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Visible Light Promoted Hydroxylation of a Si−C(sp^3) Bond Catalyzed by Rhodium Porphyrins in Water

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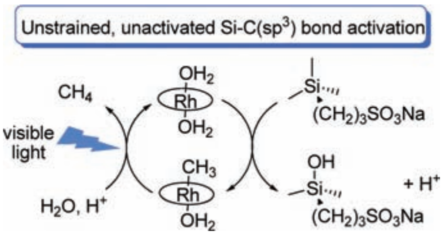
S *Supporting Information*

ABSTRACT: Catalytic activation of an unstrained, unactivated Si−C(sp^3) bond in water to form methane and silanol by electrophilic rhodium(III) porphyrin [(por)Rh^{III}] in acidic aqueous solutions under visible light ($\lambda \geq 420$ nm) has been developed. Activation of the Si−C(sp^3) bond occurs through direct Si−C bond cleavage, with methyl group transfer to rhodium to give a porphyrin rhodium methyl complex. Photolysis of (por)Rh-CH_3 in water yields methyl radical and (por)Rh^{II}. Subsequently, (por)Rh^{II} reacts with water rapidly to produce (por)Rh-H and (por)Rh-OH. (por)Rh-OH is then protonated to regenerate (por)Rh^{III}-OH_2, and (por)Rh-H undergoes hydrogen atom abstraction by methyl radical to form the observed methane.

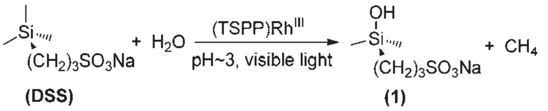
The Si−C bond activation catalyzed by transition metal complexes affords a novel route for selective functionalization of organosilanes. Si−C(sp^2) bond activation processes are often observed and well documented.[1] Although stoichiometric cleavages of unstrained Si−C(sp^3) bonds of transition metal organosilyl complexes through intramolecular[2,3] and intermolecular reactions[4] have been established, examples of catalytic cleavage of unstrained, unactivated Si−C(sp^3) bonds in the coordination sphere of a transition metal complex are quite rare.[5]

Rhodium(III) porphyrins undergo a wide range of substrate reactions in water[6] and have been reported to activate inert chemical bonds as electrophiles in organic solvents.[7] Herein, we report on an unprecedented catalytic hydroxylation of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (($(CH_3)_3Si(CH_2)_3SO_3Na$, DSS) mediated by tetra(*p*-sulfonatophenyl)porphyrin rhodium(III) ((TSPP)Rh^{III}) to yield sodium 3-(hydroxydimethylsilyl)propane-1-sulfonate ($HO\text{-}Si(CH_3)_2(CH_2)_3SO_3Na$) (**1**) and methane in acidic aqueous solutions under visible light. Stoichiometric Si−C(sp^3) bond activation of DSS occurs in the dark with formation of **1** and (TSPP)Rh-$CH_3(H_2O)$ (**2**), and photolysis of complex **2** in water completes the catalytic cycle (Scheme 1).

Scheme 1. Hydroxylation of DSS Catalyzed by (TSPP)Rh^{III}



Upon irradiation with visible light provided by a 500 W mercury lamp with a 420 nm UV-cutoff filter, acidic aqueous solutions containing (TSPP)Rh^{III} and DSS (150 equiv) were heated at 80 °C to form **1** and methane under anaerobic conditions (eq 1). The ^1H and ^{13}C NMR resonances of the methyl groups of **1** shifted to δ 0.14 and −1.12 ppm, respectively.[8,9] The ratios of the integrated intensity for the methyl groups of DSS and **1** in the ^1HNMR spectrum indicated 77% conversion of DSS after 12 h.[10] ESI-MS of **1** in water gave a peak at m/z = 197.03136, corresponding to the anion $HO\text{-}Si(CH_3)_2(CH_2)_3SO_3^-$. In addition, CH_4 was identified by gas-phase IR spectroscopy, and CH_3D was detected when the reaction was carried out in D_2O.[11]



(1)

To better understand the reaction steps in the catalytic cycles, the stoichiometric Si−C activation was studied. When an acidic solution of DSS and (TSPP)Rh^{III} was heated in the dark, equal amounts of **1** and **2** were formed through transfer of a methyl group from silicon to rhodium (eq 2). The methyl group of **2** exhibited the same ^1H NMR signal as that of an independently synthesized sample [$\delta(Rh{-}CH_3) = -6.60$ ppm, $^2J(Rh{-}CH) = 2.4$ Hz in DMSO-d_6; $\delta(Rh{-}CH_3) = -6.59$ ppm, $^2J(Rh{-}CH) = 2.4$ Hz in CD_3OD].[12] ESI-MS of **2** in water gave an envelope of peaks at m/z = 261.48951 and 356.31778, corresponding to $[(TSPP)Rh\text{-}CH_3]^{4-}$ and $[(TSPP)Rh\text{-}CH_3]Na^{3-}$, respectively.

$$[(TSPP)Rh(H_2O)_2]^{3-} + (CH_3)_3SiR \rightarrow \underset{(\mathbf{2})}{[(TSPP)Rh\text{-}CH_3(H_2O)]^{4-}} + \underset{(\mathbf{1})}{HO\text{-}Si(CH_3)_2R} + H^+$$
$$(R = (CH_2)_3SO_3Na) \qquad (2)$$

$$\text{rate} = k_{obs}[(TSPP)Rh^{III}(H_2O)_2] \qquad (3)$$

$$k_{obs} = k[DSS] \qquad (4)$$

The progress of reaction 2 was conveniently followed by monitoring the appearance of **1** and **2** with decreasing (TSPP)-Rh^{III} by ^1H NMR with at least 30-fold excess of DSS. The reaction

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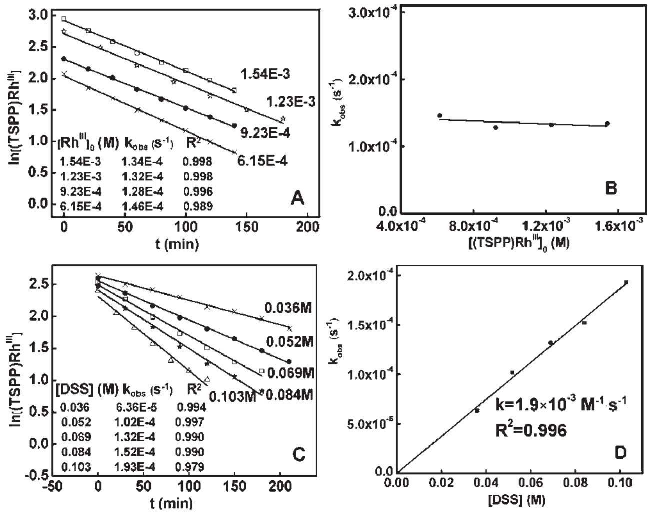
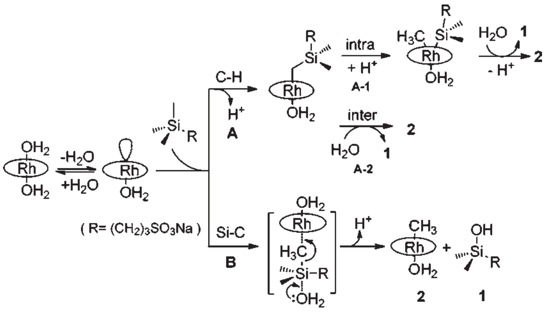


Figure 1. Values of the observed rate constant, k_{obs}, were determined from the slopes of first-order rate plots on $(TSPP)Rh^{III}$ (A,C). Dependence of k_{obs} on the concentration of initial concentration of $(TSPP)Rh^{III}$ (B) and DSS (D) at 353 K and pH 3. Conditions: (A) $[(TSPP)Rh^{III}]_0$ = 1.5 mM to 0.62 mM, [DSS] = 0.069 M; (C) $[(TSPP)Rh^{III}]_0$ = 1.2 mM, [DSS] = 0.036−0.103 M.

Scheme 2. Proposed Mechanism of Si−C Bond Cleavage by $(TSPP)Rh^{III}$



rate exhibited first-order dependence on $(TSPP)Rh^{III}(H_2O)_2$ (Figure 1A,C). The observed rate constant, k_{obs}, was independent of the initial concentration of $(TSPP)Rh^{III}(H_2O)_2$ (Figure 1B). The rate law obtained by kinetic studies is shown in eq 3. Evaluating the rate constant for reaction 2 at 353 K and pH 3 with different concentration of DSS in D_2O gave the rate constant $k = 1.9 \times 10^{-3}\ M^{-1} \cdot s^{-1}$ (Figure 1D), in accord with eq 4. Therefore, stoichiometric cleavage of the Si−C bond shows first-order dependence on both $(TSPP)Rh^{III}(H_2O)_2$ and DSS.

Rhodium(III) porphyrins have been reported to activate sp^3 and sp^2 C−H bonds,[13] and Si−C bond cleavage involving an initial C−H activation pathway has been previously reported. The organometallic intermediate ($L_nM-CH_2SiMe_3$) in the Si−C bond reaction subsequently undergoes intramolecular rearrangement[2b,e] or intermolecular nucleophilic attack[5a] to cleave Si−C bonds. To assess whether the observed Si−C bond cleavage of DSS occurred via prior C−H activation, the C−H activation intermediate of $Si(CH_3)_4$ by (TSPP)Rh(III), (TSPP)Rh-$CH_2SiMe_3(H_2O)$ (**3**), was independently synthesized.[14] When the acidic solution of complex **3** was heated at 80 °C in the dark for 52 h, 7% of **3** was converted to $(TSPP)Rh^{III}$, with formation of trace amounts of trimethylsilanol[15] and methanediol.[16] Thus, if reaction 2 occurred through the initial C−H bond activation (Scheme 2, path A), the analogous intermediate of complex **3** would have been detected in the ^{1}H NMR spectrum. Moreover, intramolecular rearrangement of complex **3** would occur through a crowded seven-coordinated Rh(IV) complex, an unusually high-energy intermediate, by α-migration of the trimethylsilyl group from carbon to rhodium (Scheme 2, path A-1). Additionally, concerted hydrolysis of complex **3** by water would produce silanol and **2** (Scheme 2, path A-2), which was inconsistent with results of thermolysis of complex **3**. The exclusive formation of **2** in the stoichiometric reaction of $(TSPP)Rh^{III}$ with DSS and the thermal stability of complex **3** rule out pathways involving C−H bond activation prior to Si−C bond cleavage.

A mechanism consistent with experimental results is proposed which involves a direct Si−C cleavage of DSS to transfer a methyl group to (TSPP)Rh(III) (Scheme 2, path B). (TSPP)-$Rh^{III}(OH_2)_2$ is a dominant species at pH ∼3, so the labile coordinated water molecules provide access to a coordinately unsaturated, highly electrophilic Rh(III) center. Assisted by the attack of water at the electropositive silicon atom of DSS, the Si−C bond cleaves heterolytically, and the methyl group is transferred to (TSPP)Rh(III) simultaneously to produce **1** and **2**. Thus, activation of the Si−C bond is thermodynamically driven by the formation of a very strong Si−O bond in the concerted process.[17]

Rhodium porphyrins accomplish a remarkable scope of selective activation of C−H[18] and C−C[19] bonds of organic molecules to form organo-rhodium porphyrin complexes. However, the resulting Rh−C bonds have high kinetic stability, which inhibits further applications in catalytic transformations. Photolysis (>350 nm) of porphyrin rhodium methyl complexes in benzene is a common method to generate porphyrin rhodium(II) metalloradicals. Interestingly, we observed that irradiation of an acidic aqueous solution of complex **2** with visible light (>420 nm) at ambient temperature resulted in the production of methane and $(TSPP)Rh^{III}(H_2O)_2$. Analogous results were also obtained for photolysis of (TSPP)Rh-$CH_2C_6H_5(H_2O)$ (**4**) to form toluene (eq 5). In the presence of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), TEMPO-$CH_2C_6H_5$ was observed, which indicated formation of a $C_6H_5CH_2$ radical in the photolysis process. $(TSPP)Rh^{III}(H_2O)_2$ was identified as the only product of (TSPP)Rh species in the photolysis process.

$$[(TSPP)Rh\text{-}R(H_2O)]^{4-} + H_2O + H^+ \xrightarrow{\text{visible light}} [(TSPP)Rh^{III}(H_2O)_2]^{3-} + R\text{-}H \quad (R = CH_3,\ CH_2C_6H_5) \qquad (5)$$

These observations suggest that photolysis of (TSPP)Rh-CH_3 in water with visible light leads to homolysis of the Rh−C bond to form $(TSPP)Rh^{II}$ and a CH_3 radical. $(TSPP)Rh^{II}$ reacts with water thermally to give $(TSPP)Rh^{III}$-OH and (TSPP)Rh-H.[12,20] Subsequently, (TSPP)Rh-H reacts with methyl radical readily to yield $(TSPP)Rh^{II}$ and methane, which accounts for the absence of (TSPP)Rh-H, and thus $(TSPP)Rh^{III}$-OH accumulates (eqs 6−8). The overall reaction is that (TSPP)Rh and a methyl group formally seize OH and H atoms from water, respectively, to form (TSPP)Rh-OH and methane (eq 9). $(TSPP)Rh^{III}$-OH is rapidly protonated to form (TSPP)Rh^{III}-OH_2 (eq 10).[21]

$$[Rh\text{-}CH_3]^{4-} \xrightleftharpoons{\text{visible light}} [Rh^{II}\bullet]^{4-} + \bullet CH_3 \tag{6}$$

$$2[Rh^{II}\bullet]^{4-} + H_2O \rightleftharpoons [Rh^{III}\text{-}OH]^{4-} + [Rh\text{-}H]^{4-} \tag{7}$$

$$[Rh\text{-}H]^{4-} + \bullet CH_3 \rightarrow [Rh^{II}\bullet]^{4-} + CH_4 \tag{8}$$

$$[Rh\text{-}CH_3]^{4-} + H_2O \xrightarrow{\text{visible light}} [Rh^{III}\text{-}OH]^{4-} + CH_4 \tag{9}$$

$$[Rh^{III}\text{-}OH]^{4-} + H^+ \rightarrow [Rh^{III}\text{-}OH_2]^{3-} \tag{10}$$

Studies of individual steps in the catalytic hydroxylation of DSS appear to be most consistent with the mechanism described in Scheme 1. The facile dissociation of H_2O from (TSPP)Rh-$(H_2O)_2$ in acidic solutions provides an opportunity for substrate access to the metal center. The formation of a Si−OH bond produces a favorable energy term and drives the cleavage of the Si−C bond, and the catalyst is regenerated by photolysis of the resulting (TSPP)Rh-CH_3 in acidic solutions with evolution of methane.

In summary, we have described a novel route to catalyze the functionalization of Si−C bonds in water. To the best of our knowledge, this is the first catalytic activation of an unstrained, unactivated Si−C(sp^3) bond in water by transition metal complexes.[22] This reaction proceeds through the direct cleavage of Si−C bond by electrophilic (TSPP)Rh^{III}, and the irradiation of (TSPP)Rh-CH_3 with visible light in water recovers the catalyst. This first Si−C(sp^3) bond activation by rhodium porphyrins reported in this article not only expands the scope of organometallic transformations of metalloporphyrins but also provides new insight into incorporation of valuable organometallic intermediates of organo-rhodium porphyrin complexes into novel catalytic transformations. Specifically, the unusual direct Si−C bond cleavage in water affords a novel strategy and synthetic tools to accomplish challenging catalytic reactions of new processes.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) For $Rh-CH_3$, Rh-H, $Rh^{II}\bullet$, Rh-OH, and $Rh-OH_2$, a coordinated water is omitted for clarity.

(22) Platinum complex catalyzes the reaction of TMS with CF_3CH_2OH to give $Me_3Si-OCH_2CF_3$ and methane, and it is the first example of a catalytic Si−C bond cleavage mediated by a transition metal complex in alcohol. See ref 5a.