

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

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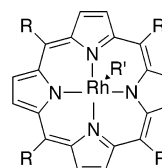
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Rhodium(III) porphyrin silyls were synthesized in high yields conveniently from the reactions of rhodium(III) porphyrin halides and methyls with silanes, via silicon–hydrogen bond activation (SiHA) in solvent-free conditions. Preliminary mechanistic 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 properties⁵ such as metal silyl $d\pi$ 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



ttp = 5, 10, 15, 20-tetratolylporphyrinato

ttmp = 5,10,15,20-tetramesitylporphyrinato

R' = Cl, Me or $\text{SiR}_1\text{R}_2\text{R}_3$

Figure 1. Structures of rhodium porphyrin complexes.

porphyrin phosphoryls. This approach is likely not amenable to prepare rhodium porphyrin silyls.

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 successfully¹ 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 $\text{Rh}(\text{ttp})\text{Cl}$ (**1**) (Figure 1) was reacted with HSiEt_3 (**2a**) (100 equiv, 0.6 M) in benzene at 100 °C for 1 day, $\text{Rh}(\text{ttp})\text{SiEt}_3$ (**2b**) was obtained with 52% yield (Table 1, entry 1). When the reaction temperature was increased to 200 °C, a lower yield of $\text{Rh}(\text{ttp})\text{SiEt}_3$ (**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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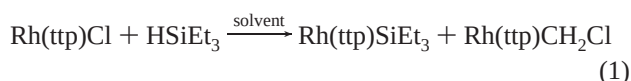
Table 1. Optimization of the Synthesis of Rh(ttp)SiEt₃, 2b

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)SiPh ₂ H, 8b (82)
14		Rh(tmp)I, 1c	1 h	Rh(tmp)SiPh ₂ H, 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 ⁱ BuMe ₂ , 13a	Rh(tmp)Cl, 1b	1 d	Rh(tmp)Si ⁱ BuMe ₂ , 13b (10)
25		Rh(tmp)I, 1c	1 d	Rh(tmp)Si ⁱ BuMe ₂ , 13b (7)

triflate is known to react with arenes via electrophilic aromatic substitution at lower temperature¹⁴ since no Rh(ttp)Ph was detected in the reaction mixture. When dichloromethane was used as the solvent, Rh(ttp)Cl reacted with HSiEt₃ (2a) (100 equiv, 0.6 M) at 100 °C for 2 days to give Rh(ttp)SiEt₃ (2b) and Rh(ttp)CH₂Cl (3). Both benzene and CH₂Cl₂ 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.



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.

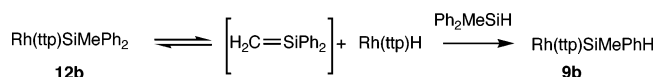


The yields of the products depended on the steric hindrance of silanes. The cone angles of silanes are identical with the cone angles of phosphines¹⁵ [Et₃SiH (132°), Pr₃SiH (132°), ⁱPr₃SiH (160°), SiH₂Ph₂ (128°), and HSiMe₂Ph (122°)]¹⁶ and have been used as a measure of steric hindrance. In general, more bulky silanes with larger cone angles reacted with slower rates and gave lower product yields. For example, the reactivity trend

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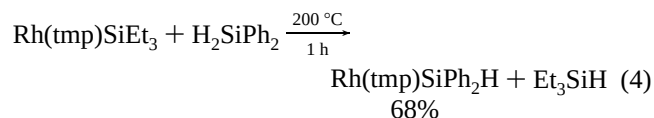
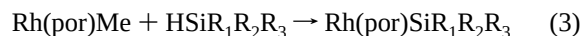
Scheme 1**Table 3. Si–H Activation of Silanes by Rh(por)Me**

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)

decreased with the increasing steric hindrance of silanes: HSiEt₃ (2a) > HSiⁱPr₃ (6a) > HSiⁱBuMe₂ (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 HSiPh₂Me (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)SiPh₂Me (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 HSiPh₂Me to give 9b. However, 9b did not react with HSiPh₂Me to give 12b at 200 °C in 2 days. Therefore, Rh(tmp)-SiPhMeH is thermodynamically more stable than Rh(tmp)-SiPh₂Me; presumably the latter is a secondary rather than a tertiary Rh-silyl complex. 12b remained stable in benzene in the absence of HSiPh₂Me, so a highly reactive intermediate likely formed from 12b and reacted rapidly with excess HSiPh₂Me to give 9b. We propose that 12b undergoes a β-hydride elimination to give Ph₂Si=CH₂ and Rh(tmp)H, which then reacts with HSiPh₂Me to give 9b (Scheme 1).

Besides rhodium porphyrin halides, rhodium porphyrin methyls reacted with silanes successfully to give rhodium porphyrin silyls with comparable yields and rates (eq 3, Table 3). The metathesis reactions appear to be general and applicable to Rh(tmp)SiEt₃. In a silyl exchange reaction, Rh(tmp)SiEt₃ (2c) reacted with H₂SiPh₂ (7a) at 200 °C in 1 h to give 68% of Rh(tmp)SiPh₂H (7b) and presumably also Et₃SiH (eq 4).¹⁷



X-ray Structure. The structures of Rh(tmp)SiPh₂Me (12b) and Rh(tmp)SiPhMe₂ (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)SiPh₂Me (12b) forms a square pyramidal geometry with the four porphyrinato nitrogen atoms

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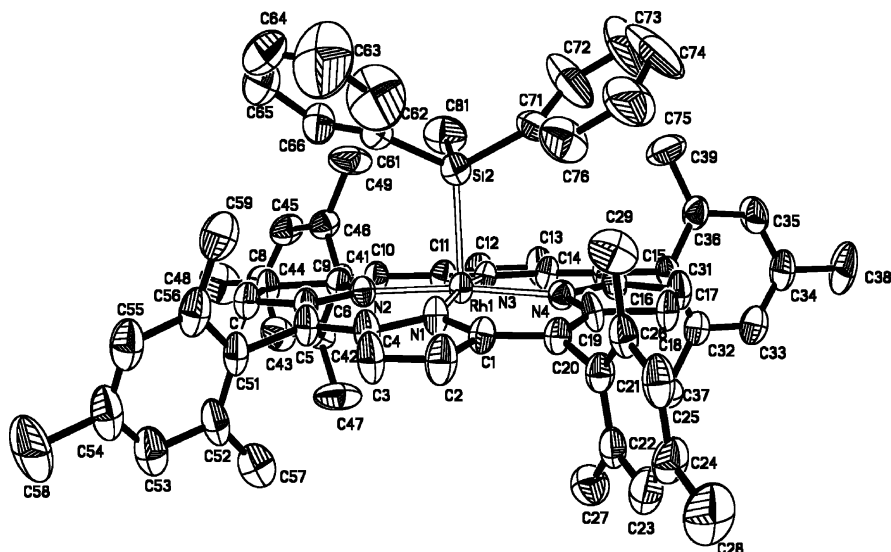


Figure 2. Molecular structure of Rh(tmp)SiPh₂Me, **12b**.

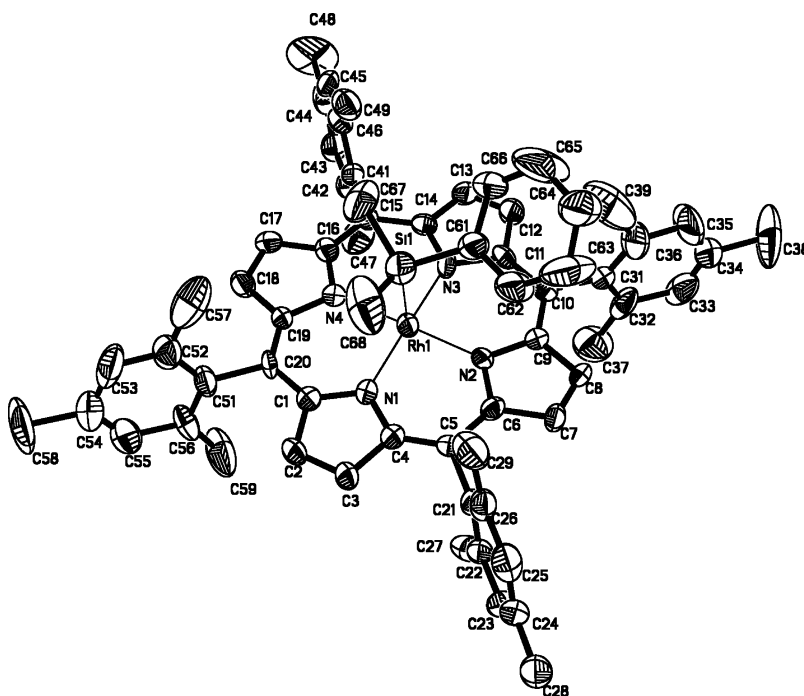


Figure 3. Molecular structure of Rh(tmp)SiPhMe₂, **11c**.

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)-SiMe₃ (Rh–Si = 2.305 Å)⁸ and Rh(oep)SiEt₃ (Rh–Si = 2.305

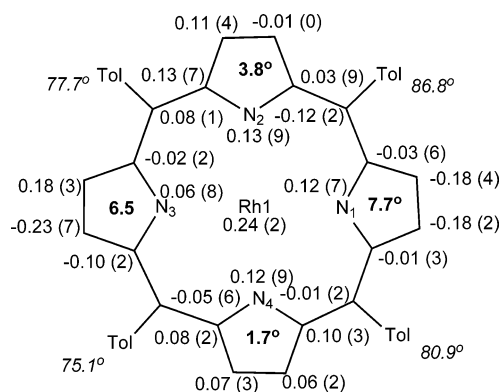


Figure 4. Displacement of the atoms of the Rh(tmp)SiPh₂Me (**12b**) porphyrin core.

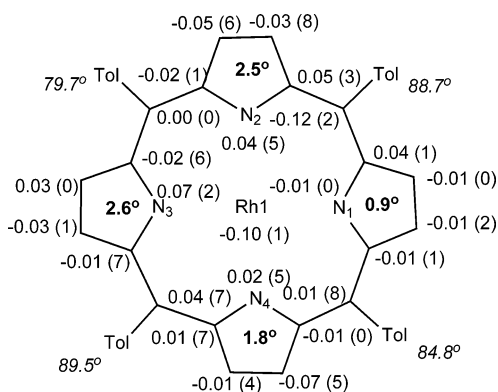


Figure 5. Displacement of the atoms of the Rh(tmp)SiPhMe₂ (**11c**) porphyrin core.

Table 4. Crystal Data for Rh(tmp)SiPhMe₂ (11c) and Rh(tmp)SiPh₂Me (12b)

	11c	12b
empirical formula	C ₆₄ H ₆₅ N ₄ RhSi	C ₆₉ H ₆₅ N ₄ RhSi
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 rflns 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 > 2σ(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)SiPh₂Me, 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)SiPhMe₂, 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(1)–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 C₁₂ (0.2371 Å), whereas N₂ 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 NC₄ pyrroles and the mean plane are 7.7°, 1.7°, 6.5°, and 3.8°, respectively.

The Rh–Si length of Rh(tmp)SiPhMe₂ (11c) is 2.438 Å and is longer than that of Rh(tpp)SiMe₃ (Rh–Si = 2.305 Å)⁸ and Rh(tmp)SiPh₂Me (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 NC₄ pyrrole rings are nearly planar. The largest deviation relative to the mean plane of the four pyrrole rings is at C₈ (0.0753 Å), whereas N₂ 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 NC₄ 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 ioniza-

tion 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(tpp)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(tpp)Ph in 21%. Even in a nonpolar solvent, ionization of Rh(por)Cl is still possible. Second, Rh(tpp)OTf²² (**1f**) is much more reactive than Rh(tpp)Cl toward Et₃SiH (Table 7). At 150 °C, Rh(tpp)Cl required 15 h to give Rh(tpp)SiEt₃ in 51% yield, while Rh(tpp)OTf only took 15 min to give a much higher yield of Rh(tpp)SiEt₃ at 78% (Table 7, entry 1 vs 3). A less coordinating OTf facilitates the formation of the Rh(tpp) 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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obtained. $R_f = 0.40$ (hexane/ $\text{CH}_2\text{Cl}_2 = 5:1$). ^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 $(\text{C}_{62}\text{H}_{67}\text{N}_4\text{O}_3\text{-SiRh})^+$ m/z 1046.4032; found m/z 1046.4046. Anal. Calcd for $\text{C}_{62}\text{H}_{67}\text{N}_4\text{O}_3\text{SiRh}$: 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)SiPr₃ (**5b**) (5.8 mg, 0.006 mmol, 51%) was obtained. $R_f = 0.47$ (hexane/ $\text{CH}_2\text{Cl}_2 = 5:1$). ^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 $(\text{C}_{65}\text{H}_{73}\text{N}_4\text{SiRh})^+$ m/z 1040.4654; found m/z 1040.4707. Anal. Calcd for $\text{C}_{65}\text{H}_{73}\text{N}_4\text{SiRh}$: 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)SiⁱPr₃ (**6b**) (1.8 mg, 0.002 mmol, 16%) was obtained. $R_f = 0.50$ (hexane/ $\text{CH}_2\text{Cl}_2 = 5:1$). ^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 $(\text{C}_{65}\text{H}_{73}\text{N}_4\text{SiRh})^+$ m/z 1041.4732; found m/z 1041.4786. Anal. Calcd for $\text{C}_{65}\text{H}_{73}\text{N}_4\text{SiRh}$: 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)SiPh₂H (**7b**) (7.3 mg, 0.0068 mmol, 62%) was obtained. $R_f = 0.27$ (hexane/ $\text{CH}_2\text{Cl}_2 = 5:1$). ^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 $(\text{C}_{68}\text{H}_{63}\text{N}_4\text{SiRh})^+$ m/z 1066.3872; found m/z 1066.3869. Anal. Calcd for $\text{C}_{68}\text{H}_{63}\text{N}_4\text{SiRh}$: 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)SiPhH₂ (**8b**) (8.9 mg, 0.009 mmol, 82%) was obtained. $R_f = 0.40$ (hexane/ $\text{CH}_2\text{Cl}_2 = 5:1$). ^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 $(\text{C}_{62}\text{H}_{59}\text{N}_4\text{SiRh})^+$ m/z 990.3506; found m/z 990.3559. Anal. Calcd for $\text{C}_{62}\text{H}_{59}\text{N}_4\text{SiRh}$: C, 75.13; H, 6.00; N, 5.65. Found: C, 74.63; H, 6.18; N, 5.17. IR (KBr, cm^{-1}): $\nu_{\text{Si-H}}$ 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/ $\text{CH}_2\text{Cl}_2 = 5:1$). ^1H

NMR (CDCl_3 , 300 MHz): δ -3.36 (d, 3 H, $J = 3.3$ Hz), -1.09 (d, 1 H, $^2J_{\text{Rh-H}} = 3$ Hz, $J_{\text{Si-H}} = 0.9$ 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 $(\text{C}_{63}\text{H}_{61}\text{N}_4\text{SiRh})^+$ m/z 1004.3715; found m/z 1004.3677. Anal. Calcd for $\text{C}_{63}\text{H}_{61}\text{N}_4\text{-SiRh}$: C, 75.28; H, 6.12; N, 5.57. Found: C, 74.75; H, 6.05; N, 5.50. IR (KBr, cm^{-1}): $\nu_{\text{Si-H}}$ 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)SiBnMe₂ (**10c**) (10.3 mg, 0.010 mmol, 91%) was obtained. $R_f = 0.30$ (hexane/ $\text{CH}_2\text{Cl}_2 = 5:1$). ^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 $(\text{C}_{65}\text{H}_{65}\text{N}_4\text{-SiRh})^+$ m/z 1032.4028; found m/z 1032.4022. Anal. Calcd for $\text{C}_{65}\text{H}_{65}\text{N}_4\text{SiRh}$: 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)SiPhMe₂ (**11c**) (6.2 mg, 0.006 mmol, 56%) was obtained. $R_f = 0.37$ (hexane/ $\text{CH}_2\text{Cl}_2 = 5:1$). ^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 $(\text{C}_{64}\text{H}_{63}\text{N}_4\text{SiRh})^+$ m/z 1018.3872; found m/z 1018.3903. Anal. Calcd for $\text{C}_{64}\text{H}_{63}\text{N}_4\text{-SiRh}$: 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)SiPh₂Me (**12b**) (2.8 mg, 0.003 mmol, 26%) was obtained with $R_f = 0.30$ (hexane/ $\text{CH}_2\text{Cl}_2 = 5:1$). ^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 $(\text{C}_{69}\text{H}_{65}\text{N}_4\text{SiRh})^+$ m/z 1080.4028; found m/z 1080.3979. Anal. Calcd for $\text{C}_{69}\text{H}_{65}\text{N}_4\text{SiRh}$: 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)I²⁷ 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)-SiEt₃ (**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(tp)*Si*(OEt)₃ (**4b**) (7.6 mg, 0.007 mmol, 74%) was obtained.

Reaction between [Rh(tp)I] (1c) and Tripropylsilane (5a). Tripropylsilane (0.5 mL) and Rh(tp)I (10 mg, 0.010 mmol) were heated at 200 °C for 2 days under N₂ in the absence of light. An orange solid of Rh(tp)*Si*Pr₃ (**5b**) (4.6 mg, 0.004 mmol, 45%) was obtained.

Reaction between [Rh(tp)I] (1c) and Triisopropylsilane (6a). Triisopropylsilane (0.5 mL) and Rh(tp)I (10 mg, 0.010 mmol) were heated at 200 °C for 2 days under N₂ in the absence of light. An orange solid of Rh(tp)*Si*iPr₃ (**6b**) (2.4 mg, 0.002 mmol, 23%) was obtained.

Reaction between [Rh(tp)I] (1c) and Diphenylsilane (7a). Diphenylsilane (0.5 mL) and Rh(tp)I (10 mg, 0.010 mmol) were heated at 200 °C for 1 h under N₂ in the absence of light. An orange solid of Rh(tp)*Si*Ph₂H (**7b**) (6 mg, 0.006 mmol, 56%) was obtained.

Reaction between [Rh(tp)I] (1c) and Phenylsilane (8a). Phenylsilane (0.5 mL) and Rh(tp)I (10 mg, 0.010 mmol) were heated at 200 °C for 1 h under N₂ in the absence of light. An orange solid of Rh(tp)*Si*PhH₂ (**8b**) (7.3 mg, 0.007 mmol, 75%) was obtained.

Reaction between [Rh(tp)I] (1c) and Phenylmethylsilane (9a). Phenylmethylsilane (0.5 mL) and Rh(tp)I (10 mg, 0.010 mmol) were heated at 200 °C for 3 h under N₂ in the absence of light. An orange solid of Rh(tp)*Si*PhMeH (**9b**) (6.5 mg, 0.006 mmol, 66%) was obtained.

Reaction between [Rh(tp)I] (1c) and Benzyltrimethylsilane (10a). Benzyltrimethylsilane (0.5 mL) and Rh(tp)I (10 mg, 0.010 mmol) were heated at 200 °C for 6 h under N₂ in the absence of light. An orange solid of Rh(tp)*Si*BnMe₂ (**10c**) (7.8 mg, 0.007 mmol, 77%) was obtained.

Reaction between [Rh(tp)I] (1c) and Dimethylphenylsilane (11a). Dimethylphenylsilane (0.5 mL) and Rh(tp)I (10 mg, 0.010 mmol) were heated at 200 °C for 1 day under N₂ in the absence of light. The suspension slowly became transparent upon heating, and a red solution was finally formed. An orange solid of Rh(tp)*Si*PhMe₂ (**11c**) (4.8 mg, 0.005 mmol, 48%) was obtained.

Reaction between [Rh(tp)SiPh₂Me] (12b) and Diphenylmethylsilane (12a). Rh(tp)*Si*Ph₂Me (3 mg, 0.003 mmol) and diphenylmethylsilane (0.5 mL) were heated at 200 °C for 2 days under N₂ in the absence of light. After removing **12a**, the reaction mixture was subjected to NMR, which suggested that **12b** had completely converted to Rh(tp)*Si*PhMeH (**9b**) (100% NMR yield).

Reaction between [Rh(tp)SiPhMeH] (9b) and Diphenylmethylsilane (12a). Rh(tp)*Si*PhMeH (**9b**) (3 mg, 0.003 mmol) and diphenylmethylsilane (**12a**) (0.5 mL) were heated at 200 °C for 3 days under N₂ in the absence of light. No Rh(tp)*Si*Ph₂Me (**12b**) signals were observed in the NMR spectrum.

Reaction of [Rh(tp)Cl] (1a) with Triethylsilane (2a). General Procedure. The reaction between triethylsilane and Rh(tp)Cl is described as a typical example. Triethylsilane (0.5 mL) was added to Rh(tp)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 N₂ in the absence of light. The crude product was purified by chromatography on silica gel eluting with hexane/CH₂Cl₂ (4:1) to hexane/CH₂Cl₂ (2:1). An orange solid of Rh(tp)*Si*Et₃ (**2b**) (8.9 mg, 0.010 mmol, 81%) was obtained.

Reaction between [Rh(tp)Cl] (1a) and Diphenylsilane (7a). Diphenylsilane (0.5 mL) and Rh(tp)Cl (10 mg, 0.012 mmol) were heated at 200 °C for 0.5 h under N₂ in the absence of light. An orange solid of Rh(tp)*Si*Ph₂H (**7c**) (8.5 mg, 0.009 mmol, 72%) was obtained. *R*_f = 0.53 (hexane/CH₂Cl₂ = 2:1). ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 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 (C₆₀H₄₇N₄SiRh)⁺ *m/z* 954.2620; found *m/z* 954.2650. Anal. Calcd for C₆₀H₄₇N₄SiRh: C, 75.46; H, 4.96; N, 5.86. Found: C, 75.69; H, 5.15; N, 5.56.

Reaction between [Rh(tp)Cl] (1a) and Benzyltrimethylsilane (10a). Benzyltrimethylsilane (0.5 mL) and Rh(tp)Cl (10 mg, 0.012 mmol) were heated at 200 °C for 1 h under N₂ in the absence of light. An orange solid of Rh(tp)*Si*BnMe₂ (**10b**) (10.0 mg, 0.011 mmol, 88%) was obtained. *R*_f = 0.62 (hexane/CH₂Cl₂ = 2:1). ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 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 (C₅₇H₄₉N₄SiRh)⁺ *m/z* 920.2776; found *m/z* 920.2708. Anal. Calcd for C₅₇H₄₉N₄SiRh: C, 74.33; H, 5.36; N, 6.08. Found: C, 73.78; H, 5.36; N, 5.96.

Reaction between [Rh(tp)Cl] (1a) and Dimethylphenylsilane (11a). Dimethylphenylsilane (0.5 mL) and Rh(tp)Cl (10 mg, 0.012 mmol) were heated at 200 °C for 1 h under N₂ in the absence of light. An orange solid of Rh(tp)*Si*PhMe₂ (**11b**) (10.2 mg, 0.011 mmol, 91%) was obtained. *R*_f = 0.58 (hexane/CH₂Cl₂ = 5:1). ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 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 (C₅₆H₄₇N₄SiRh)⁺ *m/z* 906.2620; found *m/z* 906.2600. Anal. Calcd for C₅₆H₄₇N₄SiRh: C, 74.16; H, 5.22; N, 6.17. Found: C, 73.86; H, 5.02; N, 6.13.

Reaction between [Rh(tp)Me] (1d) and Triethylsilane (2a). General Procedure. The reaction between triethylsilane and Rh(tp)Me²⁶ is described as a typical example. Triethylsilane (0.5 mL) was added to Rh(tp)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 N₂ in the absence of light. The crude product was purified by chromatography on silica gel eluting with hexane/CH₂Cl₂ (4:1) to hexane/CH₂Cl₂ (2:1). An orange solid of Rh(tp)*Si*Et₃ (**2b**) (9.9 mg, 0.011 mmol, 86%) was obtained.

Reaction between [Rh(tp)Me] (1d) and Triethoxysilane (4a). Triethoxysilane (0.5 mL) and Rh(tp)Me (10 mg, 0.013 mmol) were heated at 200 °C for 1 h under N₂ in the absence of light. An orange solid of Rh(tp)*Si*(OEt)₃ (**4c**) (10.4 mg, 0.011 mmol, 86%) was obtained. *R*_f = 0.52 (hexane/CH₂Cl₂ = 2:1). ¹H NMR (CDCl₃, 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). ¹³C NMR (CDCl₃, 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 (C₅₄H₅₁N₄O₃SiRh)⁺ *m/z* 934.2002; found *m/z* 934.2009. Anal. Calcd for C₅₄H₅₁N₄O₃SiRh: C, 69.37; H, 5.50; N, 5.99. Found: C, 69.35; H, 5.60; N, 5.95.

Reaction between [Rh(tp)Me] (1d) and Diphenylsilane (7a). Diphenylsilane (0.5 mL) and Rh(tp)Me (10 mg, 0.013 mmol) were heated at 200 °C for 0.5 h under N₂ in the absence of light. An orange solid of Rh(tp)*Si*Ph₂H (**7c**) (8.2 mg, 0.008 mmol, 67%) was obtained.

Reaction between [Rh(tp)Me] (1d) and Phenylmethylsilane (9a). Phenylmethylsilane (0.5 mL) and Rh(tp)Me (10 mg, 0.013 mmol) were heated at 200 °C for 3 h under N₂ in the absence of light. An orange solid of Rh(tp)*Si*PhMeH (**9c**) (7.7 mg, 0.0086 mmol, 68%) was obtained. *R*_f = 0.44 (hexane/CH₂Cl₂ = 2:1). ¹H NMR (CDCl₃, 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 $(\text{C}_{55}\text{H}_{45}\text{N}_4\text{SiRh})^+$ m/z 892.3718; found m/z 892.3702. Anal. Calcd for $\text{C}_{55}\text{H}_{45}\text{N}_4\text{SiRh}$: C, 73.98; H, 5.08; N, 6.27. Found: C, 73.87; H, 4.99; N, 5.81. IR (KBr, cm^{-1}): $\nu_{\text{Si-H}}$ 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)SiBnMe₂ (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)SiPhMe₂ (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)SiPh₂Me (12c) (9.4 mg, 0.0078 mmol, 78%) was obtained. $R_f = 0.56$ (hexane/ $\text{CH}_2\text{Cl}_2 = 2:1$). ^1H 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 $(\text{C}_{61}\text{H}_{49}\text{N}_4\text{SiRh})^+$ m/z 968.2776; found m/z 968.2768. Anal. Calcd for $\text{C}_{61}\text{H}_{49}\text{N}_4\text{SiRh}$: 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)Me²⁷ (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)SiEt₃ (2c) (4.9 mg, 0.0056 mmol, 56%) was produced.

Reaction between [Rh(tmp)Me] (1e) and Triethoxysilane (4a). Triethoxysilane (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)SiEt₃] (2c) and Diphenylsilane (7a). Rh(tmp)SiEt₃ (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)SiPh₂H (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/ $\text{CH}_2\text{Cl}_2 = 2:1$). ^1H 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 $(\text{C}_{54}\text{H}_{41}\text{N}_4\text{Rh})^+$ 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)SiEt₃ (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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