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Communication

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

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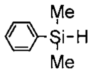
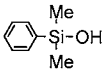
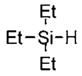
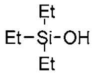
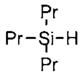
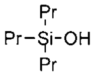
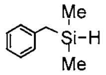
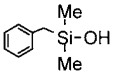
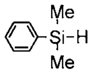
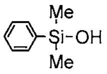
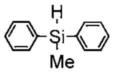
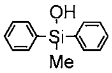
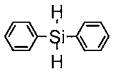
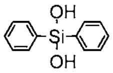
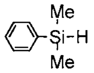
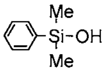
Supporting Information

ABSTRACT: Catalytic hydrolysis of silanes mediated by chlorodicarbonylrhodium(I) dimer $[RhCl(CO)_2]_2$ 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 $[RhCl(CO)_2]_2$ and $HSiCl_3$ results in rapid formation of a rhodium silane σ complex.

Silanols are widely used as key synthons for silicon-based polymers[1] 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 solution[3] 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 $[RhCl(CO)_2]_2$ 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.

Table 1. Hydrolysis of Various Silanes Catalyzed by $[RhCl(CO)_2]_2$[d]

Entry	Silane	Silanol	Time (min)	H_2 (%)	Yield (%)[a]	silanol: disiloxane[a]
1[b]			6	5	-	-
2	 $Et_3Si{-}H$	 $Et_3Si{-}OH$	8	99	>99	>99:1
3	 $Pr_3Si{-}H$	 $Pr_3Si{-}OH$	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

[a]The conversions were determined by isolated yield except entries 2 and 3, which were determined by gas chromatography. [b]Without the addition of water. [c]The addition of excess mercury (0.48 mmol). n.d. = not determined. [d]Conditions: silanes, 0.8 mmol; H_2O, 8 mmol; $[RhCl(CO)_2]_2$, 0.0016 mmol; room temperature, 25 ± 1 °C; N_2, 2 mL of THF.

The complex $[RhCl(CO)_2]_2$ 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). Diphenylsilane was also quantitatively transformed into diphenylsilanediol (entry 7). A mercury poisoning experiment was performed[10] 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 $[Cp(P^iPr_3)(NCMe)Ru(\eta^2\text{-}HSiCl_3)]^+$ and $[Cp(P^iPr_3)(NCMe)Ru(\eta^2\text{-}HSiMeCl_2)]^+$ were remarkably more stable than other silanes with alkyl substitutions.[9c] So, $HSiCl_3$ was used to react with $[RhCl(CO)_2]_2$ to observe the possible intermediate. A variable-temperature ^1H NMR technique was used to follow the reaction. The mixing of $[RhCl(CO)_2]_2$ 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_{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 ($^1J_{Si-H}$ = 49 Hz) in the ^1H NMR spectra (Figure 1). The observed Si−H coupling constant[12] was much larger than 20 Hz, proposed to be the boundary value for classical silyl hydride metal complexes,[13] and close to the $^1J_{Si-H}$ values observed in the silane σ complexes (53 Hz for $[Cp(P^iPr_3)(NCMe)Ru(\eta^2\text{-}HSiCl_3)]^+$;[9c] 54.8 Hz for $Cp'(CO)_2Mn(\eta^2\text{-}HSiCl_3)$;[14] 48 Hz for $[Cp(PMe_3)_2Ru(\eta^2\text{-}HSiCl_3)]^+$[15]) and thus in good agreement with the σ-coordinated compound $(CO)_2ClRh(\eta^2\text{-}HSiCl_3)$.

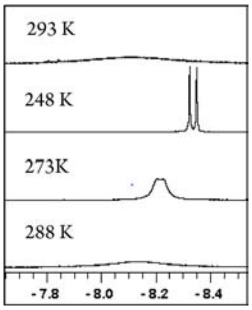


Figure 1. Variable-temperature ^1H NMR of rhodium silane σ complexes.

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 Hiden 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 $[H_2O]$ 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 $[RhCl(CO)_2]_2$ 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 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]

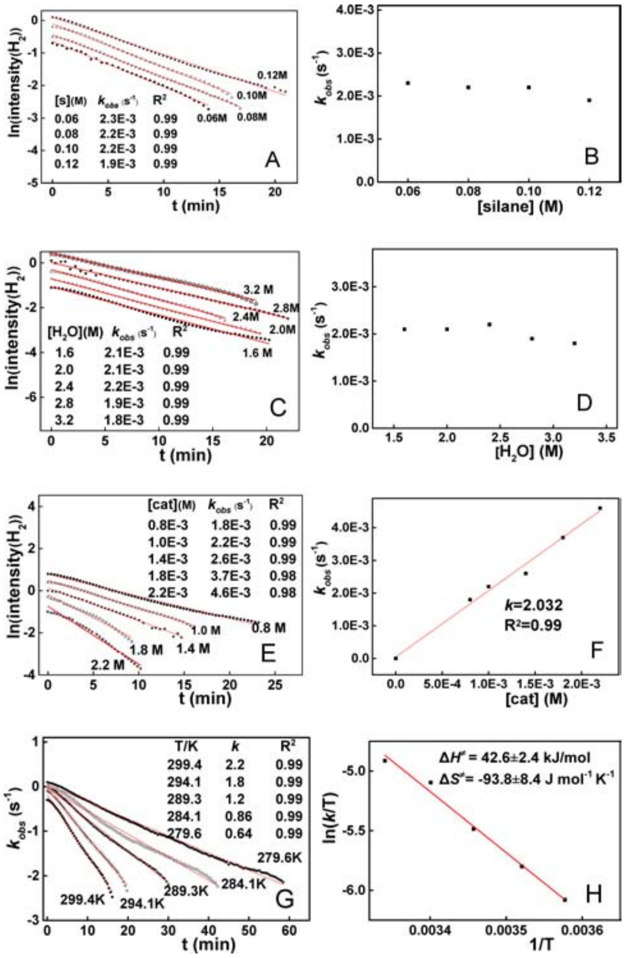


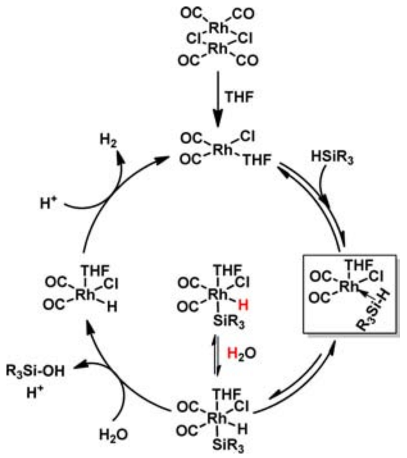
Figure 2. Kinetic studies of hydrolysis of $MePh_2SiH$ catalyzed by $[RhCl(CO)_2]_2$. Conditions: (A) $c(H_2O)$ = 2.4 M and $c([RhCl(CO)_2]_2)$ = 1.0 mM; (C) c(silane) = 0.1 M and $c([RhCl(CO)_2]_2)$ = 1.0 mM; (E) $c(H_2O)$ = 2.4 M and c(silane) = 0.1 M; (G) $c(H_2O)$ = 2.4 M, c(silane) = 0.1 M, and $c([RhCl(CO)_2]_2)$ = 1.0 mM.

$$\text{rate} = \frac{d[H_2]}{dt} = k_{obs}[\text{silane}] \tag{1}$$

$$k_{obs} = k[\text{catalyst}] \tag{2}$$

A mechanism consistent with the experimental results is proposed in Scheme 1. The first step involves dissociation of a dinuclear complex into monomer $RhCl(CO)_2$, 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 $(THF)(CO)_2ClRhH$(silyl) complex. The lack of kinetic isotope effects is due to H/D exchange of $(THF)(CO)_2ClRhD$(silyl) with water and rapid equilibrium between $(THF)(CO)_2ClRh$, silane, and $(THF)(CO)_2ClRhD$(silyl). Then water attacks the coordinated silyl group to give silanol and $(THF)(CO)_2RhH$, 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 $[RhCl(CO)_2]_2$



(Figure 4S in the SI). The second-order kinetics and large negative value of $\Delta S^{\ddagger}$ indicate that the bimolecular reaction of $(THF)RhCl(CO)_2$ with silane to form $(THF)(CO)_2ClRhH$(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 $[Et_3SiOHMe]^+$ 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 $[H_2OR_3Si]^+$ 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 $[H_2OR_3Si]^+$ 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 $[RhCl(CO)_2]_2$ 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 $[RhCl(CO)_2]_2$. 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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