

Highly Efficient Generation of Hydrogen from the Hydrolysis of Silanes Catalyzed by $[\text{RhCl}(\text{CO})_2]_2$

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Supporting Information

ABSTRACT: Catalytic hydrolysis of silanes mediated by chlorodicarbonylrhodium(I) dimer $[\text{RhCl}(\text{CO})_2]_2$ to produce silanols and dihydrogen efficiently under mild conditions is reported. Second-order kinetics and activation parameters are determined by monitoring the rate of dihydrogen evolution. The mixing of $[\text{RhCl}(\text{CO})_2]_2$ and HSiCl_3 results in rapid formation of a rhodium silane σ complex.

Silanols are widely used as key synthons for silicon-based polymers¹ and nucleophilic partners in metal-catalyzed cross-coupling reactions.² Silanols are generally synthesized by (1) hydrolysis of corresponding chlorosilanes in a strictly controlled pH buffer solution³ and (2) oxidation of Si–H bonds in organosilanes using stoichiometric oxidants producing vast amounts of environmentally damaging wastes.⁴ Clean catalytic activation of hydrosilanes through Si–H bond cleavage to produce silanols along with dihydrogen (H_2) as the sole byproduct is an attractive alternative method. Alcoholysis of silanes catalyzed by transition-metal complexes has been extensively studied;⁵ however, only a limited number of transition-metal complexes,⁶ as well as heterogeneous systems,⁷ have been reported to catalyze hydrolysis of silanes with the simultaneous evolution of H_2 . Abu-Omar et al. reported the production of H_2 from hydrolysis of silanes mediated by cationic oxorhenium(V) complexes with modest turnover number (TON) under mild conditions.^{6c} Fan's group developed an efficient system with higher TONs using dimeric ruthenium(II) complexes as catalysts.^{6f} However, mechanistic studies on transition-metal-complex-mediated catalytic hydrolysis of silanes remain scarce.^{8,9} In this Communication, we report that the commercially available rhodium(I) complex $[\text{RhCl}(\text{CO})_2]_2$ efficiently catalyzes hydrolysis of silanes to silanols with production of an equal amount of H_2 at room temperature. This system permits direct observation of a rhodium silane σ complex and determination of second-order kinetics and activation parameters.

The complex $[\text{RhCl}(\text{CO})_2]_2$ efficiently catalyzed hydrolysis of silanes to silanols with evolution of H_2 in high yield and excellent selectivity under mild conditions (Table 1). Without the addition of water, only trace amounts of H_2 were produced in anhydrous THF (entry 1). Both aliphatic and aromatic silanes were effectively converted to the corresponding silanols in the presence of 10 equiv of water (entries 2–7). Hydrolysis of the bulkier silanes required longer reaction time (entries 3 and 6).

Table 1. Hydrolysis of Various Silanes Catalyzed by $[\text{RhCl}(\text{CO})_2]_2$ ^d

Entry	Silane	Silanol	Time (min)	H_2 (%)	Yield (%) ^a	silanol: disiloxane ^a
1 ^b			6	5	-	-
2			8	99	>99	>99:1
3			10	99	98	>99:1
4			6	99	95	>99:1
5			6	96	91	>99:1
6			40	96	96	98:2
7			25	95	93	n.d.
8 ^c			6	99	95	>99:1

^aThe conversions were determined by isolated yield except entries 2 and 3, which were determined by gas chromatography. ^bWithout the addition of water. ^cThe addition of excess mercury (0.48 mmol). n.d. = not determined. ^dConditions: silanes, 0.8 mmol; H_2O , 8 mmol; $[\text{RhCl}(\text{CO})_2]_2$, 0.0016 mmol; room temperature, $25 \pm 1^\circ\text{C}$; N_2 , 2 mL of THF.

Diphenylsilane was also quantitatively transformed into diphenylsilanediol (entry 7). A mercury poisoning experiment was performed¹⁰ and was found to have no effect on the rate of reaction, which demonstrated that this system was a homogeneous catalyst (entry 8).

Although silane σ complexes were observed previously,¹¹ direct observation of this key intermediate in catalytic hydrolysis

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of silanes is rare.^{9c} Nikonov's group reported that $[\text{Cp}(\text{P}^i\text{Pr}_3)(\text{NCMe})\text{Ru}(\eta^2\text{-HSiCl}_3)]^+$ and $[\text{Cp}(\text{P}^i\text{Pr}_3)(\text{NCMe})\text{Ru}(\eta^2\text{-HSiMeCl}_2)]^+$ were remarkably more stable than other silanes with alkyl substitutions.^{9c} So, HSiCl_3 was used to react with $[\text{RhCl}(\text{CO})_2]_2$ to observe the possible intermediate. A variable-temperature ^1H NMR technique was used to follow the reaction. The mixing of $[\text{RhCl}(\text{CO})_2]_2$ and HSiCl_3 resulted in rapid formation of a rhodium(I) silane σ complex at 288 K, which showed a broad resonance at -8.15 ppm due to fast exchange between coordinated and free HSiCl_3 on the NMR time scale. When the temperature was decreased to 248 K, the static spectrum showed a doublet at -8.26 ppm ($J_{\text{Rh-H}} = 13$ Hz), which was broadened at elevated temperature and eventually coalesced to one broad peak again at 293 K. Additionally, the Si–H coupling constant was measured from the ^{29}Si satellites ($^1J_{\text{Si-H}} = 49$ Hz) in the ^1H NMR spectra (Figure 1). The observed Si–H

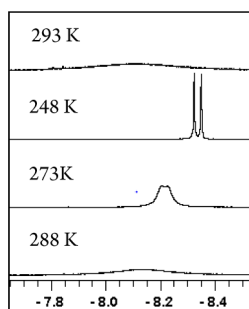


Figure 1. Variable-temperature ^1H NMR of rhodium silane σ complexes.

coupling constant¹² was much larger than 20 Hz, proposed to be the boundary value for classical silyl hydride metal complexes,¹³ and close to the $^1J_{\text{Si-H}}$ values observed in the silane σ complexes (53 Hz for $[\text{Cp}(\text{P}^i\text{Pr}_3)(\text{NCMe})\text{Ru}(\eta^2\text{-HSiCl}_3)]^+$; ^{9c} 54.8 Hz for $\text{Cp}'(\text{CO})_2\text{Mn}(\eta^2\text{-HSiCl}_3)$; ¹⁴ 48 Hz for $[\text{Cp}(\text{PMe}_3)_2\text{Ru}(\eta^2\text{-HSiCl}_3)]^+$ ¹⁵) and thus in good agreement with the σ -coordinated compound $(\text{CO})_2\text{ClRh}(\eta^2\text{-HSiCl}_3)$.

For a further understanding of the pathway of Si–H bond hydrolysis, the kinetic studies of hydrolysis of MePh_2SiH were performed by following H_2 evolution using a Hidden Analytic HPR20 mass spectrometer for at least 3 half-lives. The pseudo-first-order rate on silane was observed with at least 16-fold excess water over silane (eq 1). The observed rate constants k_{obs} , independent of the initial concentration of silane, firmly established first-order dependence on silane (Figure 2A,B). Variation in $[\text{H}_2\text{O}]$ had no influence on the observed rate constant (Figure 2C,D). The plot of k_{obs} versus the concentration of the catalyst yielded a straight line that passed through the origin (Figure 2E,F), in accordance with eq 2. All of these kinetic studies indicated that the reaction of water and MePh_2SiH mediated by $[\text{RhCl}(\text{CO})_2]_2$ was first-order on both silane and catalyst. Also, the lack of a rate dependence on water suggested that the reaction step involving water might occur after the rate-determining step. In an investigation of the kinetic isotope effect by comparing the k_{H} and k_{D} of MePh_2SiH and MePh_2SiD , m/z 2–4 values were observed corresponding to the formation of H_2 , HD, and D_2 (Figure 1S in the Supporting Information, SI). It was also difficult to determine the kinetic isotope effect by following the consumption of MePh_2SiH and MePh_2SiD , respectively, in ^1H NMR because of the rapid conversion of MePh_2SiD to MePh_2SiH . Evaluation of the activation parameters by measuring k over the temperature 279–299 K yielded $\Delta H^\ddagger = 42.6 \pm 2.4$ kJ

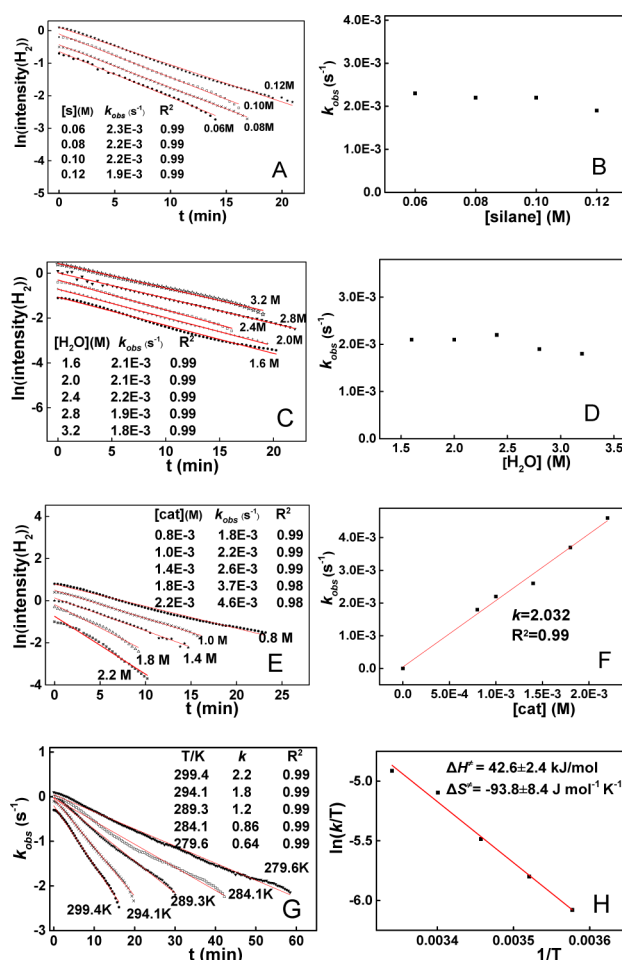


Figure 2. Kinetic studies of hydrolysis of MePh_2SiH catalyzed by $[\text{RhCl}(\text{CO})_2]_2$. Conditions: (A) $c(\text{H}_2\text{O}) = 2.4$ M and $c([\text{RhCl}(\text{CO})_2]_2) = 1.0$ mM; (C) $c(\text{silane}) = 0.1$ M and $c([\text{RhCl}(\text{CO})_2]_2) = 1.0$ mM; (E) $c(\text{H}_2\text{O}) = 2.4$ M and $c(\text{silane}) = 0.1$ M; (G) $c(\text{H}_2\text{O}) = 2.4$ M, $c(\text{silane}) = 0.1$ M, and $c([\text{RhCl}(\text{CO})_2]_2) = 1.0$ mM.

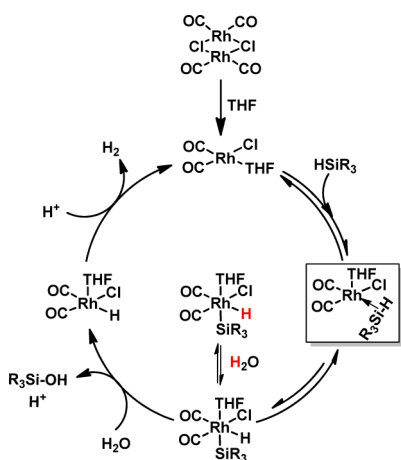
mol^{-1} , $\Delta S^\ddagger = -93.8 \pm 8.4$ J mol^{-1} K^{-1} , and $\Delta G^\ddagger(298 \text{ K}) = 70.6$ kJ mol^{-1} for hydrolysis of MePh_2SiH (Figure 2G,H). The activation parameters were close to the values reported for hydrolysis of Et_3SiH by oxorhenium(V) complexes in which Si–H bond activation was suggested as the rate-determining step ($\Delta H^\ddagger = 32.4$ kJ mol^{-1} ; $\Delta S^\ddagger = -148$ J mol^{-1} K^{-1}).⁸

$$\text{rate} = \frac{d[\text{H}_2]}{dt} = k_{\text{obs}}[\text{silane}] \quad (1)$$

$$k_{\text{obs}} = k[\text{catalyst}] \quad (2)$$

A mechanism consistent with the experimental results is proposed in Scheme 1. The first step involves dissociation of a dinuclear complex into monomer $\text{RhCl}(\text{CO})_2$, which is stabilized by coordination of THF. Subsequently, a silane σ complex is formed by coordination of silane to the rhodium center, which undergoes an oxidative addition reaction to give a $(\text{THF})(\text{CO})_2\text{ClRhH}(\text{silyl})$ complex. The lack of kinetic isotope effects is due to H/D exchange of $(\text{THF})(\text{CO})_2\text{ClRhH}(\text{silyl})$ with water and rapid equilibrium between $(\text{THF})(\text{CO})_2\text{ClRh}$, silane, and $(\text{THF})(\text{CO})_2\text{ClRhD}(\text{silyl})$. Then water attacks the coordinated silyl group to give silanol and $(\text{THF})(\text{CO})_2\text{RhH}$, which is driven by formation of a strong Si–O bond. The rhodium hydride species releases H_2 and regenerates the catalyst

Scheme 1. Proposed Pathway for Hydrolysis of Silanes Catalyzed by $[\text{RhCl}(\text{CO})_2]_2$



(Figure 4S in the SI). The second-order kinetics and large negative value of $\Delta S^\ddagger$ indicate that the bimolecular reaction of $(\text{THF})\text{RhCl}(\text{CO})_2$ with silane to form $(\text{THF})(\text{CO})_2\text{ClRhH}$ (silyl) might be the rate-determining step in the catalytic cycle.

An alternate pathway has been proposed for alcoholysis of silanes by Crabtree's group in which $[\text{Et}_3\text{SiOHMe}]^+$ was formed and the step of formation of final products was supposed to be the rate-determining step.¹⁶ In our system, if the analogous $[\text{H}_2\text{OR}_3\text{Si}]^+$ was formed through internal water attack, it should exhibit a first-order dependence on water, which was inconsistent with our observation of zero order on water. Moreover, the bonded-water intramolecular attack of η^2 -silane disagreed with the observed large negative value of the activation entropy. So, the pathway involving formation of $[\text{H}_2\text{OR}_3\text{Si}]^+$ could be ruled out.

In summary, hydrolysis of various silanes catalyzed by a rhodium(I) complex gives silanols and H_2 with high yield and excellent selectivity under mild conditions employing water as the oxygen source. A rhodium silane σ -complex intermediate is directly observed. Kinetic studies indicate first-order dependence on both silane and catalyst. Catalytic hydrolysis of silanes by $[\text{RhCl}(\text{CO})_2]_2$ provides new insight into incorporation of the analogous transition-metal silane σ complex into catalytic hydrolysis of silanes.

■ ASSOCIATED CONTENT

Supporting Information

Listing of the typical procedures for catalytic hydrolysis of silanes and kinetic studies of catalytic hydrolysis of MePh_2SiH mediated by $[\text{RhCl}(\text{CO})_2]_2$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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