# Visible-Light-Promoted Generation of Hydrogen from the Hydrolysis of Silanes Catalyzed by Rhodium(III) Porphyrins

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S *Supporting Information*

ABSTRACT: Visible-light-promoted hydrolysis of silanes catalyzed by (TAP)Rh−I to produce silanols and dihydrogen efficiently under mild conditions was reported. (TAP)Rh−H was observed as the key intermediate through stoichiometric activation of the Si−H bond by (TAP)Rh−I. Addition of water drove the stoichiometric activation of Si−H into catalysis.
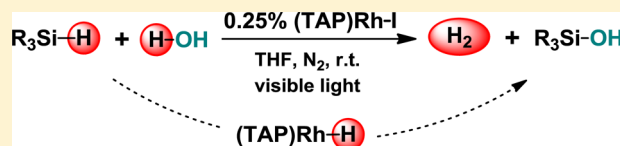
INTRODUCTION

Silanols are widely used as building blocks for silicon-based polymeric materials[1] as well as nucleophilic partners in organometallic cross-coupling reactions.[2] However, they are generally synthesized by hydrolysis of the corresponding chlorosilanes in a strictly controlled buffer solution[3] or oxidation of Si−H bonds in organosilanes using stoichiometric oxidants with the formation of vast amounts of environmentally damaging wastes.[4] To overcome these drawbacks, clean catalytic activation of hydrosilanes through Si−H bond cleavage to produce silyl ethers and silanols along with dihydrogen as the sole byproduct has been recently developed and the metal-catalyzed couplings of hydrosilanes with alcohols and water has been a highly active research field.[5,6] Rhodium porphyrins have a wide range of substrate reactions and have been reported to activate small molecules with inert chemical bonds.[7] The Chan group reported stoichiometric Si−H bond activation with formation of porphyrin rhodium silyl complexes at high temperature ((ttp)Rh−Cl + H−SiR$_3$ → (ttp)Rh−SiR$_3$ + HCl).[8] We previously reported catalytic hydroxylation of an unstrained, unactivated Si−C(sp^3) bond by combination of thermal and photochemical reactions mediated by rhodium porphyrins in water.[9] Therefore, we anticipate that catalytic hydrolysis of a more active and less sterically hindered Si−H bond in silanes also could occur through a similar pathway by using rhodium porphyrins as catalysts ((por)Rh^{III}L$_2$ + R$_3$Si−H → (por)Rh^{III}−H(L) + R$_3$Si−L, L = solvent or iodide ion). Herein, we report the visible-light-promoted catalytic hydrolysis of hydrosilanes with evolution of dihydrogen mediated by rhodium porphyrins under mild conditions. This system permits the direct observation of a porphyrin rhodium hydride as a key intermediate and determination of second-order kinetics for stoichiometric Si−H bond activation.

RESULTS AND DISCUSSION

5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin rhodium iodide ((TAP)Rh−I)) efficiently catalyzed hydrolysis of silanes to silanols with evolution of an equal amount of dihydrogen in

high yield and excellent selectivity under visible light irradiation (Table 1). Without addition of the catalyst, only trace amounts of dihydrogen were produced (Table 1, entry 1). When the reaction of dimethylphenylsilane and water was carried out in the dark, the yields of dihydrogen and silanol were moderate (Table 1, entry 2). However, the reaction rate increased significantly under irradiation by a 500 W mercury lamp equipped with a 420−780 nm filter (Table 1, entry 2 vs 5). Both aromatic and aliphatic silanes were efficiently converted to the corresponding silanols with evolution of an equal amount of H$_2$ in the presence of 10 equiv of water (Table 1, entries 5−9). Hydrolysis of methyldiphenylsilane required a longer reaction time due to its large steric hindrance (Table 1, entry 7). We further studied the effects of iodide and acid on this reaction. Addition of 1 equiv of n-Bu$_4$NI with respect to the catalyst resulted in a significant inhibition of reaction with the yield decreased to 50% in comparison to that of without additional iodide (>95%) (Table 1, entries 3 vs 5). Addition of 1 equiv of acid has no obvious effect on the yields (Table 1, entry 4 vs 5).

To better understand the reaction steps in the catalytic cycles, the stoichiometric Si−H bond activation was studied. Addition of 12.5 equiv of EtMe$_2$Si−H to a solution of (TAP)Rh^{III}−I in THF-d_8 under a nitrogen atmosphere at room temperature resulted in quantitative formation of (TAP)Rh−H instantly (eq 1). The doublet at −38.1 ppm
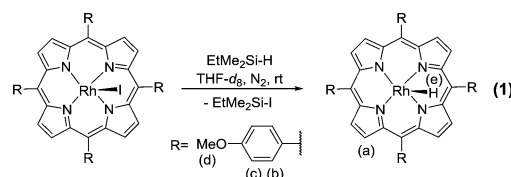
with $J_{Rh−H}$ = 31.7 Hz in the ^{1}H NMR spectrum was assigned to a typical porphyrin rhodium hydride complex, as confirmed by the 1:8 ratio of the integrals of Rh−H to pyrrole hydrogens of

A

**Table 1. Hydrolysis of Various Silanes Catalyzed by (TAP)Rh−I[f]**

Entry	Silane	Silanol	Time (h)	H_2 (%)	Yield (%)[a]	silanol: disiloxane[a]
1[b]	Ph(Me)(Me)Si−H	Ph(Me)(Me)Si−OH	1.5	4	-	-
2[c]	Ph(Me)(Me)Si−H	Ph(Me)(Me)Si−OH	1.5	40	48	>99:1
3[d]	Ph(Me)(Me)Si−H	Ph(Me)(Me)Si−OH	1.5	53	50	>99:1
4[e]	Ph(Me)(Me)Si−H	Ph(Me)(Me)Si−OH	1.5	92	95	96:4
5	Ph(Me)(Me)Si−H	Ph(Me)(Me)Si−OH	1.5	95	>95	97:3
6	Bn(Me)(Me)Si−H	Bn(Me)(Me)Si−OH	2.3	82	85	96:4
7	Ph(Ph)(Me)Si−H	Ph(Ph)(Me)Si−OH	6	74	85	>99:1
8	Et(Me)Si−H	Et(Me)Si−OH	1.2	78	79	98:2
9	Et(Et)(Et)Si−H	Et(Et)(Et)Si−OH	2.5	84	94	n.d.

[a]The yield and selectivity were determined by ^{1}H NMR, except for entry 9, which was determined by gas chromatography. [b]No catalyst. [c]In the dark. [d]1 equiv of n-Bu$_4$NI. [e]1 equiv of CF$_3$COOH. [f]Conditions: 30 °C, N$_2$, 500 W mercury lamp; entries 1, 2, and 5−9, (TAP)Rh−I (3.2×10^{-3} mmol), silanes (0.8 mmol), H$_2$O (8.0 mmol), 2 mL of THF; entries 3 and 4, (TAP)Rh−I (1.6×10^{-3} mmol), silanes (0.4 mmol), H$_2$O (4.0 mmol), 1 mL of THF. n.d. = not determined.

porphyrin (Figure 1). The observed chemical shift and Rh−H coupling constant were close to the values previously reported in (TSPP)Rh−H ($\delta_{Rh−H}$ −38 ppm, $J_{Rh−H}$ = 31 Hz in DMF-d_7; TSPP = tetrakis(p-sulfonatophenyl)porphyrin),[10a] consistent with the assumption of (TAP)Rh−H as the key intermediate in the Si−H bond activation.
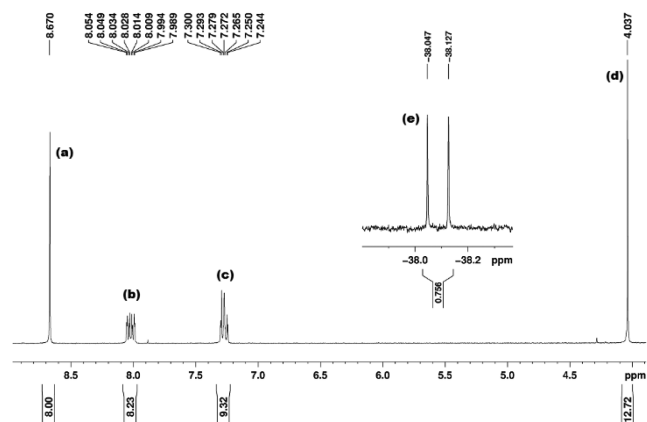
Figure 1. ^{1}H NMR spectra of (TAP)Rh−H in THF-d_8 (400 MHz).

To further study the pathway of Si−H bond activation, the kinetic experiments were carried out in dried THF-d_8 at 35 °C under an N$_2$ atmosphere. The reaction of Ph$_3$Si−H with (TAP)Rh−I with a moderate reaction rate was a good candidate to be conveniently monitored by the appearance of (TAP)Rh−H with the decreasing (TAP)Rh−I in ^{1}H NMR spectrum. The reaction rate exhibited first-order dependence on (TAP)Rh−I (Figure 2A,C), and the observed rate constant
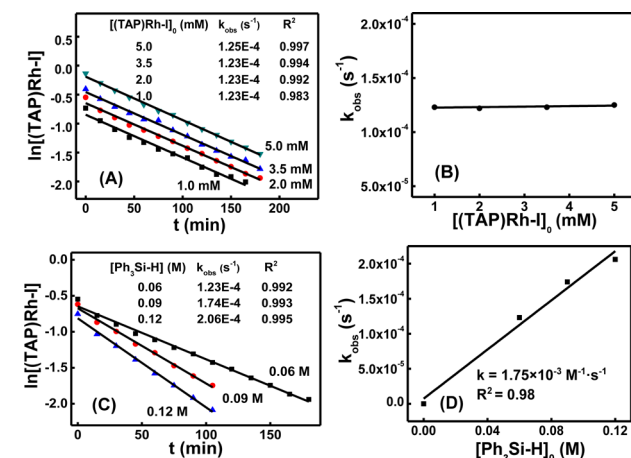
Figure 2. Kinetic study for stoichiometric Si−H bond activation. k_{obs} values were determined from the slopes of first-order rate plots on (TAP)Rh−I (A, C). Dependence of k_{obs} on the concentration of the initial concentration of (TAP)Rh−I (B) and Ph$_3$Si−H (D) at 308 K in 0.3 mL of dried THF-d_8. Conditions: (A) [(TAP)Rh−I]$_0$ = 1.0−5.0 mM, [Ph$_3$Si−H] = 0.06 M; (C) [(TAP)Rh−I]$_0$ = 2.0 mM, [Ph$_3$Si−H] = 0.06−0.12 M.

(k_{obs}) was independent of the initial concentration of (TAP)Rh−I, which further confirmed the first-order dependence on (TAP)Rh−I (Figure 2B). The observed rate constant (k_{obs}) versus the initial concentration of triphenylsilane showed a straight line passing through the origin (Figure 2D), indicating that Si−H activation is first order in the concentration of silane. The rate constant at 308 K was determined to be $k = 1.75 \times 10^{-3}$ M^{-1} s^{-1} (eq 2). Thus, stoichiometric activation of the Si−H bond showed first-order dependence on both (TAP)Rh−I and triphenylsilane. The rate law obtained by kinetic studies is given in eq 3.

$$k_{obs} = k[Ph_3Si−H] \tag{2}$$
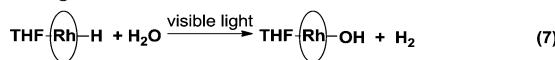
$$rate = k_{obs}[(TAP)Rh−I] \tag{3}$$

A stoichiometric mechanism of Si−H bond activation in the absence of water consistent with experimental results was envisioned through the following pathways in Scheme 1: (1) dissociation of coordinated iodide resulted in a coordinately unsaturated, highly electrophilic rhodium(III) center, which provided an opportunity for silane access to the metal center;

Scheme 1. Proposed Mechanism of Stoichiometric Si−H Bond Activation by (TAP)Rh−I in Tetrahydrofuran
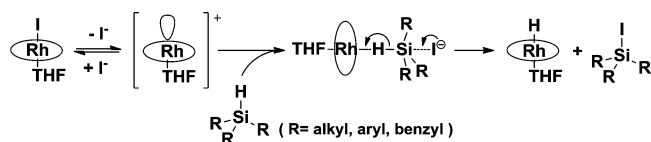
(2) assisted by the attack of dissociated iodide ion at silicon atom, the Si−H bond was cleaved heterolytically with formation of porphyrin rhodium hydride and R_3Si−I.

Porphyrin rhodium hydride complexes have been reported to accomplish various reactions with carbon monoxide, olefins, and aldehydes by the Wayland group.[7a,b,10] In these reactions, H_2 was generally pressurized in order to prevent the slow conversion of porphyrin rhodium hydride complexes into porphyrin rhodium radical and H_2. In addition, porphyrin rhodium(II) radicals have been reported to react with methanol or water to produce (por)Rh−H and (por)Rh-OCH_3 or (por)Rh−OH.[11,12] Moreover, the Bakac group has reported that UV photolysis of N_4-macrocyclic rhodium hydride complexes $(([14]aneN_4)RhH^{2+})$ resulted in the homolysis of the Rh−H bond, which could be followed by hydrogen atom abstraction from rhodium hydride complexes by hydrogen radical to yield H_2. The rate constant of subsequent hydrogen atom abstraction was estimated as $>3 \times 10^8$ M^{-1} s^{-1}.[13] In our system, the photolysis of (TAP)Rh−H in the presence of water under visible light irradiation led to homolytic cleavage of the Rh−H bond to form the (TAP)Rh^{II} radical and a H radical (eq 4). The resulting (TAP)Rh^{II} radical was converted to

$$\text{THF-Rh-H} \underset{\text{visible light}}{\overset{\text{visible light}}{\rightleftharpoons}} \overset{\bullet}{\text{Rh}} + \text{THF} + \text{H}^{\bullet} \quad (4)$$

$$2\,\overset{\bullet}{\text{Rh}} + 2\,\text{THF} + \text{H}_2\text{O} \rightleftharpoons \text{THF-Rh-H} + \text{THF-Rh-OH} \quad (5)$$

$$\text{THF-Rh-H} + \text{H}^{\bullet} \longrightarrow \overset{\bullet}{\text{Rh}} + \text{THF} + \text{H}_2 \quad (6)$$

$$\text{THF-Rh-H} + \text{H}_2\text{O} \overset{\text{visible light}}{\longrightarrow} \text{THF-Rh-OH} + \text{H}_2 \quad (7)$$
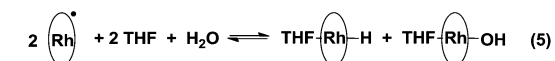
(TAP)Rh−H and (TAP)Rh−OH by reaction with water (eq 5). Subsequently, rapid hydrogen atom abstraction from (TAP)Rh−H by a H radical occurred with the production of (TAP)Rh^{II} and H_2 (eq 6). The overall reaction is that (TAP)Rh−OH and H_2 were formed through the photolysis of (TAP)Rh−H in the presence of water (eq 7). Irradiation of (TAP)Rh−H in anhydrous C_6D_6 led to the observation of $[(TAP)Rh]_2$ dimer and hydrogen, which supported the homolytic cleavage of the Rh−H bond under irradiation to regenerate catalyst. However, the regeneration of porphyrin rhodium(III) through heterolysis of Rh−H with acid could be ruled out due to the negligible effect of additional acid on the reaction yield (Table 1, entry 4 vs 5).

The rate enhancement was observed under visible light due to the photolysis of the Rh−H bond (Table 1, entries 2 and 3). Without addition of water, the mixture of (TAP)Rh−I and 9.8 equiv of $EtMe_2Si$−H in C_6D_6 was heated to 60 °C for 10 h; (TAP)Rh−$SiEtMe_2$ was observed in the yield of 76%, which was very similar to the results reported by Chan.[8] As we observed the instant formation of (TAP)Rh−H by mixing $EtMe_2Si$−H with a solution of (TAP)Rh−I, the porphyrin rhodium silyl compound must be produced by the reaction of (TAP)Rh−H with $EtMe_2Si$−H.[16] These results demonstrated that water played a critical role in regeneratng (TAP)Rh^{III} from the reaction intermediate (TAP)Rh−H and avoiding side reactions of (TAP)Rh−H.

In the catalytic cycle, coordinated unsaturated electrophilic porphyrin rhodium(III) is formed through dissociation of labile iodide ion (Scheme 2). Subsequently, assisted by the attack of highly nucleophilic water, the Si−H bond is cleaved heterolyti-

Scheme 2. Proposed Mechanism of Catalytic Hydrolysis of Silanes by Rhodium Porphyrin
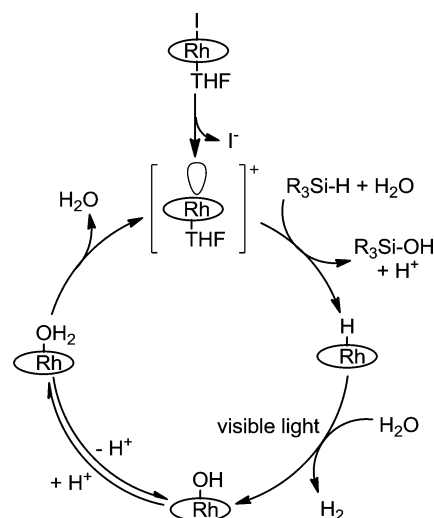
cally with formation of the corresponding silanol and porphyrin rhodium hydride, which converts to a porphyrin rhodium hydroxyl complex under visible light. (TAP)Rh−OH is protonated to give (TAP)Rh−OH_2. Dissociation of labile coordinated water regenerates the reactive catalyst species and completes the catalytic cycle.

■ CONCLUSIONS

In summary, visible-light-catalyzed hydrolysis of various silanes catalyzed by porphyrin rhodium produces the corresponding silanols and an equal amount of H_2 with high yields and excellent selectivity under mild conditions. The porphyrin rhodium hydride complex is directly observed, and kinetic studies of stoichiometric Si−H bond activation indicate that the reaction rate is first order in both porphyrin rhodium and silane. Addition of iodide ion has a significantly inhibitory effect on the catalytic reaction.[15] Addition of water provides a novel pathway for the conversion of the reaction intermediate which is significantly different from the stoichiometric Si−H bond activation reported by the Chan group to form porphyrin rhodium silyl complexes. The rapid Si−H bond activation by porphyrin rhodium we observed at room temperature provides a facile and general route to prepare porphyrin rhodium hydride, which has previously been a cumbersome process.

■ EXPERIMENTAL SECTION

General Information. All manipulations were performed under nitrogen. THF-d_8, C_6D_6 and $CDCl_3$ were obtained from Cambridge Isotope Laboratory Inc. THF was refluxed over sodium benzophenone until the indicator turned blue. $[Rh(CO)_2Cl]_2$ was purchased from Strem Chemical Inc., and other reagents were obtained from Sigma-Aldrich, Alfa Aesar, and Tokyo Chemical Industry (TCI) and used as received. ^1H NMR spectra were recorded on a Bruker Avance III400 or Bruker Avance III 500 MHz spectrometer at ambient temperature. Gas chromatography was performed on an Agilent 7890A GC instrument, and GC-MS was carried out on an Agilent 7890A/5975C GC/MSD instrument. IR spectra were recorded on a Nicolet Avatar 330 FT-IR spectrometer. A CEL-M500 mercury lamp was used for irradiation with a 420−780 nm filter. The synthesis of $TAPH_2$ was according to Adler's report.[14]

Synthesis of (TAP)Rh−I. A 21.0 mg portion (0.054 mmol) of $[RhCl(CO)_2]_2$ dissolved in 0.5 mL of chloroform was added dropwise into a two-neck flask through a syringe to a suspension containing 40.0

mg (0.054 mmol) of TAPH$_2$ and 45.0 mg (0.55 mmol) of anhydrous sodium acetate in 15 mL of chloroform under nitrogen. The resulting mixture was stirred at room temperature for 1 h. A 28.0 mg portion (0.11 mmol) of I$_2$ was dissolved in 2.0 mL of chloroform and added to the mixture in two stages: 1.0 mL initially and an additional 1.0 mL after 30 min. The reaction mixture was then stirred at room temperature for an additional 3 h. The crude product was concentrated by rotary evaporation after filtration to remove the inorganic salts and chromatographed on neutral alumina using 4/1 (v/v) dichloromethane/ethyl acetate as the eluent to give (TAP)Rh−I in an overall yield of 65%. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 4.08 (s, 12H; CH$_3$), 7.23−7.29 (m, 8H; *meta*-H), 8.07−8.15 (m, 8H; *ortho*-H), 8.89 (s, 8H; β-pyrrole H). ^{1}H NMR (400 MHz, THF-d_8) δ (ppm): 4.06 (s, 12H; CH$_3$), 7.27−7.33 (m, 8H; *meta*-H), 8.07−8.09 (m, 8H; *ortho*-H), 8.83 (s, 8H; β-pyrrole H).

Hydrolysis Reaction of Silanes. A 3.1 mg portion (3.2 × 10^{-3} mmol) of (TAP)Rh−I dissolved in 2.0 mL of THF was mixed with 144 μL (8.0 mmol) of water in a 10 mL two-neck flask with one neck attached to a gas buret filled with dibutyl phthalate. A 500 W mercury lamp was used for irradiation. Silanes (0.8 mmol) were added to the solution through a syringe, resulting in the immediate formation of dihydrogen. Concentrations of the residual silane and silanol production were measured by the ratio of the intensity integration of the ^{1}H NMR with respect to a known concentration of hexamethylbenzene as an internal standard. In the cases of Et$_3$Si−H and Et$_3$Si−OH, concentrations were measured by gas chromatography with a standard curve.

Hydrolysis Reaction of PhMe$_2$SiH with Additional Iodide or Acid. A 1.0 mL portion of a THF solution of (TAP)Rh−I (1.6 × 10^{-3} mmol) and 72 μL (4.0 mmol) of water were mixed in a 10 mL two-neck flask with one neck attached to a gas buret filled with dibutyl phthalate. A 10 μL portion of 0.16 M n-Bu$_4$NI THF solution or 3 μL of a 0.50 M THF solution of CF$_3$COOH was added before irradiation by a 500 W mercury lamp. A 64 μL portion of PhMe$_2$SiH (0.4 mmol) was added to the solution through a syringe. Concentrations of the residual silane and silanol produced were measured by the ratio of intensity integration of the ^{1}H NMR with respect to a known concentration of CH$_2$Br$_2$ as an internal standard.

Synthesis of (TAP)Rh−H. A 92 μL portion of 6.5 mM (6.0 × 10^{-4} mmol) (TAP)Rh−I chloroform solution was evaporated and then dissolved in 0.3 mL of THF-d_8 and mixed with 1.0 μL (7.6 × 10^{-3} mmol) of EtMe$_2$Si−H in a J. Young valve NMR tube to instantly produce an orange solution of stoichiometric (TAP)Rh−H. ^{1}H NMR (400 MHz, THF-d_8) δ (ppm): −38.09 (d, 1H, ^1J(Rh,H) = 31.7 Hz; Rh-H), 4.04 (s, 12H; CH$_3$), 7.25−7.30 (m, 8H; *meta*-H), 7.99−8.05 (m, 8H; *ortho*-H), 8.67 (s, 8H; β-pyrrole H).

Kinetic Studies. (TAP)Rh−I was mixed with 0.3 mL of dried THF-d_8 and Ph$_3$Si−H in a J. Young valve NMR tube. The reaction was monitored by ^{1}H NMR at 35 °C in the dark under nitrogen. Different initial concentrations of (TAP)Rh−I and Ph$_3$Si−H were used respectively to determine the order of the reaction.

Generation of [(TAP)Rh]$_2$. A 6.0 × 10^{-4} mmol portion of (TAP)Rh−H was dissolved in 0.3 mL of anhydrous C$_6$D$_6$ and irradiated for 1 h to generate [(TAP)Rh]$_2$. ^{1}H NMR (400 MHz, C$_6$D$_6$) δ (ppm): 3.61 (s, 24H; CH$_3$), 7.15 (*meta*-phenyl H obscured by solvent), 7.60 (d, 8H; ^3J(H,H)= 7.4 Hz; *ortho*-H), 8.69 (s, 16H; β-pyrrole H), 9.70 (d, 8H; ^3J(H,H) = 7.8 Hz; *ortho*-H).

Reactions of EtMe$_2$SiH and (TAP)Rh−I To Produce (TAP)Rh-SiEtMe$_2$. A 153 μL portion of 6.5 mM (1.0 × 10^{-3} mmol) (TAP)Rh−I chloroform solution was evaporated, and then the residue was dissolved in 0.4 mL of C$_6$D$_6$ and mixed with 1.3 μL (9.8 × 10^{-3} mmol) of EtMe$_2$Si−H in a J. Young valve NMR tube. The reaction mixture was heated at 60 °C for 10 h to form (TAP)Rh−SiEtMe$_2$ in a yield of 76%. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): −3.84 (s, 6H; methyl CH$_3$), −3.71 (q, 2H; ^3J(H,H) = 7.9 Hz; CH$_2$), −1.27 (t, 3H; ^3J(H,H) = 8.0 Hz; ethyl CH$_3$), 4.09 (s, 12H; OCH$_3$), 7.23−7.28 (m, 8H; *meta*-H), 7.98−8.10 (m, 8H; *ortho*-H), 8.67 (s, 8H; β-pyrrole H). HRMS (ESI): calcd for C$_{52}$H$_{48}$N$_4$O$_4$RhSi [M + H]$^+$ 923.25136; found 923.24944.

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Notes
The authors declare no competing financial interest.

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