane (0.5 mL) and Rh(ttp)Me (10 mg, 0.013 mmol) were heated at 200 °C for 6 h under N_2 in the absence of light. An orange solid of Rh(ttp)SiPhMe$_2$ (**11b**) (8.5 mg, 0.009 mmol, 79%) was obtained.

Reaction between [Rh(ttp)Me] (1d) and Diphenylmethylsilane (12a). Diphenylmethylsilane (0.5 mL) and Rh(ttp)Me (10 mg, 0.013 mmol) were heated at 200 °C for 0.5 h under N_2 in the absence of light. An orange solid of Rh(ttp)SiPh$_2$Me (**12c**) (9.4 mg, 0.0078 mmol, 78%) was obtained. $R_f = 0.56$ (hexane/CH_2Cl_2 = 2:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ −3.17 (s, 3 H), 2.68 (s, 12 H), 4.46 (d, 4 H, $J = 7.5$ Hz), 6.43 (t, 4 H, $J = 7.5$ Hz), 6.74 (t, 2 H, $J = 7.5$ Hz), 7.49 (dd, 8 H, $J = 9$ Hz, 7.5 Hz), 7.81 (d, 4 H, $J = 7.5$ Hz), 7.91 (d, 4 H, $J = 7.5$ Hz), 8.56 (s, 8 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ −5.40, 22.20, 31.59, 123.44, 126.38, 127.70, 127.96, 128.06, 132.01, 134.38, 134.59, 135.94, 137.73, 139.88, 143.99. HRMS (FAB): calcd for $(C_{61}H_{49}N_4SiRh)^+$ m/z 968.2776; found m/z 968.2768. Anal. Calcd for $C_{61}H_{49}N_4SiRh$: C, 75.61; H, 5.10; N, 5.78. Found: C, 75.83; H, 5.18; N, 5.56.

Reactions of [Rh(tmp)Me] (1e) with Silanes. General Procedure. The reaction of Rh(tmp)Me[27] (**1e**) with triethylsilane (**2a**) is described as a typical example. Triethylsilane (0.5 mL) was added to Rh(tmp)Me (10 mg, 0.011 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 in the absence of light. The crude product was purified by chromatography on silica gel eluting with hexane/CH_2Cl_2 (10:1) to hexane/CH_2Cl_2 (5:1). An orange solid of Rh(tmp)SiEt$_3$ (**2c**) (4.9 mg, 0.0056 mmol, 56%) was produced.

Reaction between [Rh(tmp)Me] (1e) and Triethoxysilane (4a). Triethoxylsilane (0.5 mL) and Rh(tmp)Me (10 mg, 0.011 mmol) were heated at 200 °C for 0.5 h under N_2 in the absence of light. An orange solid of Rh(tmp)Si(OEt)$_3$ (**4b**) (7.9 mg, 0.0075 mmol, 68%) was produced.

Reaction between [Rh(tmp)SiEt$_3$] (2c) and Diphenylsilane (7a). Rh(tmp)SiEt$_3$ (5 mg, 0.005 mmol) and diphenylsilane (0.5 mL) were heated at 200 °C for 1 h under N_2 in the absence of light, and **2c** was consumed completely. After removing **7a**, the mixture was eluted with hexane/CH_2Cl_2 (5:1) to give an orange solid of Rh(tmp)SiPh$_2$H (**7b**) (3.6 mg, 0.0036 mmol, 68%).

Reaction between [Rh(ttp)Cl] (1a) and Trimethylphenylsilane (14a). Rh(ttp)Cl (10 mg, 0.012 mmol) and trimethylphenylsilane (0.5 mL) were heated at 200 °C for 1 day under N_2 in the absence of light. An orange solid of Rh(ttp)Ph (**14b**) (2.0 mg, 0.0024 mmol, 18%) was formed. $R_f = 0.50$ (hexane/CH_2Cl_2 = 2:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.24 (d, 2 H, $J = 8.4$ Hz), 2.69 (s, 12 H), 4.73 (t, 2 H, $J = 8.4$ Hz), 5.20 (t, 1 H, $J = 6.9$ Hz), 7.54 (t, 8 H, $J = 6.9$ Hz), 7.99 (dd, 8 H, $J = 7.5$, 7.8 Hz), 8.76 (s, 8 H). HRMS (FAB): calcd for $(C_{54}H_{41}N_4Rh)^+$ m/z 848.2381; found m/z 848.2390.

Reaction between [Rh(ttp)OTf] (1f) and Triethylsilane (2a). Rh(ttp)OTf[22,29] (10 mg, 0.011 mmol) and trimethylphenylsilane (0.5 mL) were heated at 150 °C for 15 min under N_2 in the absence of light. Rh(ttp)SiEt$_3$ (**2b**) (6.5 mg, 0.006 mmol, 78%) was obtained.

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Supporting Information Available: Text and crystallographic data for **11c** and **12b** (pdf and cif).This material is available free of charge via the Internet at http://pubs.acs.org.

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